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Electrochemically Active Polymers for Rechargeable Batteries

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Contents

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1. Introduction

Electrochemical energy storage systems (batteries) have a tremendous role in technical applications. They are used in computers, communication devices, industrial controls, electric vehicles, spaceships, laboratory equipment, *etc.* They are of crucial importance for portable instruments, remote control, solar power, pacemakers, and toys, to name only a selection of familiar uses. With technologies emerging today, an even higher demand for rechargeable batteries with high specific energy and power is expected. In this review we examine the prospects of electroactive polymers in view of the properties required for such batteries. Conducting organic polymers are considered here in the light of their rugged chemical environment: organic solvents, acids, and alkalis.

Fundamental electrochemical aspects of conducting organic polymers (including their electronic conductivity) have been discussed in a review paper[1] citing 395 references and covering the literature up to 1989. However, in it there is little discussion as to applications of polymers in batteries and the state of the art of these batteries. Some battery applications of electroactive polymers are discussed in a recent book edited by Scrosati.[2] The goal of the present article is to provide, first of all in tabular form, a survey of electroactive polymers in view of potential applications in rechargeable batteries. It reviews the preparative methods and the electrochemical performance of polymers as rechargeable battery electrodes.

The theoretical values of specific charge of the polymers are comparable to those of metal oxide electrodes, but are not as high as those of most of the metal electrodes normally used in batteries. Therefore, it is an advantage in conventional battery designs to use the conducting polymer as a positive electrode material in combination with a negative electrode such as Li, Na, Mg, Zn, MeH_x, etc.

Most of the common conducting polymers exchange anions during the charging and discharging process. Therefore, the salt concentration in the electrolyte changes during cycling (salt is formed during discharge from the cations of the negative and anions of the positive electrode, and enough solvent must be provided to leave this salt dissolved), which is unfavorable for the specific energy and operation of the battery. But even with such a system, batteries with high specific energies at mean cell voltages of up to 3.5 V are feasible.

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Dr. Klaus Müller is Senior Research Chemist in the Environment group of Battelle's Geneva Laboratories. At Battelle since 1987, he has worked on batteries and corrosion as well as on problems of air pollution, soil pollution, and environmental impact. A graduate of Dresden Technical University and of the University of Pennsylvania at Philadelphia, he has worked also on electric double-layer theory, adsorption, fuel cells, electrocatalysis, and organic electrochemistry in the research laboratories of Hokkaido University, American Cyanamid, Hoffmann-LaRoche, and Brown Boveri. He is the author or co-author of over 50 papers and patents.

Dr. K. S. V. Santhanam is Senior professor at the Tata Institute of Fundamental Research in Mumbai, India. Earlier on he did research in association with A. J. Bard at the University of Texas and P. J. Elving at the University of Michigan. He is active in the Society for the Advancement of Electrochemical Science and Technology, the Bioelectrochemical Society of India, and the Indian Society for Radiation and Photochemical Sciences, and he serves on the editorial board of several journals. He is the author of over 120 papers in international journals.

Dr. Otto Haas is Head of the Electrochemistry Section, Paul Scherrer Institute, Villigen, Switzerland, where he is directing several electrochemical energy storage and conversion projects. He started his research on redox polymers and conducting polymers about 20 years ago, and he performed much of this work as a visiting associate in the research groups of M. S. Wrighton, H. Gerischer, J. M. Savéant, E. J. Cairns, and R. W. Murray. The present review on conducting polymers was initiated by Otto Haas on the occasion of the 60th birthday of Professor A. von Zelewsky, University of Fribourg, Switzerland, to honor his excellent qualities in teaching and research and his talent for spreading enthusiasm to his students. It was in fact Professor von Zelewsky who provided Otto Haas with the opportunity to carry out pioneering work on the subject of this review.

After the discovery of Shirakawa *et al.*[3] that virgin polyacetylene, $(CH)_x$, can be reversibly oxidized and reduced and so switched reversibly from the insulating to a semiconducting or conducting state, innumerable attempts have been made to utilize the redox reactions of $(CH)_x$ for storing charge. Other conducting polymers such as polyphenylene, polypyrrole, polythiophene, and polyaniline have been proposed and investigated for charge storage, and the key parameters of organic polymer batteries have been critically discussed.[4] Among the many conducting polymers, polyacetylene is regarded as a "model" material, on one hand because of its bivalence (as a host, both for positive and for negative charge) and on the other hand because of the vast theoretical knowledge acquired by physicists.

During their electrochemical oxidation and reduction, polymer electrodes must take up or give off ions in order to maintain electroneutrality of the material. This process is often called polymer doping/undoping. The doping is an ion insertion process[5,6] that raises the redox state and electronic conductivity of the polymer. The charge-compensating ions can move within the polymer. Thus, a conducting polymer is actually an electronic as well as an ionic conductor.

Conventional battery electrode materials often have a distinct redox potential, more or less independent of their state of charge or discharge (the Li/Li^+ couple—typically suggested for polymer batteries—has such a rather constant potential), while conducting polymers have as it were a "floating" redox potential, *i.e.*, one that strongly depends on their state of charge or discharge.

Thus, for conventional electrode materials the end of discharge or of charging is indicated by the fact that their potential ceases to be relatively constant. Intermediate states of charge or discharge are difficult to recognize by measurements of potential, and only deep discharge produces a distinct potential change. For conducting polymers, the potential is an indication for the state of charge or discharge (which is an advantage), even though this implies that the discharge characteristic is sloping (which is generally considered to be a disadvantage).

Polymers can be utilized as positive and/or negative electrodes in rechargeable cells. (Infrequently, conducting polymers have been used as a catalytic surface rather than as an electroactive material, *e.g.* in $Li/SOCl_2$ and Li/SO_2Cl_2 cells.[7,8]) Although the terminology is only correct for the discharge of rechargeable batteries, negative electrodes are often regarded as "anodes" and positive electrodes as "cathodes" throughout the battery literature. In this review, these terms are accepted. Also, it should be remembered that often a device described as a battery is merely a single electrochemical cell. The former term often appears to have been used with a connotation of rechargeability, which is at variance with the realities of the battery market.

Figure 1.1 shows schematically how polymers can be used in cell assemblies as electroactive materials. In this figure, M stands for a metal, M^+ for cations (typically metal ions), A^- for anions, P for a neutral polymer, P^- for a polymer in its reduced state, and P^+ for a polymer in its oxidized state (transfer of one electron is assumed). A polymer electrode can be combined with a metal electrode (cases *a* and *e*) or with a metal oxide or sulfide electrode (case *f*). Using two polymers with different redox potentials, one can design three different basic cell types (cases *b*, *c*, and *d*).

In cases *a* and *b*, the ions formed (liberated) at the electrodes during charging and discharging have to be stored in the electrolyte. This means that a substantial electrolyte (and solvent) volume is necessary. In all other cases, ions are merely transferred from one electrode to the other during the charging and discharging processes, and the electrolyte volume actually required is negligibly small. In fact, very thin ionically conducting membranes may be used to separate the electrodes in these cases, thus, in

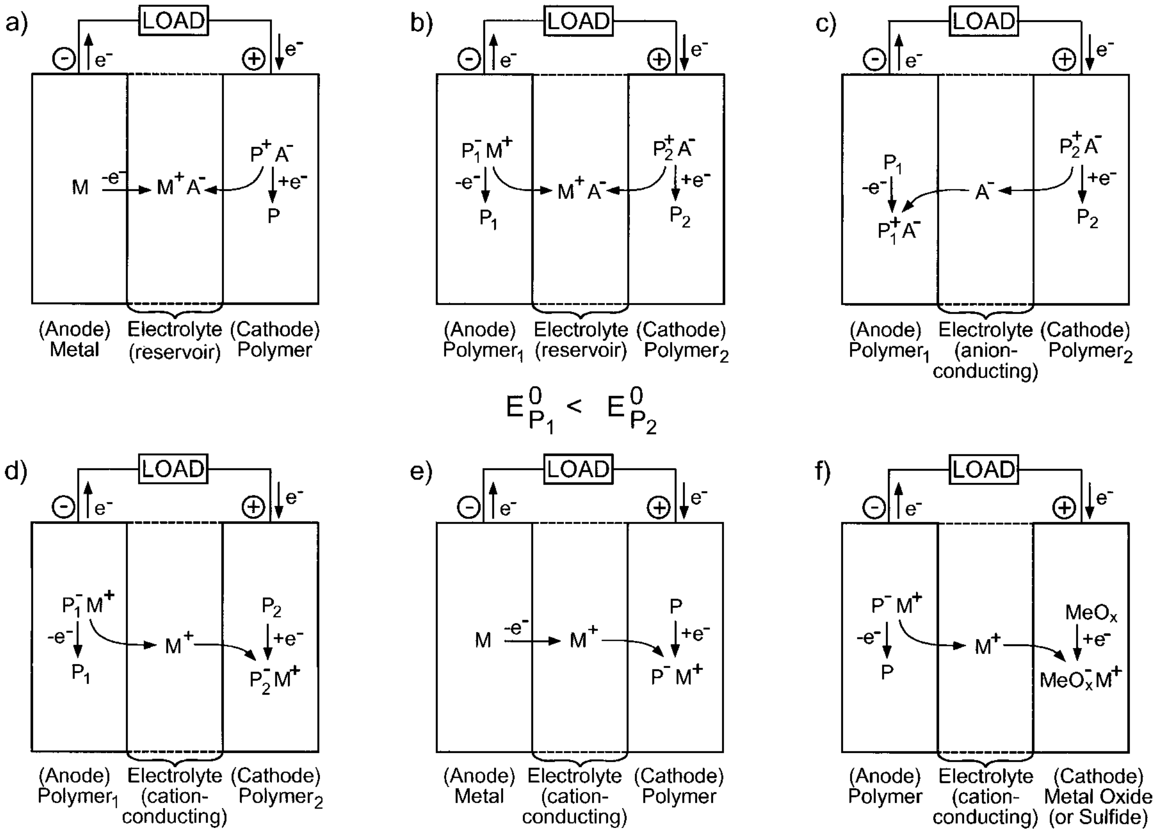


Figure 1.1. Polymers (P) as electroactive materials in cell assemblies: (a) metal/polymer (P is anion-inserting)—most common configuration for cells assembled with the model polymers of Table 1.1; (b) polymer/polymer (P_1 is cation, P_2 is anion-inserting); (c) polymer/polymer (both anion-inserting); (d) polymer/polymer (both cation-inserting); (e) metal/polymer (P is cation-inserting)—most common configuration for cells assembled with redox dimerization and polymerization electrodes; (f) polymer/metal oxide or sulfide (P is cation-inserting)—most common configuration when carbonaceous materials replace P. All cells are shown in their discharge configuration. For further details see Introduction.

principle higher specific energies and energy densities are attainable.

The specific charge (in A h kg^{-1}) or charge density (in A h dm^{-3}) of an electroactive polymer is calculated from the polymer mass or volume required per exchangeable unit charge (one Faraday = 96487 C mol^{-1} = 26.8 A h mol^{-1}). (In battery literature, the term "capacity" is often used instead of "specific charge", both for individual electrodes and the entire cell or battery. It is useful to remember at this occasion that in any cell or battery, the capacity (in A h) of the assembly is limited by the electrode(s) (anodes or cathodes) having the lower capacity.) The polymer's equivalent weight (or mass) is defined as the mass of the polymer's repeating unit divided by the number of electrons exchanged or stored by it (which may be a fractional number), or as the mass of the polymer's set of repeating units exchanging (storing) one electron. For instance, in polypyrrole and polyaniline which, in their charged state, typically have an electron deficiency of one unit distributed over two to five pyrrole or aniline rings in the polymer chain, the equivalent weights are accessible through an experimental determination of charge acceptance/charge delivery and associated weights. In redox polymerization/depolymerization electrodes where charge storage/release is linked to the making/breaking of a distinct bond, the equivalent weights are accessible through simple stoichiometry.

However, concerning the values reported for specific charge (or charge density), it should be pointed out that the figures provided by different workers in the literature are not always calculated on the same basis. Adequate corrections may be needed for a valid comparison of cited values. Common bases are the following:

(1) Specific charge based on the polymer's equivalent weight.

(2) Specific charge based on the polymer's equivalent weight and the equivalent weight of counterions needed for charge compensation (for the doping process).

(3) Specific charge based on the polymer's equivalent weight and the equivalent weight of all electrolyte and solvent molecules involved in the exchange reaction. This figure is obtained experimentally by actually weighing the active material in the doped state and counting the coulombs passed while the electrode is charged and discharged.

(4) Specific charge as in 2 or 3, but also including the weights of inactive components of the electrode mass like carbon, binders, *etc.*

(5) Specific charge including also the weights of the counter electrode and amount of electrolyte (salt and solvent) required.

The most important performance parameters that need to be reported when considering conducting polymers as potential battery electrode materials are the following: Charge density, preferably >200 A h kg^{-1}; voltage difference to the counter electrode, preferably >2 V; Coulombic efficiency, preferably close to 100%; voltage efficiency, preferably >80%;

cycle life; preferably >500 cycles; self-discharge (parasitic reactions, *e.g.* with the electrolyte), preferably <1%/day; chemical stability: shelf life >1 year (in the charged or, more commonly, discharged state).

The theoretical specific energy of a complete cell is given by the product of specific charge (counting the masses of both electrodes and the stoichiometric amount of the electrolyte) and the potential difference between the electrodes. Since polymer electrodes exhibit potentials which, in most cases, undergo a considerable decrease during discharge, the potential difference used in calculating the theoretical or practical specific energy should be a properly selected mean value between the start and end of discharge.

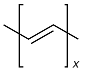
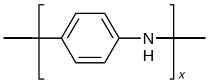
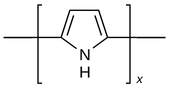
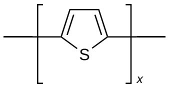
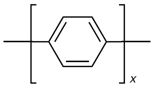
The highest specific energies of cells or batteries are expected when metal electrodes with high specific charge such as Li, Na, Mg, Al, and Zn are combined with the appropriate cation-exchanging polymer of low equivalent weight functioning as a cation-insertion electrode. However, most of the reports in the literature refer to work on battery designs corresponding to scheme *a* of Figure 1.1, which implies lower specific energies than the arrangement of scheme *e*. This is due to the fact that cation-exchanging polymers have not been explored extensively until now. Thiol-based redox polymerization electrodes are naturally advantageous in this respect.

Generally, lithium electrodes have been preferred as the negative battery electrodes in polymer batteries, since they have a very high theoretical specific charge (although their rechargeability may be limited). The properties of Li and LiAl electrodes are well documented in the literature[9,10] and, hence, will not be discussed here. However, several attempts have been made to use polymer negative electrodes instead, so that an all-plastic (completely organic) battery could be designed according to Figure 1.1, parts *b*−*d*. Lithium ion-inserting carbon negatives have been used most often (and are marketed) in the configuration corresponding to Figure 1.1*f*.

Note that an anion-inserting (*p*-dopable) polymer can be combined into a cell with another similar polymer, and the same is true for two cation-inserting (*n*-dopable) polymers, so long as their *relative* oxidation and reduction potentials are sufficiently different.

Many conducting polymers have been reported in the literature,[1,11−19] but only few basic ("model") polymers have been investigated in depth for rechargeable batteries. These are the polymers prepared from monomers (possibly substituted) like acetylene, aniline, pyrrole, thiophene, and benzene. The molecular structures of these polymers and typical electronic conductivities in the doped state are listed in Table 1.1. The latter values are not the highest that can be found in the literature for a given polymer but represent those of samples used in the battery investigations reported. It has to be stressed that the conductivity very strongly depends on the redox state (doping level) of the polymer, which changes during the cycling of the electrode in proportion to the depth of charge−discharge. For battery performance, polymer conductivity will be crucial only at extreme levels of discharge. Rate limitations rather arise from low ionic mobilities in the polymers as well as in the electrolytes. The molecular structures of other polymers discussed (condensed thiophenes, redox polymers, redox polymerization materials, and polyacenes) are reported below in Tables 2.2 and 2.3.

Table 1.1. Model Conducting Polymers Examined for Rechargeable Batteries[a]

structure	MW monomer unit	conductivity ($S\ cm^{-1}$) of the oxidized polymer	ref(s)
	13 (26)	3−1000	12,20−25
	91	0.01−5	20,26−28
	65	0.3−100	25,28−30
	82	2−150	28,31
	76	10−500	24,28,32

[a] Significantly higher conductivities have been published for the polymers listed but not in the context of battery work.

2. Preparation of Polymer Electrodes

Electrochemically active polymers can be prepared, both by electrochemical and by chemical methods. Electrochemical methods are often preferred, because they offer the advantage of a precise control of potential and state of charge of the resulting polymer. Potentiostatic, potentiodynamic, and galvanostatic techniques have been typically used for electropolymerization.[1,33−35] Work in which the chemical preparation has also been employed includes refs 36−39. Detailed conditions for preparation of the most important polymers are discussed below.

Table 2.1 summarizes the details of preparation of the polymers for their use as cathode (positive electrode) materials. The table lists the media, the electrolytes, the concentrations of the monomer (wherever reported), and the method used for the polymerization. A pretreatment or conditioning of the polymer which is sometimes required prior to use of the polymer in a battery arrangement is also indicated in the table.

Polymers obtained from the corresponding monomer by oxidation are produced in the oxidized, *p*-doped (charged) state, and hence contain the anions required (or desired) for charge compensation. However, some polymers, notably $(CH)_x$, are not in an oxidized state as prepared; they are typically oxidized (charged) prior to any battery experiments. Hence, the table also lists the conditions used for the oxidation of $(CH)_x$ as well as the degree of doping thus attained (in the columns labeled medium, electrolyte, and pretreatment).

Table 2.1 also lists the conditions employed in the preparation of anode (negative electrode) materials. Such entries are preceded by "A:" (for "anode mate-

Table 2.1. Preparation of Polymer Electrodes[a]

polymer electrode[b,c]	medium	electrolyte	concentration of monomer (or polymer)	polymerization method	substrate (contact)	pretreatment (conditioning)	ref
				Polyacetylene			
$(CH)_x$	H_2O	~0.5 M $NaAsF_6$ + 52% HF		chem. polym.	free $(CH)_x$ film	electrochem. ox., $y = 0.03$	23
$(CH)_x$	H_2O	7.4 M HBF_4 or sat. $Pb(ClO_4)_2$		chem. polym., Shirakawa's method		electrochem. ox., $y = 0.02-0.04$	20
$(CH)_x$	H_2O	0.5 M KI		chem. polym.	free $(CH)_x$ film	PS ox. at +9 V, $y = 0.07$	57
$(CH)_x$	CH_2Cl_2	0.5 M Bu_4NClO_4		chem. polym.	free $(CH)_x$ film	PS ox. at +9 V, $y = 0.06$	57
$(CH)_x$	CH_2Cl_2	Bu_4NAsF_6		chem. polym., Shirakawa's method		electrochem. ox., $y = 0.08$	22
$(CH)_x$	THF or PC	0.5 M Bu_4NClO_4		chem. polym.	free $(CH)_x$ film	electrochem. ox., $y = 0.05$	50
$(CH)_x$	THF or PC	0.3 M $LiClO_4$		chem. polym.	free $(CH)_x$ film	electrochem. ox., $y = 0.06$	50
$(CH)_x$	PC or SL	~1 M $LiClO_4$		chem. polym.	Pt or Ni wire	electrochem. ox.	23
$(CH)_x$	PC or SL	0.5−1 M $LiClO_4$		chem. polym. on the grid, Ziegler−Natta cat.	electron microscopy grid	PS ox. at $E < +4.1$ V (Li/Li$^+$), $y = 0.06$	48
$(CH)_x$	PC or SL	~1 M Bu_4NPF_6		chem. polym.	Pt or Ni wire	electrochem. ox., $y = 0.06$	23
$(CH)_x$	PC	0.95 M $LiAsF_6$		chem. polym., Shirakawa's method	Pt mesh envelope	PS ox. at +3.5 to +3.9 V (Li/Li$^+$), $y = 0.02$	56
$(CH)_x$	PC	$LiClO_4$ or $LiAsF_6$		chem. polym.	Pt mesh	GS ox. at 50 μA cm^{-2} [+3.6 to +3.9 V (Li/Li$^+$)], $0 < y < 0.10$	45
$(CH)_x$	PC	0.35 M $LiBF_4$		chem. polym. on the grid, Ziegler−Natta cat.	electron microscopy grid	PS ox. at $E < +4.1$ V (Li/Li$^+$), $y = 0.06$	48
$(CH)_x$	PC	0.1−1 M $LiClO_4$ or 1 M $LiBF_4$ or 1 M $LiPF_6$			films of compacted $(CH)_x$ powder on a Pt foil	PS ox. at +3.8 V (Li/Li$^+$)	47
$(CH)_x$	PC	1 M $LiClO_4$		chem. polym., Shirakawa's method	Au evaporated on $(CH)_x$ film	GS ox. at 0.1 mA cm^{-2}, $y \approx 0.02$	44
$(CH)_x$	PC	$LiClO_4$		chem. polym., Shirakawa's method	$(CH)_x$ sandwiched in a Pt mesh	GS ox. at 50 μA cm^{-2}, $y = 0.05$	53
$(CH)_x$	PC	0.3 M $LiClO_4$		chem. polym., Shirakawa's method	Pt wire attached to one side of a $(CH)_x$ film	GS or PS ox. at 2 mA cm^{-2} or at +1.0 V (Ag/Ag$^+$), $y = 0.04-0.06$	21,22
$(CH)_x$	PC	1 M $LiClO_4$		chem. polym., Shirakawa's method	Pt plate	GS ox. at 0.5 mA cm^{-2}, $y = 0.06$	51
$(CH)_x$	PC	0.3 M $LiClO_4$		chem. polym.	free $(CH)_x$ film	PS ox. at +3.8 V (Li/Li$^+$), $y > 0.06$	49
$(CH)_x$	PC	1 M $LiClO_4$		chem. polym.	free $(CH)_x$ film	GS ox. at 12 μA cm^{-2}, $y \le 0.07$	23
$(CH)_x$	PC	1 M $LiClO_4$		chem. polym., Shirakawa's method	Pt mesh	GS ox. at 50 μA cm^{-2}, $y \le 0.10$	56
A: $(CH)_x$	PC	1 M $LiClO_4$		chem. polym., Shirakawa's method	Au evaporated on $(CH)_x$ film	GS red. at 0.1 mA cm^{-2}, $y \sim 0.02$	44

A: $(CH)_x$	PC	1 M Bu_4NClO_4		chem. polym., Shirakawa's method	Pt sheet, permanent pressure	$(CH)_x$ film abraded with fine emery paper, electrochem. red. $y = 0.02-0.05$	52
A: $(CH)_x$	THF or PC	0.5 M Bu_4NClO_4		chem. polym.	free $(CH)_x$ film	electrochem. red., $y = 0.02-0.07$	50
A: $(CH)_x$	THF or PC	0.3 M Bu_4NPF_6		chem. polym.	free $(CH)_x$ film	electrochem. red., $y = 0.06$	49,50
A: $(CH)_x$	THF	$LiClO_4$		chem. polym.	free $(CH)_x$ film	$(CH)_x$ strip shorted to Li, $y = 0.06$	49,50
A: $(CH)_x$	THF	0.3 M $LiClO_4$		chem. polym.	free $(CH)_x$ film	electrochem. red., $y = 0.06$	49,50
A: $(CH)_x$	THF	0.8 M $LiClO_4$		chem. polym.	Pt mesh	PS red. at +0.7 V (Li/Li^+), $y = 0.09-0.10$	45
A: $(CH)_x$	THF	$LiClO_4$		chem. polym.	free $(CH)_x$ film	GS red. at 0.18 mA cm^{-2}, $y = 0.10$	58
A: $(CH)_x$	THF	1 M $LiClO_4$		chem. polym.	free $(CH)_x$ film	$(CH)_x$ film shorted to Li, $y \leq 0.10$	23
A: $(CH)_x$	THF	1 M $LiClO_4$ or 1 M $NaPF_6$		chem. polym. Shirakawa's method	Pt gauze	GS red. at 0.14 mA cm^{-2}, $y = 0.10$	5
A: $(CH)_x$ + Li_zAl or Li_zPb (composite)	THF or MTHF	0.25 M $LiB(C_6H_5)_4$ or 1.5 M $LiPF_6$		acetylene polym. on Al or Pb surface		electrochem. red.	59
A: $(CH)_x$ + Li_zAl or Li_zPb (composite)				Shirakawa's polym., Li_zAl or Li_zPb alloy		mixing of polymer, alloy, and a PE binder	59
				Polyaniline			
PAni (powder)	H_2O	NH_4F, HF	0.05 M	chem. ox. with 0.04 M $(NH_4)_2S_2O_8$	SS or Al screen	mixture of PAni and 20 wt % of AB compressed on the substrate, vacuum drying at 80 °C	36
PAni (powder)	H_2O	0.1 M HCl		chem. ox. with $(NH_4)_2S_2O_8$	Pt screen	rolling of a mixture of dried PAni and 20 wt % PTFE	68
PAni (powder)	H_2O	HCl		chem. ox. with $(NH_4)_2S_2O_8$		drying, mixing with 10% of Teflonized AB	20,75
PAni (powder)	H_2O	1 M HCl		chem. ox. with $(NH_4)_2S_2O_8$	Pt disk	treatment with aqueous 0.1 M NH_4OH, mixing with 5−17 wt % of CB and 0−5 wt % PTFE	83,84, 86
PAni (powder)	AN	Ani-HBF_4:AN = 1:15		chem. ox. with stoich. $Cu(BF_4)_2$		add 16% AB	87
PAni (powder)	H_2O	1 M HCl	0.2 M	PS ox. at +0.8 V (SCE)	Pt foil	rolling of a mixture of dried PAni and 20 wt % PTFE	68
PAni (powder)	H_2O	$HClO_4$		GS ox. at 1 mA cm^{-2}	Pt-coated Ti	vacuum drying at 50 °C, grinding to 60−80 mesh	65
PAni (granular)	H_2O	0.5 M H_2SO_4	0.5 M	GS ox. at 5 mA cm^{-2} (6 C cm^{-2})^d	Pt sheet	vacuum drying at room temperature	61
PAni (fibrous)	H_2O	1 M $HClO_4$	0.5 M	GS ox. at 5 mA cm^{-2} (6 C cm^{-2})^d	Pt sheet	vacuum drying at room temperature	61
PAni (mossy film)	H_2O (10 °C)	2 M HBF_4		GS ox. at 1 mA cm^{-2} (21.6 C cm^{-2})^d	GC	dry, peel-off film, press on PAni-plated Ti	63
PAni (dendritic film)	H_2O	0.25 M or 0.5 M H_2SO_4	0.35 M	PSw ox. at 20 mV s^{-1} from −0.05 V to +0.8 V (SCE)	GC		79
PAni (membrane)	H_2O	$HClO_4$		GS ox. at 1 mA cm^{-2}	Pt-coated Ti	drying, grinding to 60−80 mesh, dissolving in MP, casting	65
PAni (film 300 μm)	H_2O	2 M $HClO_4$	1 M	GS ox. at 1 mA cm^{-2} (20 C cm^{-2})^d	Pt	vacuum drying at 100 °C	62
PAni (film)	H_2O	2 M HBF_4	1 M	GS ox. at 5 mA cm^{-2}	Au	drying in a desiccator	64
PAni (film)	H_2O	HBF_4		electrochem. ox.	Pt foil	treatment with aqueous/methanolic alkali solution	20
PAni (film)	H_2O	0.1 M H_2SO_4	0.1 M	PSw ox. at 100 mV s^{-1} from −0.2 V to +0.8 V (SCE)	Pt plate	vacuum drying overnight	73
PAni (film)	H_2O	1 M HCl	0.2 M	PSw ox. at 50 mV s^{-1} from −0.2 V to +0.8 V (SCE)	Pt or SnO_2	vacuum drying at 90 °C for 48 h	68,72
PAni (film)	H_2O	1 M HCl	0.1 M	PSw ox. from +0.15 V to +1.0 V (NHE) (2 mC cm^{-2})^d	Au or GC		77

Table 2.1 (Continued)

polymer electrode[b,c]	medium	electrolyte	concentration of monomer (or polymer)	polymerization method	substrate (contact)	pretreatment (conditioning)	ref
				Polyaniline (continued)			
PAni (film)	H_2O	2 M acid (H_2SO_4, HCl, HF, HNO_3, CF_3SO_3H or CF_3COOH)	0.1 M	PSw ox. at 50 mV/s from −0.1 V to +0.9 V (NaSCE)	Pt		74,76
PAni (film)	H_2O	0.1 M H_2SO_4 + 0.5 M Na_2SO_4	0.1 M	PSw ox. from −0.2 V to +0.7 to +0.8 V (SCE)	Pt, Au, PG, or SS		75
PAni	H_2O	0.5 M H_2SO_4	1.5%	PS ox. at +0.8 V (SCE) (25 C cm^{-2})[d]	high porosity reticulated vitreous carbon	equilibrated in 1.5 M ZnI_2 + 1 M NH_4I (pH 4)	69,70
PAni (film)	H_2O	1 M $HClO_4$	0.5 M	PS ox. at +0.8 V (Ag/AgCl)	SS (polished and cathodically etched)	rinse ($HClO_4$), dry (vacuum)	71
PAni (film)	H_2O	1 M H_2SO_4	0.1 M	PSw ox. from 0 to +0.8 V (SCE) or GS ox. at 1.25 mA cm^{-2}	graphite or ITO	30 min at −0.2 V (SCE), H_2O rinse, vacuum dry	67
PAni	H_2O	2 M HBF_4	1.0 M	GS ox. at 0.01 to 5 mA cm^{-2}	Pt	wash with water and acetone	66
PAni (film)	AN	1 M Ani·HBF_4	1 M	GS ox. at 10 μA cm^{-2}	Pt	remove, make pellets with AB and PTFE, dry	93
PAni + carbon (composite)	H_2O	$HClO_4$		GS ox. at 1 mA cm^{-2}	Pt-coated Ti	drying, grinding to 60−80 mesh, dissolving in MP, impregnation of a carbon cloth	65
PAni (film)	PC	0.5 M $LiClO_4$ + CF_3COOH (>0.5 M)	0.5 M	PSw ox. at 10 mV s^{-1} from −0.7 V to +0.4 V (Ag/Ag^+)	Pt		88,89
PAni (film)	PC	0.5 M $LiClO_4$ + CF_3COOH (>0.5 M)	0.5 M	GS ox. at 0.5 mA cm^{-2} (≤20 C cm^{-2})[d]			88
PAni (film)	AN	0.5 M $LiClO_4$	0.1 M	PSw ox. at 50 mV/s from −0.2 V to +1.3 V (SCE)	Au		92
				Polypyrrole			
PPy (powder)	H_2O		0.3 M	chem. ox. with 0.7 M $Fe(ClO_4)_3$	SS	PPy pressed into pellets	37
PPy (film)	H_2O	0.01 M $K_4Fe(CN)_6$	0.5 M	3-s PS pulses from +0.50 V to +0.68 V (SCE)	Pt	wash	159
PPy (film)	AN + 1% H_2O	0.1 M Et_4NTos	0.1 M	GS ox. at 1.6 mA cm^{-2}	GC		160
PPy (composite)	H_2O with methylcellulose or (hydroxypropyl)cellulose			chem. ox. with $FeCl_3$	SS	mixing colloidal PPy sol. with a $P(EO)_8$·$LiClO_4$ sol., casting, drying	132
PPy (film)	PC + trace water	ClO_4^-		GS ox. at 0.25 mA cm^{-2}	metal	PPy peeled off after the synthesis	124, 126
PPy (film)	PC	0.5 M $LiClO_4$	0.05−0.1 M	GS ox. at 0.006−4 mA cm^{-2} [~3.7 V (Li/Li^+)]	Pt wire		129
PPy (film)	PC	0.1 M $LiClO_4$	0.1 M	GS ox. at 1 mA cm^{-2} (0.24 C cm^{-2})[d]	Pt		121
PPy (film)	PC	1 M $LiClO_4$	0.5 M	electrochem. ox.	Pt foil		114
PPy (film)	PC	0.2 M $LiClO_4$ or $LiPF_6$ or $LiCF_3SO_3$ or $LiBF_4$	0.2 M	PS ox. at +0.22 to +0.84 V (Ag/Ag^+)	Pt plate	anion UD	111, 112
PPy (film)	PC	0.2 M $LiPF_6$	0.2 M	PS ox. at +3.9 V (Li/Li^+)	Pt plate	PF_6^- UD	110
PPy (film)	PC	0.2 M $LiClO_4$	0.2 M	PS ox. at +0.8 V (Ag/Ag^+) (1 C cm^{-2})[d]	Pt coated with 2 μm NBR	NBR removed after the PPy growth	141
PPy (film)	AN	0.05 M $LiClO_4$	0.02 M	GS ox.	Pt foil	galvanostatic UD in the same sol.	119
PPy (film)	AN	0.1 M Et_4NClO_4	0.1 M	GS ox. at 0.7 mA cm^{-2} (0.7 C cm^{-2})[d]	Pt		120

PPy (film)	AN	0.1 M Et_4NBF_4 or Et_4NClO_4	0.1 M	PS or GS ox. at +1 V (SCE) or at 1 mA cm^{-2}	Au		113
PPy (film)	AN	0.1 M Bu_4NBF_4 or Bu_4NClO_4	0.25 M	GS ox. at 0.5 mA cm^{-2} (3.6 C cm^{-2})^d	CFP		127
PPy (film)	NB	0.1 M Bu_4NBF_4	0.2 M	GS ox. at 0.5 mA cm^{-2} (3.6 C cm^{-2})^d	CFP		38
PPy	vacuum		pyrrole vapor	chem. ox. with $FeCl_3$ on the separator	glass fiber separator	washing with ethanol, vacuum drying at room temperature	131
PPy (film)	H_2O	0.025 M DBS	0.05 M	GS ox. at 1 mA cm^{-2}	Pt	wash (H_2O, AN), soak (PC)	161
PPy (composite film)	PC or PC + DME	Nafion or PSS	0.1 M	GS ox. at 0.5 mA cm^{-2} (4.8 C cm^{-2})^d			122
PPy-Nafion (composite film)	AN	0.1 M Et_4NTos	1 M	GS ox. at +0.55 V (SCE)	GC, Au	substrate precoated from Nafion sol.	162
PPy-PSS (composite film)	H_2O	PSSNa, ~0.5 M SO_3^- equivalent	0.25 M	PS ox. at ~+0.6 V (Ag/AgCl)	Pt	cycling in WE	145
PPy-PSS (composite film)	H_2O	10 wt % PSSNa	6 wt %	GS ox. at 3−6 mA cm^{-2} (GS ox. at 10 mA cm^{-2})	CFP (Pt)	dry, soak with PTFE dispersion, hot-dry, press	144
PPy-CB (composite film)	PC + C particles 3 mg mL^{-1}	1 M $LiClO_4$	0.2 M	GS ox. at 5.5 mA cm^{-2}	SS		150
PPy-CB (composite film)	H_2O + C particles ≤50 mg mL^{-1}	0.1 M KCl	0.1 M	PS ox. at +0.85 V (Ag/AgCl)	GC, SS	deposition sol. sonicated	151
PIn	AN/BN/H_2O	0.1 M Et_4NBF_4	0.2 M	PS ox. at +0.7 V (Ag/AgCl)	Pt	AN rinse, vacuum dry	163
PIn	AN	0.1 M $LiClO_4$	0.01 M	PS ox. at +0.9 to +1.0 V (SCE)	Pt, ITO		158
				Polythiophene			
PT	AN, THF, CH_2Cl_2	Bu_4NClO_4 Bu_4NBF_4 $LiClO_4$			Pt, Au, ITO		166
	AN	0.1 M Bu_4NClO_4	0.01 M	PS ox. at >1.6 V (SCE)	Pt		
Pt (cathode + anode)	AN	0.5 M $LiClO_4$	0.4 M	CCV ox. at ~20 mA cm^{-2}	ITO	ClO_4^- + Li^+ UD by shorting, BF_4^- + Bu_4N^+ doping in AN, 0.2 M Bu_4NBF_4	167
PT	PC	0.03 M Et_4NPF_6	0.2 M	GS ox. at 10 mA cm^{-2}	ITO, Pt		170
PT	BN	0.5 M $LiBF_4$	0.4 M	CCV ox. at ~20 mA cm^{-2}	ITO		168
PT (PBT)	AN	0.5 M $LiClO_4$	0.1 M (T or BT)	GS ox. at 50 μA cm^{-2}	Pt, ITO	washing	169
PT (PBT)	AN	0.5 M $LiClO_4$	(T or BT)	GS ox. at 1−7 mA cm^{-2} 5 °C (T), 25 °C (BT)	Pt	UD/GS, washing, 50 cycles WE	171
PT	$CHCl_3$, dioxane	Lewis acids $FeCl_3$, $MoCl_5$, $RuCl_3$	VP	chem. ox. (in film on glass plate)			165
PT			2,5-dihalo-thiophene	chem. dehalogenation polycondensation	CFP	dissolving in $CHCl_3$, addition of carbon powder, spreading on the plate	38
PT	NB	0.1 M Bu_4NClO_4 or Bu_4NClO_4	0.25 M	GS ox. at 0.5 mA cm^{-2} (3.6 C cm^{-2})^d	CFP		38, 127
PBT	AN	0.5 M $LiClO_4$	0.02 M	GS ox. at 1.6 mA cm^{-2}	SS	washing, ~50 cycles WE	172
PT (film)	PC	0.5 M $LiClO_4$	0.2−1.0 M	GS ox. at ≥1 mA cm^{-2} (0.24 C cm^{-2})^d	Pt	10 cycles WE	173
PT (PBT)	AN	0.5 M $LiClO_4$	0.01 M BT	GS ox. at 1.6 mA cm^{-2}	Pt, ITO	several cycles WE	174
PT (PBT)	AN	0.5 M $LiClO_4$	0.01 M BT	GS ox. at 1.6 mA cm^{-2}	[Pt, C, ITO]		175
PT (P3T)	AN	0.1 M Et_4NBF_4		ox. by potential steps to +1.00 to +1.05 V (SCE)	Pt gauze	potential control	178
PT	PC	0.5 M $LiClO_4$	1 M	GS ox. at 0.25 mA cm^{-2}	Pt	wash, undope slowly before cycling	471
PBT	PC	0.5 M $LiClO_4$	0.05 M	GS ox. at 0.25 mA cm^{-2}	Pt		
P3T	PC	0.5 M $LiClO_4$	0.05 M	GS ox. at 0.25 mA cm^{-2}	Pt		
PTT	AN	0.1 M Bu_4NBF_4	0.001−0.002 M	PS or PSw ox. ?	ITO	washing	198

Table 2.1 (Continued)

polymer electrode[b,c]	medium	electrolyte	concentration of monomer (or polymer)	polymerization method	substrate (contact)	pretreatment (conditioning)	ref
				Polythiophene (continued)			
PTT	CH_2Cl_2	0.2 M Bu_4NClO_4	0.002 M	GS ox. at 1 mA cm^{-2}	Pt, ITO	several cycles WE	174
PTT	CH_2Cl_2	0.2 M Bu_4NClO_4	0.005 M	GS ox. at 0.4 mA cm^{-2}	Pt, C, ITO		175
	PC	0.5 M $LiClO_4$	0.01 M	GS ox. at 0.15−0.3 mA cm^{-2}			
PDTT	AN	0.1 M Bu_4NBF_4	0.001−0.002 M	PS or PSw ox.	ITO	washing	198
PDTT	AN	0.1 M $LiClO_4$ or 0.1 M Et_4NBF_4	0.015 M	GS ox. at 0.4 mA cm^{-2}	Pt, C paper, ITO	anodic conditioning in Et_4NBF_4/PC to eliminate $LiClO_4$	202
PDTT	CH_2Cl_2	Bu_4NPF_6, Bu_4NClO_4		GS ox.	Pt, ITO	UD in SE	207
PDTT	CH_2Cl_2	0.1 M Bu_4NClO_4 Bu_4NPF_6	0.002 M	GS ox. at 0.4 mA cm^{-2}	Pt, ITO		199
PDTT	CH_2Cl_2	0.1 M Bu_4NClO_4	0.002 M	GS ox. at 0.16−0.4 mA cm^{-2}	Pt	UD in SE, washed	200
	PC	0.1 M $LiClO_4$	0.002 M	GS ox. at <0.2 mA cm^{-2}			
PDTT	CH_2Cl_2	0.1 M Bu_4NClO_4	0.002 M	GS ox. at 0.4 mA cm^{-2}	ITO, Pt	UD in SE, washed	201
PDTT	CH_2Cl_2	0.2 M Bu_4NClO_4	0.002 M	GS ox. at 0.4 mA cm^{-2}	Pt, ITO		174
PDTT	CH_2Cl_2	0.2 M Bu_4NClO_4	0.002 M	GS ox. at 0.4 mA cm^{-2}			175
PMOT	CH_2Cl_2 0 °C	?	?	PS ox. at +1.8 V (Ag/AgCl)	ITO, Pt?		187,188
PEDOT	PC	0.1 M Bu_4NPF_6	0.017 M	PS ox. at +1.1 V (Ag/Cl)	Pt, ITO		189
	CH_2Cl_2 0 °C	0.1 M Bu_4NPF_6		PS ox. at +1.58 V (Ag/Cl)	Pt		189
PMT		$Bu_4NCF_3SO_3$			Pt	opt.: removed, rinsed, dried	179
PMT	PC	0.03 M Et_4NPF_6	0.2 M	GS ox. at 10 mA cm^{-2}	ITO, Pt		170,183
PMT	PC	0.1 M $LiBF_4$ or $LiAsF_6$	0.2 M	GS ox. at 1−10 mA cm^{-2}	Au film	UD by shorting, washing in CH_3OH	181,182
PMT	PC	0.5 M $LiClO_4$		GS ox.	Pt		208
PMT	AN	0.2 M $LiClO_4$	0.2 M	PS ox. at +1.25 V (Ag/Ag^+)	Pt		209
PMT	AN	0.1 M Et_4NBF_4	0.1 M	GS ox. at 10 mA cm^{-2}	Pt, GC	rinsed, vacuum dried	210
PAT, POT				chem. ox./$FeCl_3$		break-in cycles WE	186; see 165,185
PAT, POT	NB	0.02 M Bu_4NClO_4, 0.02 M Bu_4NPF_6	0.2 M	GS ox. at 5−10 mA cm^{-2}	Pt		185
PPT	AN	0.1 M $LiClO_4$, 0.1 M $NaClO_4$, or 0.1 M Bu_4NClO_4	0.01 M	GS ox. at 10 mA cm^{-2}	Pt	UD in SE, washing AN	190
PPT	PC	0.03 M Et_4NPF_6	0.1 M	GS ox. at 1 mA cm^{-2}	ITO, Pt	AN rinse	191
PFPT	AN	1 M $Me_4NCF_3SO_3$	0.1 M	GS ox. at 5 mA cm^{-2}	FCP		192
PFAK (Poly(3))	NB	0.02 M Bu_4NPF_6	0.1 M	PS ox. at +1.7 V (SCE)	Pt		211
PTE	BN	0.1 M Bu_4NBF_4		CCV ox.	Pt	UD, washing AN, CH_3OH, H_2O, break-in cycles	194
PTE, PTB	AN	0.1 M Et_4NBF_4	0.1 M	CCV ox.	ITO	UD, washing	195
PBTI	CH_2Cl_2	0.1 M Bu_4NClO_4	~0.002 M	PS ox.	Pt, Au	UD in 0.2 M $LiClO_4$/H_2O	205,206
PIBT	AN	0.1 M PPh_4Cl	0.1 M	PS ox. at +1.0 V (Ag/Ag^+)	ITO	UD 0.0 V (Ag/Ag^+), treat. NH_3 aq., wash. OS, dry	203
				Poly(*p*-phenylene)			
PPP	AsF_5 VP	−	solid powders or single crystals of benzene oligomers	gas−solid reaction	−	doped as prepared	218
PPP	PC	0.5 M Et_4NPF_6 (Pt CE)	−	chem. polym. (Kovacic)		powder processed powder metallurgically to films to be doped electrochemically after chem. predoping	24,219,220
A: PPP	THF	0.5 M $LiClO_4$ (Li CE)	−	[ref 212−214]			

PPP (powder)	H_2O	14 M H_2SO_4 or 11.3 M $HClO_4$ or 8 M HBF_4	–	chem. polym. (Kovacic)	self-supported pellets	powder compressed with 7.5% soot, formation	39,216
PPP	PC	$LiClO_4$	–	chem. polym. (Kovacic)	Pt mesh	powder annealed (400 °C), then pressed on Pt	221
A: PPP	THF	$LiClO_4$	–				
PPP	NB	0.1 M $CuCl_2$ + 0.1 M $LiAsF_6$	1.2 M benzene	CCV ox. at +30 V (∼3 mA cm^{-2})	ITO, Pt	UD by cathodic red.	228,229,232
	BN	0.1 M $CuCl_2$ + 0.1 M $LiBF_4$	BP				
PPP	THF	$LiBPh_4$ or $NaBPh_4$	–	chem. polym. (Kovacic)	Ni screen (expanded)	powder (80%) + CB (10%) + Halar binder (10%) warm-pressed, cured (175 °C)	222
PPP	SO_2 (−40 °C)	0.1 M Bu_4NPF_6	0.02 M	CCV ox. at +2.3 V			18
PPP	NB	0.1 M $CuCl_2$ + 0.1 M $LiAsF_6$	1.2 M	CCV ox. at +30 V (3 mA cm^{-2})	ITO	UD (WE), benzene wash, vacuum anneal (24 h, 400 °C)	230,231
A: PPP	DME	1 M $NaPF_6$	PPP powder	electrochem. red. at $0 < E < +1$ V *vs* Na/Na^+	expanded Ni screen	mixing with carbon powder	223
A: PPP/Li_xPb A: PPP/Na_xPb				chem. polym. (Kovacic)	expanded Ni screen	mechanical blending of PPP powder, PE binder, alloy powder, pressing into screen	59,223−226
PPP	AN	0.1 M Bu_4NClO_4	0.002−0.005 M *p*-terphenyl	PS or PSw ox.	GC, Pt, ITO		234
				Poly(triphenylene)			
PTP	AN	0.1 M Bu_4NClO_4	0.002−0.005 M *o*-terphenyl or TP	PS or PSw ox.	GC, Pt, ITO		234
				Polyazulene			
PAz	AN	0.1 M Et_4NBF_4	0.0001−0.001 M	PS ox. ?	Pt		236
PAz	PC	0.1 M $LiClO_4$	0.05 M	GS ox. at 0.6−1.6 mA cm^{-2} (5 C cm^{-2})^d	Pt		239
PAz	PC	0.1 M $LiClO_4$	0.01 M	GS ox. at 0.3 mA cm^{-2} (1 C cm^{-2})^d (0.6−10 C cm^{-2})^d	Pt		237,238
P(Az-*co*-Py)	PC	0.1 M $LiClO_4$	0.05 M (Az+Py)	PS ox. at +4.2 V (Li/Li^+), 2 C cm^{-2}	Pt		240
				Polyfluorene			
PFl	AN	0.1 M Bu_4NBF_4	0.01 M	PS or PSw ox.	Pt, GC, HOPG	wash, dry when desired	243−245
PFl	MS	–	0.001−0.1 M	PS, GS or PSw ox.	Pt, W, GC		246
				Polyfuran			
PFu	AN +0.01 M H_2O	0.1 M ? Bu_4NBF_4	0.01 M ?	PS ox. at >+1.85 V (SCE)	Pt		166
PFu	$CHCl_3$/vapor interface	Lewis acid cat.	(VP)	$FeCl_3$ or $MoCl_3$ (in $CHCl_3$) for a chem. reaction	glass plate		165
				Polycarbazole			
PCz (film)	DMF	0.1 M Bu_4NClO_4	0.06 M	GS ox. at ≤2.5 mA cm^{-2}	Pt, Au		250−252
PCz (powder)	H_2O or organic solvent	–	?	chem. ox. with $NOBF_4$		washing, pressing pellets	29
PCz, PECz, PPCz	MeOH (75%) H_2O (25%)	5 M $HClO_4$	0.005 M	PS or PSw ox.	Au, Pt, GC	CV cycles	248,249
P(V)Cz (film)	AN	0.5 M $LiClO_4$ + 0.55 M H_2O	0.0085 M	PS ox. at +1.0 V to +1.2 V (SCE) or by potential pulses	Pt		253
P(Py-*co*-(V)Cz)	AN wet	Bu_4NClO_4	0.1 M	PS ox. at +1.2 V (Ag/Ag^+)	Pt		254
				A Tetrathiafulvalene-Substituted Polystyrene			
PS-PTTF	THF	–	–	grafting of PTTF to PS, dissol., spin-coating	Pt, ITO	formation (activation) cycles	255

Table 2.1 (Continued)

polymer electrode[b,c]	medium	electrolyte	concentration of monomer (or polymer)	polymerization method	substrate (contact)	pretreatment (conditioning)	ref
				Ferrocene-Substituted Polyethylene			
PVFc	CH_2Cl_2	0.1 M Bu_4NClO_4	0.01 M PVFc	free-radical polym. of VFc in benzene	NESA, Pt	precip. by CPE (~0.1 mA cm^{-2}), wash CH_2Cl_2, vacuum dry	256
	THF	–	2% (wt)		NESA, Pt	film casting, doping in AN electrolyte	
PVFc	benzene	–	1–3% PVFc	free-radical polym. of VFc in benzene	Pt	film casting	257
	–	–	–		Pt	pelletize powder with graphite (1:1)	
PVFc	CH_2Cl_2	–	~0.05% PVFc	commercial polymer	Pt	film casting, dry 2 min 118 °C	258
				Carbazole-Substituted Polyethylene			
PVCz (film)	CH_2Cl_2	0.2 M Bu_4NClO_4 or 0.1 M Bu_4NClO_4	0.005 M VCz	ox. by CPE (1–2 mA cm^{-2}) [+1.0 V (Ag/Ag^+)]	Pt	wash CH_2Cl_2, vacuum dry	259,260
PVCz (film)	AN	0.1 M $LiClO_4$	0.01 M	PS or PSw ox.	Pt rotated	AN rinse	261
PVCz	Tl–CH (1:1)	–	~0.1% PVCz	commercial polymer	Pt	film casting, wet with AN, dry, heat 90 °C	262
				Polyoxyphenazine			
POPh	H_2O	1 M H_2SO_4	0.001–0.002 M	PSw ox.	GC, Au	formation cycles	263–265
POPh	H_2O	1 M H_2SO_4		chem. ox. with $(NH_4)_2S_2O_8$, $FeSO_4$ as a cat.	GC	wash 1 M H_2SO_4, dry, dissolve acetone, spin or dip coat	264
				Polymer Adducts			
nylon-6/I_2 adduct	H_2O	ZnI_2		electrochem. I^- ox., I_2 absorption by nylon-6	CFP	mixing nylon-6 with 17 wt % carbon powder	267

polymer electrode	medium	electrolyte	preparation of active material	substrate (contact)	pretreatment (conditioning)	ref(s)
			Graphite, Pitch-Based Carbons			
A: C [PG]	VP	–	HT (1000 °C) of benzene vapor	Ni	press pyrolytic carbon into Ni screen, charge/discharge in WE	327
A: C [PCk] A: C [SG]	–	–	ground petroleum coke, ground graphite	Ni	prepare slurry from C powder with EPDM binder in CH, evaporate on substrate, dope electrochemically	331
A: C [NG]	–	–		SS screen	apply 97% NG + 3% PTFE binder to substrate, dry	318,328
A: C [PCF]	–	–	HT (up to 2900 °C) of pitch-based carbon fiber	Ni	dry bundle of C fibers having Ni wire as tie and current collector	343–345
A: C [PCk]	–	–	HT (up to 2900 °C) of pitch coke	Ni	press flexible sheet of PCk with 5% PTFE binder into Ni screen, dry	339
A: C [Gr]	see Table 3.1	see Table 3.1	dried graphite powder	Ni	prepare composite electrode from C and WE (2:3) on Ni screen	332
A: C [PCP]	–	–	pitch-based carbon powder (HT 1400 °C)	SS	prepare pellet with 5% PTFE binder, assemble SS cell	346
A: C [SG] A: C [PCk]	–	–		SS	prepare electrode with 6% PVDF binder on SS screen	333–335
A: C [SC, HC]	–	–	HT (550–2850 °C)	Cu	Slurry of C + 2% EPDM binder + 5% CB conducting filler dried on substrate, compressed, cut to coin cell electrodes	316
A: C [GW]	–	–	vapor-grown carbon whiskers, graphitized	Ni	mix C with PVDF in MP, spread paste on Ni screen, dry	348,349
A: C [Ck] A: C [Gr]	– –	– –	cokes ground, pyrolyzed; graphites used as received	C mat	prepare slurry with binder (8% PTFE or 6% PVDF or polymer-derived carbon) in acetone, apply to C fiber mat, dry, hot press	340

A: C [PCF]	–	–	mesophase pitch C fibers: HT at 900–3000 °C	SS	mix C + 3% PTFE binder, press into SS screen	330,341
A: C [PCk]	–	–				
A: C [SG, NG]	–	–				
A: C [NG]	–	–	grinding of NG, HT (1000 or 2800 °C) of MCMB	SS	mix C + PEO binder + AB conductive filler (6:3:1) to slurry in AN, spread onto substrate, dry	329
A: C [MCMB]	–	–				
A: C [PG]	VP	–	CVD of C from hydrocarbon vapor on porous cat.	Cu	Mix C with binder, coat onto substrate	350
A: C [MPC]	–	–	pyrene pyrolysis at 700 °C in pillared clay, demineralization	Cu	Slurry C with CB, PVDF binder in MP, dry, press	351
A: C [PCF]	–	–	mesophase carbon fiber mats (different degrees of graphitization)	Ni	surface treatments: vacuum + heat, partial air ox., electrochem., or silane coupling	347
A: C [SG, NG]	–	–		Cu	mix Gr powder with 10% PVDF binder, slurry with MP, spread onto substrate, dry	317
A: C [SG]	–	–		(Glass)	cast composite electrodes of C + PEO + $NaCF_3SO_3$ + C dispersant in AN onto glass, dry, cut	336
A: C [PCk]	–	–				
A: C [SB]	–	–				
			Heteroelement-Substituted Carbons			
A: BC_2N	VP	–	$CH_3CN + BCl_3$: CVD (1000 °C) followed by HT (best: 1500 °C)		pellets made with 10–20% PTFE binder	360
A: CN_z (z = 0.02–0.08)	VP	–	CVD ($C_2H_2 + NH_3$) 900–1000 °C, pyrolysis (C_6H_6, CH_3CN, C_5H_5N)	Cu	powders mixed with 10% PVDF binder in MP to slurry, spread on substrate, dried, cut	362
A: $B_{0.05}C_{0.95}$	VP	–	CVD ($C_6H_6 + BCl_3$) 900 °C, 5 Torr, 5 h	Cu	powder slurry prepared with 2% EPDM binder + 5% CB conductive filler, spread on Cu foil, dried, pressed, cut	316
A: B_zC_{1-z} (z = 0.03–0.17)	VP	–	CVD ($C_6H_6 + BCl_3$) 900 °C	Cu	powders mixed with 10% PVDF binder in MP to slurry, spread on substrate, dried, cut	361
A: $C_{1-z}Si_z$ (z = 0.02–0.10)	VP	–	CVD [$C_6H_6 + (CH_3)_2Cl_2Si$] 850–1050 °C	Cu	powders mixed with 10% PVDF binder in MP to slurry, spread on substrate, dried, cut	363
			Polyacenes			
C [ACF]	see Table 3.1	see Table 3.1	HT of cellulose or HT of phenolic resin	Pt	prepare felt, cloth, paper; dope electrochemically in WE	364,365
A: C[ACF]				Pt		
PAS-PF	VP	–	cure resole sol. to PF resin, mold sheet, pyrolyze 400–800 °C nonox. atm.		I_2 dope, RT	366,367
A: PAS-PF	THF	–			Na dope, Na naphthalide	
PAS-PF A: PAS-PF	see Table 3.1	see Table 3.1	cure resole sol. with added $ZnCl_2$ at 100 °C to PF resin, pyrolyze at 700 °C, wash with dil. aq. HCl sol., water	Pt	Au evaporation for contact, doping in WE	368–370
PAS-PF A: PAS-PF	see Table 3.1	see Table 3.1	as above (refs 368–370), but pyrolysis at 510 °C	SS	crush, mix powder with PTFE binder and CB conductive filler, press, evaporate Au contact, dope in WE	371
A: PAS-PF	see Table 3.1	see Table 3.1	as above (refs 368–371)	SS	Li^+ dope in WE	373
A: PAS-PF			as above (refs 368–371)		crush, slurry powder with 10% PTFE dispersion, press to film	372
PAS-SD [A: PAS-SD]	see Table 3.1	see Table 3.1	pyrolyze (“thermally structurize”) SD copolymer at ≤700 °C in inert gas or vacuum	SS screen	crush, mix with 3% PTFE, press into screen, vacuum dry, vacuum impregnate with WE	374,375
			as above, adding pore-forming salts Na_2CO_3 or $NaHCO_3$ or HCOONa or NH_2COONa to evolve gas during pyrolysis			376
A: PPFA	–	–	polym. furfuryl alcohol in aq. H_3PO_4, pyrolyze at 500 °C in N_2, HT at 1100 °C	SS	paste powder with 10% PVDF in DMF, press into screen, dry, cut	40,377,378
A: PPFA	–	–	Polym. furfuryl alcohol in aq. H_3PO_4 (5%) adding benzene (1:1) at 85 °C, HT black polymer at 1100 °C for 2 h in Ar	Cu	Crush, mix with 2% EPDM and 5% CB conductive filler, slurry in CH, apply to foil, dry, cut	316

Table 2.1 (Continued)

polymer electrode	medium	electrolyte	preparation of active material	substrate (contact)	pretreatment (conditioning)	ref(s)
Polyacenes (continued)						
A: PPPP	see Table 3.1	see Table 3.1	HT of Kovacic PPP (ref 214) at 700 °C in H_2 flow		prepare pellet with PE binder, dope electrochem. in WE	379
A: PPPP	see Table 3.1	see Table 3.1	as above (ref 379), pyrolysis at 700 or 775 °C		composite electrodes: mix C with WE	380
C_{60}-F	–	–	extract enriched Texas soot, purify chromatographically	Pt	deposit film from toluene sol.	381
C_{70}-F	–	–				
A: C [model]	–	–	carbonize acenaphthylene, coronene, phenolphthalein at 800 or 1000 °C in N_2, graphitize at 2780 °C	Ni	paste from C and 4% aq. PTFE dispersion spread into screen, pressed, vacuum dried	382
PPCNAc	VP	–	$CH{\equiv}C{-}CN$ thermally polym. at 200–1000 °C in N_2			390
TSPAN A: TSPAN	–	–	PAN powder and pore-forming salt (ref 376) dispersed 1:3 in DMF, HT first to 150–200 °C, then to final HTT (2 h) in N_2; wash, dry, crush	SS	press compressed TSPAN powder with 5–6% PTFE binder into SS grid, soak with alcoholic poly(vinylbutyral) binder sol., vacuum dry	385–388
PPAN	–	–	Courtauld's PAN yarn or fabric oxidized (230–290 °C, air), then pyrolyzed (900 or 1100 °C, Ar)	Ni, SS	fibers enclosed in Ni grid, cloth pressed against SS disk	389
PP	–	–	heat brominated sat. or unsat. heterocyclic monomers in vacuum (ex.: pyrrole, indole, thiazole, triazine) at 100–700 °C		form electrodes with binder	391
POAP	H_2O	0.1 M $HClO_4$ + 0.4 M $NaClO_4$	0.001 M monomer sol. ox. by PSw	Pt, GC, Au		392
POPDA	H_2O	0.5 M Na_2SO_4	0.05 M monomer sol. ox. by PSw	HOPG	rinse: H_2SO_4, then H_2O	393
A: BC_3N	–	–	PAN and BCl_3 heated to 400 °C in N_2, HT 1000 °C in N_2 (1 h) AN and BCl_3 heated to 1000 °C in N_2, HT 1000 °C in N_2 (1 h)		Li-doped with lithium naphthalide sol. in THF	394
A: BC_7N	–	–	ABS and BCl_3 heated to 400 °C in N_2, HT 1000 °C in N_2 (1 h) AS and BCl_3 heated to 400 °C in N_2, HT 1000 °C in N_2 (1 h)			394
A: $BC_{10}N$	H_2O	–	saccharose, boric acid, urea (polym.) reaction in water at 200 °C, then HT in N_2 at 1000 °C		pellets made with 10% PTFE binder	395
A: $BC_{10}NLi_{0.44}$	H_2O	–	same, adding LiOH		pellets made with 10% PTFE binder	395
A: $C_{1-z}P_z$	H_2O	–	PFA + H_3PO_4 cured at 160 °C, 1 h; carbonized at 500 °C, 1 h; milled; heat-treated 1 h (500–1300 °C)	Ni	pellets made with 10% PVDF binder, Ni screen	396
A: $C_{1-z}Si_z$	–	–	pyrolyze DOW 710 fluid (polymethylphenylsiloxane) at 900, 1000, 1100 °C in Ar	Cu	powder mixed with 10% PVDF binder in MP slurry, spread on substrate, dried, cut	363

[a] Abbreviations used in the tables are explained in a separate list. [b] A: *Anodes*; otherwise *Cathodes* [Note: Polymer cathodes are typically prepared in the doped (oxidized) form.] [c] The starting material for the preparation of $(CH)_x$ electrodes is neutral polyacetylene. This must be oxidized or reduced; the conditions used for the oxidation or reduction, the substrate used for mounting the polyacetylene, and the medium and electrolyte employed are indicated in the table. [d] Represents the number of Coulombs passed in the preparation of the cathode.

rial"). It further gives information concerning the media, electrolytes, methods used for the *n*-doping (reduction), and substrates (current collectors) used in the experiments. For the preparation of $(CH)_x$ electrodes, the starting material is acetylene polymerized typically by Shirakawa's method. The process of *n*-doping conducted by, *e.g.*, potentiostatic reduction as well as the degree of doping thus attained is described by the details given in the columns labeled medium, electrolyte, and pretreatment.

Degrees of doping, y, express the numbers (fractions) of unit charge per monomer unit of the polymer, except for polyacetylene, where CH is the unit referred to.

2.1. Polyacetylene (PAc)

Although alternative synthetic routes for polyacetylene, PAc or $(CH)_x$, starting, *e.g.*, from poly(vinyl chloride) exist,[490] a simple version of Shirakawa's method based on the catalytic polymerization of acetylene[41−43] was used for polymer preparation in a majority of the published work. Acetylene gas at pressures ranging from a few Torr to one atmosphere and concentrated solutions of Ziegler-type catalysts such as $Ti(OC_4H_9)_4{-}Al(C_2H_5)_3$ are needed for the polymerization reaction, in which a $(CH)_x$ film (or, at low catalyst concentrations, a $(CH)_x$ powder) is formed on surfaces wetted with the catalyst solution. Generally, *cis*-polyacetylene is formed when synthesized at low temperatures (≤ -78 °C).[43,44] During heating or electrochemical cycling of the *cis*-$(CH)_x$, the thermodynamically more stable *trans*-polyacetylene is formed. The polymer synthesized at -78 °C has a randomly oriented fibrillar structure with fibrils of 5 to 20 nm; the fibril diameter increases to 30 nm when synthesis occurs at $+100$ °C.[43,45] The specific surface area of polyacetylene films is typically about 40−60 $m^2\ g^{-1}$. Polyacetylene is oxygen sensitive and, therefore, contact with air should be avoided.[44]

Unfortunately, the Shirakawa-type polyacetylene typically contains residues of the Ziegler catalyst which cannot be washed out completely. A much more complicated method comprising several synthetic steps was therefore developed by Edwards and Feast.[46] It yields polyacetylene samples free of any contaminants.

Both positive and negative battery electrodes are typically constructed using as-synthesized (virgin, undoped) polyacetylene films. This material is insulating and has to be anion- or cation-doped by electrochemical or chemical oxidation or reduction to become electronically conducting before its utilization as a battery electrode.[5,21−23,44,45,47−56] The doping is often performed electrochemically after the battery is assembled. However, especially for the negative electrodes, the use of electrochemically prereduced (precharged) polymer is convenient. The reduction can for instance be performed potentiostatically in tetrahydrofuran (THF) containing $LiClO_4$ with metallic Li as the counter electrode.[45] This preparation leads to maximum Li^+ doping levels of $y \approx 0.1$ at $+0.7$ V *vs* Li/Li^+.[45]

Several doping procedures of polyacetylene were discussed by MacDiarmid and co-workers.[22] The electrochemical anion doping reaction (sometimes described as *p*-doping, since introduction of the anions into the polymer correlates with the appearance of positive charge in the polymer) can be formulated, *e.g.* for univalent anions, A^-, as follows:

$$(CH)_x + xyA^- \Leftrightarrow [(CH)^{y+}{\cdot}yA^-]_x + xye^- \quad (2.1)$$

The degree of polymerization is denoted as x; the doping level is y. The doping reaction with univalent cations (M^+), sometimes analogously described as *n*-doping of the polymer, can be formulated in a similar way:

$$(CH)_x + xyM^+ + xye^- \rightleftharpoons [(CH)^{y-}{\cdot}yM^+]_x \quad (2.2)$$

The degree of doping (doping level) can be estimated by integrating the current during an electrochemical experiment. A simultaneous *n*- and *p*-doping of two $(CH)_x$ electrodes can be achieved in a single electrochemical cell when using $(CH)_x$ both as the cathode and as the anode.[50]

A wide variety of solvents and electrolytes has been used for the electrochemical anion doping; *e.g.* propylene carbonate (PC), CH_2Cl_2, and THF with $LiClO_4$,[5,21−23,44,45,47−51,53−56] $LiBF_4$,[47,48] $(C_4H_9)_4NClO_4$,[22,49,50,57] and $LiAsF_6$.[45,56] The choice of the solvent seems to have insignificant influence on the anion doping level attained (Table 2.1).

The discovery that $(CH)_x$ can be reduced electrochemically to the *n*-doped state in the presence of alkali metal ions has resulted in a large number of publications on Li^+ doping.[5,23,44,45,49,50,55,58] The doping levels and, thus, the specific charge that can be imparted to polyacetylene negative electrodes appear to be higher when THF, rather than PC, is used as the solvent (Table 2.1). Sodium ion-doped $(CH)_x$ battery electrodes have also been prepared.[5] Moreover, *n*-doping by tetrabutylammonium ions has been achieved,[49,50,52] but somewhat lower doping levels were reported for them (Table 2.1).

Polyacetylene has also been used as an electron- and ion-conducting, electroactive matrix for finely dispersed alkali metal alloys of Pb or Al; the corresponding composites were proposed as negative electrodes for batteries.[59]

Performance data for PAc are described in section 3.1 and Table 3.1.

2.2. Polyaniline (PAni)

Until recently, polyaniline seemed to be the electroactive polymer most investigated for battery applications, as it satisfies most of the basic requirements of an electrode material in a light-weight battery. The polymer can be produced by anodic or chemical oxidation of aniline monomer. Sometimes low molecular mass material is solvent-extracted from the polymers produced.[60]

The electrochemical oxidation of aniline has been typically carried out in aqueous electrolytes, either galvanostatically,[61−67] potentiostatically,[68−71] or by cycling the potential of the substrate anode, *e.g.* between -0.2 or 0.0 V and $+0.8$ V *vs* SCE in 1 M HCl,[68,72] 0.1 M H_2SO_4,[73] or 1 M H_2SO_4.[67] Several electrolytes have been successfully used:

$HClO_4$,[16,60−62,65,71,74] HCl,[68,72] H_2SO_4,[67,69,70,75,76] CF_3-COOH,[74,76] and HBF_4.[20,63,64,66] The polymer has been deposited on substrates ranging from the metals Au,[64,75,77] Pt,[20,61,66,72,74,76] Pt-coated Ti,[65] and stainless steel[60,71,75,78] to SnO_2[68,72] and carbon.[63,67,69,70,75,77,79,80]

Polyaniline deposition starts with the formation of a rather compact globular structure, whereas porous fibrous structures are formed later on.[72,80,81] Soft and spongy PAni deposits have been reported to grow to maximum thicknesses of several millimeters at 1 mA cm^{-2} in an acidic perchlorate electrolyte.[65] At higher current density (5 mA cm^{-2}), aniline oxidation in 1 M $HClO_4$ resulted in fibrillar polyaniline[61] with fiber diameters of ~0.1 μm. Galvanostatic oxidation of aniline under similar conditions, but using 0.5 M H_2SO_4, gave a granular PAni structure with individual granules having a diameter of ~0.5 μm.[61] The fibril radius of porous fibrillar PAni produced galvanostatically in aqueous 2 M HBF_4 strongly decreased (from 1.3 to 0.2 μm) with increasing current density (0.01 to 5 mA cm^{-2})[66] while film porosity remained constant at about 50%. A denser cross-linked structure of the polymer was obtained when 0.25 mol % of *p*-phenylenediamine was added to the aqueous acidic aniline solution used for electropolymerization.[72,82]

Polyaniline preparation by chemical oxidation of aniline has also been investigated.[20,36,68,75,82−86] The oxidative polymerization of aniline in an acid produces the protonated, partially oxidized form of the polymer,[83] which can be converted to the corresponding base by treatment with alkali solution.[20,84,86] A particularly successful preparation was found to be by the oxidation of anilinium tetrafluoroborate with $Cu(BF_4)_2$ in acetonitrile.[87] Carbon black (about 5 wt %) and PTFE (5−20 wt %) are typically added to the chemically synthesized PAni powder in order to improve the electronic conductivity as well as the mechanical stability of the electrodes.[20,75,84] The blend can be rolled into sheets.[68] A similar approach was used by Geniès *et al.*,[36] who compressed a mixture of PAni and 20 wt % of acetylene black into a pellet while incorporating a stainless steel or aluminum grid as the mechanical support and current collector.

The electrochemical polymerization of aniline has also been studied in organic media such as propylene carbonate and acetonitrile (AN).[88−93] The electrochemical polymerization process occurring in acidified PC was systematically investigated while changing the aniline-to-acid ratio from 1:1 to 1:4. SEM investigations showed that smoother PAni layers grow at higher acid concentrations.[88] The properties of the PAni films produced in nonaqueous media have been compared with those produced in aqueous electrolytes.[91] The properties and performance figures are almost identical, but a polymerization in nonaqueous media has the advantage of excluding water from materials to be used in nonaqueous media.

The fact that PAni powder produced by electrochemical oxidation is soluble in *N*-methyl-2-pyrrolidone (MP) has been used to prepare PAni membranes.[65] The viscous solution of PAni in this solvent can be spread on a glass plate. A membrane is then formed using a “doctor blade” technique while the solvent is allowed to evaporate. With this procedure, PAni membranes have been produced in thicknesses of 15 to several tens of micrometers. The membranes can be removed from the glass plate after drying in vacuum at 100 °C. A similar procedure has been used for the preparation of PAni composite membranes incorporating carbon cloth[65] or DMcT (see below).

Sulfonated polyaniline, which behaves as a cation exchanger, can be prepared by sulfonation of emeraldine or polyaniline base.[94−97] Aniline and *o*-aminobenzenesulfonic acid can be copolymerized to a self-doped conductive polymer.[98] Another cation-exchanging PAni film was prepared as PAni-PSSA-*co*-MOEGA composite [PSSA = poly(*p*-styrenesulfonic acid), MOEGA = methoxy-oligo(ethylene glycol)-acrylate].[99] Layered PAni positive electrodes having an inner layer with small inorganic counterions and merely an outer layer with the larger organic polymeric counterions (anions) were prepared in order to obtain a lower electrochemical equivalent of the active material.[100,101]

Fiber-reinforced “multiporous” PAni was prepared in the form of large sheets for lithium ion batteries (with pyrolyzed polyimide carbon for the negatives).[102]

Recent polyaniline work has focused on the preparation of PAni composites with inorganic (FeOCl,[103] V_2O_5[104]) or organic (disulfide polymers[105−109]) active materials, which may in addition contain conductive fillers and/or binders. Results for the organic composites are presented in section 3.8. By way of example, a PAni-DMcT composite (DMcT = 2,5-dimercapto-1,3,4-thiadiazole) was cast as a film from a solution of these active materials in MP and combined with a lithium foil anode while plasticized acrylonitrile−acrylate copolymer served as the electrolyte.[107]

2.3. Polypyrrole (PPy)

Polypyrrole has been produced by potentiostatic and potential-sweep techniques;[110−118] galvanostatic[38,113,118−130] and chemical[29,37,131−135] oxidation routes have also been utilized for the polymerization of pyrrole.

For instance, with Pt or Au sheet as the substrate, polypyrrole was typically electropolymerized at 3.7−4.5 V *vs* Li/Li^+ in propylene carbonate or acetonitrile containing $LiClO_4$ and ≥ 0.2 M pyrrole monomer.[110,112,136] Actually, owing to the increased risk of polymer overoxidation during electrosynthesis, polymerization potentials of >3.9 V *vs* Li/Li^+ are not recommended.[136,137] Trace water (≤ 0.5 M) was added to the electrolyte in some cases to improve the electrochemical performance of the polymer film.[124,125,138] In AN, the more basic BF_4^- ion is supposed to lead to better quality PPy films than ClO_4^- as the counterion during electrochemical synthesis.[139] The amount of polymer deposited can be controlled in terms of the charge consumed for the polymerization.[110,140] A value of about 2.3 e^- per monomer unit is commonly found to be consumed in synthesis when working quantitatively.

Osaka *et al.*[90,91,141−143] developed a method of producing a favorable morphology of PPy normal to the substrate. Pyrrole is polymerized at a Pt electrode covered with nitrile butadiene rubber (NBR), where the polymer grows in the form of whiskers or poles from the electrode surface through the NBR film acting as a matrix that is removed with methyl ethyl ketone after polymerization. The electrochemical doping/undoping of NBR matrix-grown polypyrrole is claimed to be faster than that of common PPy. In another matrix approach, PPy was prepared by galvanostatic electrolysis at 0.5 mA cm^{-2} using 0.1 M pyrrole in alcoholic Nafion solution.[122] A SEM analysis showed that a PPy-Nafion composite film was formed which contained an agglomeration of PPy fibrils, again oriented in a direction normal to the electrode. Composite films with Nafion or PSS as the immobile counterion, which are cation-inserting, can readily be prepared from corresponding solutions[144−147] or by pyrrole electropolymerization into a preexisting Nafion film.[162]

Polypyrrole for battery electrodes can be produced by chemical oxidation, too, preferably at about 0 °C and under an Ar atmosphere, with oxidizing agents such as $Fe(ClO_4)_3$. When the PPy powder thus synthesized was pressed into pellets, conductivities of up to 20 S cm^{-1} were measured.[37]

In an aqueous $FeCl_3$ solution containing pyrrole and methylcellulose or hydroxypropylcellulose, a colloidal PPy composite material processable owing to its "solubility" is formed.[148] Composites based on polyethylene oxide (PEO) and PPy were prepared from the above aqueous colloidal dispersion by adding an aqueous solution containing PEO and electrolyte salt. Composite PPy-PEO electrodes were produced from this mixture by film casting on stainless steel current collectors.[132,133,149] Composites of carbon black (CB) and PPy can be obtained, both in aqueous and nonaqueous solutions, when pyrrole is electropolymerized in the presence of suspended carbon particles,[150,151] which are readily incorporated. These composites exhibit higher conductivity while CB may also contribute to the charge storage capacity. Conversely, in $PPy\cdot MnO_2$ composites the polymer acted as a conductive filler and also contributed between 10% and 60% of the combined charge storage capacity.[152,153]

Substituted polypyrroles such as poly-*N*-methylpyrrole[137,154−157] and polyindole[158] can be prepared in a similar manner as polypyrrole.

2.4. Polythiophene (PT)

A thorough review on the synthesis, mechanism of synthesis, structure, and properties of the polythiophenes was published in this Journal.[164] It will be of particular interest, among others, for its wealth of conductivity data.

Thiophene and its oligomers as well as substituted thiophenes can be polymerized chemically[38,165] or electrochemically. (Abbreviations and structures of these compounds are listed in Table 2.2.) Electrochemical oxidation of the monomers in nonaqueous solvents such as acetonitrile, propylene carbonate, CH_2Cl_2, and $C_6H_5NO_2$ containing $(C_4H_9)_4NClO_4$, $LiClO_4$ or other salts has been used to obtain polymer films on suitable conducting substrates.[127,166−175] Typically, galvanostatic synthesis at current densities[167,168,170] of 0.1−20 mA cm^{-2} from rather concentrated monomer solutions (0.1−5 M), frequently carefully deaerated with argon,[31,127,167,168,170,176] was used. The relatively high potential of 1.6 V *vs* SCE must be exceeded in order to form true polymer films on the electrode: this is 0.8 V more positive than in the case of pyrrole oxidation to polypyrrole films.[166] Approximately the same degree of oxidation as in the PPy case (about 0.3 charges per monomer unit) is attained upon electrochemical synthesis.[168]

As-synthesized PT films exhibit conductivities which, depending on the precise synthesis conditions, may exceed 100 S cm^{-1}. Such "doped" films were found by some workers not to be stable in air or protic solvents such as water and methanol, but neutral ("undoped") films can be heated in air up to 200 °C without decomposing.

Careful observers at Neste Oy in Finland[177] found that dry PT-ClO_4 films are hazardous when heated to temperatures above 100 °C or strongly compressed, although entirely stable under the normal conditions encountered in their use as active electrodes in secondary lithium batteries. They recommend that a safer doping agent than perchlorate be selected.

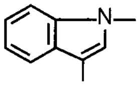
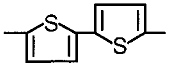
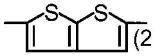
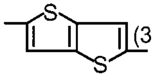
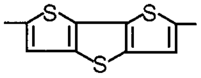
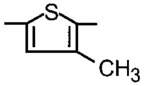
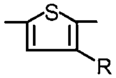
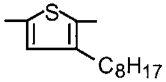
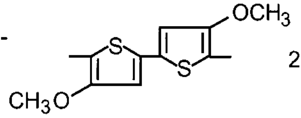
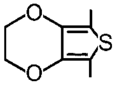
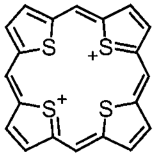
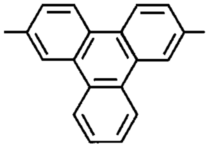
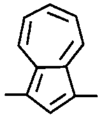
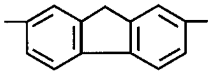
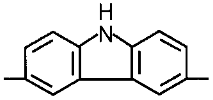
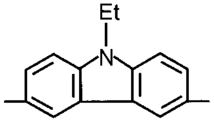
In contrast to polypyrrole, the preparation of good-quality polythiophene films must be performed in dry solutions. The polymer cannot be formed electrochemically when the electrolyte contains about 1 M H_2O.[176] Polymers prepared at 5 °C show a higher conductivity than those prepared at room temperature or at 40 °C.[31] Dimers (bithiophene) and trimers (terthiophene) as the starting material yield more regular polymers.[171,172,174,175] Terthiophene yields a polymer which can be *n*-doped more easily.[178]

Poly(3-methylthiophene) (PMT) has been investigated as much as the unsubstituted polythiophene. As-synthesized PMT films were five times more conductive than similar PT films and superior mechanically, too.[170] *p*-Doped films were stable in air;[179] their work function varied little with time.[180] *n*-Doped films were unstable in air, according to their work function change.[180] The morphology of the polymer films depends on the current density used for synthesis. At high current densities (up to 10 mA cm^{-2}) a granular morphology with an average grain diameter of up to 13 μm is obtained.[181,182] Sato *et al.*[183] must be mentioned for a careful optimization of electrochemical polymerization conditions for 3-methylthiophene (see Table 2.1). Temperatures during synthesis should be between −15 and +5 °C, according to the conductivity criterion. The superiority of PMT over PT could be shown to be due to clean 2,5-polymerization.[183]

The reproducibility of preparation and properties of PMT films was checked for three substrates and three film thicknesses among a set of three laboratories,[184] in order to define the parameters for optimization of the properties.

Longer straight-chain 3-substituents were found to be even more favorable for certain polymer properties: between *n*-heptyl and *n*-nonyl, the conjugation length, porosity, and electrochemical reversibility of the poly(3-alkylthiophene)s were found to exhibit

Table 2.2. Structures and Abbreviations of Materials in the Text and Tables

Abbre-viation	Name	Formula monomer unit	MW monomer	MW monomer unit in polymer
PIn	Polyindole		117	115
PT	Polythiophene Polythienylene		84	82
PBT	Poly (bithiophene) Polythiophene		166	164 82
PTT	Poly (thienothiophene)	 (2,3-b)	140	138
		 (3,2-b)	140	138
PDTT	Poly (dithienothiophene)	 (3,2-b; 2',3'-d)	172	170
PMT	Poly (3-methylthiophene)		98	96
PAT	Poly (3-alkylthiophene)		83+MW_R	81+MW_R
POT	Poly (3-n-octylthiophene)		196	194
PMOT	Poly (4,4'-dimethoxy-bithiophene)		226	224
PEDOT	Poly (3,4-ethylenedioxy-thiophene)		142	140
TTP	Tetrathiaporphyrin		110	108
PPP	Poly (p-phenylene) Poly (1,4-phenylene) Polybenzene Polyphenyl		78	76
PTP	Poly (triphenylene)		228	226
PAz	Polyazulene Poly (bicyclo[5,3,0]deca-pentaene)		128	126
PFl	Polyfluorene		166	164
PFu	Polyfuran		68	66
PCz	Polycarbazole		167	165
PECz	Poly (N-ethylcarbazole)		195	193

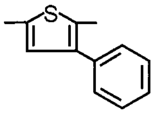
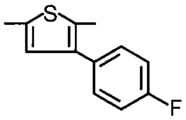
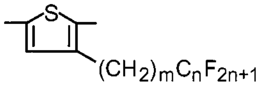
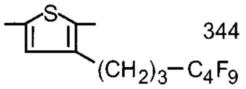
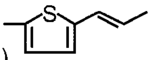
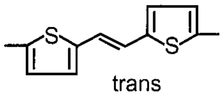
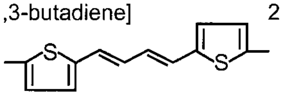
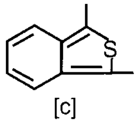
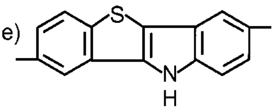
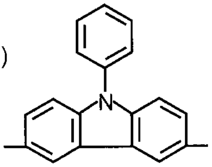
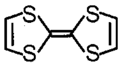
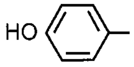
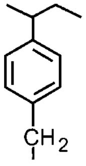
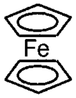
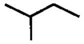
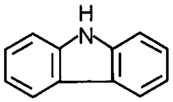
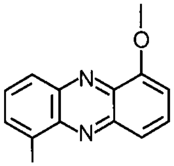
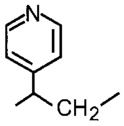
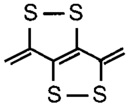
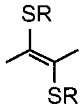
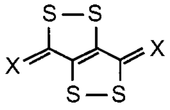
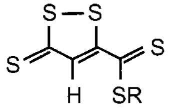
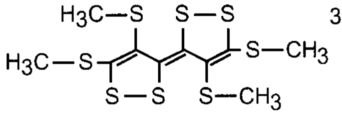
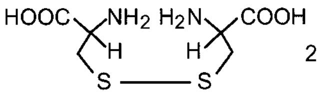
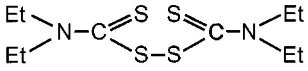
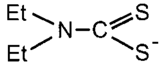
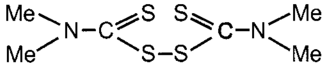
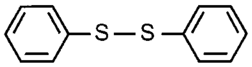
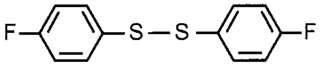
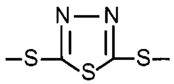
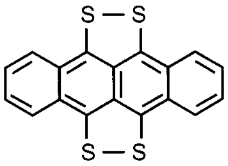
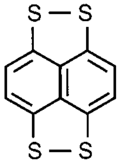
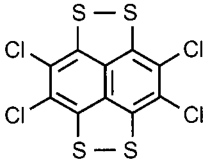
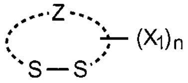
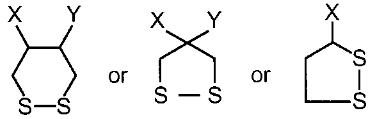
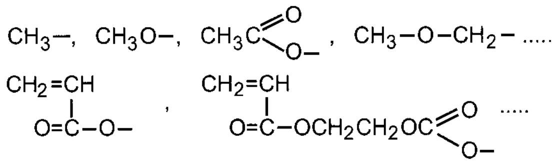
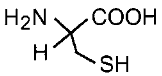
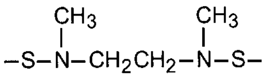
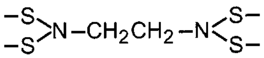
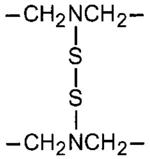
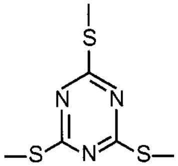
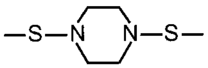
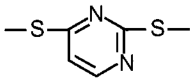
PPT	Poly (3-phenylthiophene)		160	158
PFPT	Poly (3-[4-fluorophenyl]thiophene)		178	176
PFAK	Poly ([fluoro-3-alkyl]thiophene)	 $(CH_2)_mC_nF_{2n+1}$		
	Poly (3) [ref 211]	 $(CH_2)_3-C_4F_9$	344	342
PTV	Poly (2,5-thienylene vinylene) (Poly[acetylene-co-thiophene])		110	108
PTE	Poly [1,2-di(2-thienyl) ethylene]		192	190
PTB	Poly [1,4-di(2-thienyl)-1,3-butadiene]		218	216
PIBT	Polyisobenzo[c]thiophene Polyisothianaphthene Polyisothionaphthene		134	132
PBTI	Poly(benzothienoindole)		223	221
PPCz	Poly (N-phenylcarbazole)		243	241
TTF	Tetrathiafulvalene		204	203
P-	Phenoxy-			296
PSP-	Polystyryl-Phenoxy-			414
Fc	Ferrocene Dicyclopentadienyliron		186	185
PV-	Polyvinyl-			212
Cz	Carbazole		167	166
PV-	Polyvinyl-			193
POPh	Polyoxyphenazine		196	194
PAm	Nylon-6	$-CO-(CH_2)_5-NH-$		113
	I_2-Nylon 6 1:1			367

Table 2.2 (Continued)

Abbreviation	*Name*	*Formula monomer unit*	*MW monomer*	*MW monomer unit in polymer*
PTHF	Poly (tetrahydrofuran)	 (opened)	72	70
	I_2-PTHF 1:1			324
PVP	Poly (vinylpyridine)		105	105
Ru-	Ru (bipy)$_2$ Cl - PVP 1:1			553
$(CS)_n$	Carbon-sulfur polymer		[44 or 176]	[44 or 176]
DATA	Dialkylthioacetylene polymer		90 + 2MW$_R$	88 + 2MW$_R$
DTDT	Dithiolodithiol X = S or N-Acyl		240 (X=S)	-
DT-TCA	Thioxodithiolyl-dithiocarbonic acid alkyl ester		224 R=CH_3	-
MTBT	Tetramethylthio-bis(dithiol)		388	-
	Cystine (D−)		240	-
TETD	Tetraethylthiuram disulfide		296	-
DEDC	Diethyldithio-carbamate		148	-
HEDS	Bis(hydroxyethyl) disulfide	$HOCH_2CH_2SSCH_2CH_2OH$	154	-
EEDS	Bis(ethoxyethyl) disulfide	$EtOCH_2CH_2SSCH_2CH_2OEt$	210	-
TMTD	Tetramethylthiuram disulfide		240	-
DMS	Dimethyl disulfide	$CH_3-S-S-CH_3$	94	-
PDS	Diphenyl disulfide Phenyl disulfide		218	-
FPDS	Bis(fluorophenyl) disulfide		254	-
X0	Bis(2-mercapto-ethyl) ether polymer	$-SCH_2CH_2-O-CH_2CH_2S-$	138	136
X1 DMcT	Dimercaptothiadiazole polymer		150	148

TTT	Tetrathiotetracene Tetrathionaphthacene		352	-
TTN	Tetrathionaphthalene		252	-
TCTTN	Tetrachlorotetrathio-naphthalene		390	-
	Cyclodisulfide, general			
	Cyclodisulfides, more specific			
	X, Y =  CH_3-, CH_3O-, $CH_3C(=O)O-$, CH_3-O-CH_2- ....., $CH_2=CH-C(=O)-O-$, $CH_2=CH-C(=O)-OCH_2CH_2OC(=O)O-$			
	Cysteine		121	120
X2	N,N'-dimethyl-N,N'-dimercaptoethylene-diamine polymer	 $-S-N(CH_3)-CH_2CH_2-N(CH_3)-S-$	152	150
X3	N,N,N',N'-tetramercapto-ethylenediamine polymer	 $(-S)_2N-CH_2CH_2-N(S-)_2$	188	184
X4	Polyethylenimine, –S–S– crosslinked		152	148
X5	2,4,6-Trimercaptotriazole polymer Trithiocyanuric acid polymer		177	174
X6	N,N'-Dimercapto-piperazine polymer		150	148
X7	2,4-Dimercaptopyrimidine polymer 2,4-Dithiouracil polymer		144	142
X8	1,2-Ethanedithiol polymer	$-S-CH_2CH_2-S-$	94	92
X9	Bis(2-mercapto-ethyl) sulfide polymer	$-S-CH_2CH_2-S-CH_2CH_2-S-$	154	152

maxima. Polymerization always gave cisoid structures. Chain branching close to the thiophene ring, as in 3-(2-propyl)thiophene, completely prohibits polymerization. Chain branching far from the thiophene ring does not prohibit polymerization but instead can be used to produce lower-density polymers in a controlled manner.[185]

Longer-chain poly(3-alkylthiophene)s chemically prepared[186] exhibit fusibility, solubility, and gel characteristics. Interesting alkoxy- and alkylenedioxy-substituted polythiophenes were synthesized by Heinze *et al.*[187−189] Their poly(4,4′-dimethoxybithiophene) (PMOT) and poly(3,4-(ethylenedioxy)-thiophene) (PEDOT) exhibited an extreme electrochemical stability in cyclic voltammetry.

A phenyl group,[190,191] better yet a *p*-fluorophenyl group[192] in the 3-position of thiophene is instrumental for the preparation of polythiophenes which can insert both anions and cations (*p*- and *n*-doping). Similar properties were expected for vinylene thienylene polymers: one named poly(thienylene vinylene) (PTV) which has vinylthiophene as its monomer unit, was prepared by a rather complex chemical route,[193] and can be regarded as ABAB-type acetylene−thiophene copolymer, and two others named poly(1,2-dithienylethylene) and poly(1,4-dithienyl-1,3-butadiene) for their constituent monomer units, which were prepared electrochemically[194−196] and can be regarded as ABBABB and AABBAABB-type acetylene−thiophene copolymers. (The names are those used in the original papers.) The −CH=CH− units enhance the coplanarity of the polymer chain and the effective conjugation length.[194]

The macrocyclic, nonplanar tetrathiaporphyrin which could be interpreted as cyclic tetramer of 2-methylene-substituted thiophene was prepared by a chemical route[197] as a dication. Its ion-insertion and deinsertion properties could be interesting but, of course, its conjugation length is minimal.

Composite polythiophene cathodes were prepared by dissolving a soluble fraction of chemically synthesized polythiophene in $CHCl_3$. Carbon powder (20 wt % relative to the polymer) was dispersed in this solution and the resulting suspension spread on a carbon fiber plate for drying. This sheet with composite film was then used as a positive electrode material capable of forming iodine adducts.[38]

The numerous polymers made in basically similar fashion from condensed species with two and more aromatic rings (at least one of them thiophene) and their derivatives are cited in section 3.4 and/or Table 3.1. Many of them require lower current densities, lower oxidation potentials, and lower monomer concentrations for their electrochemical synthesis (refs 174, 175, and 198 for PTT; refs 174, 175, and 199−202 for PDTT). The PDTT described most recently[202] could be *n*-doped. Poly(isobenzo[*c*]thiophene) or poly(isothianaphthene) is another polythiophene for which *n*-dopability is expected. In this instance, it was found that the spin density is extremely low as compared to the doping level, suggesting that the carriers are mostly spinless bipolarons.[203] The *n*-doping was recently demonstrated.[204]

A curiosity of sorts is the polymer of benzothienoindole, called thionaphthene-indole by the authors.[205,206] Its electrochemical polymerization (head-to-tail[206]) gives a protonated product which is proton-conducting when it contains 10% water.

2.5. Poly(*p*-phenylene) (PPP)

Poly-*p*-phenylene is the only benzene polymer significant as an ion-inserting organic battery material. Polybenzene would be a more appropriate name when considering the naming of other polymers in this review, yet it was rarely used. Nomenclature and chemical synthesis have been reviewed.[212]

Oxidative cationic polymerization of benzene under remarkably mild conditions (aluminum chloride as a Lewis acid catalyst, cupric chloride as an oxidizing agent, and a small amount of water) produces high surface area PPP powder within 30 min at 35 °C.[212−214] The product is infusible, insoluble, and stable in air below 400 °C and in inert atmosphere below 550 °C.[212] It has a high degree of orientation: the rings are nearly fully coplanar and very purely *p*-polymerized, which is believed to be the reason for the good crystallinity and for electrochemical intercalation properties resembling those of graphite.[39,215−217]

Doped PPP suitable for electrochemical testing or uses has been prepared by the reaction of terphenyl and similar oligomers with AsF_5,[218] by chemical predoping followed by electrochemical doping of the compressed Kovacic powder product,[24,219,220] by electrochemical doping of PPP powder annealed at 400 °C and then pressed to pellets with a Pt screen,[221] by electrochemical doping of powder cold-pressed to pellets with carbon black,[39] or by electrochemical doping of pellets produced by hot-pressing from powder mixed with carbon black and binder.[222]

Composite PPP−metal alloy electrodes have been prepared by mechanical blending of PPP powder, PE binder, and alkali−lead alloys and pressing into screens.[59,223−226] Formation cycles proved to be beneficial for all electrodes involving PPP powder of chemical origin.[39,216,225]

Early attempts at an electrochemical polymerization of benzene failed to give PPP films of good quality,[227] until Japanese workers added cupric chloride to the usual salt−organic solvent system.[228−232] Another successful approach was found when working at low temperatures in liquid SO_2.[18] Liquid hydrofluoric acid was used to produce PPP, but is inconvenient as a medium for electrochemical synthesis, owing to its corrosiveness and health hazards.[18]

Considering the importance of a graphitelike structure in the highly regular PPP, it is not surprising to find that substitution is highly detrimental for the properties of benzene polymers.[233] Somewhat surprisingly, biphenyl also yields inferior PPP qualities.[228,234] From *p*-terphenyl, a structure is produced which contains triphenylene islands in addition to PPP segments,[234] so again no improvement can be realized.

In studies involving different synthesis potentials, Meerholz and Heinze[235] found that cross-linking and thus a less regular structure of the polymers is favored at more positive potentials. Long, ideally linked chains are found at less positive potentials.

2.6. Other Conducting Polymers

Conducting polymers of variable electrochemical activity have been produced from many aromatic compounds other than those considered in earlier chapters, notably from azulene, fluorene, and carbazole. These and a few others will be considered briefly in this chapter (and section 3.6). Synthesis conditions are summarized in Table 2.1. Structures and abbreviations are given in Table 2.2.

2.6.1. Poly(triphenylene) (PTP)

Triphenylene (9,10-benzophenanthrene) was found to polymerize anodically without branching to a poly(*p*-phenylene) in which each consecutive pair of biphenyl units is bridged by a benzene ring.[234] A quinonoid structure was formulated for this polymer.

2.6.2. Polyazulene (PAz)

Azulene has been polymerized electrochemically.[166,236–239] The conditions listed for the work of Naoi *et al.*[239] in Table 2.1 constitute the result of optimization in one electrolyte, presumably selected arbitrarily. Random copolymers of azulene and pyrrole can readily be produced under similar conditions.[240,241]

The PAz films are very stable even in air.[236] For their structure, a *trans* configuration of alternate seven-membered rings along the chain of linked five-membered rings was proposed.[242]

2.6.3. Polyfluorene (PFl)

Fluorene (both the unsubstituted, the 9-monosubstituted, and the 9,9-disubstituted) have been oxidized anodically to slightly conducting polymers. Their chains form by coupling at the 2- and 7-position.[243–245] From coulometry during and after synthesis and from chemical analysis, doping levels between 0.5 and 1 were deduced. All these fluorene polymers are sensitive to overoxidation. The polymers of unsubstituted and 9-monosubstituted fluorene are sensitive as well against cathodic reduction. The voltammetric behavior is rather complex in the organic medium of the above work but was found to be much less complex in a room-temperature molten salt.[246]

2.6.4. Polynaphthalene (PNap) and Polyanthracene (PAnt)

The composite electrolytes containing $CuCl_2$ in addition to a suitable organic solvent and dopant ion electrolyte which were successful for electrochemical benzene polymerization have been used for the polymerization of naphthalene and anthracene.[247] The resulting polymers had much lower conductivities than PPP (0.1 mS cm^{-1} for PNap, 1 mS cm^{-1} for PAnt), although were said to be reversibly *p*-dopable.

2.6.5. Polyfuran (PFu)

Tourillon and Garnier[166] found furan to be the heterocycle with the highest oxidation potential (pyrrole, +0.8; thiophene, +1.6; furan, +1.85 V *vs* SCE), and obtained well-conducting films in AN + 0.1 M Bu_4NBF_4. Yoshino *et al.*[165] produced similar films by a chemical method by exposing the monomer vapors to a liquid film of Lewis acid solution ($FeCl_3$, $MoCl_3$) present on a glass plate, but their PFu product was far less conducting than PPy and PT. Nishio *et al.*[29] made PFu by chemical oxidation with $NOBF_4$.

2.6.6. Polycarbazole (PCz)

Polycarbazole, too, can be prepared chemically or electrochemically. Chemical synthesis, like that of PFu, was successful with nitrosyl tetrafluoroborate ($NOBF_4$) as an oxidant.[29] The electrochemical preparation of polycarbazoles, *N*-substituted or not, is successful in aqueous acidic media by CV scans or potentiostatic oxidation. Continued CV cycles serve to activate the polymer but must not be extended beyond the first (reversible) oxidation peak. Only poly(*N*-ethylcarbazole) was more stable at more anodic potentials.[248,249]

Electrochemical synthesis of unsubstituted PCz was also performed galvanostatically in DMF with $(C_4H_9)_4NClO_4$ as an electrolyte.[250,251] Current densities higher than 2.5 mA cm^{-2} gave poorly adhering films. Galvanostatic pulses, preferably asymmetric,[252] or deposition in a magnetic field[251] yield higher-quality films (smoother, pinhole-free).

N-Vinylcarbazole, when subjected to aqueous polymerization conditions, rather than polymerizing loses the vinyl group hydrolytically.[249] In acetonitrile, an addition of small amounts of water to the electrolyte (*e.g.*, AN + 0.5 M $LiClO_4$) inhibits the undesirable chemical polymerization of vinylcarbazole via the vinyl groups: the polymer is then linked via the benzene rings.[253] For poly(vinylcarbazole) as a polyvinyl-type polymer, see section 2.7.

The synthesis of pyrrole/*N*-vinylcarbazole copolymers has been described.[254] Here the monomers may link up through their aromatic sites, but vinyl group linkage as a competing or alternative reaction ought to be considered, depending on the conditions employed. Water was added in some of the different routes to copolymers[254] to prevent the formation of nonconducting PVCz[253] precipitating in dry AN.

2.7 Redox Polymers

Redox polymers is a term of distinction used in the present section (and section 3.7) for a group of polymers with an ordinary, nonconjugated backbone and redox centers localized, for the most part, in pendant groups. The redox centers, not the polymer chain, govern the redox behavior. Conductivity arises when these centers can exchange charge, *e.g.*, on account of mixed valency.[255–257] In contrast, the polymers of previous sections (2.1 to 2.6) have a conjugated backbone where optional groups (substituents) merely modify the spectrum of redox states offered by the polymer chain.

Redox polymers to be considered include the polyvinyl polymers with tetrathiafulvalene, ferrocene, and carbazole groups, polyoxyphenazine, and the adduct-forming polyamides. Selected examples reported in the literature will be considered so that some comparison and perspective can be gained. Synthesis conditions are summarized in Table 2.1; abbrevations and structures can be found in Table 2.2.

2.7.1. A Tetrathiafulvalene-Substituted Polystyrene (PS-PTTF)

Tetrathiafulvalene (TTF), more precisely its *p*-hydroxyphenyl derivative, constituted the pendant groups in a polystyrene (PS) used by Kaufman *et al.*[255] for the preparation of electroactive modified electrodes. The polymer was applied to the substrates by spin coating from its THF solution. In films of different thickness, TTF groups were spaced about 8 Å apart (which translates to a molar concentration of 3.5 M for these redox groups). Facile electronic conduction through the amorphous films was explained in terms of electron exchange between these closely spaced TTF groups. The electron movement along these groups is accompanied by counterion movement through the polymer matrix.

2.7.2. Ferrocene-Substituted Polyethylene (PVFc)

Shirota *et al.*[256] transformed poly(vinylferrocene) (PVFc) dissolved in dichloromethane to the insoluble doped polymer (polyethylene with ferricenium salt and ferrocene as mixed-valence substituents) by potentiostatic oxidation, which led to precipitation on the electrode. Depending on the conditions, these films had degrees of doping of 0.59 to 0.91 and very modest conductivities inversely depending on the degree of doping. Insulating neutral polymer produced by film casting from a THF solution of PVFc was also transformed into conducting doped polymer by electrochemical oxidation in AN electrolyte; here a degree of doping of 0.22 was attained.

Iwakura *et al.*[258] cast their films from CH_2Cl_2 solutions, and recalled that for such films a redox site concentration of about 2 M had been reported previously.

2.7.3. Carbazole-Substituted Polyethylene (PVCz)

N-Vinylcarbazole when subjected to controlled-potential electrolysis in dry nonaqueous solutions polymerizes via its vinyl group to poly(vinylcarbazole), PVCz, an *N*-carbazole-substituted polyethylene. Doped polymer is obtained at once.[259,260] Its conductivity was found to be mediocre. Poor solubility of the oxidized (doped) product was attributed to partial cross-linking via the pendant carbazole groups. (This cross-linking is electrochemically analogous to the formation of S–S bridges in the redox dimerization and redox polymerization materials to be discussed in sections 2.8 and 3.8.)

More recently, kinetic control of the potentiostatic growth of PVCz films by the use of rotating electrodes was found to yield compact, well-adhering films.[261] Electrodes with PVCz have also been produced by film casting from true solutions of the polymer in toluene–cyclohexanone mixtures.[262]

2.7.4. Polyoxyphenazine (POPh)

Polyoxyphenazine or polyphenazenylene oxide, generally reported as poly(1-hydroxyphenazine), can be generated electrochemically (usually in potentiodynamic scans) in strongly acidic aqueous solutions by the polymerization of 1-hydroxyphenazine (1-phenazinol).[263-265] Polymerization occurs via the formation of ether bridges;[265] hence, the monomer units do not form a conjugated chain. A certain overlap of the oxygen lone-pair electrons with the aromatic sp^2 electrons is of course possible and was inferred as well from the position of a (poorly defined) IR band at 1220 cm^{-1};[266] but essentially, the redox centers are isolated.

The POPh can also be produced chemically as a brown powder by persulfate oxidation in similar solutions containing $FeSO_4$ in catalytic amounts.[264]

2.7.5. Polymer Adducts (PAm•I_2, PTHF•I_2)

Certain nonconducting polymers have an affinity to electroactive molecules such as I_2, with which they form adducts. When combined with a conductive filler, they can then be used as positive electrode materials in rechargeable batteries. Thus, a rechargeable electrode was made by preparing a 5:1 composite from nylon-6 (a polyamide, PAm, in the form of powder or of solution in formic acid) and carbon black, and using a carbon fiber plate as the current collector.[267,268] A 5:1 polymer–carbon composite was similarly made using poly(tetrahydrofuran) (PTHF),[268] a linear polymer produced chemically[269] from THF via chain opening which should more properly be regarded as a polyalkylene oxide, and not named poly-THF.

These two polymers were found to be superior to others (such as polymethacrylate) in their ability to form I_2 adducts when operated as the rechargeable positive electrode in aqueous $Zn/ZnI_2/I_2$ systems.[268]

2.7.6. A Polymer Complex (PVP–Ru)

Ruthenium, in the form of its bipyridine-complexed ions, can be incorporated into poly(vinylpyridine) (PVP) to form a PVP–Ru complex. A film of this material can be formed on a substrate (GC, Au, Pt, *etc.*) from solutions by spin coating.[270] Binding of the Ru complex occurs when the pendant pyridine in PVP becomes one of the Ru ion ligands. In the paper cited, one ruthenium complex was bound to one out of four to 20 PVP monomer units.

2.8 Sulfur and Redox Polymerization Electrodes

Sulfur as a heteroelement in an important group of conducting polymers storing charge by delocalization along the polymer chains has been considered in section 2.4. In the present section, sulfur will be discussed as an electropositive element in molecules where bond breaking/bond making is the basis for charge storage. In both cases, charge-compensating counterions must be taken up or repelled in the process.

In the polythiophenes, the level of charge storage is related to the degree of doping. In the compounds to be discussed below, it is related to the extent to which the polymerization/depolymerization reaction occurs. The maximum of charge storage would evidently be attained in a device where the oxidation state of sulfur changes from 0 to −2, which would correspond to an equivalent mass of 16 g $faraday^{-1}$. In practical systems, at most one electron is exchanged per sulfur atom, and usually less than one electron. Refer to Table 3.2 for further figures calculated to provide comparison, even though on the basis of certain arbitrary assumptions concerning the values of y and n for representative electroactive materials.

Table 2.2 provides the names, abbreviations, structures and "monomer" molecular weights for a number of the sulfur compounds prepared or used for charge storage and mentioned in the papers and patents cited in sections 2.8 and 3.8. Not all are polymers: their inclusion was justified by analogies in the charge-storage reaction. Data for preparation have not been collected in Table 2.1; data for performance are collected so far as available in Table 3.1.

2.8.1. Activation of Sulfur (–S–)

The best-known example for sulfur activation is the sodium/sulfur cell. In it, sulfur reactivity is obtained by working at high temperatures (about 350 °C) with compounds Na_2S_x stored in a matrix of special graphite felt. Sodium ions cross from the sodium anode through the β-alumina electrolyte into the "sulfur" electrode where, during discharge, Na_2S_x is converted to $Na_2S_{x-\delta}$ (x is about 5, δ is about 2). The sodium polysulfide melt takes up sodium ions during discharge, and gives them off during charging. A closer look at this system is beyond the scope of this review.

Problems such as those related to corrosion and operating safety have induced electrochemists to search for ways to activate sulfur at lower temperatures. A few unconventional approaches will be mentioned in the remainder of this section, while sections 2.8.2 and 2.8.3 will deal with the redox dimerization and polymerization electrodes, respectively.

Workers at Berkeley[271] achieved satisfactory activation in half-cells for redox batteries when using moderately alkaline (pH 12) aqueous sodium polysulfide solutions (1.3 M S^{2-}, 1 M S^0) with some DMF cosolvent (13 mol %) as a dissolved cathode material flowing through a porous, catalytically activated current collector electrode (a stack of Ni screens plated with Co catalyst, or a stack of expanded Mo sheet coated with MoS_2 catalyst) at 25–50 °C. In their active material, S_4^{2-} was found to be the major polysulfide species.

Much earlier, workers at Tel Aviv University[272] had built nonaqueous cells where a sulfur-loaded porous current collector (PTFE-bonded carbon in expanded Ni) was combined with a lithium anode in an organic solvent (1:1 THF–toluene) containing lithium polysulfide (about 0.3 M Li_2S_8) as additional cathode material and 1 M $LiClO_4$ as an electrolyte salt.

In these two examples, during discharge the cations are taken up by the dissolved electrode material. Conceptually, this is a situation intermediate between the conventional batteries and batteries with ion-inserting/deinserting electrodes.

It is interesting to mention a recent paper where electrochemical sulfur activation at Pt electrodes was utilized to produce electrophilic species S^{2+} which can react with nucleophiles to thioorganic compounds (monosulfides, trisulfides).[273] Here the sulfur-impregnated carbon electrode exhibited either an entry of anions or exit of cations during oxidation, just as would a battery electrode, since sulfur oxidation occurred within the electrode.

The electrochemistry of sulfur adsorbed (for its activation) on carbon was reviewed and studied further by Kavan *et al.*[274] Different carbon materials were prepared from lithium amalgam-reduced PTFE, reacted with sulfur, made into electrodes with PTFE-carbon black mixture, and tested in cells with 1 M $LiClO_4$ in PC as the electrolyte. Solid-state cells were prepared with $P(EO)_8{\cdot}LiClO_4$ as the electrolyte, which was also added to the electrodes.

Degott[275] prepared active materials: $(CS_{0.7})_n$ by the reaction of polysulfide with poly(chlorotrifluoroethylene), and $(CS_x)_n$, where $x = 0.15-1$, by reaction of elemental sulfur with the highly reactive carbon obtained by (electro)chemical reduction of PTFE. Physical characterization led him to propose that chains of sulfur heterocycles are present (ideal formula: $(CS)_n$) and that C–C cross-linking at the stage of synthesis leads to sulfur substoichiometry.

Reduction of halogenated carbon polymers in the presence of sulfur can be visualized as passing through a stage resembling polyacetylene. Perichaud and Le Mehaute[276] prepared polyacetylene by reduction of PVC and heated the product with elemental sulfur to obtain a polyacetylene polysulfide; they speak of an attachment of polysulfide chains to the polyacetylene chain, which would lead to a structure different from that of Degott's $(CS)_n$. Electrodes for tests in cells were then prepared with the addition of acetylene black and PTFE dispersion. Sulfur-modified polyacetylene for rechargeable batteries was also claimed by Stiehl *et al.*[277]

A chemically more definite form of such a compound, apparently more stable, are the dialkyldithioacetylene polymers.[278] However, more favorable (lower) equivalent weights, hence higher energy densities, are found in the (conceptually) acetylene-derived dithiols also claimed by Stiehl *et al.*: DT-DT,[279] a thiocarbonic acid alkyl ester (TCA) of DT,[280] and a methylthio-substituted bis(dithiol), MTBT.[281] The compounds can be regarded as disulfides which, upon discharge, undergo scission of the S–S bond, two ionic groups RS^- are formed and two alkali metal ions must be supplied to compensate this charge.

Disulfides have been claimed in a number of patents. Only two more will be mentioned here, and they are not a source of performance data. The naphthalene-derived disulfides of Teo,[282] *viz.* his tetrathiotetracene, tetrathionaphthalene, and tetrachlorotetrathionaphthalene, were described as compounds which are transformed to polymers by the formation of metal complexes (*e.g.*, by Ni bridging the four S atoms of two disulfide groups belonging to two different molecules) and becoming electroactive by the intercalation (presumably) of I_2 or Br_2, in which case Li or Na are used as the negative electrode. These complex polymers are said also to operate as negative electrodes, when combined with iodine- or bromine-containing poly(2-vinylpyridine) (PVP). Their electrochemical activity does not involve the breaking of S–S bonds.

2.8.2. Thiol Dimerization Electrodes

Quite recently the discovery and possible applications of redox dimerization and polymerization electrodes were recounted and well illustrated in Japanese by Visco *et al.*[283] (For reviews concentrating on redox polymerization electrodes, see section 2.8.3.)

It was realized in the late 1980s that disulfide bridges, so common in protein reactions involving the cysteine–cystine couple,[284] could have a potential for electrochemical uses. The electrochemistry of cysteine and cystine had for instance been studied by Zagal and Herrera,[285] who found that phthalocyanines (that of Co for the oxidation of cysteine, and that of Mn for the reduction of cystine) provide acceleration of the reactions, which at a bare graphite electrode were sluggish or absent. Here an activation occurred by the strong interaction of these amino acid molecules with the catalytic electrode surface.

For a battery reaction, activation of the sulfur atom should preferably occur from within the molecule. Also, chemical stability and a suitable state of aggregation are essential for electrode materials. For combination with a molten sodium electrode with β''-alumina electrolyte or separator, a melt or solution of the disulfide exhibiting dissolving power for the sodium thiolate produced upon reduction (discharge) will be required.[286–289] The system should exhibit good conductivity[290] and should be stable and operative above 100 °C (above the melting point of sodium). For good function of the sodium ion-conducting β''-alumina electrolyte, a number of precautions should be taken, otherwise severe polarization phenomena unknown at the operating temperatures of sodium/sulfur cells will appear when temperatures appropriate for the operation of sodium/organosulfur cells are used.[291]

For combination with a (solid) lithium electrode, either a solution of the thiolate–disulfide system in a solvent will be feasible as the positive electrode, provided a passivating layer protecting the lithium is formed *in situ*;[292,293] or a solid disulfide system, provided a “solid” but elastomeric electrolyte is present in the form of polyethylene oxide (for instance, with Armand’s plasticizing salt $LiN(CF_3SO_2)_2$, in order to attain room temperature operation), which is also added as an ionic conductor to the positive electrode cast as a thin film from the disulfide.[294]

Mailhe[286] showed that tetraethylthiuram disulfide (TETD) was a suitable, stable electrode material. In its anion, diethyldithiocarbamate (DEDC), formed upon reduction, charge delocalization is strong, the sodium salt is readily soluble in the molten TETD (to the extent of 60%; more when 10–20% DMSO are added as a solvent). Conductivity of this system is satisfactory as soon as 2% NaDEDC is present in the TETD (which corresponds to 2% discharge).[290] Water and excessive temperatures must be avoided. The TETD can be synthesized from CS_2 and amines in alkaline media. An aluminum current collector is suitable, since an electronically conducting passive layer is formed on the aluminum surface.

Theoretically, dialkyl disulfides should be of interest as positive electrodes. Their stability is satisfactory, but the solubility of the corresponding reduced forms (the alkali alkylthiolates) is not high enough.[286] Ether functions in the alkyl chain should improve the solubility of the alkali salts.[286] However, as such compounds were not commercially available,[288] bis(hydroxyethyl) disulfide (HEDS) was tested at first,[287] then bis(ethoxyethyl) disulfide was prepared and also tested.[287] Graphite felt catalytically activated with phthalocyanines helped the kinetics.

The TETD system was studied in detail.[288] With a sodium counter electrode and β''-alumina as the electrolyte, it can be operated at about 130 °C. It was evident that the Na/TETD cell has greatly reduced corrosion problems as compared to the Na/S cell, and that it is reliable and safe. The low melting point of the reduced form, sodium dithiocarbamate, is due to resonance stabilization of the anion.[290] This phenomenon is at the same time a key to the electrochemical reversibility.

Kinetic studies were performed for a family of these compounds:[295,296] TMTD (the methyl analog of TETD), TETD itself, diphenyl disulfide (PDS), and its fluorine-substituted analog (FPDS). All proved to be chemically reversible in their reduction to the thiolates, kinetically slow (as seen from the sweep-rate dependence and magnitude of peak separation in the voltammograms), chemically stable in both forms, and little or not adsorbed on the electrode. Graphite was a better electrode material than glassy carbon or platinum, yet catalysts were found to be required for the use of this system in batteries. Thus, graphite felt impregnated with catalyst is a suitable current collector for these positive electrodes. A suitable catalyst is cobalt phthalocyanine (CoPc).[296]

The TETD system was subsequently studied with lithium as an anode, a microporous separator, and DMSO as a solvent in which the active material of the positive electrode is dissolved.[292] A passivating layer forms on the lithium, which is a favorable condition for storage in the charged state.

The search for compounds commercially available, and the realization that in the thiuram systems there are two electrochemically *in*active sulfur atoms present for every electrochemically active –S–S– disulfide bridge, rapidly led the group at Berkeley to systems where *di*mercapto compounds or *di*thiolates are the reduced form, and disulfide polymers are the oxidized form[283] (see section 2.8.3).

A hierarchy of disulfides for use in secondary batteries was described in a patent by Kubota.[297] A battery reaction was not formulated, but the extensive references to the work of Visco and colleagues (see above) suggest that Kubota claims cyclodisulfides as an alternative to the dimeric disulfides. It can be seen from the formulas reproduced in the patent that groups activating the molecules are present as substituent(s) of the (mostly) five- or six-membered nonaromatic cyclodisulfide ring. These groups can also be such that polymers are formed which contain the disulfidic rings in or at the polymer chain. Opening of the S–S bond and formation of dithiolates is the likely event during discharge. It is not obvious whether, during recharge, the same compounds would be re-formed or some polymerization would occur as in redox polymerization electrodes.

2.8.3. Thiol Polymerization Electrodes

The redox polymerization electrodes with S–S bonds have been reviewed by the group who discovered them.[298–300] The more recent development of composites of these materials with polyaniline can be appreciated from a detailed patent description[301] and a number of papers, mainly by Japanese workers.[105−107,302,303]

The disulfide polymers were discovered in the instance of bis(2-mercaptoethyl) ether.[283] Its polymer is actually a commercial product (a Thiokol of the Morton Thiokol Company). Rapidly an entire list of dimercapto (or more generally polymercapto) compounds was identified commercially or synthesized, and converted to polymers with X designations (see Table 2.2). Upon oxidation, dimercapto monomers will give rise to linear polymers; trimercapto compounds will yield cross-linked products. When a mixture of monomers is used as the starting material in a positive battery electrode, the charge−discharge cycles will lead to copolymers of different kinds (block, random, regular).

In the very general patent from the Berkeley group,[289] the scope of the disulfide polymers was represented in terms of the general formula $[R(S)_y]_n$, where R could be an aliphatic or aromatic group, y could be an integer between 1 and 6, n could be between 2 and 20; R could contain additional heteroatoms. Preferred values of y are unity (section 2.8.2) and two (this section). These dimers and polymers could be combined with, preferably but not exclusively, a Na or Li anode. For cells with liquid anode and cathode, a solid electrolyte (doubling as a separator) is preferred. For cells with solid anode and cathode, the electrolyte is preferably liquid or a plasticized polymer. Carbon fibers (graphite felt[293]) or aluminum fibers would be used to reinforce the cathode's conductivity (and rigidity). A phthalocyanine (Pc) catalyst such as CoPc or MnPc could be used to lower the charge-transfer resistance between graphite felt and liquid cathode materials.[289] A barrier layer was found to form when a lithium anode is in contact with a liquid cathode,[293] which is a very valuable feature. These patents[289,293] refer mainly, but not exclusively, to dimerization systems in the examples given.

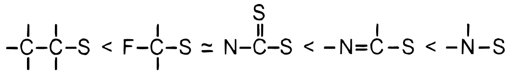
The preference for linear polymers (X1, X2, X3, X6) was clearly expressed in an early conference paper;[304] X4 forming ladder-type polymers and X5 becoming a cross-linked polymer are inferior in kinetics and performance.

The advantages of sodium over lithium were pointed out in a companion conference paper:[294] it is cheaper, and its kinetics is more favorable, so that the equivalent weight penalty relative to lithium is not important.

The advantages of the plasticized solid polymer electrolyte mentioned previously were outlined in a patent of 1991[305] and in a paper of 1993.[306] Both documents refer to the polymer X1 (the monomer is commercially available as Bismuthiol I) as the preferred cathode material, which can be combined with Li or Na as an anode. The paper[306] focuses on warm solid-state lithium cells with X1.

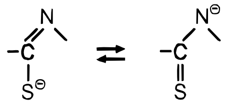
Synthetic information concerning the redox polymerization systems can best be found in papers from 1991 and 1992,[307,308] while fabrication of the electrodes and cells is described in the 1991 pair of papers.[307,309] It was pointed out that electrolyte salt should be incorporated into the cathode, although in a low concentration, since salt-saturated cathodes will polarize during discharge.[309] A typical electrode preparation can be described as follows.[310] The perfectly water-free sulfur compound, *e.g.* X1, is mixed with 10% carbon as an electronically conductive filler and with PEO containing lithium salt as an ionically conductive filler. The mixture is slurried up and dissolved in AN, and the electrode is produced by casting on a smooth substrate. Such electrodes, which are foils about 20 μm thick, are then combined with a thin PEO−Li salt foil (also produced by solvent casting) and suitable anode in a complete cell.

An important finding from kinetics studies[309] was the sequence



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-S < F-\overset{|}{\underset{|}{C}}-S \simeq N-\overset{\overset{S}{\|}}{C}-S < -N=\overset{|}{C}-S < -\overset{|}{N}-S$$

for the order of molecular structure next to the sulfur atom in which the redox reactions become faster. This is a more detailed statement than that found in the patent of Gauthier,[311] *viz.*, that partial delocalization of the charge on the nitrogen atom



is responsible for better kinetics and a higher cell potential. Gauthier's favorite polymers are X1 and X7. His claims are largely overlapping with those of the group at Berkeley.

Work with X1 was also pursued in Japan[105−107,109,301,303,312,313] (using DMcT as an abbreviation for the monomer), where electropolymerized polyaniline was found to be a catalyst for enhancing the kinetics of the disulfide polymers, as well as an electrode material. Naoi and his colleagues put forward the same delocalization scheme as reproduced above.[312] High-performance X1-PAni electrodes have been prepared[107] by dissolving X1 and PAni (oxidized to the extent of 35%) in MP (in a 2:1:5 weight ratio) and spreading and drying this mixture on a carbon film so as to obtain a 20-μm film of electrode material.

Workers in Canada[314] reported that instead of polyaniline, one could use polypyrrole to enhance the kinetics of X1.

It should be mentioned in closing this section that polymeric (or cyclic oligomeric) thiophene disulfides had been reported as early as 1979; *cf.* the recent review of Todres.[315]

2.9. Polyacenes and Carbons

A flowing transition exists among polymers, polyacenes, and the various carbons, both in their genesis and in their properties. Graphite, for instance, can in a wider sense be regarded structurally as carbon polymer chains cross-linked in the plane. Polyacenes truly constitute a transition between polymers and graphitic carbons.

It has already been pointed out in the section on poly(p-phenylene) that similarities in the ion-inserting properties exist between this true polymer and graphite.[39] It will be justified, therefore, to conclude this review with some information on materials which stretch the definition of organic polymers. Most of it is from very recent papers. A possibility of comparison with the data in the earlier chapters, rather than a complete survey, is the aim. Table 2.3 lists structures and abbreviations.

By the hierarchy of their structural order, carbon materials range from carbon blacks and petroleum coke to carbon fibers, "supercarbons", and graphite. By their genesis, materials can be distinguished which have been made from known polymer precursors. By their composition, materials with heteroatoms can be distinguished. Such heteroatoms can be introduced during synthesis of the carbon material itself or during synthesis of a polymer precursor. These genetic distinctions, which reveal more clearly the connection with the materials in earlier sections, were used when creating the four subsections of the present section and of section 3.9.

It will be appropriate at the outset to remark that a number of carbons in their composition are closer to polyacetylene $(CH)_n$ than to ideal polymeric carbon C_n. Hydrogen is gradually eliminated from the lattice with increasing pyrolysis or heat treatment temperature. Likewise, carbons exhibit structures where the stacking of adjacent hexagonal carbon layers occurs with elements of disorder (turbostratic, *viz.*, random rotations and translations) which are gradually eliminated with increasing temperature, and depending on whether the carbon is "soft" or "hard".[316] This structure is decisive for the properties.[316] In disordered carbons heated to temperatures above 2000 °C, Dahn[316] found a correlation according to which x in Li_xC_6 will come closest to the intercalation limit of $x = 1$ when the random stacking probability (probability of finding a random rotation or translation) is zero. No lithium can be inserted between randomly stacked adjacent parallel layers.[316] To the contrary, in highly oriented pyrolytic or natural graphite, intercalation is attended by phase transitions between stages,[317] which are seen as a series of voltage plateaus in the charge−discharge cycles.[317,318]

The formation of graphite compounds by intercalation (commonly by the intercalation of anions) has been known for a long time and is textbook knowledge. The ion-exchanging properties of graphite surfaces have also been studied long ago.[319] Graphite salts are oxidation products. In aqueous acidic solutions, anions are intercalated together with water and neutral acid molecules.[216,217] In sulfuric acid, for instance, a compound $C_{36}^+HSO_4^-\cdot 2H_2SO_4$ can be formed reversibly.[216]

However, graphite is readily overoxidized.[320] Graphite intercalation compounds with anions have not found great favor in research on rechargeable batteries. This may be attributed as much to their relatively low specific charge (37 A h kg^{-1} for the sulfate formulated above) as to the lack of compatible anodes.

Carbon intercalation with cations, chiefly Li^+, on the other hand, has been studied vigorously in recent years.[40,321] Such anodes provide the highly desirable, apparently safe substitute for lithium metal and lithium alloy anodes. They can be used to design cells (similar to those of Figure 1.1, part *d* and *f*) where during discharge, Li^+ ions are released from the anode and incorporated into cathodes such as those based on conducting polymers or the oxides of, *e.g.*, cobalt, nickel, vanadium. Such systems have been called shuttlecock, rocking-chair, swing, or simply lithium ion batteries.[322] Here only the electrodes, not the electrolyte, function as the ion reservoir, thus high specific energies/energy densities can be achieved on principle, and commercial development is under way.[153,322−325]

Anodes (negative electrodes) for lithium ion batteries can basically be realized, not only with the lithium ion-inserting carbon materials and with truly Li^+-doped conducting polymers but also with *p*-doped conducting polymers, when the latter are prepared with a large, immobile dopant anion. The most frequent example described in the past was polypyrrole poly(styrenesulfonate). Such electrodes have been studied repeatedly as cathodes (positive electrodes). As an anode, though not in a lithium ion battery), such an electrode was described in very recent work.[326] Probably its working potential is too positive, and its specific charge too low, owing to the weight of the immobile anion, for this anode to be competitive with the carbon-based anodes described in the present section. (This weight penalty can be avoided when the immobilized anion is constituted by sulfonation of the pyrrole or similar polymer, as discussed in the polyaniline section.)

Information on electrode preparation can be found in Table 2.1. Powders (for instance of the materials described in section 2.9.4) were generally compressed to electrodes with binders. Certain pyrolyzed materials (carbon fibers or carbonized fabrics) could be contacted directly.

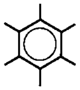
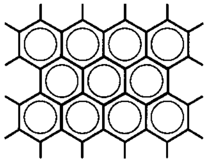
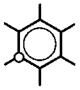
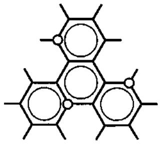
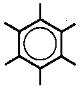
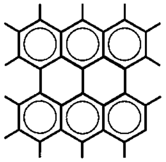
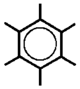
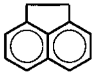
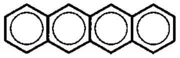
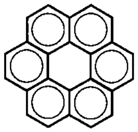
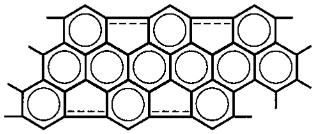
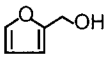
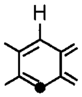
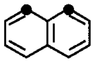
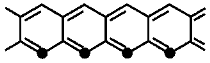
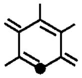
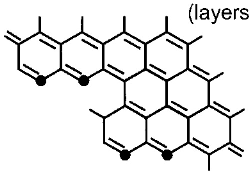
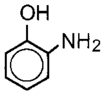
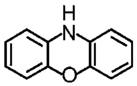
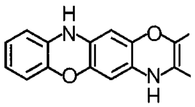
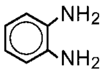
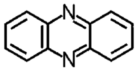
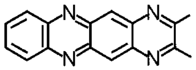
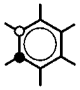
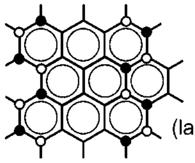
2.9.1. Graphite, Pitch-Based Carbons (C)

In the review of Fauteux and Koksbang[40] written in 1991, the best carbon intercalation material available at that time was that of Mohri *et al.*,[327] which was prepared by pyrolysis of benzene vapor at 1000 °C. Slightly better results were quoted in 1994 from recent Japanese conference papers by Iijima[321] for natural graphite and graphite whiskers.

The diversity of materials, both in their origin and treatment, can be gathered from Table 2.1. Natural graphites,[317,318,328−330] synthetic graphites,[316,317,330−338] products based on petroleum coke,[316,330,331,333−336,339−342] and pitch[316,329,330,333−336,341,343−347] are largely from the commercial sector. Pyrolytic products were prepared by vapor-phase processes from benzene[327] and other hydrocarbons not disclosed in the publications,[348−350] some of them again by industrial suppliers (graphite whiskers[348,349]). Sandí *et al.*[351] used a pillared clay as the matrix during pyrolysis of pyrene and removed this matrix after pyrolysis to obtain a molecularly porous carbon.

Electrodes were prepared from these carbon materials in the conventional way. Binders, sometimes a conductive filler, and for cells with polymer electrolytes, a high proportion of this electrolyte were incorporated into the electrodes, as described in Table

Table 2.3. Structures and Abbreviations of Materials in the Text and Tables

Abbreviation	*Name*	*Formula (Monomeric "unit" or precursor)*	*Hypothetical or idealized structure*
Gr NG SG	Graphite Natural graphite Synthetic graphite	 C_6 MW 72	 (layers)
(also valid for other graphitized carbons: PCF, PCk, PCP)			
$(B_zC_{1-z})_n$	Boron-substituted carbons	 C_5B for z=0.17 MW 71 ○ = B	 (layers)
PAS-SD	Polyacenic semiconductor from styrene-divinylbenzene copolymer	 C_6 MW 72	 (layers)
PAS-PF	Polyacenic semiconductor from phenol-formaldehyde resin	 C_6 MW 72  acenaphthene  acenaphthylene  tetracene  coronene	 (layers)
PPFA	Pyrolyzed poly(furfuryl alcohol)	 $C_5H_6O_2$ MW 98 furfuryl alcohol	
PPCNAc	Pyrolyzed poly(cyano-acetylene)	 C_5HN MW 75 ● = N  1,8-naphthyridine	 (lower T; will form graphite-like structure with less nitrogen at higher T)
TSPAN	Thermally structured polyacrylonitrile	 C_5N MW 74	(layers) 
POAP	Poly(o-aminophenol)	 C_6H_7NO MW 109  phenoxazine	 (ladder)
POPDA	Poly(o-phenylenediamine)	 $C_6H_8N_2$ MW 108  phenazine	 (ladder)
BC_3N		 C_3BN MW 61 C_4BN MW 73 ○ = B ● = N	 (layers)

2.1. Specific surface treatments were studied for their effects on the electrochemical properties.[338,347] Lithium incorporation was studied in all cases except for the one publication related to sodium insertion[336] and for work where the starting material for a lithium-intercalating graphite electrode was the potassium compound KC_8.[352]

Crystal structure, which is highly important for the electrochemical properties,[316] depends on the heat treatment, mainly the temperature. In "soft" carbons (petroleum coke, heat-treated petroleum pitch), turbostratic disorder is readily relieved by heat treatment.[316] In "hard" carbons such as those produced from polymer precursors, disorder is highly persistent with respect to heat treatment;[316] see sections 2.9.3 and 2.9.4.

It has frequently been noticed that electrolyte composition is highly important for the ability of a carbon (in particular graphite) to incorporate lithium ions. This is because a Li^+-permeable layer must be formed at the surface which will prevent co-insertion of solvent molecules.[353] Solvent co-insertion causes exfoliation of the graphene layers.[353] Such surface layers are formed from electrolyte reduction products. Propylene carbonate, the "default" solvent in so many nonaqueous electrochemical systems, is reducible well before Li^+ incorporation/reduction, but its reduction products do not prevent solvent co-insertion; to the contrary, they may prevent Li^+ insertion.[332] Crown ethers added to the electrolyte, which preferentially solvate the Li^+ ions, are helpful in preventing undesired solvent incorporation into the carbon,[316,333] but lower the conductivity of the solution. In studies of carbon materials, liquid electrolytes with mixed solvents (EC, DME, DMC, MF) and additives (*e.g.*, CO_2) are preferred. Most of the recent studies of carbon materials were performed in such systems.[102,354−358] Chloroethylene carbonate was found to be a new advantageous cosolvent.[359] A detailed study of solvent mixtures was published.[335]

The interlayer spacing measurably widens during lithium incorporation.[332] The (002) lattice spacing increases from 3.37 to 3.72 Å in the case of graphite.[332] The reversibility of this process is important; if for reasons of solvent incorporation, for instance, this is not the case, destructive exfoliation will occur.[333] Less-ordered carbons are more resistent to exfoliation.[333] Potassium-intercalated graphite was found to retain its wider lattice spacing in lithium ion electrolyte.[352]

The radial structure of carbon fibers appears to be important in preventing solvent cointercalation with the ions.[339] The reason could be kinetic, since fibers offer better ingress and diffusional motion to the ions.[330] Mesophase pitch-based carbon fibers graphitized at 3000 °C exhibited the highest lithium diffusion coefficient.[330]

As mentioned above, intercalation may be attended by solvent decomposition (especially EC and/or PC decomposition) during the first cycle, which gives rise to the ion-conducting passivating layer on the electrode.[331] This layer, as its name implies, prevents the continuation of solvent decomposition during subsequent cycles, hence starting with the first discharge (or second cycle) the intercalation behavior becomes reversible. The passivating layers are improved in the presence of CO_2.[334,335] The irreversible charge consumed during the first cycle is proportional to the carbon's surface area.[331] Anions also may undergo reduction, and may lead to the formation of passivating layers, prior to lithium incorporation.[332]

The first-cycle loss of charge, often referred to as "irreversible capacity", is detrimental, because the underlying reactions consume lithium ions (and sometimes anions as well) from the electrolyte. In the instance of a petroleum coke, additional losses were found to occur during an initial storage period, when part of the intercalated lithium reacted with the electrolyte.[342]

2.9.2. Heteroelement-Substituted Carbons (CHet)

Carbons substituted (interstitially or by lattice-site substitution) with other elements can be prepared from suitable polymer precursors (section 2.94) or by CVD (this section). The layered-structure compound BC_2N was produced from acetonitrile and boron trichloride,[360] while a series of carbons B_zC_{1-z} were prepared from benzene and boron trichloride as the precursors.[316,361] Here, boron as an electron acceptor has been introduced into the carbon lattice, so a higher affinity for lithium uptake into the lattice is expected.

Nitrogen substitution was achieved with pyridine, acetonitrile, or acetylene and ammonia as the precursors.[362] Some of the nitrogen introduced is substitutional in the carbon lattice, thus acting as an electron donor like lithium itself. This competition lowers the affinity for lithium uptake into the lattice. Another fraction of the nitrogen is "chemical nitrogen",[362] probably some interstitial or substituent-type species, which reacts with Li irreversibly. These two effects make nitrogen-containing carbons undesirable as anodes in lithium ion cells.[362]

Silicon was introduced in a "nanodisperse" fashion by a CVD process with benzene and dimethyldichlorosilane as the precursors.[363] Its incorporation was visualized as taking part in a pregraphitic carbon structure in which room for the foreign atoms is left where carbon layers fold or buckle (regions of unorganized carbon). Each silicon atom appears to host 1.5 Li atoms in the lattice upon charging, in addition to lithium held in the graphitic part of the carbon lattice.[363]

2.9.3. Polyacenes (PAS)

Pyrolysis of polymers such as phenol formaldehyde resin or cellulose was found to give "activated carbon fibers" (ACF)[364,365] or materials called "polyacenic semiconductors" (PAS).[366−373] Their chemical doping produced striking conductivity effects, only when the heat-treatment temperature (HTT) was relatively low.[366,368] Metallic conductivity arises at higher HTT, the band gap shrinks and vanishes,[367,370] but "dopability" is maintained and can be used for electrochemical energy storage.

Similar materials can be produced by pyrolysis (or "thermal structuring") of styrene-divinylbenzene copolymers,[374−376] poly(furfuryl alcohol),[40,316,377,378] or poly(*p*-phenylene).[379,380] The structures, which are reported in Table 2.3, are both speculative and approximative idealized. “Ladder”-type structures of linearly associated, fused rings appear particularly unlikely. A two- or three-dimensional networking is certainly more realistic. Disorder is prevalent, and lithium ion doping may further increase it.[379]

The common elements of these pyrolyzed materials are fused C_6 rings, although smaller rings may be present. Residual hydrogen is common, it may even be important for energy storage,[370] although the reasons have not been elucidated. Similar structures with heteroatoms can be produced in analogous fashion from suitable precursors (see section 2.9.4). On account of their structural similarity to the polyacenes, a reference to fullerenes is included in the present section.[381] Finally, model polyacenic carbons have been synthesized from compounds which could be called oligoacenes.[382]

The methods of pyrolysis briefly indicated in Table 2.1 are conventional (inert gas; hydrogen for PPPP). The salt $ZnCl_2$ was added at the stage of polymerization when preparing PAS-PF,[368,369] and the acid H_3PO_4 was added at the stage of polymerization when preparing PPFA.[377] These substances undoubtedly influence the pyrolysis stage as well. Pore-forming salts are important in order to avoid the formation of structures too compact for electrolyte access to the intercalating crystallographic units.[376] It is of particular interest for economic reasons[325] that commercial resin mixes (resole, novolak) can be used as the starting materials for pyrolysis.[383,384]

Many of the pyrolyzed materials have extremely large surface areas, *e.g.*, 1500 to 2500 $m^2\ g^{-1}$ for the activated carbon fibers[364,365] or $>2000\ m^2\ g^{-1}$ for PAS made from phenol−formaldehyde resin.[368] In addition to macroporosity, microporosity is present, which may be decisive for their dopability with ions larger than those admitted by graphite.[369] The double porosity is of great importance for fast charging kinetics.[371] Ion entry and accomodation is also facilitated by the distance between carbon ring layers, which is considerably larger, for instance, between 0.37 and 0.40 nm, than the lattice spacing of 0.337 nm in graphite.[372,373] Such distances are held responsible for the higher structural stability during charge−discharge cycles, as compared to graphite.[373] In the case of pyrolyzed epoxy novolak resins,[384] the pore structure was found to undergo a strong deterioration upon slight oxidation (burnoff), quite in contrast to what was found for graphite.[338]

Even at high levels of Li^+ doping, the state of Li in the lattice is nonmetallic.[373,375] Pyrolyzed PPP offers sites, not only for the insertion of Li^+ ions (like all other materials) but also for a fixation of additional lithium.[379]

The distance between adjacent layers and the disorder decrease when the HTT is raised, and the carbon materials become more crystalline.[378] This is particularly evident in “soft” carbons (materials carbonizing in the liquid phase, graphitizable carbons). “Hard” carbons (nongraphitizable carbons, materials carbonizing in the solid phase, such as those made by pyrolysis of PFA) remain amorphous or highly disordered even at very high HTT.[316,378]

The polyacenes are infusible, insoluble, and stable in air. If the raw materials are suitably shaped, then the pyrolytic materials, too, can be obtained in the form of felt, cloth, or sheets resembling paper, even foam. Otherwise, the carbonized polymers are crushed and made into conventional electrodes with the aid of binders. Test results obtained with such electrodes are reported in Table 3.1 and section 3.9.3.

2.9.4. Poly(heteroacenes) (PHAS)

Like the polyacenes (PAS) of section 2.9.3, the poly(heteroacenes) or poly(heteroacenic) semiconductors (PHAS) can be obtained by pyrolysis of polymers. The products of oxygen-containing polymers have been included in section 2.9.3, since most of the oxygen is lost on pyrolysis.[366] Pyrolysis products of nitrogen-containing polymers preserve nitrogen, although some is eliminated;[327,385,386] its loss can be monitored via the decrease in paramagnetism.[385] In these products, the remaining nitrogen atoms substitute carbon in polyacenic structures.

The basic structural element of the poly(azaacenes) has been described as naphthyridine (quite consistently misspelled naphtiridine or naphthiridine by most authors[266,385]). However, naphthyridine chains are unlikely to exist beyond a narrow temperature range: a planar structure of condensed rings further cross-linked is then formed, explaining conductivities as high as 100 $S\ cm^{-1}$ of the resulting PAS material.[385]

Polyacrylonitrile was the most common polymer precursor made into PHAS.[340,375,385−389] The starting materials were PAN powder,[385−388] yarn or fabric.[389] Cyanoacetylene when thermally polymerized yields a cyano-substituted polyacetylene reacting further to the same material as PAN when the temperature is raised sufficiently.[390]

Contrary to what was found for nitrogen-substituted graphites produced by CVD,[362] the polyacenic nitrogen atoms appear to favor lithium ion insertion.[375] The potential of lithium ion insertion, however, was found to be rather positive, around 2 V *vs* Li/Li^+, according to curves described[375] as discharge curves. On the other hand, Tran *et al.*[340] claimed that their PAN-derived foam-carbon electrode had a significant part of its specific charge due to lithium ion insertion below 0.4 V *vs* Li/Li^+. Their curves look quite different from those of Schwarzenberg *et al.*[375]

Polyamines of undisclosed structure, presumably on the basis of aniline and naphthylamine, have been pyrolyzed. The structures proposed for these products contain nitrogen atoms outside the C_6 rings.[375]

The workers in Dresden called their material “thermally structured” (“TS”). The preparation of pyropolymers from brominated heterocyclic monomers described by the same group[375,391] can likewise be imagined to involve a polymer intermediate. As in the pyrolysis of phenol−formaldehyde resins, pore-forming salts (carbonate, bicarbonate, formate) have been added in the thermal structuring of PAN.[376,385] The resulting microporous materials have very high surface areas.[386]

The polymerization of *o*-aminophenol and *o*-phenylenediamine by potential sweeps in acidic solutions presumably leads to largely linear polyacenes (phenoxazine and phenazine chains[392,393]). Their electrochemistry has not been explored in greater depth.

Boron-substituted PHAS have been prepared by pyrolyzing an acrylonitrile copolymer or PAN itself in the presence of BCl_3 so as to obtain almost graphitelike structures.[394] Here, the distinction between polyacenes and graphites becomes tedious. A saccharose−urea condensation copolymer can be assumed to function as the intermediate in the products made by Ishikawa *et al.*[395] Here, too, layered (or quasi-layered) structures are obtained. It is an interesting approach in this work, that lithium ions were already incorporated into the anodes during synthesis:[395] this should be compared to the "predoping" referred to in section 3.9.3.[373]

A phosphorus-containing material was made in the presence of H_3PO_4 from PFA as a polymer precursor.[396] The phosphoric acid is actually the polymerization catalyst; used in larger quantities, some of it is then incorporated into the pyropolymer, depending on the HTT, predominantly as $(C_6H_5O)_2POOH$, $(C_6H_5O)(C_6H_5)POOH$, or $(C_6H_5)_2POOH$.[396]

Finally, an interesting silicon-containing carbon was made from poly(methylphenylsiloxane) as a precursor.[363] This method opens up a more convenient and cheaper route to the materials originally prepared by CVD from benzene and dimethyldichlorosilane.[363] This route was explored in a study of pyrolyzed epoxy−silane composites.[397]

3. Electrochemical Performance of Polymers as Battery Electrodes

Published parameters of a few complete polymer batteries as well as of various polymer (and polymer-containing) electrodes claimed to be suitable for batteries are listed in Table 3.1. Polymer "batteries" (usually just single experimental cells with a few milligrams of a polymer and a very large excess of an electrolyte) are commonly assembled with conducting polymers in their doped (oxidized or reduced) state. Therefore, the table lists not only the polymers but also the ions and solvents used for doping (and cycling). A metal, often excess lithium, in contact with the corresponding salt solution is typically used as the negative electrode. The few published exceptions where a polymer electrode was utilized as the negative electrode of a battery are also included. More promising ion-inserting materials for negatives are carbon-based,[40] see section 3.9.

Table 3.1 further lists the doping (oxidation or reduction) levels of the polymers (y), the open-circuit voltages of the fully charged cells, experimentally measured values of specific charge, energy, and power, Coulombic efficiencies recorded during cycling, as well as reported cycle lives of the polymer electrodes or cells. Pertinent aspects concerning these parameters are discussed in the following sections. The abbreviations used in the text and table are explained in a special listing at the end of this review. Note that the table contains the maximum values of specific charge, energy, and power (or sometimes, with suitable indications, the corresponding densities of charge, energy, and power) as claimed in the publications, thus reflecting upper limits of these particular electrochemical parameters rather than values that can be expected for a scaled-up commercial product. As a reference for comparison among highly disparate materials, Table 3.2 lists theoretical values of specific charge based on the (admittedly arbitrary) assumption of a "typical" doping level taken from Table 3.1 for the conducting polymers, and on the assumption of a two-electron reaction for the redox polymerization electrodes.

For high values of specific energy and power in a complete battery, the ideal choice for the negative electrode is metallic lithium or sodium. For the Li/Li^+ couple the standard potential, $E°$, is −3.05 V, which is the most negative value known for metal/metal ion couples. In addition, lithium metal has a very low equivalent weight, of 7 g faraday^{-1}, which is advantageous for the design of light-weight batteries. Therefore, in the majority of the polymer cells listed in Table 3.1 the Li/Li^+ couple was utilized as the negative (or counter) electrode. This should not be understood as representing the solution for practical battery systems. The review of Fauteux and Koksbang[40] should be consulted for more realistic anode materials. Of these, only the carbon-based lithium-inserting materials will be discussed in the present review (section 3.9).

Deterioration of cell parameters during cycling can happen due to failure of either or both of the two electrodes. The cycling behavior of bare lithium is quite unsatisfactory,[398,399] therefore, the short cycle life of some of the polymer-containing systems listed in Table 3.1 might actually be due to failure of the lithium counter electrode, and the feasible cycle life of the polymer might be much longer.

3.1. Polyacetylene (PAc)

3.1.1. Specific Charge and Energy

In numerous papers,[5,12,21−23,49,50,58] MacDiarmid and his co-workers have reported values of specific energy determined for cells containing polyacetylene, PAc or $(CH)_x$. For example, for a cell with an anion-doped $(CH)_x$ (doping level $y = 0.06$) as the positive electrode and metallic Li as the negative electrode, a specific energy of 176 W h kg^{-1} based on $[CH^{0.06+}(ClO_4^-)_{0.06}]_x$ and the Li consumed (*i.e.*, neglecting the electrolyte, solvent and cell hardware weights) was claimed.[21,22,49,50] Apart from this restrictive definition of specific energy (which is entirely justified for purposes of comparison), most values published by MacDiarmid's group (and others) were extrapolated from measurements on single, very small electrodes or pairs of electrodes. For example,[58] specific energies ranging from 202 to 167 W h kg^{-1} (based on $(CH)_x$ and the Li consumed) have been calculated for discharge rates ranging from 50 to 400 A kg^{-1} of $(CH)_x$. The actual experiments were performed at current densities of a few mA cm^{-2} or less in cells containing ∼0.1 mm thick $(CH)_x$ films having an area of 0.9 cm^2 and weighing ∼3−4 mg.[58] Chien and Schlenoff[48] extrapolated to a specific energy of 250 W h kg^{-1} from experiments involving ultrathin (<0.1 μm, 20−500 ng) $(CH)_x$ films comprised of 2−3 nm microfibrils. A still higher specific energy of 270 W h kg^{-1} (based on the weight of only the doped polymer) was published by Shinozaki *et al.*[400] for a $(CH)_x/LiClO_4/Li$ system comprising a 1 cm × 1 cm $(CH)_x$ film and an excess of electrolyte.

The $(CH)_x$ morphology was found to be very important for the doping level that can be attained. More porous $(CH)_x$ material admitted a higher doping level and hence higher specific energy (the energy density might decrease, though). Values of 70 and 27 W h kg^{-1} (of total electrode mass) were found for samples having the same mass but thicknesses of 1.6 and 0.4 mm, respectively; here the thinner electrode was made from the same $(CH)_x$ sheet, which was compressed to one-fourth the original thickness.[52] This compression must have been detrimental to utilizability of the active mass.

The ability of $(CH)_x$-containing cells to store charge has been studied by many groups.[19,29,45,47,51−53,56,375,401,402] A value of 424 W h kg^{-1} of $(CH)_x$ (based on ∼8 mg for the mass of both electrodes and $y = 0.364$) was found by Nagatomo *et al.*[44] for a cell having the configuration n-$(CH)_x$/1 M $LiClO_4$-PC/p-$(CH)_x$. This is a surprisingly high value, but unfortunately no data on cycle life or Coulombic efficiency were given. In the same paragraph of their paper, the authors stated that no degradation had occurred during >2000 cycles, but the long-term cycling was performed at the very low values of $y = 0.026$ for the degree of doping (charging) and $\Delta y = 0.002$ for the change in the degree of doping (charging) during a given cycle, *i.e.*, with very shallow cycles.[44] For larger cells, Nagatomo *et al.*[54] when studying p-$(CH)_x$/$LiClO_4$/Al cells with a cathode area of 54 cm^2 later found specific energies of 114, 110, and 100 W h kg^{-1} of $(CH)_x$ at discharge currents of 5, 10, and 15 mA, respectively.

The specific energies achieved in practical battery systems are expected to decrease by at least a factor of 5 relative to the theoretical ones.[403] Nigrey *et al.*[21] therefore suggested that a reasonably conservative estimate of the specific energy available from PAc batteries which considers all materials needed for a completely packaged cell stack can be obtained when dividing the figure of 176 W h kg^{-1} by 7 (the same factor as found for an average lead−acid automotive battery), which gives a value of 25 W h kg^{-1}.

MacDiarmid's group[5] proposed combining reduced $(CH)_x$ as an anode with TiS_2 as the cathode; the electrolytes used were $LiClO_4$ and $NaPF_6$ in THF. Such rechargeable cells gave experimental specific energies between 8 and 34 W h kg^{-1} only (based on the weights of TiS_2 and $[(CH)^{y-}\cdot(M^+)_y]_x$, where M was Na or Li).

All-solid-state $(CH)_x$ cells with several solid electrolytes ($RbAg_4I_5$ or AgI,[404] PEO,[11] and PVDF+PC[55,181]) have also been studied, and gave specific energies between 10 and 47 W h kg^{-1} (since these figures are based on the polymer weight alone, they are significantly inferior to those found with liquid-electrolyte cells).

3.1.2. Electrode Potential/Cell Voltage

The open-circuit voltages of charged experimental cells combining anion-doped $(CH)_x$ with metallic Li are rather high, typically between 3.4 and 3.7 V, depending mainly on the doping level of $(CH)_x$ films used in the cells.[12,21,22,48−50,58] When Li^+-doped $(CH)_x$ is used as the negative electrode instead of the Li/Li^+ couple, lower open-circuit voltages of 2.5−3.5 V are measured.[44,55,58] True ion-transfer cells, *e.g.* Li/$[(CH)^{0.07-}\cdot(Li^+)_{0.07}]_x$ with 7% n-doped $(CH)_x$, have much lower open-circuit voltages: ∼1.1 V when assembled with the doped polymer, and ∼2.0 V when fully charged until the $(CH)_x$ becomes neutral (undoped).[23] When cation-doped $(CH)_x$ as a negative electrode is combined with TiS_2 as the positive electrode, the cell has also a relatively low open-circuit voltage of about 1.7−1.8 V.[5]

Farrington *et al.* have shown that $(CH)_x$ electrodes can be charged up to open-circuit potentials of 3.9 V *vs* Li/Li^+ in $LiAsF_6$ or $LiClO_4$-containing, PC-based electrolytes,[56] but then the Coulombic efficiency of the charging is poor. At potentials more positive than 3.9 V *vs* Li/Li^+ the nonaqueous electrolyte significantly decomposes.[405]

3.1.3. Charging Rate/Specific Power

The charge and discharge current densities of PAc electrodes are relatively low (≤2.5 mA cm^{-2}, ref 44), but the total current of the battery can be increased by using electrodes constituting piles of several thin PAc sheets. The low current densities have been attributed to slow kinetics of the doping/undoping process controlled by solid-state diffusion of the dopants.[406] Only the ions at or close to the polymer/electrolyte interface easily move between the polymer and the solution during the charge−discharge cycles.[406−408]

This capacitance-like behavior is also manifest in an illusive, low charge−discharge efficiency (see section 3.1.4). The charge immediately available for discharge decreases when the electrode is stored in its charged state, when time is available for diffusion of a progressively increasing number of counterions from the surface to the bulk of the polymer.[19,51] Accordingly, no steady-state potentials are attained by $(CH)_x$ electrodes within any reasonable time interval.[407] This diffusion process has been investigated in detail.[409] The diffusion coefficients of anions in $(CH)_x$ fibrils were reported to be very low, ranging from 10^{-18} to 10^{-12} cm^2 s^{-1} at room temperature.[409−411] The wide spread of the values can be explained by differences in the (usually unknown) real, solution-wetted surface areas as well as by different morphologies of the $(CH)_x$ samples, which were not properly taken into account when calculating the diffusion coefficients in the studies published.[409]

The specific power found for complete Li/$(CH)_x$ cells with $LiClO_4$ electrolyte (see Table 3.1) was, on an average, 591 W kg^{-1} when $(CH)_x$ was anion-doped, and 192 W kg^{-1} when it was cation-doped.[23] The difference appears mainly to arise from the lower cell voltage recorded in the latter case. The peak values of specific power reported for Li/$(CH)_x$ and $(CH)_x$/$(CH)_x$ cells with liquid electrolytes are typically in the range of about 20 to 30 kW kg^{-1} of the polymer,[21,23,49,55,400] but much lower figures, of the order of 1 kW kg^{-1}, were found for particular systems,[12,23,50,52,55,58] see Table 3.1. On the other hand, for extremely thin $(CH)_x$ layers (less than 0.1 μm thick: 400 ng of 2−3 nm diameter microfibrils on an electron microscopy grid delivering 1 mA during 0.1 s) a specific power of 8 MW kg^{-1} has been measured by Chien and Schlenoff.[48] It should be acknowledged

Table 3.1. Reported Performance of Laboratory Cells with Electroactive Polymers

positive electrode		negative electrode										
electroactive material	inserted ion	electroactive material	inserted ion	electrolyte/ solvent	doping level (y)†	OCV^a (V)	specific charge^b (A h kg^{-1})	specific energy^b (W h kg^{-1})	specific power^b (W kg^{-1})	Coulombic efficiency, (%)	cycle life (cycles/conditions or definition)	ref
						Polyacetylene						
$(CH)_x$	BF_4^- or ClO_4^-	Pb	–	7.4 M HBF_4 or sat. $Pb(ClO_4)_2/H_2O$	$0.02-0.04^A$					60–90		20
$(CH)_x$	I^-	Ag	–	$RbAg_4I_5$ or AgI	0.07^A	0.65		10			“many possible recharges”	404
$(CH)_x$	I^-	Na	–	NaI/PEO		2.8–3.5		20	250		>20	11
$(CH)_x$	ClO_4^-	Li	–	1 M $LiClO_4$/PC	$\leq 0.10^A$		200	270^c	23700^c	35–91	<20–40/drop of efficiency	400
$(CH)_x$	ClO_4^-	Li	–	1 M $LiClO_4$/PC	$0.06-0.07^A$			255^d	$30000;^d\ 591^{d,e}$	86		23
$(CH)_x$ (film <0.1 μm)	ClO_4^-	Li	–	1 M $LiClO_4$/PC	0.06^A	3.5		250	8×10^6	>95		48
$(CH)_x$	ClO_4^-	Li	–	$LiClO_4$/PC	0.07^A	3.6		$\leq 217^d$	$\leq 9100^d$	≤60		12,58
$(CH)_x$	ClO_4^-	Li	–	1 M $LiClO_4$/PC	0.06^A	3.7		$176;\ 30^f$	$30000;^d\ 5000^f$			49
$(CH)_x$	ClO_4^-	Li	–	0.3 M $LiClO_4$/PC	0.06^A	3.7		$176;^d\ 25^f$	$19000;^d\ 680^f$		>326/to 7% $C_{max.}$	21
$(CH)_x$	ClO_4^-	Li	–	0.3 M $LiClO_4$/PC	0.06^A	~3.7		176^d		~100		22,50
$(CH)_x$	ClO_4^- or AsF_6^-	Li	–	$LiClO_4$ or $LiAsF_6$/PC	$\leq 0.11^A$	≤3.9		“low to moderate”		87–100 ($y \leq 0.10$) 22 ($y = 0.11$)		45,56
$(CH)_x$	ClO_4^-	Al	–	1 M $LiClO_4$/ EC+PC (4:1)	0.14^A			114		45	>30	54
$(CH)_x$	ClO_4^-	$(CH)_x$	ClO_4^-	0.5 M Bu_4NClO_4/ PC	$0.05^A + 0.02^A$	0.5						50
$(CH)_x$	I^-	$(CH)_x$	Na^+	NaI/PEO		2.8–3.5			10–20		>20	11
$(CH)_x$	ClO_4^-	$(CH)_x$	Li^+	$LiClO_4$/PVDF+PC	$0.008^{A,C}$	3.4	17^h	47^h	3200^h	60–82	>300/$\Delta y = 0.002$	55
$(CH)_x$	ClO_4^-	$(CH)_x$(+Al)	Li^+	1 M $LiClO_4$/PC	$0.36^{A,C}$		157^g	424^g		42		44
					$0.07^{A,C}$	3.5		$45-142^g$		33–71	>2000/$\Delta y = 0.002$	
$(CH)_x$	ClO_4^-	$(CH)_x$	Li^+	$LiClO_4$/EC+PC	$0.06^{A,C}$	3.5	125^h	270^h	30000^h		>500/$\Delta y = 0.02$	55
$(CH)_x$	ClO_4^-	$(CH)_x$	Li^+	$LiClO_4$	$0.06^{A,C}$	~2.5						58
$(CH)_x$	ClO_4^-	$(CH)_x$	Bu_4N^+	0.5 M Bu_4NClO_4/ PC	$0.024^{A,C}$	2.5						50
$(CH)_x$	ClO_4^-	$(CH)_x$	Bu_4N^+	Bu_4NClO_4/PC	$0.20^{A,C}$	3.4		72^g	1250^g	24		52
$(CH)_x$	PF_6^-	$(CH)_x$	Bu_4N^+	Bu_4NPF_6/PC, THF or SL	0.06^A	2.5–2.7						23,49, 50
$(CH)_x$	Bu_4N^+	$(CH)_x$	Bu_4N^+	0.5 M Bu_4NClO_4/ PC	$0.02^C + 0.07^C$	0.66						50
$(CH)_x$	Li^+	$(CH)_x$	Li^+	1 M $LiClO_4$/THF	$0.00^C + 0.07^C$	~1.0				~100		23
$(CH)_x$	Li^+	Li	–	1 M $LiClO_4$/THF	$\leq 0.10^C$	~2.04 ($y = 0$) ~1.05 ($y = 0.07$)		137^i	$2900;^i\ 192^{i,e}$	~100 ($y \leq$ 0.06); <100 ($y > 0.06$)		23
$(CH)_x$	Li^+	Li	–	$LiClO_4$/THF	$\leq 0.10^C$	1.9		$\leq 202^i$	$\leq 323^i$	~100	100/to 60% C	12,50, 58
$(CH)_x$	Na^+	Na	–	$NaPF_6$/THF	$\leq 0.10^C$			$\leq 115^i$	$\leq 206^i$	~100		12
		$(CH)_x$	Li^+	0.8 M $LiClO_4$/ THF	$<0.10^C$	[≥0.7 *vs* Li]		“low to moderate”		92–98		45
		$(CH)_x$	Li^+		$0.06^C < y < 0.18^C$	[0.7 *vs* Li]	226				90/to 80% C	415
TiS_2	Li^+	$(CH)_x$	Li^+	1 M $LiClO_4$/THF	0.10^C	~1.65		27^j		49–78		5
TiS_2	Na^+	$(CH)_x$	Na^+	1 M $NaPF_6$/THF	0.10^C	~1.8		34^j		50–64		5
		Li-Al+$(CH)_x$ (11:89)					220				80/to 80% C	415
		$Li_{4.3}Pb+(CH)_x$ (24:69)					280				100/to 80% C	415

Polyaniline												
PAni	SO_4^{2-}	Zn	–	1 M $ZnSO_4/H_2O$		<1.35	108^c	111^c		~100 (≤80% $C_{max.}$)	500/to 40 A h kg^{-1}	73
							135^k	139^k			2000/to 38 A h kg^{-1}	
PAni	SO_4^{2-}	Zn	–	$ZnSO_4/H_2O$	≤0.20^A		100			~100	120/drop of efficiency	427
PAni	Cl^-	Zn	–	1 M $ZnCl_2/H_2O$ (pH ≈ 4)		1.18	152^l	159^l	916^d	96–98	30/to 95% C	83
							109^d	115^d				
PAni	Cl^-	Zn	–	2 M $ZnCl_2$ + 0.5 M NH_4Cl/H_2O (pH ≈ 4)	0.50^A	1.3–1.5	90–95			45–99		70
PAni	Cl^-	Zn	–	sat. $ZnCl_2$ (+ 1 M NH_4Cl)/H_2O		>1.1	60–86^l	67–93^l		87–94		68
PAni	Cl^-	Zn	–	1 M $ZnCl_2$ + 0.5 M NH_4Cl/H_2O		~1.3		50–100		70–100	>100/to 90% C	429
PAni	H^+, Cl^-	Zn(Hg)	–	1 M $ZnCl_2$ + 0.5 M NH_4Cl + 0.1 M $NaBF_4/H_2O$ (pH = 4–5)		<1.4	~25^m	95^d		92–99 200/to 88% C	46/to 96% C	20
PAni	Br^-/Br_3^-	Zn	–	2 M $ZnBr_2$ + 1 M NH_4Cl/H_2O	0.50^A	1.5	90–95			73–99	"not completely stable"	70
PAni	I^-/I_3^-	Zn	–	1.5 M ZnI_2 + 1 M NH_4I/H_2O (pH = 4)		1.2	143^l			>88		69
PAni	ClO_4^-	Li	–	1 M $LiClO_4$/PC			90^{aa}					87
PbO_2	–	PAni	H^+, SO_4^{2-}	4 M H_2SO_4/H_2O		<1.7	40^c			95–100	4000/ to 25 A h kg^{-1}	73
PAni (composite with $LiClO_4$/PEO)	ClO_4^-	Li	–	$LiClO_4$/PEO(+EC)		3.6	48^l			98	250/to 80% $C_{max.}$	425
PAni theoretical	*ClO_4^-*	*Li*	–	*4 M $LiClO_4$/PC*	*0.80^A*	*4.0*		*152^n*	*1.6 × 10^8 (1 μm)^n* *1.6 × 10^6 (10 μm)^n* *1.6 × 10^4 (100 μm)^n*			423,432
PAni	ClO_4^-	Li	–	$LiClO_4$/PC	0.92^A		270;^{k} 160^o	87^n				418
PAni	ClO_4^-	Li	–	1 M $LiClO_4$/PC	0.70^A		164^k			~100 (<130 A h kg^{-1})	>500/50% $C_{max.}$	61
PAni	ClO_4^-	Li	–	1 M $LiClO_4$/PC	0.50^A		148;^{l} 93^d	539;^{l} 340^d		>98	"good"	84
PAni	ClO_4^-	Li	–	$LiClO_4$/PC+DME	0.50^A	<4.0	140^l				100/to 80 A h kg^{-1}	75
PAni	ClO_4^-	Li	–	$LiClO_4$/PC	0.60^A	3.0	127^l	382^l				90,91
PAni	ClO_4^-	Li	–	1 M $LiClO_4$/PC		3.2	120^k			~100 (≤120 A h kg^{-1})	~150	62
PAni	ClO_4^-	Li	–	1 M $LiClO_4$/PC	0.45^A		106	352		98–100	>50	421
PAni	ClO_4^-	Li	–	1 M $LiClO_4$/ EC+PC (2:1)			100^l	31^p			>25	63
PAni	ClO_4^-	Li–Al	–	1 M $LiClO_4$/PC		3.6	100^l	300^l		100	"hundreds"	36
PAni	ClO_4^-	Li	–	$LiClO_4$	0.60^A		100					6
PAni	ClO_4^-	Li	–	1 M $LiClO_4$/ PC+DME (1:1)		~4		260^l		~95	>30	430
PAni (+ carbon cloth)	ClO_4^-	Li–Al	–	1 M $LiClO_4$/ PC+DME (1:1)	0.18^A	~3.0	80–100^c			80–95	~300/to 60% C	65
PAni	BF_4^-			BF_4^-	0.50^A		100^c					415
PAni	BF_4^-	Li	–	1 M $LiBF_4$/ EC+PC (2:1)			75^l	20^p			20/to 50% C	63
PAni	BF_4^-	Li–Al	–	1 M $LiBF_4$/ PC+DME (1:1)		3.0 (3.5)	60^l (120^l)	160^l (370^l)		~100	>200/to 50% C	78
PAni	PF_6^-	Li	–	1 M $LiPF_6$/ EC+PC (2:1)			90^l	26^p			>25	63

Table 3.1 (Continued)

positive electrode		negative electrode										
electroactive material	inserted ion	electroactive material	inserted ion	electrolyte/ solvent	doping level (y)†	OCV^a (V)	specific charge^b (A h kg^{-1})	specific energy^b (W h kg^{-1})	specific power^b (W kg^{-1})	Coulombic efficiency, (%)	cycle life (cycles/conditions or definition)	ref
Polyaniline (continued)												
PAni fiber-reinforced	BF_4^-	PAPI	Li^+	3 M $LiBF_4$/ PC+DME			119;^{c} 91^h				>100	102
PAni	ClO_4^- (and H^+ leaving)	PAni	ClO_4^- (leaving)	0.1 M Et_4NClO_4/ PC	0.5					≤60		71
PAni	ClO_4^- (and H^+ leaving)	PPy	ClO_4^- (leaving)	0.1 M Et_4NClO_4/ PC	0.018					≤60	≥10	71
PAni	BF_4^-	Li	–	1 M $LiBF_4$/PC			130					93
PAni sulfonated	Li^+ (leaving)	–	–	0.5 M $LiClO_4$/AN	0.2		44					95
PAni sulfonated	Cl^- (and H^+ leaving)	–	–	1 M HCl/H_2O			37 (first ox. step)				~1000 (CV)	96
PAni sulfonated	ClO_4^- (and H^+ leaving)	–	–	0.5 M $LiClO_4$/AN			68 (both ox. steps)					96
PAni self-doped	H^+ (leaving)	–	–	1 M HCl/H_2O			47					98
PAni-Cl/ PAni-PSS bilayer	Li^+ (leaving)	Li	–	1 M $LiClO_4$/ PC+DME (1:1)			84^c			~100		100
Polypyrrole												
PPy	Cl^-	PPy·PD	K^+	KCl/H_2O	0.17^{A,C}	~1.6						15
PPy (composite with $LiClO_4$/PEO)	ClO_4^-	Li	–	$LiClO_4$/PEO	0.09^A	3.1		55^q		92–99	170/to 60% C	132,133
PPy theoretical	*ClO_4^-*	*Li*	–	*4 M $LiClO_4$/PC*	*0.40^A*	*3.5*		*140^n*	*1.2 × 10^8 (1 μm)^n* *1.2 × 10^6 (10 μm)^n* *1.2 × 10^4 (100 μm)^n*			423, 432
PPy	ClO_4^-	Li	–	$LiClO_4$/PC	0.45^A	3.0	130^l	390^l		100		90,91
PPy	ClO_4^-	Li	–	0.5 M $LiClO_4$/PC	≤0.45^A					~99	20000/to 80% C	125,136, 457
PPy	ClO_4^-	Li	–	$LiClO_4$/PC	0.33^A	3.6	82^r	40–60^f 15,^{s} 30^t			1000/to 80% C	124,126, 450
PPy	ClO_4^-	Li	–	1 M $LiClO_4$/PC	≤0.33^A	~3.9	54^d	151^d		81–98		119
PPy	ClO_4^-	Li	–	1 M $LiClO_4$/PC				134^h				439
PPy	ClO_4^-	Li–Al	–	0.1 M $LiClO_4$/PC	0.33^A	3.0				>90	50/to 30% C	121
PPy	ClO_4^-	Li	–	1 M $LiClO_4$/PC	0.24^A			85		92	>1800	110
PPy (NBR-guided)	ClO_4^-	Li	–	1 M $LiClO_4$/PC	~0.33^A					100		91,141, 143
PPy (on glass fiber separator)	ClO_4^-	Li	–	1 M $LiClO_4$/PC	0.27^A	3.8	50^l			>90	660/to 80% $C_{max.}$	131
PPy	BF_4^-	Li	–	$LiBF_4$/PC	<0.33^A		170^k	360^i				126
PPy	BF_4^-			BF_4^-	0.33^A		95^c					415
PPy	BF_4^-	Li	–	$LiBF_4$	0.3^A		90					6
PPy	BF_4^-	Li	–	1 M $LiBF_4$/ PC+DME (1:4)	0.22^A	4.0		135^d		91–100	~50	127
PPy-DBS	Li^+	Li	–	1 M $LiClO_4$/PC	0.4	3.2	53	170		~100	70/to 70% C	161
PPy-PSS	Li^+ (leaving)	Li	–	1 M $LiClO_4$/ DMSO		>3.0		220^c [W h L^{-1}]		>90	300	145
PPy-PSS	Li^+ (leaving)	Li	–	1 M $LiClO_4$/PC	0.3	3.55	57^c			~100	>30	144
PPy	ClO_4^-	PAQ/p-InP (photoassisted)		0.1 M Et_4NClO_4/ AN	≤0.31^A	2.0	14^g	28^g		82–90	>25	120

$C_{24}\cdot ClO_4^-$	ClO_4^-	PPy	ClO_4^-	0.2 M $LiClO_4/PC$	0.33^A	>2.0		78^j				438
								$20-30^f$		>90		138
PPy	ClO_4^-	Li	−	$P(EO)_{8-20}\cdot LiClO_4$						90−95	1400	460
PIn	ClO_4^-	−	−	0.1 M $LiClO_4/AN$	0.16							158
					Polythiophene							
PT	ClO_4^-	−	−	0.1 M Bu_4NClO_4/AN	0.25^A							166
PT	BF_4^-	−	−	0.5 M $LiBF_4/BN$	0.30^A	4.2	$98;^k 73^c$					168
PT	BF_4^-	PT	Bu_4N^+	0.2 M Bu_4NBF_4/AN	$0.24^{A,C}$	3.1	37^g	93^g	89000^g		"satisfactory"	167
							24^c	63^c	61000^c			
									$>300000^{g,v}$			
PT (PBT)	ClO_4^-	Li/Ni mesh	−	1 M $LiClO_4/PC$	0.10^A					>95		169
					0.18^A	3.8				>85		
					0.24^A	4.2		140^k	25000^k			
PT (PBT)	ClO_4^-	Li	−	1 M $LiClO_4/PC$ or PC+DME (1:1)	0.025^A to					~85 (PT) ~95 (PBT)		171
					0.10^A		30^c	100^c			>100	
PT	I_5^-	Zn	−	0.5 M ZnI_2/H_2O		1.3				~100	>200	38
PT	ClO_4^-	Li	−	1 M $LiClO_4$/ PC+DME (1:4)	0.16^A	4.0	52	83		76	~50	127
PT	PF_6^-	−	−	0.1 M Et_4NPF_6/AN	0.69^A (CV)			102^c				191
−	−	PT	Et_4N^+	0.1 M Et_4NPF_6/AN	0.24^C (CV)			57^c				191
PBT	ClO_4^-	Li	−	$P(EO)_{20}\cdot LiClO_4$, 70 °C	0.17^A	3.9−3.8	56^k			99−98	~300	172
PT	ClO_4^-	Li	−	0.5 M $LiClO_4/PC$		~4.0					200/to 90% C	173,176
PT (PBT)	ClO_4^-	(Li)	−	1 M $LiClO_4/PC$	0.16^A		$44;^c 37^d$			86		174
PT (PBT)	ClO_4^-	(Li)	−	1 M $LiClO_4/PC$	0.126^A		$44;^k 37^c$			99	700/to 75% C	175
					0.16^A		$56;^k 46^c$					
					0.32^A	~3.2						
PT (P3T)	BF_4^-	−	−	0.1 M Et_4NBF_4/AN	0.25							178
−	−	PT(P3T)	Et_4N^+	0.1 M Et_4NBF_4/AN	0.1							178
PT	ClO_4^-	(Li)	−	0.5 M $LiClO_4/PC$	$0.19/0.11^{bb}$						>600	471
PBT	ClO_4^-	(Li)	−	0.5 M $LiClO_4/PC$	$0.24/0.20^{bb}$						>600	
P3T	ClO_4^-	(Li)	−	0.5 M $LiClO_4/PC$	$0.37/0.32^{bb}$						>1500	
PTT	BF_4^-	−	−	0.1 M Bu_4NBF_4/AN								198
PTT	ClO_4^-	(Li)	−	1 M $LiClO_4/PC$	0.062^A		$29;^k 26^c$			95		174
PTT	ClO_4^-	(Li)	−	1 M $LiClO_4/PC$	$\leq 0.19^A$	~3.2	$32;^k 28^c$			99−98	~700; ~1000/ to 60% C	175
PDTT	ClO_4^-	(Li)	−	1 M $LiClO_4/PC$	0.41^A to 0.50^A		$57-69^k$			≤93		198
	$CF_3SO_3^-$	(Li)	−	1 M $LiCF_3SO_3$	0.50^A							
PDTT	ClO_4^-	(Li)	−	$LiClO_4/PC$			69^k			~75		207
PDTT	ClO_4^-	(Li)	−	0.1 M Bu_4NClO_4/ CH_2Cl_2		1.0 (SCE)	54^c			~100 (CV) decreasing <70 (GS)	100 (CV)	199
PDTT	ClO_4^-	Li	−	1 M $LiClO_4/PC$	0.50^A		54^c			~100 (CV) 90−100 (GS)	1000 (CV) >400 (GS)	200
PDTT	Br^-/Br_3^-	Zn	−	0.2 M $ZnBr_2/H_2O$			$\sim 90;^c \sim 30$			<50		201
PDTT	ClO_4^-	Li	−	1 M $LiClO_4/PC$	0.44^A		$51;^k 42^c$					174
PDTT	ClO_4^-	Li	−	1 M $LiClO_4/PC$	0.45^A	~3.3	$51;^k 42^c$			99	700/to 66% C	175
PDTT	BF_4^-	−	−	0.2 M Et_4NBF_4/PC	0.37 max.							202
					0.2−0.3		23^l	77^l		93		
−	−	PDTT	Et_4N^+	0.2 M Et_4NBF_4/PC	0.2−0.3							
PMT	PF_6^-	−	−	Bu_4NPF_6/AN	0.25^A (CA)							179

Table 3.1 (Continued)

positive electrode		negative electrode										
electroactive material	inserted ion	electroactive material	inserted ion	electrolyte/ solvent	doping level (y)†	OCV^a (V)	specific charge^b (A h kg^{-1})	specific energy^b (W h kg^{-1})	specific power^b (W kg^{-1})	Coulombic efficiency, (%)	cycle life (cycles/conditions or definition)	ref
Polythiophene (continued)												
PMT	PF_6^-	–	–	0.1 M Et_4NPF_6/AN								183
PMT	BF_4^-	Li–Al	–	1 M $LiBF_4$/EC+PC (4:1)	0.38^A		97^k	326		>96	>1200 (9% DL, 142 A kg^{-1})	181,182, 473
PMT	ClO_4^-	Li	–	0.5 M $LiClO_4$/PC	0.28^A		92^k			98 (CV)		208
							54^d	162		92–81	80	
PAT	BF_4^-	–	–	0.1 M Bu_4NBF_4/NB	0.49^A		68			47		186
POT					0.33^A		46			94		
PAT	ClO_4^-,	–	–	0.02 M Bu_4NClO_4/NB,	0.15^A to							185
POT	PF_6^-			0.02 M Bu_4NPF_6/NB	0.18^A							
PMOT	PF_6^-	–	–	0.1 M Bu_4NPF_6/CH_2Cl_2	2.0							187,188
PEDOT (ex PC)	PF_6^-	–	–	0.1 M Bu_4NPF_6/PC	0.30		57^l			>99		189
PEDOT (ex CH_2Cl_2)	PF_6^-	–	–	0.1 M Bu_4NPF_6/CH_2Cl_2	0.75		140^l			>99		189
PPT	PF_6^-	–	–	0.03 M Et_4NPF_6/PC	0.19^A (as grown)							191
				0.1 M Et_4NPF_6/AN	0.78^A (CV)			77^c				
–	–	PPT	Et_4N^+	0.1 M Et_4NPF_6/AN	0.72^C (CV)			77^c				191
PFPT	$CF_3SO_3^-$	PFPT	Me_4N^+	1 M $Me_4NCF_3SO_3$/ AN				18^g [W h L^{-1}]	35000^g			192
PFAK (Poly(3))	ClO_4^-	–	–	0.1 M $LiClO_4$/AN	0.33^A		26				>5000 (CV)	211
PTV	BF_4^-	–	–	1 M $LiBF_4$/PC	0.30^A		74.5^k	260		>90		193
PTE (trans)	BF_4^-	Li	–	0.1 M Bu_4NBF_4						>99	100	194,196
ex trans				PC	0.28^A		48					
ex cis				NB	0.55^A		94					
PTE	BF_4^-	(Li)	–	$LiBF_4$/PC	0.3^A		42^k	148^k				195
PTB					0.3^A		37^k	130^k				
PIBT	ClO_4^-	Li	–	1 M $LiClO_4$/PC	0.072^A		15^k			>80		203
					[at 3.5 V (Li/Li^+), much more at 4.0 V]		14^c					
PBTI 10% H_2O	ClO_4^-	Mg	–	none	0.9^A		80^d	148^d			primary cell	206
Poly(*p*-phenylene)												
PPP	AsF_6^-	PPP	K^+			0.4^{A,C}	3.3	141^k	150			24
PPP	PF_6^-	Li–Al	–	0.5 M $LiPF_6$/PC		0.4^A	4.4		320	91		24
	AsF_6^-					0.4^A	4.4		285			
PPP/7.5% soot	HSO_4^-	–	–	14 M H_2SO_4/H_2O	0.14^A–0.17^A			49–60^k		~100	~200	39,216
	ClO_4^-			11.3 M $HClO_4/H_2O$						~100		
	BF_4^-			8 M HBF_4/H_2O						~30		
PPP	ClO_4^-	Li	–	$LiClO_4$/PC	0.10^A	3.47	35^k		6700 [A kg^{-1}]	64		221
	PF_6^-	Li	–	$LiPF_6$/PC		3.20				70		
Li (?)	–	PPP	Li^+	$LiClO_4$/THF	0.22^C	2.85	78^k			90		221
PPP	AsF_6^-	Li	–	1 M $LiAsF_6$/SL	>0.16^A		>56^k			>80		215
		PPP	Li^+	$LiClO_4$/THF	>0.35^C		>123^k					
PPP/7.5% soot	HF_2^-	–	–	20–24 M H_2F_2/H_2O	0.15^A		53^k			~100		217
PPP	AsF_6^-	(Li)	–	0.1 M $LiAsF_6$ + 0.1 M $CuCl_2$/NB	0.06^A	4.5	21^k					228,229

PPP	AsF_6^-	Li	–	0.1 M $LiAsF_6$/PC	0.39^A		140^k	570^k 300^c	10000 (A kg^{-1})	87		230
–	–	PPP	Li^+	Bu_4NClO_4/AN	0.06^C		21^k					231
PPP	PF_6^-	–	–	Bu_4NPF_6/SO_2	0.25^A		87^k				44 (CV)	18
–	–	PPP/10% C, 10% PE	Li^+	$LiBPh_4$/THF $LiBMe_4$/THF $LiPF_6$/THF	0.45^C		159^k 153^c 145^k					222,475
			Na^+	$NaBPh_4$/THF	0.41^C		129^c					
$Li_xV_6O_{13}$	Li^+	$(Li_{4.3}Pb)_{80}$ PPP_{18}	Li^+	1.5 M $LiPF_6$/MTHF			A: 230 A: 450 (A h L^{-1})	70^u 170^u (W h L^{-1})		98	1000/to 80% C	59,223, 224
Na_xCoO_2	Na^+	$(Na_{3.75}Pb)_{79}$ PPP_{19}	Na^+	1 M $NaPF_6$/DME			A: 234 A: 430 (A h L^{-1})	65^u 160^u (W h L^{-1})	90 (A kg^{-1})	99−100	500/to 80% C	225,226, 415
Na_xCoO_2	Na^+	$(Na_{3.75}Pb)_{50}$ PPP_{43}	Na^+	1 M $NaPF_6$/DME			A: 200 A: 400 (A h L^{-1})				1000/to 80% C	
PPP	PF_6^-, AsF_6^-, ClO_4^-, BF_4^-, $CF_3SO_3^-$	Li	–	1.0 M Li salts/PC	$\leq 0.16^A$		27^k (initial) 23^k (100 cycles) 55^k (maximum)			>90 shallow (4%)	100 shallow (4%)	232
					Poly(triphenylene)							
PTP	ClO_4^-	–	–	0.1 M Bu_4NClO_4/AN	0.5^A							234
					Polyazulene							
PAz	BF_4^-	PAz^0	(BF_4^-)	0.1 M Et_4NBF_4/AN	0.25^A	2.3	53^k		~2000 (A kg^{-1})			236
PAz	ClO_4^-	Li	–	1 M $LiClO_4$/PC	0.18^A		42^k	130^k		97−99	540	237,238
PAz	ClO_4^-	Li	–	1 M $LiClO_4$/PC	0.20^A 0.45^A	3.3	102^l	338^l		100 90	900	90,91, 239
P(Az-*co*-Py) Az > 50%	ClO_4^-	Li	–	1 M $LiClO_4$/PC						100		240
					A Tetrathiafulvalene-Substituted Polystyrene							
PS-PTTF	ClO_4^- BF_4^-	–	–	Et_4NClO_4/AN Bu_4NBF_4/AN	$\sim 1^A$		$\sim 100^k$ (A h L^{-1})				many 1000 (CV)	255
					Ferrocene-Substituted Polyethylene							
PVFc	ClO_4^-	–	–	1 M $LiClO_4$/ AN or H_2O	0.6^A−0.99^A		75−125 $(110-180)^w$			97−100	50	257
PVFc	ClO_4^-	–	–	0.1 M Bu_4NClO_4/AN	0.8^A							258
PVFc theoretical	ClO_4^-	*Li*	–	*4 M* $LiClO_4$*/PC*	1.00^A	*3.85*		128^n $(140)^w$	2.9×10^9 $(1\ \mu m)^n$ 2.9×10^7 $(10\ \mu m)^n$ 2.9×10^5 $(100\ \mu m)^n$			423,432
					Carbazole-Substituted Polyethylene							
PVCz	ClO_4^-	Li	–	1 M $LiClO_4$/PC		4.1				86−90	100	260
PVCz	ClO_4^-	Li	–	1 M $LiClO_4$/PC	$\leq 0.05^A$		6^k			76−96		253
PVCz	ClO_4^-			0.5 M $LiClO_4$/AN	$\leq 0.50^A$		34^k				<1000/to $y \leq 0.07$	253
PVCz	ClO_4^-	–	–	0.1 M Bu_4NClO_4/AN	$\sim 1^A$		~70					262

Table 3.1 (Continued)

positive electrode		negative electrode										
electroactive material	inserted ion	electroactive material	inserted ion	electrolyte/ solvent	doping level (y)†	OCV^a (V)	specific charge^b (A h kg^{-1})	specific energy^b (W h kg^{-1})	specific power^b (W kg^{-1})	Coulombic efficiency, (%)	cycle life (cycles/conditions or definition)	ref
Polyoxyphenazine												
–	–	POPh	H^+	1 M H_2SO_4/H_2O	2^C						>5000 (CV)	263
PbO_2	(SO_4^{2-})	POPh	H^+	1 M H_2SO_4/H_2O		1.65				75–97	400	476
Polymer Adducts												
PAm-C 5:1 (I_2 adduct)	I^-	Zn	(Zn^{2+})	0.5 M ZnI_2/H_2O		1.5	151	181 for the pos	2100 (A kg^{-1})	100	300/to 80% C 1000/to 50% C	267,268
							128	154 for the cell				
PTHF-C 5:1 (I_2 adduct)	I^-	Zn	(Zn^{2+})	0.5 M ZnI_2/H_2O			168	201 for the pos		100	500	268
							138	166 for the cell				
Sulfur and Redox Polymerization Electrodes												
Na_2S_4 1.3 M solution	Na^+			NaOH aq. pH 12 13 mol % DMF	1.5^C				10–20 [mA cm^{-2}]			271
C(S) [$(CS)_n$]	Li^+	Li	–	1 M $LiClO_4$/PC $P(EO)_8{\cdot}LiClO_4$	0.3^C 0.22^C	3.05–3.49	105 175→100					274
$(CS_x)_n$ [$(CS)_n$]	Li^+	Li	–	$P(EO)_8{\cdot}LiClO_4$	$\sim 0.5^C$	(2.03)	310	630 ($x = 0.25$)				275
						(1.98)	490	970 ($x = 0.75$)				
DTDT +50% soot	Li^+	Li	–	1 M $LiClO_4$/ DME+PC (1:1)		2.7	>300 disch., 56 cycling				–	279
DTDT solution in DME	Li^+	Li	–	1 M $LiClO_4$/DME		3.0	>500 disch.					
DT-TCA +50% (AB+PTFE 65:35)	Li^+	Li	–	1 M $LiClO_4$/ DME+PC (1:1)		3.0	>430 disch., 70 cycling					280
TETD	Na^+	Na	–	NaDEDC/TETD/ 20% DMSO or SL				≥100				286
					$\sim 2^C$	2.3		80–110	40–60 peak, 6 steady			288,289, 295
HEDS	Na^+	Na	–					200				288
DMS	Na^+	Na	–	CH_3SNa/DMS/ 40% DMSO				540 ?				288
TETD	Li^+	Li	–	LiDEDC/TETD/ 75% DMSO		2.6		82–156			135 (10%)	292
X1 (film with C and electrolyte)	Li^+	Li	–	$P(EO)_8{\cdot}LiN(SO_2CF_3)_2$		3.0		264 $(241)^w$ 200	160 $(144)^w$ 2400		350 (77–93 °C) (100 °C)	304,305, 307, 308
X1 (film with C and electrolyte)	Li^+	Li	–	$P(EO)_8{\cdot}LiN(SO_2CF_3)_2$		3.0		136 $(166)^w$	67 $(83)^w$			306
X1	Na^+	Na	–	β''-alumina		2.81					32	294,309
X2						2.56					–	
X3						2.48					–	
X4						2.61					–	
X5						2.82					40	
X6						2.56					–	

X0	Li^+	Li	–	$P(EO)_{20}\cdot LiCF_3SO_3$		2.5	120	240			308,309
X1						3.0	110	330			
X2						2.8					
X3						2.7					
X4						2.8					
X5						3.0					
X6						2.7					
X7						2.6					
X8						2.5	170	350			
X9						2.3					
X1/PAni/GE (1:0.25:2.3)	Li^+	Li	–	$LiCF_3SO_3$/GE		>3.0 (3.7)		>220			105
X1/C/GE (1:0.25:2.3)	Li^+	Li	–	$LiCF_3SO_3$/GE		(3.7)		170			
X1/PAni/GE (1:1.2:2.5; 6% C)	Li^+	Li	–	$LiBF_4$/GE		3.07	88 (cath.)	203 (cell)		50	106
X1/PAni/MP (2:1:1.5)	Li^+	Li	–	$LiBF_4$/GE			180 (cath.)	600 (cath.) 450 (cell)^y		100	107,313
Graphite, Pitch-Based Carbons											
$LiCr_3O_8$, LiV_2O_5	Li^+	C [PG]	Li^+	1 M $LiClO_4$/PC	~0.95^x		~350		~99	~500/to 80% C	327
(Li)	–	C [PCk]	Li^+	1 M $LiAsF_6$/ EC+PC (1:1)	~0.5^x		~180			>100/to 95% C	331
(Li)	–	C [SG]	Li^+	1 M $LiAsF_6$/ EC+PC (1:1)	~1.0^x		~370			>20/to 98% C	
(Li)	–	C [PCk]	Li^+	1 M $LiCF_3SO_3$/ EC+PC+DMC (1:1:3)			200		99		356
$LiNiO_2$	Li^+	C [NG]	Li^+	1 M $LiClO_4$/ EC+DME (1:1)	~1.0^x	~4.0	325 (Gr) 88 (A+C)		98		318,328
(Li)	–	C [PCF]	Li^+	1 M $LiClO_4$/PC	~0.6^x		220 (C)		~100	>20	343
LiV_3O_8	Li^+	C [PCF]	Li^+	1 M $LiClO_4$/PC			50 (A+C)	~150 (A+C)			
(Li)	–	C [PCF]	Li^+	1 M $LiCF_3SO_3$/ EC+DME (1:1)	0.55^x		~200 (C)		98	>20	345
$LiCoO_2$	Li^+	C [PCF, graphitized]	Li^+	1 M $LiPF_6$/EC+DEC		4.2	120	[310 W h L^{-1}]		>400	358
(Li)	–	C [PCk]	Li^+	1 M $LiClO_4$/ EC+PC (1:1)			140–280 (C)			>50	339
(Li)	–	C [Gr]	Li^+	$LiPF_6$/PAN+EC	1.0^x	0.02					332
(Li)	–	C [PCP]	Li^+	$LiPF_6$ (11.6 wt %)/ EC+DEC	0.4^x		150 (C)			>10	346
(Li)	–	C [SG]	Li^+	1 M $LiAsF_6$/ THF+MF (1:1) –6 atm CO_2	0.95^x					>10	335
(Li)	–	C [GW]	Li^+	1 M $LiClO_4$/ EC+DEC			363 (C)		100		349,355
$LiCoO_2$	Li^+	C [GW]	Li^+	1 M $LiClO_4$/ EC+DEC			158 (“system”)		100		
(Li)	–	C [SG]	Li^+	0.5 M $LiN(CF_3SO_2)_2$/ EC+DMC	0.92^x						340
(Li)	–	C [PCF] C [SG]	Li^+	1 M $LiPF_6$/ EC+PC (1:1)	≤0.96^x						330,341
(Li)	–	C [MCMB] C [NG]	Li^+	$P(EO)_8\cdot LiClO_4$			410 (C) 280 (C)				329
(Li)	–	C [MCMB] HTT 700 °C	Li^+				750				354

Table 3.1 (Continued)

positive electrode		negative electrode										
electroactive material	inserted ion	electroactive material	inserted ion	electrolyte/ solvent	doping level (y)†	OCV^a (V)	specific charge^b (A h kg^{-1})	specific energy^b (W h kg^{-1})	specific power^b (W kg^{-1})	Coulombic efficiency, (%)	cycle life (cycles/conditions or definition)	ref
Graphite, Pitch-Based Carbons (continued)												
(Li)	–	C [MPC]	Li$^+$	1 M $LiPF_6$/ EC+DEC (3:7)			825				20	351
(Li)	–	C [PCF]	Li$^+$	1 M $LiClO_4$/ EC+PC (1:1), EC+DMC (1:1)			>300 (C)					347
Na	–	C [SG]	Na$^+$	$P(EO)_8{\cdot}NaCF_3SO_3$	[NaC_{70}]							336
Na	–	C [PCk]	Na$^+$	$P(EO)_8{\cdot}NaCF_3SO_3$	[NaC_{30}]							
Na	–	C [SB]	Na$^+$	$P(EO)_8{\cdot}NaCF_3SO_3$	[NaC_{15}]							
Heteroelement-Substituted Carbons												
(Li)	–	BC_2N	Li$^+$	1 M $LiClO_4$/PC or EC+DME			50–100^k					360
(Li)	–	CN_z	Li$^+$	1 M $LiPF_6$/ EC+PC+DME (1:1:2)	0.6–0.7^x							362
(Li)	–	B_zC_{1-z}	Li$^+$	1 M $LiN(CF_3SO_2)_2$/ EC+PC (1:1)	0.75–1.16^x		≤437^k					361
Li	–	$C_{1-z}Si_z$	Li$^+$	1 M $LiN(CF_3SO_2)_2$/ EC+PC (1:1)			400–500^k				>35	363
(Li)	–	$B_{0.05}C_{0.95}$	Li$^+$	1 M $LiN(CF_3SO_2)_2$/ EC+DME (1:1)	0.94^x		~350					316
Pyrolyzed Cellulose or Phenolic Resin												
C [ACF]	ClO_4^-	Li	–	$LiClO_4$/DME+PC	0.036^z	3.9		110	20000^i	~94	>10/to 66% C	364
C [ACF]	ClO_4^-	C [ACF]	Bu_4N^+	1.06 M Bu_4NClO_4/ PC	0.024^z	3.6	[27 F g^{-1}] (capacitor)			95	>200	364
C [ACF]	ClO_4^-	C [ACF]	Li$^+$	1 M $LiClO_4$/BL	0.0315^z	3.0	[36.5 F g^{-1}] (capacitor)	36.2^c	11100	≥96	>130/to 96% C	365
C [ACF]	ClO_4^-	Li	–		0.05^z	4.6			14800		>50/to 83% C	365
Polyacenes												
–	–	PAS-PF	Na$^+$	[Na naphthalide/ THF]	0.03–0.13^z							366,367
PAS-PF	I$^-$	–	–	[I_2 vapor]	0.06–0.07^z							
PAS-PF (4.5–1.0 V)	ClO_4^- + Li$^+$	Li	–	1 M $LiClO_4$/ SL+BL (1:1)			220^k	550^k				368
PAS-PF (4.0–2.0 V)	ClO_4^-	Li	–	1 M $LiClO_4$/ SL+BL (1:1)			71–82		≤380 (A kg^{-1})			
PAS-PF (2.0–0.0 V)	ClO_4^-	PAS-PF	Li$^+$	1 M $LiClO_4$/ SL+BL (1:1)			[37 F g^{-1}] 38–42				3000/deep	
PAS-PF	ClO_4^- or BF_4^- + Li$^+$	[Li]	–	1 M $LiClO_4$ or $LiBF_4$/PC	0.03^z p 0.04^z n					~100	>200 (CV)	370
PAS-PF (4.0–1.5 V)	BF_4^- + Li$^+$	Li	–	2 M $LiBF_4$/PC	0.02^z p 0.06^z n	4.0		110 (W h L^{-1})				371
PAS-PF (2.5–0.0 V)	BF_4^-	PAS-PF	Et_4N^+	1 M Et_4NBF_4/PC							several thousand; 2000/to 90% C at +70 °C	
[Li]	–	PAS-PF	Li$^+$				530			~100	>10/deep >100 (CV)	373
[Li]	–	PAS-PF	Li$^+$	$LiPF_6$/EC+DEC			>450					350
PAni	ClO_4^-	PAS-PF	Li$^+$	1 M $LiClO_4$/ EC+PC (1:1)			35					372
PAS-PF	Li$^+$	[Li]	–				71			>95		
PAS-SD	ClO_4^-	Li	–	1 M $LiClO_4$/PC		~3.4	~160				>10	375

$Li(Ni,Co)O_2$	Li^+	PPFA	Li^+	1 M $LiClO_4$/ DME+PC (1:1)			320 (PPFA)			97	>60	377
											1200/2-h disch.,	40
							∼400			98	>120/to 80% C	378
[Li]	–	PPFA	Li^+	1 M $LiN(CF_3SO_2)_2$/ EC+DME (1:1) or EC+PC			330					316
[Li]	–	PPPP	Li^+	1 M $LiPF_6$/ DME+PC (1:1)			680			“excellent”		379
[Li]	–	PPPP	Li^+	$LiClO_4$/PAN+EC			610			99		380
[Li]	–	C_{60}-F	Li^+	0.5 M $LiClO_4$/PC	0.05^z		108^c	217^c				381
[Li]	–	C [model]	Li^+	1 M $LiClO_4$/ EC+DEC			134−497					382
TSPAN	ClO_4^-	Li	–	1 M $LiClO_4$/PC	0.011^z	3.8				100		375,386 387
					0.016^z	4.0	∼33			93		
	Li^+	Li	–		0.092^z	2.0	∼185			100		
					0.13^z	1.6				100		
	$ClO_4^- + Li^+$	Li	–		$0.016^z p$ $0.09^z n$		∼200				100 (CV)	
TSPAN	ClO_4^-	TSPAN	Li^+	1*M* $LiClO_4$/PC						96−100	2000	388
TSPAN	ClO_4^-	Li	–		$0.045-0.0475^z$		90−95	250−270		100	2000/shallow 130/deep	
PPAN	$N(CF_3SO_2)_2^-$	Li	–	1*M* $LiN(CF_3SO_2)_2$/ DME+PC (1:1)			333					389
Li	–	PAN-FC	Li^+		0.15^z		327 425					340
PAni	Li^+	PAPI	Li^+	3*M* $LiClO_4$/ DME+PC		3.7	61 (+) 270 (−)	(in cell)			100	102
(Li)	–	PAPI	Li^+	3*M* $LiClO_4$/ DME+PC			500^c	(half-cell)				102
Li	–	$BC_{10}N$	Li^+	1*M* $LiCF_3SO_3$/ EC+DME (1:1)			97^k		30 (A kg^{-1})	95	>20	395
		$BC_{10}NLi_{0.44}$	Li^+				109^k			94	>20	
(Li)	–	$C_{1-z}P_z$ ($z = 0.04$)	Li^+	1*M* $LiClO_4$/ DME+PC (1:1)			450^k					396
Li	–	$C_{1-z}Si_z$	Li^+	1*M* $LiN(CF_3SO_2)_2$/ EC+PC (1:1)			$540-580^k$					363

[†] A, anion; C, cation. [a] Open circuit voltage, charged cells. [b] Maximum values. Whenever no superscript appears, the basis of the specific charge/energy/power is not given. [c] Based on the weight of the doped polymer(s) [or active material(s)]. [d] Based on the weight of the doped polymer and the weight of the consumed metal. [e] Average specific power. [f] Estimated value for a practical battery. [g] Based on the weight of both polymer film electrodes. [h] Based on the weight of one polymer film electrode. [i] Based on the weight of the undoped polymer (or active material) and the weight of the consumed metal. [j] Based on the weight of both electroactive materials. [k] Based on the weight of the undoped polymer (or active material). [l] Based on the weight of the electroactive polymer [m] Complete packaged battery, AAA size. [n] Theoretical specific energy/power for a cell without hardware or separator. [o] Based on the weight of the undoped polymer with co-inserted solvent. [p] Based on the gross weight of the cell (10% PAni, 3% Li, 34% electrolyte, 53% hardware). [q] Based on the weight of the composite material. [r] Based on the weight of the doped polymer with co-inserted solvent. [s] Practical specific energy, cylindrical cell of Mignon size (not optimized). [t] Practical specific energy, flat cell (not optimized). [u] Prototype AF- or AA-size cells. [v] Thinner films. [w] Per liter. [x] x in Li_xC_6. [y] Expected value. [z] Ions per C atom. [aa] Based on the weight of electroactive material plus conductive filler. [bb] First number: cycle 10; second number: cycle 600.

Table 3.2. Typical Values of Specific Charge[a]

polymer or dimer	y	equiv wt [g/MU; g/dimer]	spec. charge (without counterions) [A h kg^{-1}]
PAc	0.07	13	144
PAni (aq.)	0.5	91	147
PAni (org.)	1.0	91	295
PPy	0.33	65	136
PT	0.25	82	82
PMT	0.25	96	70
PPP	0.4	76	141
PAz	0.25	126	53
PCz	0.25	165	41
TETD		296	181
DMS		94	570
EEDS		210	255
X1		148	362
X7		142	377

[a] For polymers typical values of y from Table 3.1; for dimers $n = 2$.

that these high values of specific power were measured over very short periods of time and are actually an extrapolation from so little active electrode material that they reflect surface,[21] rather than bulk, properties of the polymer (stated otherwise: they reflect a capacitor rather than battery parameter). Moreover, such values are calculated while disregarding the masses of conducting substrate and counter electrode. For practical Li/$(CH)_x$ batteries, maximum values of specific power ranging from[21] 680 W kg^{-1} to[49] 5 kW kg^{-1} have been published. These values have been estimated by extrapolating short-circuit discharge results for laboratory cells with a few milligrams of $(CH)_x$ using an empirical reduction factor of 6 or 7. Using the data given in ref 49, *viz.*, the current of 0.55 mA sustained for 25 min with 3.8 mg of $(CH)_x$, and the same empirical reduction factor, about 70 W kg^{-1} rather than 5 kW kg^{-1} can be calculated for "sustained" power.

Solid-electrolyte cells show somewhat lower peak values of specific power, typically between 250 W kg^{-1} (PEO-based electrolyte[11]) and 3.2 kW kg^{-1} (PVDF + PC electrolyte[55]), all values being based on the weight of the polymer film alone.

3.1.4. Coulombic and Voltage Efficiency

Values for Coulombic as well as voltage efficiencies exhibiting a spread from 20% to 100% have been reported depending on the particular experimental conditions used (Table 3.1). This spread of the values can be explained by the fact that, generally, polyacetylene electrodes are rather unstable and sensitive to impurities and treatment conditions.[45]

Discrepancies between the estimates of doping levels of electrochemically doped $(CH)_x$ obtained by coulometry and elementary analysis suggest that, in many cases, a significant fraction of charge is consumed for oxidation of the electrolyte.[412] Thus, polyacetylene can be electrochemically oxidized in propylene carbonate with nearly 100% Coulombic efficiency to doping levels of less than $y = 0.10$.[45] At higher doping levels, the potential of the oxidized film rises above 3.9 V *vs* Li/Li$^+$, and the solvent is not truly stable.[412,413] Thus, experimental Coulombic efficiencies typically are functions of the polymer's doping level (which also determines the potential). Besides, the very slow diffusion of counterions from the bulk to the surface of $(CH)_x$ makes them unavailable for fast release into the electrolyte during discharge, and thus influences the measurable (apparent) Coulombic and voltage efficiency of $(CH)_x$ electrodes.[19,51]

For example, in propylene carbonate, Coulombic efficiencies as high as 91% with a doping level of $(CH)_x$ of $y = 0.024$ which dropped to 35% at $y = 0.194$ were reported for a particular experiment.[400] The Coulombic efficiency increased with increasing charging current density in this experiment: at 0.1 mA cm^{-2}, the value was 46%, and at 1 mA cm^{-2} it was 88%.[400] An opposite trend was found at higher current densities: at 0.5 and 1 mA cm^{-2} the Coulombic efficiency was 87%, but at 2.5 mA cm^{-2} it was only 55%.[44] The Coulombic efficiencies of $(CH)_x$ electrodes have also been measured as a function of temperature[400] and were found to be significantly higher at −20 °C than at room temperature. Farrington *et al.*[56] performed more sophisticated discharge cycles after charging a Li/$(CH)_x$ cell with a constant current of 50 μA cm^{-2} (which caused the polymer potential to rise to 3.9 V *vs* Li/Li$^+$, already at $y = 0.07$): the cell was discharged with constant currents of 500, 250, or 120 μA cm^{-2}. About 50−65% of the charge was removed before the potential reached 2.5 V, at which point cell discharge was continued at a controlled potential of 2.5 V, which added 30−40% of the initial oxidation level to the Coulombic yield and brought the total yield to 85−95%.

The above examples show that, depending on the particular experimental conditions, either electrolyte oxidation (and/or other parasitic reactions) or the slow dopant diffusion can prevail during experiments exhibiting low apparent Coulombic efficiencies.

3.1.5. Cycling Properties

No satisfactory cycling experiments on polyacetylene electrodes are available yet. Although statements like "many possible recharges" as well as cycle lives of up to >2000 cycles have been published in the past, one has to be very careful when short-time and/or shallow cycling experiments are extrapolated to predict the behavior of real-size cells.

Nagatomo *et al.*[44] claimed that their n-$(CH)_x$/LiClO$_4$-PC/p-$(CH)_x$ cells exhibited no observable degradation even after 2000 cycles, but the cycling had been performed only with $\Delta y = 0.002$, which translates to a specific energy of only about 5 W h kg^{-1}. Each cycle was limited to 10 min discharge at a constant resistance of 50 kΩ and 10 min charge at 0.05 mA cm^{-2}. The cell was reported to be usable over the temperature range from −20 to +50 °C.[44] The above cell was later modified to the configuration n-$(CH)_x$/PVDF·LiClO$_4$-PC/p-$(CH)_x$ by using a solid electrolyte, and 300 very shallow cycles, again with $\Delta y = 0.002$, were reported.[55]

Deep cycling obviously causes rapid deterioration of the cells. Very fast loss of charge has been reported for $(CH)_x$/$(C_4H_9)_4NClO_4$-PC/$(CH)_x$ cells by Broich and Hocker,[52] who found that cells charged with a constant voltage of 4 V and discharged through a load resistance of 1−100 Ω were damaged within about five charge−discharge cycles, in the event that they were completely discharged in each cycle. These results were confirmed by Nagatomo *et al.*[54] for two types of larger-size Al/$LiClO_4$-(PC + EC)/$(CH)_x$ cells with electrode areas of 20 and 54 cm^2 where currents of up to 20 mA were used for charging and discharging (which raised the cell voltages after charging to values in excess of 4.5 V). Degradation of $(CH)_x$ as well as a decomposition of the organic solvent due to the excess amount of charge and high charging voltage were observed.[54]

Farrington *et al.*[56] pointed out that, in order to reach an efficient cycling of polyacetylene, a minimum of liquid electrolyte and ultraclean conditions should be used. To avoid undesirable side reactions during cycling, an upper limit of $y < 0.10$ has been recommended for the anion as well as cation doping.[19,45,400] Then the $(CH)_x$-containing cells will exhibit rather stable voltages and high Coulombic efficiencies. However, a degradation of the $(CH)_x$ film surface can occur at current densities of ≥ 1 mA cm^{-2}, when due to the slow solid-state diffusion of dopants into the bulk polymer the dopant concentration at the surface, and thus the potential, increases to excessive values. This phenomenon has been made responsible for the low cycle life, of about 20 cycles, observed even at the rather low overall doping level of $y \approx 0.06$.[400]

Long-term deep-cycling data are not available at all for polyacetylene.

3.1.6. Chemical Stability/Self-Discharge

Polyacetylene is air-sensitive.[44] When not in contact with an electrolyte, both virgin and doped $(CH)_x$ react rapidly with oxygen.[45,56] Oxidation takes two general forms. When PAc is exposed to small concentrations of oxygen at low pressures, oxidation appears to be reversible, at least for short times of exposure. Upon exposure to oxygen for longer periods of time, the reaction becomes irreversible, the polymer becomes brittle and even more insulating than a virgin film. The latter reaction involves irreversible oxidation of the polymer chains and a degradation of the conjugated bond network.[45] In addition, there is no doubt that many of the oxidized polyacetylene/electrolyte/solvent combinations reported in the literature are thermodynamically unstable, and hence PAc will suffer irreversible oxidation of the conjugated-polymer backbone.[56] Doped $(CH)_x$ films are unstable already at moderate temperatures (~50 °C). Their decomposition involves irreversible reactions of the guest ion with the polymer, which decreases the electronic conductivity of the material.[45] Polyacetylene also self-reacts, forming cross-links and defects.[56] Nevertheless, at least during the time needed for doping in aqueous electrolytes, no reaction with water was found to take place.[23]

The stability of $(CH)_x$ electrodes in electrochemical cells has been examined in a number of laboratories,[5,21−23,45,51,52,55,56,400] but the results are somewhat controversial. In a very early paper[21] it had been claimed that, in Li/$LiClO_4$-PC/$(CH)_x$ cells, no degradation of the polyacetylene electrode was observed. It was also noted that such cells did not spontaneously lose their charge.[21,22]

Polyacetylene that has been *n*-doped with Li^+, as well as neutral $(CH)_x$, appear to be quite stable toward reaction with $LiClO_4$-THF electrolyte.[23] For $(CH)_x$ reduced to a y value of 0.04, near 100% Coulombic efficiency was observed for 16 cycles when the film was reoxidized immediately after reduction. When it was allowed to stand on open circuit for 24 h after reduction to $y = 0.04$, a slight decrease in efficiency to 95% was observed.[45] The loss of capacity by $(CH)_x$ electrodes can be attributed to the difficulty of recovering dopant species which have diffused deeper into the polymer film.[53] Another study[23] claimed that, in the same electrolyte, the potential of a $(CH)_x$ electrode reduced to a y value of 0.07 remained remarkably constant at ~1.05 V *vs* Li/Li^+ for 40 days. When reoxidized back to neutral $(CH)_x$ the electrode displayed a stable OCV of ~2.04 V for at least 40 days.[23]

The conservation of charge during storage of *n*-$(CH)_x$/*p*-$(CH)_x$ cells is not as good as shown in the above examples for reduced and neutral $(CH)_x$ electrodes.[23] It was reported that the OCV of $(CH)_x$/$(C_4H_9)_4NClO_4$-PC/$(CH)_x$ cells decreases from 3.4 to 1.0 V within about 20 h.[52] Shinozaki *et al.*[400] reported that the Coulombic efficiency of a Li/$LiClO_4$-PC/$(CH)_x$ cell dropped to <50% after 20 h of storage. The OCV of these cells decreased from 3.96 to 3.49 V during the same period. Other studies[45,56] revealed that oxidized polyacetylene is unstable toward, and will react with, electrolytes containing $LiClO_4$ and propylene carbonate. For example, a $(CH)_x$ sample oxidized to $y = 0.03$ lost about 40% of its stored charge during 40 h at open circuit in this electrolyte. Moreover, extended electrochemical cycling of polyacetylene with ClO_4^- as the counterion may result in its slow, irreversible chlorination.[56]

Nagatomo *et al.*[55] compared cells with liquid electrolyte: $(CH)_x$/$LiClO_4$-(PC+EC)/$(CH)_x$, and cells with plasticized polymer electrolyte: $(CH)_x$/PVDF·$LiClO_4$-PC/$(CH)_x$, which lost 50% of their charge at open circuit, the times required for this loss being 1 day and 5 h, respectively. The rapid self-discharge is not caused by $(CH)_x$ degradation but by reactions of the $(CH)_x$ film with the electrolyte and/or with residual impurities.[55] The polymer itself can be recharged without loss of charge acceptance. In studies of self-discharge of Li/$LiClO_4$-PC/$(CH)_x$ cells by electrochemical impedance spectroscopy, it was found that the component R_r in the equivalent circuit (which is related to the self-discharge reaction rate) clearly correlates with the open-circuit voltage regardless of the charging current.[51] Spontaneous undoping has been cited as a reason for self-discharge.[414] A mechanism (recombination?) is not evident so far.

The rapid loss of charge which occurs when common-quality liquid or solid electrolytes are used must obviously be considered as an important limitation for practical applications of $(CH)_x$ cells. It is hardly possible to draw serious conclusions concerning the stability of $(CH)_x$, because the exact experimental conditions used in the various laboratories are difficult to compare or (in some papers) even to find out. However, many of the divergent results reported for $(CH)_x$ cells can be rationalized in terms of an extreme sensitivity of $(CH)_x$ electrodes to traces of impurities in the electrolyte. Therefore, polyacetylene must be handled carefully during cell assembly, used only with high-purity electrolytes, and cycled within strict potential limits.[56] As pointed out by Schlenoff and Chien[412] who reinvestigated the efficiency, stability, and self-discharge of electrochemically doped $(CH)_x$ in propylene carbonate in the absence of impurities and metallic lithium, the stability of *p*-type $(CH)_x$ is actually much higher than had been previously estimated for $(CH)_x$ batteries. The authors were able to show that at the $(CH)_x$ electrode, an oxidation product of the solvent is generated which is mobile in the electrolyte and mediates or accelerates the discharge of *p*-doped $(CH)_x$ by metallic lithium in a Li/$(CH)_x$ battery. Furthermore, it was found that the stability of *p*-type $(CH)_x$ is in reality much greater than that of *n*-type $(CH)_x$.[412]

3.2. Polyaniline (PAni)

Polyaniline has been investigated, both in nonaqueous electrolytes, typically in combination with a Li or Li-Al negative electrode, and in aqueous electrolytes, typically with a Zn negative electrode. Both cell types are treated below. In addition, polyaniline–polypyrrole dual layers have been characterized as electrodes for lithium secondary batteries.[416,417]

3.2.1. Specific Charge and Energy

Values of specific energy ranging from 87 to 540 W h kg^{-1} have been measured for Li/PAni and Li-Al/PAni cells with *liquid nonaqueous electrolytes*. As for other electroactive polymers, most of these values have been derived from cells containing $LiClO_4$-PC as the electrolyte,[36,84,90,91,418] and are typically based on the weight of the electroactive polymer only. For example, an experimental specific charge of 148 A h kg^{-1} was reported when referring to the weight of the polymer, which translates to 93 A h kg^{-1} when the weight of ClO_4^- and the Li consumed is included.[84] Referring to the polymer weight alone, a specific energy of 540 W h kg^{-1} was obtained at an average discharge voltage of 3.65 V *vs* Li/Li^+ for Li/PAni cells, in contrast to the 340 W h kg^{-1} calculated by referring to the weights of Li, ClO_4^-, as well as the polymer.[84] Some other representative values are listed in Table 3.1.

The specific charge values were determined directly *in situ* in aqueous and nonaqueous electrolytes.[418] A specific charge of 270 A h kg^{-1} of PAni was found from the doping level of 0.9 attained in $LiClO_4$-PC, but due to solvent uptake and to incomplete doping (oxidation), only 160 A h kg^{-1} of PAni could be realized during cycling. Still lower values are calculated when the weight of the anion is included.

The specific charge of PAni in $LiClO_4$-PC generally improves with the number of charge–discharge cycles, and reaches a maximum after about 30 cycles, which is believed to be due to the electrolyte progressively penetrating into the polymer and supplying sufficient quantities of anions for enhanced doping of the PAni.[36] The specific charge available from PAni during discharge also increases with the operating temperature. For example, at a given current density of 0.5 mA cm^{-2}, it was 100 A h kg^{-1} at 25 °C, 140 A h kg^{-1} at 40 °C, and 150 A h kg^{-1} at 60 °C. This temperature effect, actually a kinetic effect, has been attributed to the increase in electrolyte conductivity and to higher diffusion coefficients of the ions inside the polymer.[36] On the other hand, no capacity loss was found to occur between 40 and 0 °C, and only 20% capacity loss occurred down to −20 °C.[60]

The PAni film morphology strongly depends on the polymerization method and temperature. Polymerization of aniline at higher temperatures yields larger grains.[419] Accordingly, the specific charge and other characteristics of PAni also depend on preparation conditions.[78,88,89,420] Compact PAni films have been generated by adding a small amount of *p*-phenylenediamine to the 0.2 M aniline solution during polymer growth.[72] The resulting films had a denser and more uniform structure. A denser structure is believed to provide higher values, not only of energy density but also of specific energy of the polymer film. From a comparative study conducted with Li/PAni cells,[421] it was concluded that the highest specific energy, of 352 W h kg^{-1} of PAni, is provided by electrochemically grown PAni films. Lower values are obtained with PAni in powder or pellet form (332 and 122 W h kg^{-1}, respectively). For coin-type PAni cells,[78] the best cell performance in terms of discharge capacities and other characteristics was found with PAni having a fibrillar structure that was produced at 10 mA cm^{-2} by electrochemical oxidation of aniline in HBF_4. The morphology and surface area, and thus the discharge performance, depend on the solvent,[93] acid,[66] and oxidizing agent[87] used to prepare PAni.

The effects of solvent and electrolyte salt type and of electrolyte concentration on the specific charge of polyaniline have also been investigated in the test media.[63,422] For example, in ref 422 the total charge stored in PAni was claimed to be 30% higher when using 2 M $LiClO_4$ in ethylene carbonate (EC) instead of PC. The experimental specific charge of the polymer was 100 A h kg^{-1} when the electrolyte was present in large excess, but decreased when smaller quantities of electrolyte were used. When the weight of a standard electrolyte solution, 1 M $LiClO_4$-(PC + EC), included in the cell was only about twice that of PAni, the specific charge was about 60 A h kg^{-1}.[63] This capacity reduction depends on the electrolyte type. For electrolyte salts such as $LiPF_6$ or $LiBF_4$, the capacity loss was found to be similar to that observed in the $LiClO_4$ case, but the values of specific charge themselves were significantly lower.[63] A correlation was found between the optimum electrolyte layer thickness and the thickness of the polymer cathode.[423] For example, with a 100 μm thick PAni electrode the electrolyte (4 M $LiClO_4$-PC) thickness should be about 300 μm. According to calculations concerning the influence of salt concentration on the specific energy of Li cells with PAni and other polymers, the highest salt concentrations experimentally feasible are the best.[423]

The effect of polyaniline film thickness (20–100 μm) on the polymer's experimental specific charge in coin-type model Li/PAni cells has been examined under constant current density (0.13 mA cm^{-2}) conditions.[65] The discharge capacity of cast, monolithic

PAni membranes (about 80 A h kg^{-1} for 20 μm films) was found to be an inverse function of thickness of the polyaniline. This implies that the utilization of PAni films is limited to a rather thin region next to the surface of the polymer, and that the movement of dopants (ClO_4^-) in the polyaniline matrix is comparatively slow. For composite materials of polyaniline and porous carbon cloth, it was found that, even though the composites became thicker than comparable PAni membranes, the utilization of PAni improved to 80−100 A h kg^{-1} for composites of up to 500 μm thickness.[65] A value of 119 A h kg^{-1} was found for fiber-reinforced PAni by Echigo *et al.*[102] This material was used to build a prototype 17 mW h CR-2016 cell with pyrolytic carbon anode (see section 2.9.4).

In Japan, coin-type Li-Al/$LiBF_4$-(PC + DME)/PAni secondary cells in Al920, Al2016, and Al2032 sizes have been developed and tentatively commercialized.[78] The recommended cut-off charging voltage of the cell is 3.0 V, but it can be increased to 3.5 V if slight electrolyte degradation is accepted. The discharge capacity of the Al2016 cell is 3.0 mA h with 3.0 V and 6.0 mA h with 3.5 V. For the polymer electrode, the corresponding values of specific charge are 60 A h kg^{-1} and 120 A h kg^{-1}, the values of specific energy are 160 W h kg^{-1} and 370 W h kg^{-1}, respectively.[78] These coin cells were shown to perform at temperatures between −20 °C and +40 °C. At −20 °C, about 80% and 40% of the nominal capacity are retained at discharge currents of 10 and 100 μA, respectively.[78]

All-polymer (PAni/PAni and PPy/PAni) cells were assembled by Lee *et al.*[71] Cell performance was not satisfactory (low Coulombic efficiencies, low cell voltages leading, presumably, to rather low specific energies).

All-solid-state Li/PAni laboratory cells, typically with PEO-based electrolytes, have been proposed and characterized.[424,425] However, their specific energy is significantly lower than that found in the liquid−electrolyte case,[426] namely about 50 W h kg^{-1} when based on the PAni weight.[424]

Zn/PAni cells with *liquid aqueous electrolyte* where the Zn/Zn^{2+} couple replaces the Li/Li^+ couple discussed above have been studied using PAni films formed chemically or electrochemically in aqueous media.[20,68−70,73,83,427−429] The specific charge of the polymer in aqueous electrolytes can be as high as 152 A h kg^{-1} (when only the polymer weight is taken into consideration), which is comparable to that in Li/PAni cells.[83] Of course, the voltage of a charged Zn/PAni cell is significantly lower (about 1.3 V) than the values of 3.0−3.6 V typical for Li/PAni. Moreover, the Zn/PAni cells pose problems with regard to long-term rechargeability of the Zn electrode.

With $ZnCl_2$, $ZnSO_4$, and $ZnBr_2$ as the electrolytes, the Zn/PAni cells provide specific energies in the range of 50−160 W h kg^{-1} of PAni.[68,70,73,83,429] As in the Li/PAni case, the specific energies were mostly calculated by referring to the polymer's weight alone, *i.e.*, neglecting the dopant, counter electrode, electrolyte, and cell hardware weights. For example, a value of 159 W h kg^{-1} translates to only 115 W h kg^{-1} when the weights of the Zn and Cl^- involved in the reactions are included in the calculation.[83]

With PAni electrodes in aqueous 1 M $ZnSO_4$ solutions, thermal response studies demonstrated that SO_4^{2-} ion insertion occurs in the first, H^+ ion elimination occurs in the second anodic peak or oxidation step.[67] These two steps are found only for PAni. Evidently, using both steps implies that correspondingly higher values of specific charge can be attained, but stability problems may arise (see section 3.2.6).

With $ZnCl_2$ as the electrolyte, values of specific charge of up to 100 A h kg^{-1} of the polymer can be realized. Attempts to store more charge led to rapid polymer degradation.[70] In $ZnBr_2$ media, additional charge unrelated to polymer doping can be stored via the Br_3^-/Br^- redox couple. Unfortunately, there is a tendency toward attack of the polymer by Br_2.[70] Mengoli *et al.*[69] replaced the above electrolytes in a Zn/PAni cell by ZnI_2. The specific charge was increased to about 140 A h kg^{-1} of the polymer. However, in these cells the polyaniline rather acts as a current collector: the redox reaction of the I_3^-/I^- couple proceeds rapidly in the PAni film. It was estimated that one I_3^- ion can be stored per N atom in PAni.[69]

Sulfonated polyaniline, owing to its higher molecular weight, should exhibit lower values of specific charge. However, upon charging in aqueous electrolytes, protons are expelled from the polymer, and in nonaqueous lithium salt solutions, lithium ions are expelled, i.e., the polymer is converted from an anion to a cation exchanger.[95] Considering the low equivalent weight of lithium ions, sulfonation of polyaniline could be an avenue to higher values of specific charge. A sulfonated polyaniline prepared by copolymerization of *o*-aminobenzenesulfonic acid and (minor quantities of) aniline exhibited about 47 A h kg^{-1} in aqueous solutions (first redox process only), over 80 A h kg^{-1} in nonaqueous solutions (both redox steps).[98] For a complete Li/sulfonated PAni cell with nonaqueous $LiClO_4$ electrolyte, 52 A h kg^{-1} and 130 W h kg^{-1} were calculated on the basis of experimental results (disregarding current collectors, separators, and the cell container).[96]

Polyaniline with poly(*p*-styrenesulfonate) as the counterions (PAni-PSS) is cation-exchanging. Due to the anionic weight penalty, its specific charge as cathode material is relatively low. When a bilayer electrode was prepared with PAni-PSS as an outer and PAni-Cl as an inner layer, where PAni-PSS functioned both as a cation-selective membrane and electroactive material, a higher specific charge (84, rather than 53, A h kg^{-1}) was observed.[100,101]

Results for the composites of PAni and organic disulfide polymers are presented in section 3.8.

3.2.2. Electrode Potential/Cell Voltage

The open-circuit voltages reported for charged Li/PAni experimental cells (which actually can be considered as potentials of the polymer electrode, because the potential of metallic lithium is practically constant) are in the range from 3.0 to 4.0 V.[36,62,90,91,430] The open-circuit voltage of the cells was found to be independent of film thickness but was strongly influenced by the method of PAni synthesis and pretreatment.[16]

In aqueous solutions, protonation equilibria are important for the development of the open-circuit voltage.[16,17] The open-circuit voltages of charged Zn/PAni cells are in the range of 1.1−1.5 V.[20.68,70,73,83,429] The rather wide variation in published data appears to arise from the different types of PAni materials synthesized and then used in electrolytes having different salt and/or acid concentrations. The values, like those of specific charge, must be assessed while considering whether the first or both the first and second redox process are involved in charge storage. Generally only the first process can be used, but a manipulation of the active site [poly(*N*-methylaniline)] may favorably alter the redox process.[431]

3.2.3. Charging Rate/Specific Power

Very few values of specific power have been reported for PAni cells. Somasiri and MacDiarmid[83] measured values of specific power as a function of discharge currents for $Zn/ZnCl_2/PAni$ cells, and obtained a maximum value of 916 W kg^{-1} at 12 mA cm^{-2}. The calculation rests on the polymer weight plus the weights of Zn and Cl^- consumed during the discharge reaction. The current collector and other cell hardware is ignored in the calculation. Theoretical maximum values of specific power of up to 1.6 MW kg^{-1} were calculated under certain rather optimistic assumptions for bipolar Li/PAni cell designs with polymer films 10 μm thick, and values of up to 16 kW kg^{-1} for films 100 μm thick.[423,432] It is obvious from a comparison between these values of specific power and the specific energy (152 W h kg^{-1}) calculated for the same designs[423,432] that such discharge would be complete within fractions of a second (minute). Even then, careful consideration should be given to heat dissipation. For comparison: the targets set by the U.S. Advanced Battery Consortium for electric vehicle batteries are much lower: >150 W kg^{-1} or >135 W L^{-1}.[325,433]

3.2.4. Coulombic Efficiency

Coulombic efficiencies of Li/PAni cells have been determined by a number of workers.[16,36,61,62,65,78,84,421,430] The Coulombic efficiency for the polymer is high, typically 95−100% (Table 3.1). Lower values measured on complete cells are usually due to insufficient reversibility of the counter electrode. (Note that, for PAni and other polymers, these efficiencies have always been measured without any waiting period between charging and discharging. This is a valid testing procedure; self-discharge (in the charged state) is a separate test.)

It was noticed[36] that, in the first few cycles, the charge recovered from PAni electrodes is in fact greater than that put in during charging. This is not surprising, because the as-synthesized PAni is partially charged. During cycling of the cell the electrolyte penetrates progressively into the polymer, making more PAni electrochemically available.[36] In repetitive, steady-state cycling the Coulombic efficiency generally stabilizes at a value close to 100%, which indicates that doping and undoping of the polymer proceed rather reversibly. However, the Coulombic efficiency decreases when the polymer is (over)charged to >130 A h kg^{-1},[61] and the polymer is partially destroyed by overoxidation.[434] By limiting the charging to 83 A h kg^{-1}, more than 500 cycles without any degradation (*i.e.* at 100% Coulombic efficiency) were demonstrated;[61] these cycles were about 3 h each. Goto *et al.*[62] have obtained similar results, but their material showed the onset of a Coulombic efficiency decrease at about 120 A h kg^{-1} of PAni.

The Coulombic efficiencies were close to 100% in cycles involving charging current densities of 10 mA cm^{-2}, but started to decrease at higher current densities, *e.g.* to ∼50% at ∼80 mA cm^{-2}.[421] High current densities may be detrimental, owing to decomposition of the electrolyte or solvent, which is possible at high potentials. In fact, the decrease in Coulombic efficiency occurring at higher voltages across a Li-Al/PAni cell was found to be caused by a reaction revealed through gas evolution.[435]

The Coulombic efficiencies of the polymer in Zn/PAni cells with $ZnCl_2$ or $ZnSO_4$ electrolyte have been reported[20,68,73,83,427] to be in the range of 85−100% when the charging was limited to potentials where the cell voltage is less than about 1.35 V, and the charging was restricted to <100 A h kg^{-1}, beyond which the cells lose capacity. As in the Li/PAni case, higher charging current densities (>10 mA cm^{-2}) and higher levels of charging lead to lower Coulombic efficiencies.[73,427] The Coulombic efficiencies of complete Zn/PAni cells sometimes decreased after several tens of cycles or after storage. This decrease was due to limited cycling capability of the Zn counter electrode.

3.2.5. Cycling Properties

The cycle life of polyaniline electrodes has been studied in several laboratories (Table 3.1). The best result was reported in ref 61: During more than 500 constant-charge cycles at 0.1 mA cm^{-2} corresponding to a specific charge of PAni of 83 A h kg^{-1}, the polymer was remarkably stable, as no degradation could be observed.

Obviously, the polymer can be cycled many times. The cycle life of complete Li/PAni cells is often limited by the negative electrode. In some Li-Al/PAni cells the apparent cell capacity decreased from one cycle to the next.[435] This was due to an accumulation of dopant ions in the polymer: the amounts of charge corresponding to the difference in Coulombic efficiency between the positive and the negative electrode remained in the positive electrode in each cycle.[435] Thus, an apparent deterioration of the cell capacity during cycling caused by an excessive uptake of doping sites by dopant ions can occur. However, this is not immediately fatal and can be avoided by a proper choice of the negative electrode.

The DOD (depth of discharge)-dependent cycle life has been reported for button-type R2020 Li-Al/PAni cells cycled at 0.56 mA cm^{-2}.[62] For 100% DOD (2.6 mAh), a cycle life of 150 cycles was estimated. Beyond the 150th cycle, failure occurred but was caused by the negative electrode. At 40% DOD the cycle life was 600 cycles. Unfortunately, the definition of the end-of-life criterion was not reported.[62] A cycle life of more than 1000 has been specified for commercial coin-type Li-Al/PAni cells;[78] however, the permitted DOD is 20−38% of their rather low nominal capacities ranging from 0.5 mAh (Al920) to 3 mAh (Al2016).

Composites of PAni and carbon cloth up to 500 μm thick have been cycled in cells with Li-Al counter electrodes. After 300 cycles the polymer's specific charge had typically decreased by about 40% of its initial value, of 80−100 A h kg^{-1}.[65]

Cycle life studies have also been conducted with aqueous PAni cells. Cycle lives of several tens up to hundreds of cycles have been estimated for the Zn/$ZnCl_2$/PAni system.[20,83,429] Somasiri and MacDiarmid[83] believe that the observed decrease in cell capacity might be related to slow formation of gas, presumably H_2 formed at the Zn electrode. The gas can gradually lower the efficiency of the contact between PAni and current collector.[83] Kitani *et al.*[73] have determined the cycle life of two different cell systems, Zn/$ZnSO_4$/PAni and PAni/H_2SO_4/PbO_2. The discharge capacity of the PAni/PbO_2 cell decreased steadily from the initial value of 40 A h kg^{-1} (based on the weight of the doped polymer) to 25 A h kg^{-1} after 4000 cycles. With the Zn/PAni cell, however, the polymer's specific charge of ∼65 A h kg^{-1} decreased during the first 500 cycles and then remained constant at ∼40 A h kg^{-1} over 1500 cycles. In contrast to these systems, a cell assembled with $ZnBr_2$ electrolyte (Zn/$ZnBr_2$/PAni) was found to be "not completely stable on cycling".[70]

Such cycle numbers become only meaningful when at the same time the duration of each cycle is consistent with the application contemplated. In general, very thin electrodes (in cycles lasting seconds) will sustain many rapid cycles. Thicker electrodes sustain fewer cycles, and shallower, low-power cycling is recommended. Thus, the coin-type Li-Al/PAni cell of Bridgestone, with a nominal capacity of 4 mAh, was designed to sustain >1000 shallow cycles (using only 1 mA h). Its application niche was reported to be, not really as a battery but as a supercapacitor buffering electronic circuitry such as found in solar energy storage.[436]

3.2.6. Chemical Stability/Self-Discharge

In the case of PAni, it is particularly important when reporting stability and self-discharge to specify whether the first or second redox stage has been attained for the material under discussion. Polyaniline exhibits two redox stages,[62] and instabilities readily arise before the second stage is completed. More fundamental differences appear to exist between aqueous and nonaqueous solutions.[63]

It was observed in certain experiments that the Coulombic efficiency of PAni decreased significantly below 100% in repetitive charge−discharge cycles. This decrease typically occurred when the polymer potential exceeded about 4 V *vs* Li/Li^+ during charging,[62] which promoted side and/or overoxidation reactions in the cell. Therefore, as in the cells assembled with other electroactive polymers such as PPy, PT, or $(CH)_x$, the voltage of Li/PAni cells should not be allowed to exceed ∼4.0 V.[117]

The potential of PAni depends on its doping level and, in other words, on the amount of charge consumed. Thus, the onset of overoxidation can also be defined via this quantity. For example, when fibrous polyaniline electrochemically synthesized was charged to >130 A h kg^{-1} (of the undoped polymer), the electrolyte (1 M $LiClO_4$-PC) became colored next to the surface of PAni, indicating that the polymer was attacked by excess charge.[61] When the polymer is charged to 110 A h kg^{-1}, no overoxidation occurs. The self-discharge rate is less than 2% per day at room temperature in this case.[61] In another laboratory, a self-discharge loss of 7% was observed after 30 days of storage for PAni charged to 120 A h kg^{-1}.[62] The self-discharge loss is temperature-dependent: About 7% per day was observed at 60 °C, and 1% per day at 0 °C.[61] Contrary to the pure PAni, PAni-Nafion composite films have a high self-discharge rate: about half of the stored charge is lost after 20 h.[437]

Geniès *et al.*[36] believe that self-discharge losses of batteries based on polyaniline are lower than those of the majority of other existing battery types. Li-Al/$LiClO_4$-PC/PAni cells stored for 3 months had lost only 8% of their discharge capacity. After recharge, the nominal capacity was recovered.[36] The self-discharge loss of commercial coin-type Li-Al/PAni cells (Al2016) at room temperature was found to be ≤15% for a storage period of 3 months. At 60 °C, the self-discharge loss increased to 30% after 60 days of storage.[78] The maximum available capacity of the Al2016 cell also decayed after storage, but the polymer cell still retained more than 80% of its initial capacity when it was stored for 100 days at 60 °C and 90% relative humidity.[78] On this basis, a shelf life of 5 years or more was estimated.

Although the mechanism of PAni self-discharge has not been completely clarified, it is believed to be closely related to the stability of the polymer toward overoxidation (which seems to be better for PAni than for the other electroactive polymers[63]) and to effects caused by impurities formed during the synthetic process.[62] Armand *et al.*[436] reason that lithium reacting with the electrolyte yields basic, nucleophilic species which in turn will react with the radical cations present in oxidized, conjugated polymers such as PAni and PPy.

3.3. Polypyrrole (PPy)

It is generally considered to be difficult to *n*-dope PPy,[6,113] hence its use as a negative electrode in rechargeable batteries is unlikely. Thus, research efforts were essentially concentrated on the utilization of polypyrrole as positive electrodes in batteries. Development of a novel metal-free secondary cell with graphite as the positive active material and polypyrrole as the negative was recently proposed by Beck and Boinowitz,[138,438] but here both electrodes are ClO_4^--inserting, so the cell voltage is lower than in cells where the carbon material is negative and Li^+-inserting. Aqueous electrolytes were widely used, but found to be appropriate for electrode preparation only, not for cell assembly and operation.

3.3.1. Specific Charge and Energy

In the literature, specific energy data ranging from 80 to 390 W h kg^{-1} have been reported for Li/PPy cells with liquid electrolytes. The values have most often been calculated from data measured with cells containing $LiClO_4$-PC as the electrolyte,[90,91,110,119,439] and are frequently based on the weight of the electroactive polymer only. Representative values reported by various laboratories are listed in Table 3.1.

The maximum doping level of polypyrrole is independent of the doping anion,[440] except for macroanions. But the doping level of polypyrrole and, consequently, the values of specific charge and energy attainable in Li/PPy cells at practical current densities strongly depend on the method used in fabricating the polymer electrode.[110,111,131] For example, Panero *et al.*[119] measured a specific energy of 151 W h kg^{-1} (based on the weights of the doped polymer and Li consumed) for a Li/$LiClO_4$-PC/PPy cell with excess electrolyte containing a PPy film about 1 μm thin and doped to a level of $y = 0.24$. The polymer film was electrochemically grown in acetonitrile[119] under the conditions generally used about 10 years ago. Much higher values of specific energy, of up to 390 W h kg^{-1} (based on the weight of the polymer), were reported by Osaka *et al.*[90,91] for their Li/$LiClO_4$-PC/PPy cells after optimizing the PPy synthesis.[111] Water trapped in the polymer (*e.g.* during the chemical synthesis in H_2O) also influences the specific charge of PPy electrodes,[37,125] which reaches a maximum when about 3 wt % of water is present in PPy.[37]

The specific charge of polypyrrole is solvent-dependent. With PPy synthesized by a chemical method in water, values of specific charge of 108 and 122 A h kg^{-1} corresponding to doping levels of $y = 0.40$ and $y = 0.45$ were reported for Li/$LiClO_4$/PPy cells with PC and AN as the solvents, respectively.[37] (These specific charge values refer to the sum of masses of the polymer and inserted anions.) Differences in the doping levels of polymers in PC and AN could be explained by the higher stability of AN at high oxidative potentials[441] allowing higher charging potentials, but in this particular case the authors attributed the difference to differences in polymer capacitance.[37] Feldberg[442] in fact contended, and demonstrated by model calculations, that in doped polymers, capacitive double-layer charging provides an important contribution to the specific charge. Using small heterogeneous rate constants he could also give an explanation for the energy lost (not recoverable) due to the rather high peak-to-peak separation, ΔE_p, exhibited in the cyclic voltammograms of polypyrrole and other conducting polymers. This does not explain, however, why ΔE_p does not vanish at very low scan rates.

Recently Deiss *et al.*[443] showed with a numerical simulation of data for PAc that this scan-rate-independent ΔE_p can only be explained when an N-shaped free energy *vs* oxidation level relation is assumed. For a discussion of the capacitor concept in the case of PAni see the paper of Barsukov and Chivikov.[444]

The total charge stored in polypyrrole was found to be 30% higher when EC, rather than PC, was used as the solvent.[422] This difference is due to steric solvation effects: up to three solvent molecules are co-inserted in the polymer with each anion.[445] With dimethyl sulfite (DMSU) as a solvent, values of specific charge ranging from about 160 A h kg^{-1} to more than 200 A h kg^{-1} have been reported and explained by Li^+ being inserted into PPy during discharge, *i.e.*, cation uptake replaces anion expulsion.[422,446−448] Unfortunately, DMSU apparently is not stable enough to be useful for practical lithium batteries.

Tölgyesi *et al.*[159] prepared cyanoferrate-doped PPy films, hoping that these electroactive anions would provide additional charge storage. It was found that, unfortunately, every polymer charge is compensated by one multivalent anion, so many cations are also incorporated into the doped polymer, and further, only 20% of the built-in anions exhibited electroactivity.

Wampler *et al.*[151] prepared PPy-CB composites. Both during pyrrole polymerization in CB slurries and in cycling of the composite electrodes (with 10 to 80 wt % of CB), enhanced charge uptake was observed. The increase in the specific charge was modest (7%), but as a further advantage, such electrodes remain fully conductive during deep discharge.

A more significant enhancement of charge storage was found in similar composites by Takamura *et al.*[150] Upon carbon incorporation, the dopability went up from $y = 0.143$ to $y = 0.389$ when referred to pyrrole units alone, but the weight percent of CB in the active material is not known. These PPy-CB films had a very fine, open morphology.

In a practical polymer cell, the most important contribution of additional weights reducing the specific energy is that of the solvent required for uptake of the ions after discharge. Considering that 3 mol kg^{-1} is approximately the maximum concentration for $LiClO_4$-PC electrolytes, it has been calculated[124] that the specific charge of polypyrrole (82 A h kg^{-1} was assumed by the authors) will decrease by a factor of about 2 to about 40 A h kg^{-1} on account of solvent requirements.

When Nafion or PSS composites of PPy[144,145,162] are considered for such cells, specific energy is lost on account of the high molecular weight counterions, but this loss may be compensated in "rocking-chair" lithium ion batteries: the electrolyte (a thin lithium ion-conducting polymer film) separates the positive (lithium ion-inserting PPy composite) from the negative (Li, LiAl, or preferably lithium ion-inserting carbons, see section 3.9), an electrolyte reservoir is not required. Thus, the energy density of 220 W h dm^{-3} reported by Osaka *et al.*[145] is of practical interest.

For practical, packaged Li/PPy cells of optimum design, specific energies of about 40−60 W h kg^{-1} have been predicted.[124,126,449] These predictions were confirmed by measurements on the only practical cells yet designed, which are those of Varta/BASF.[124,126,450] Bittihn *et al.*[124] described two cell types, a cylindrical cell (AA size) and a flat cell (4 mm thick), which at a 20-hour rate of discharge provided specific energies of 15 and 30 W h kg^{-1}, respectively. The latter cell utilized a 50 μm thick polymer foil as the positive electrode and a 100 μm thick lithium foil as the negative electrode.[450]

The experimental specific charge of polypyrrole is typically lower when solid, polymer/electrolyte salt combinations are used as electrolytes instead of liquid electrolytes. In these designs, the combined electrolyte is also present in the PPy electrode. For example, the specific energy of a Li/PPy cell was 55 W h kg^{-1} (based on the weight of the composite positive electrode) when a PPy-PEO composite and a PEO-based solid electrolyte were used.[132]

3.3.2. Electrode Potential/Cell Voltage

The open-circuit voltages of a number of laboratory Li/PPy cells have been measured.[90,91,119,121,124,126,127,131,132,161] They are between 3 and 4 V for charged cells, depending mainly on the doping level of the polymer. The potential of the lithium counter electrode is very stable and can therefore be used as a reference. At ordinary charging rates, the voltage *vs* degree of doping curve rises smoothly without any break well beyond 4.5 V *vs* Li/Li^+. Charging with extremely low currents reveals a flat portion followed by a step, features which indicate where overoxidation of PPy and electrolyte decomposition start.[117] These limits are readily transgressed at ordinary charging rates.

The open-circuit voltage of charged cells slowly decreases with time, which has been attributed to self-discharge of the polymer electrode.[413] For the discharge cut-off voltage of Li/PPy cells, an arbitrary value of 2 V is usually adopted. At this point the slope of the discharge curve becomes gradually (although noticeably) larger.

The commercial Li/PPy cell announced by Varta had an open-circuit voltage of 3.6 V when fully charged,[450] and operated between a maximum charging voltage of 4.0 V and minimum discharge voltage of 2.0 V.[126]

3.3.3. Charging Rate/Specific Power

During charging (oxidation) the discharged, undoped polypyrrole is transformed into the doped conducting form. The transformation was found to start at the electrolyte/polymer interface and to gradually proceed in the direction of the current collector.[451] This should be so when the electronic conductivity of the polymer is higher than its ionic conductivity. During discharge, a percolation-type conduction mechanism becomes evident, which implies that toward the end of discharge, some conducting clusters which have lost their contact to the electrode remain and cannot be discharged.[452]

The doping rate strongly varies with the electrolyte salt as well as with the solvent.[440] The oxidation kinetics are limited by solid-state diffusion and migration of anions in the polymer. The reduction (discharge) kinetics of the oxidized PPy are also limited by the solid-state transport of ions in the polymer. During fast discharge the electroneutrality is maintained mainly on account of solid-state transport of the faster cations (*e.g.* Li^+) into the polymer,[453] and the salt formed then diffuses slowly into the liquid phase until equilibrium is reached. During slow discharge anions solely escape from the polymer into the liquid phase.[454] Having in mind the rather complicated reaction mechanism of PPy cycling, it is not surprising that sample morphology (which is predetermined by the synthesis conditions) as well as the polymer film thickness strongly influence the charge–discharge rates.[112]

Naegele and Bittihn[126] have shown that a porous PPy structure with large specific surface area was the prerequisite for high-power applications. This condition is not compatible with high energy densities. Bittihn *et al.*[124] also examined the discharge capacity of PPy with smooth and rough surfaces. The smooth material exhibited levels of specific charge which decreased significantly with increasing charging current density, in contrast to what was found for the rough material, which was porous and could be charged to the same limits of specific charge with currents of up to 5 mA cm^{-2}.

For the diffusion coefficients of anions in polypyrrole, values ranging from 10^{-9} to 10^{-12} cm^2 s^{-1} have been reported;[112,119,454,455] they are higher than those in polyacetylene. For the apparent diffusion coefficient of ClO_4^- ions in PPy, values of 10^{-9} to 10^{-10} cm^2 s^{-1} have been estimated, the exact value depending on the electrolyte concentration, polymer potential, and direction of current flow.[455] In view of these low values of the diffusion coefficients, acceptable values of current density can only be attained when the active material is porous, *i.e.*, has a high internal surface area and pores where the electrolyte ions involved in charge storage can diffuse much faster. Diffusion becomes significantly faster with increasing temperature.[454]

Polypyrrole with ClO_4^- has lower conductivity than PPy•PSS, where cations are the mobile species. However, in the former, conductivity (and thus rate capability) increases, in the latter case it decreases with increasing degree of oxidation, in accord with the amount of mobile species present in the polymer.[146]

With the goal of increasing the cell charge–discharge rates, attempts were made to accelerate the dopant movement in the polymer film by preparing high surface area electrode structures using films of NBR as a matrix for oriented growth of PPy;[141–143] the host NBR film is subsequently removed with a solvent. The NBR matrix-grown PPy electrodes exhibit an open, porous structure admitting a faster anion doping process than ordinary PPy electrodes.[141–143] Nafion also is supposed to improve the kinetics for structural reasons.[456]

3.3.4. Coulombic and Voltage Efficiency

Coulombic efficiencies of Li/liquid electrolyte/PPy cells have been mentioned in many papers.[90,91,110,112,119,121,125,127,131,136,141,143,457] The values reported are spread out over a range of 80–100%, and apparently depend on the amount of impurities in the electrochemical system, on temperature, charging rate, time spent in the charged state (between the end of charging and the start of discharge), on the type and thickness of the PPy films, as well as on the material of the current collector. For a single PPy electrode the variety of observations reported can be rationalized in terms of fast, Pt-catalyzed self-discharge processes at the solid–liquid interface of the (often extremely thin) PPy films on Pt supports[413] and/or partial polymer overoxidation during cycling.[457] Careful experiments actually show Coulombic efficiencies approaching 100% during cycling of polypyrrole electrodes.[90,111,112,114,126,457,458]

3.3.5. Cycling Properties

In a number of experimental studies the cycle life of single PPy electrodes in liquid nonaqueous electrolytes[37,110,119,121,124−127,131,136,446,457] as well as that of the corresponding Li/PPy cells[124,450] was reported. For chemically prepared PPy, a stability over more than 50 cycles was reported.[37] More data are available for electrochemically grown PPy. In an older paper by Trinidad *et al.*[121] the cycle life of PPy was stated to be very poor. However, in a more recent reinvestigation, cycle lives (defined in this case by a capacity drop to 80% of its initial value) of up to more than 20 000 deep cycles have been demonstrated in a $LiClO_4$-PC electrolyte for 1 μm thin PPy films.[125] In several studies the Varta/BASF group has shown that the Coulombic capacity of PPy electrodes 50 μm thick decreased by 10% after 400 charge−discharge cycles,[450] and by 20% after 1000 cycles.[124,126,459] The decrease of capacity of the Li/PPy cells during cycling is higher when a limited amount of electrolyte is used; the known poor cycling efficiency of metallic lithium contributes to this result.[124]

The polymer cycle life was found to depend on the type of the PPy film used in the cell.[110,125] For example in ref 110, cells containing PPy prepared by two different methods have been compared. Films grown in PC containing $LiPF_6$ and cycled in $LiClO_4$-PC after undoping the PF_6^- anions exhibited stable Coulombic efficiencies for more than 1800 cycles. Films grown in PC containing $LiClO_4$ were inferior in their cycle life.

The cycle life of PPy-based composite electrodes for solid-state batteries has been investigated in Li/$P(EO)_8{\cdot}LiClO_4$/PPy cells. Typical PPy-PEO composite electrodes exhibited cycle lives attaining more than 700 cycles.[132] According to more recent work involving a Li/$P(EO)_{8-20}{\cdot}LiClO_4$/PPy cell with PPy synthesized in PC and the PEO electrolyte cast from AN solution directly onto the PPy, 1400 cycles were attained at 80 °C.[460]

3.3.6. Chemical Stability/Self-Discharge

Charged (doped) polypyrrole electrodes are stable and can be stored and handled in ambient air. On the other hand, discharged (undoped) PPy is oxygen-sensitive. In nonaqueous electrolyte solutions, the stability of polypyrrole is very good in the potential interval from 2.0 to about 4.0 V *vs* Li/Li$^+$.[125] However, attempts in common electrolyte solutions to increase the specific charge of PPy by extending the potential window to values more positive than 4.0 V *vs* Li/Li$^+$ result in a rather fast degradation of the polymer during cycling, which is attributed to an irreversible oxidation (overoxidation).[125,136] Overoxidation produces hydroxyl and then carbonyl groups and a net loss of mass.[160] The rate of overoxidation strongly increases in the presence of nucleophiles.[117,461] It has been shown that, for a long cycle life of PPy electrodes, the content of water (and other nucleophilic species) in the battery electrolyte solution should not exceed about 10 ppm.[117] Hence, an appropriate choice of solvent, electrolyte, and cycling conditions is important for the cycle life of the cells.

A continuing source of controversy concerning polymer batteries is their propensity to self-discharge.[4] This led to a number of studies involving PPy-containing cells with liquid electrolytes.[119,121,124,126,462] The self-discharge rates of PPy electrodes measured in different laboratories vary significantly, from more than 50% during the first day[121] to about 5% capacity loss per day during the first few days of storage[124] (the latter value decreasing to about 1% per day when averaged over a one-month period[124]) and to a mere 10% capacity loss over 4−5 weeks.[126] Because of the different experimental conditions used, the literature data on self-discharge are difficult to compare but, typically, the highest self-discharge rates were measured at thin (~1 μm), porous polymer films on platinum current collectors.[121,463] On the other hand, the lowest self-discharge rate was measured at a technical Li/PPy cell having thick PPy films (30−50 μm) as the positive electrode.[124,459,464]

The stability of PPy films strongly depends on the potential of pyrrole polymerization: stability losses are observed for films prepared at certain intermediate and at excessively high potentials.[462] Park *et al.*[462] report that water molecules will attack the quinoid (bipolaron or dicationic) form of overoxidized PPy. Acidity also enhances the degradation rates.[462] Residual bromide from Br$^-$-catalyzed PPy synthesis may be detrimental.[138]

According to Thiéblemont *et al.*,[465] water (rather than oxygen) will attack short polymer chains in the process of (chemical) polymerization.

It has been suggested[466] that the high potentials of many positive electrodes may create problems in terms of electrolyte oxidation. Both at open circuit and during cell charge, the solution may degrade oxidatively at the positive electrode, resulting in film formation, possible loss of positive electrode performance, and self-discharge.[412,466−468] In propylene carbonate-based electrolytes, Pt-catalyzed oxidation of the solvent at the solid−liquid interface of the PPy films contributes significantly to the self-discharge processes.[413] If self-discharge depends on a reaction between the polymer film material and the solution, then thin films having a higher ratio of film surface area to film volume are expected to be more susceptible to this reaction. On the other hand, the ratio of film surface area to solution volume is important when low-level solution impurities are involved in the reaction.

The self-discharge rate decreases significantly with increasing thickness of the polymer film.[413] This is encouraging for prospective practical applications. However, thick electrodes can exhibit a charge retention due to slow diffusion of counterions from the bulk to the surface of the polymer.[114,119]

The self-discharge rate of PEO-based all-solid-state Li/PPy cells is very high.[132,149] Cells with PPy-PEO composite positives lost up to 50% of their charge within 4 h at the working temperature of 85 °C, and total self-discharge of the cell occurred after one day.[132] However, the self-discharge rate rapidly decreases with decreasing working temperature.[149] (Unfortunately, the electrochemical utilization of polypyrrole also decreases with the decreasing temperature due to lower solid-state mobility of anions.) The self-discharge of PEO-based cells has been attributed to mobile redox species formed by the reaction of the Li electrode with the solid electrolyte or with impurities in it, at elevated temperatures of 80−120 °C.[149] PAN-based all-solid Li/PPy cells, although kinetically superior to the PEO-based cells, share their instability,[469] presumably owing to instability of the Li/PAN electrolyte interface.

Since PPy exhibits self-discharge only when the Li electrode is present in Li/PEO-$LiClO_4$/PPy cells,[133] Armand *et al.*[436] reason that lithium reacting with the electrolyte yields basic, nucleophilic species which in turn will react with the radical-cations present in oxidized, conjugated polymers such as PAni and PPy.

Attempts have been made to increase the ionic conductivity of PPy by modifying the polymer structure. New PPy electrodes have been prepared, *e.g.* from poly(*N*-oxyalkylpyrroles),[470] and a new solid electrolyte, $(PEO\text{-}SEO)_{20}\cdot LiClO_4$ [SEO stands for $CH_2{=}CHC_6H_4CH_2O(CH_2CH_2O)_{12}CH_3$], was conceived for room temperature applications. The Li/PEO-SEO/poly(*N*-oxyalkylpyrrole) cell lost 35% of its charge upon standing for one week at 25 °C.[470]

3.4. Polythiophenes (PT)

Performance characteristics of laboratory cells with a large variety of polythiophenes (PT) are listed in Table 3.1 (for the structures, see Table 2.2, which also explains the abbreviations and alternative names).

3.4.1 Specific Charge and Energy

For the first cells and half-cells built with electrosynthesized PT,[166−169] limiting doping levels of 0.24 to 0.30 electrons per monomer unit of the polymer (e^-/MU) were reported, corresponding to a specific charge of nearly 100 A h kg^{-1} of the active material (excluding the ions). A more realistic value found for the doping level in a number of publications is the figure of 0.16, which translates to a specific charge of 52 A h kg^{-1} of the active material, about 44 A h kg^{-1} of the active material plus ions, or 37 A h kg^{-1} for the cell including the Li anode.[127,174,175] The doping level attained with a solid-state Li/PT cell involving $P(EO)_{20}$-$LiClO_4$ as the solid electrolyte was 0.17.[172]

In remarkable early work,[167] both an anode and a cathode of PT (0.13 mg each, 0.75 or 0.2 μm thick) were used, and the performance parameters were quite impressive (Table 3.1). Apparently these results have not been directly confirmed in later work.

The improvement of performance obtained with the use of bithiophene as the starting material for PT preparation is quite interesting: 52 *vs* 34 A h kg^{-1}, 156 *vs* 102 W h kg^{-1} were found in a comparative study and attributed to the more regular structure of the polymer prepared from the dimeric thiophene.[208]

Poly(terthiophene) (P3T), another unsubstituted polythiophene, accepts *p*- and *n*-doping to levels of 0.25 and 0.10, respectively.[178] It is obvious from the voltammograms that distinct processes widely separated on the potential scale are involved. Even higher doping levels (initially over 0.4, then decreasing toward 0.3 in 1500 cycles) and spectroscopic evidence for a superior conjugation length relative to PBT and PT were obtained by Rasch and Vielstich[471] for P3T.

Polymers of the simplest condensed-ring thiophene monomer, thienothiophene, are not advantageous in terms of specific charge or energy. For poly(dithienothiophene), however, which has about double the molecular weight of the monomer unit as compared to polythiophene, doping levels about 2.5 to 3 times those of polythiophene were reported,[174,175,198,200] which makes PDTT the best candidate among PT without side chains. Mastragostino *et al.*[202,472] built a charge-balanced supercapacitor from *n*- and *p*-doped PDTT supported by carbon paper. The numbers given in Table 3.1 refer to a voltage working range of 0 to 3.3 V. The success of *n*-doping was attributed to the use of large, polarizable cations, $(C_2H_5)_4N^+$, as the counterions. In a Ragone plot of specific power against specific energy, the PDTT/PDTT supercapacitor looks very promising for electric vehicle applications.[472]

The 3-methyl-substituted thiophene can be polymerized to structures sustaining a stable doping up to 0.38 e^-/MU, corresponding to almost 100 A h kg^{-1} or 326 W h kg^{-1} (with Li anode, counting the active materials only, here taken as the weight of the films).[181,182,473] It was in fact demonstrated that a sharp conductivity maximum exists for the films produced with a current density of 10 mA cm^{-2}, where a granular structure (6 μm average grain size) develops. This is the preferred structure for high-performance PMT films.

Very high doping levels were reported[186] for poly(3-octylthiophene) when chemically synthesized, so that again a relatively attractive specific charge may be available despite the higher MU mass. Rudge *et al.*[185] who synthesized the poly(alkylthiophene)s electrochemically, did not go beyond doping levels of 0.16−0.18, implying unsatisfactory specific charge values, but interestingly, their limiting doping levels were quite independent of length of the straight alkyl chain from C_1 to C_{18}.

The highly stable methoxy- and ethylenedioxy-substituted polythiophenes of Heinze *et al.*[187−189] have the further virtue of very high levels of charge acceptance. One positive charge per thiophene ring could be stored in the PMOT film,[188] while PEDOT accepted a maximum of 0.75 charges per thiophene ring.[189] The PEDOT film was stable in cyclic voltammetry, even in aqueous solutions.[189]

Rather interesting figures were reported from half-cells built with poly(thienylene vinylene)[193] and poly(dithienylethylene),[194−196] *viz.*, doping levels between 0.28 and 0.55 corresponding to specific charge values between 48 and 94 A h kg^{-1} of the active material. A curiosity reported by Capuano *et al.*[206] is the primary aqueous Mg/poly(benzothienoindole) cell offering 148 W h kg^{-1}.

Some workers[169,473] have mentioned limiting doping levels as being about 6% per carbon atom in the system. While this may be factually true, and compatible with the statement that one delocalized charge can be distributed over four rings in the polymer chain, such a statement ignores the heteroatoms.

A frequent, more general observation has been the need for a number of "forming" ("activation", "break-in") cycles which must be performed before top cell performance in a given system is attained.[171−173,186,193,194]

A 3-substituted thiophene polymer was found to be equally *n*- and *p*-dopable after careful selection of the electrolyte (1 M $(CH_3)_4NCF_3SO_3$ in AN) and 3-substituent (4-fluorophenyl).[192] The authors achieved an energy density of 18 W h dm^{-3} for the active polymer films in a PFPT/PFPT cell. Film thicknesses of more than 10 μm could be employed.

In the instance of PPT which was studied in relation to PT by cyclic voltammetry,[191] the effect of substitution on the *n*-dopability was distinctly revealed. Despite the heavy substituent (and heavy cation!), a PPT negative appears to offer a higher specific charge than a PT negative. Krylov *et al.*[190] have demonstrated true *n*-doping for PPT.

n-Dopability is expected, too, for the dithienylethylene and -butadiene polymers[195] and for poly(isobenzothiophene) (PIBT);[203] it was demonstrated for PIBT in ref 204.

3.4.2 Electrode Potential/Cell Voltage

Polythiophene itself has a rather positive electrode potential. The OCV values against Li/Li$^+$ evidently depend on the doping level and are typically 3.8−4.2 V at *p*-doping levels between 0.17 and 0.24.[168,169,172] When polythiophene was used as an anode as well, a cell voltage of 3.1 V was observed.[167] Apparently, when certain doping levels were approached, the cell voltage "ran away" (at $y = 0.25$ for the PT/PT cell of ref 167; at $y = 0.35$ for the Al/PMT cell of ref 473), which indicates destructive electrolytic processes. It is not clear, however, whether the anode, cathode, electrolyte salt, or solvent are involved. The records of half-cell potentials against doping level for positives usually exhibit neither a runaway nor a leveling. The statement of Onoda *et al.*[193,195] that 30% is the maximum dopant concentration is at variance with the data reported graphically in these papers. This figure rather represents the doping level attained at a cutoff cell voltage selected by unrelated considerations. Extremely slow measurements of charging curves such as those reported by Novák *et al.*[117] for polypyrrole have apparently not been published for polythiophenes.

Condensed polythiophenes (polythieno- and -dithienothiophene) have even more positive electrode potentials for comparable degrees of doping,[174,175] if data recorded during (preparative) doping can be used for a judgement. To the contrary, most 3-substituted polythiophenes have less positive electrode potentials. For an Al/poly(3-methylthiophene) cell, 3.3 V was reported as the mean discharging voltage.[182] For the corresponding Li cells, a figure of about 3.6 V can be read from galvanostatic discharge curves, *e.g.*, in ref 208. About 3.5 V is the cell voltage reported for poly(2,5-thienylene vinylene).[193]

Numerical data for the electrode potential or cell voltage in polythiophene systems are actually not abundant. Further comments are due in the section on chemical stability and self-discharge.

3.4.3 Charging Rate/Specific Power

A few figures for specific power (discharge rate) are reported in Table 3.1. The early figure of more than 300 kW kg^{-1} of the polymer plus ions[167] refers to a PT/PT cell with electrodes 0.2 μm thick. Values of specific power of about 0.2−4 kW kg^{-1} of the active materials plus ions during discharge of a Li/PMT cell were reported in ref 473, where charging had occurred at about 250 A kg^{-1}. The Coulombic efficiencies were about 100% up to a discharge current of 250 A kg^{-1} or specific power of 0.8 kW kg^{-1}. For the performance of a PDTT/PDTT supercapacitor, see section 3.4.1.

The very recent figure of 35 kW kg^{-1} of active materials plus ions[192] was calculated for poly[3-(4-fluorophenyl)thiophene] from the *RC* time constant in a capacitive configuration ("supercapacitor") that would be of interest for load leveling in electric vehicle (EV) applications. Here, both electrodes were polymer electrodes having a realistic thickness in view of EV energy density requirements (18 W h dm^{-3}) and a realistic substrate material (75-μm carbon fiber paper) in view of the load-leveling requirements.

Polythiophenes appear to be kinetically superior to other conducting polymers including polyacetylene.[192] This is a feature which is relevant, not only for charge and discharge but also for (nondestructive) self-discharge (see below). A highly porous structure and at the same time high conductivity[167,168,170] may be the primary reasons for fast kinetics. In view of these kinetic features, only high-surface-area, fibrous substrates would seem to be appropriate for PT polymer electrodes.[127,192]

For PMT, a kinetic study[209] revealed that the doping and undoping occurs in two steps. The first is capacitive and fast, and involves the surfaces of aggregates of compact chains. The second is faradaic and slower, and involves ionic diffusion between the chains into the compact aggregates. During oxidation of the polymer, one such pair of processes can be distinguished. During reduction two such pairs are seen which are separated on the potential scale. A delayed phase change during oxidation (switching from an insulating to the conducting state) is responsible for the difference.

The high-capacity feature has been put to use in an application of PMT as an ("active") cathodic current collector in primary cells with SO_2, $SOCl_2$, and SO_2Cl_2 as the dissolved active material.[210] These cells were found to be capable of supplying high pulse currents.

For the PFPT/PFPT cell mentioned in section 3.4.1,[192] a specific power capability of 35 kW kg^{-1} (of active material on both electrodes) was evaluated from results of impedance measurements. This is more than adequate for capacitors in electric vehicle applications.

In conclusion, optical display applications and capacitor applications (including the load leveling in EV) may be more realistic[171,192,472] than the more classical storage battery applications for the PT group of conducting polymers.

3.4.4. Coulombic Efficiency

Coulombic efficiencies of (or close to) 100% have been found in many studies involving polythiophenes (see Table 3.1). When the Coulombic efficiencies of different polythiophenes are compared, it would appear that PBT is superior to PT,[172] PMT performs well,[208] and so does PTE.[194] However, a critical comparison is hardly possible in view of the great variety of conditions (doping level, depth of discharge, current density, film thickness).

A Coulombic efficiency of 93% for *n*-doping was reported for PDTT.[202] A numerical value was not given by Rudge *et al.*,[192] although implicitly it may be deduced from their data that with the optimized electrolyte and thiophene substituent, it was close to 100%, like that of *p*-doping.

A specific problem of the polythiophenes are the early cycles with lower Coulombic efficiencies. In most instances, the improvement recorded in subsequent cycles is due to a formation process during which a more favorable structure of the polymer develops.[172,194] In the instance of *p*- and *n*-dopable PFPT,[192] this phenomenon has been described as "trapped charge", *i.e.*, an amount of charge that cannot be reextracted and which depends on the morphology (which was more favorable when high growth current densities were used).[192]

Polythiophenes appear to be the one group of polymers for which instances have been found where Coulombic efficiencies decreased with decreasing charging and discharging rates or decreasing cyclic scan rates. This is a feature attributable to self-discharge being so rapid that it already becomes manifest during the periods of time taken for the charging and discharging of the cells.[198]

In careful quantitative studies, it was found that the Coulombic efficiency remains at or near 100% up to well-defined doping levels or charging potentials and up to well-defined discharge current densities. Beyond these limits it decreases systematically.[182,201,473] Not surprisingly, when a waiting time exists between charge and discharge, lower Coulombic efficiencies are found.[198]

A single figure of energy efficiency was provided for a PT cell in ref 127: 27% for a Li/PT cell which exhibited 76% Coulombic efficiency. The large internal cell resistance may have been responsible for the overly large differences between the two efficiency figures.

Coulombic efficiencies drop off quite "regularly" after a certain number of cycles (see, *e.g.*, refs 127, 173, and 199). One possible reason is given in section 3.4.5.

3.4.5. Cycling Properties

Like Coulombic efficiency figures, cycle numbers are meaningful and comparable only under well-defined conditions: doping level, depth of discharge, or cell-voltage limits. The number of voltammetric cycles recorded with half-cells cannot provide a reliable indication for cycle life, although it can be adduced for comparison.

In view of the frequent statements concerning fast kinetics, good stability of the polythiophenes, and nondestructive nature of self-discharge, it may be that many unsatisfactory cycle lives reported in the literature were actually due to early failure of the substrate-polythiophene bond or failure of the anode. If polymer degradation was the reason for failure on cycling, it could be demonstrated spectroscopically.[173]

As early as 1983, Kaneto *et al.*[167] pointed out that the charging voltage must be limited for satisfactory cycle life. Panero *et al.*[171] reported cyclability "with no evidence of decomposition" after an initial set of break-in cycles, while Yamamoto *et al.*[127] concluded that "presumably degradation" caused a loss of cycling efficiency after about 50 cycles. A remarkable result[70] were the 300 cycles of a lithium/PBT solid-state cell with PEO-$LiClO_4$ as the electrolyte at 70 °C. Here, too, an initial activation phase was required during cycling; after that, the Coulombic efficiencies were 98−99%. The 1500 cycles reported more recently[471] do not refer to a complete cell but demonstrate the quality of P3T films.

3.4.6. Chemical Stability/Self-Discharge

Most workers have reported that the polythiophenes are environmentally stable, both in the doped and neutral (undoped) state. However, the rather positive potential (oxidation potential of about 4.1 V *vs* Li/Li^+) implies the likelihood of secondary reactions of the doped polymer in its electrochemical environment.[474] The *p*-doped state of the polythiophenes has been found to be subject to relatively rapid self-discharge in the electrochemical cells. Reactions with the "electrolytic medium" have been suggested,[199] although not demonstrated, as the reasons for self-discharge or "spontaneous undoping".

Self-discharge was found to be negligible in the solid-state cell of ref 172 when this was stored at room temperature, rather than at its operating temperature of 70 °C, which suggests that the electrolyte provides part of the pathway of self-discharge. Other than working with highly purified chemicals, no conscious efforts appear to have been made for finding a remedy to the problem of self-discharge. The work on *n*-dopable PFPT[192] could serve as a guide in this direction.

A few typical figures for the rates of self-discharge are as follows: a decay of open-circuit voltage from 3.7 to 3.35 V within 140 h;[171] complete self-discharge after one day at 70 °C, but negligible self-discharge after one month at room temperature[172] (the solid-state cell already mentioned); 100% self-discharge within 18 to 100 h in CH_2Cl_2, but only 35% self-discharge during 240 h in air;[199] 75% self-discharge within 80 h;[200] 1% per day.[182]

Self-discharge was found not to involve degradation of the polymer,[175,198−201] but follow the same pathway as ordinary (controlled) discharge. In the instance of bromide-doped PDTT in aqueous medium, part of the self-discharge was attributed to a loss of Br_2 from the Br_3^- dopant ions.[201]

The environmental stability of PT, PMT, and PM_2T (3,4-dimethylthiophene polymer) was studied under a variety of conditions.[179] The doped and undoped polymers were found to be stable in air, oxygen, humidity, and water for 8 months. They resisted heat of 200−250 °C in air and of 700−800 °C in an inert atmosphere or vacuum. They were also stable in concentrated acidic media but were slowly attacked by basic solution. In terms of the oxidation and reduction potentials (relative to the respective values of water and oxygen), PMT is stable in its doped and undoped state,[179] in contrast to some other polymers such as polyacetylene and poly-*p*-phenylene. Environmental stability against H_2O and O_2 has also been demonstrated for PTV.[193]

Polymer stability is of course a function of the doping level. It was reported that the potential limit of stability of propylene carbonate is attained when PMT has a doping level of merely 16%.[473] Solvent mixtures may be preferable (20% PC, 80% EC were used in ref 473).

3.5. Poly(*p*-phenylene) (PPP)

Poly(*p*-phenylene) has been used for positive and for negative electrodes. The cycle lives and Coulombic efficiencies of these electrodes have not been outstanding (see Table 3.1). High values of specific power are a more distinct feature;[221,230] they have been attributed to the material's high surface area and microporosity.[24,220] High doping levels and, thus, high values of specific charge have been demonstrated[24,222,230,475] and would, combined with the high OCV and high average discharge voltages, lead to excellent specific energies,[24,230] but are difficult to realize in practical cells owing to solvent instability.[24,222,475] Relatively stable aqueous half-cells have been realized with PPP positives[39,216] when very high acid concentrations were used. However, the corresponding values of specific charge are not sufficiently attractive.

By far the most promising use of PPP has been in combination with alkali metal−lead alloys[59,223−226,415] for negative electrodes in cells where $Li_xV_6O_{13}$ and Na_xCoO_2 were the positive electrodes. Cycle lives, values of specific charge of the anodes, and values of specific energy of the AF-size cells prepared were very interesting (see Table 3.1), but here the PPP has only a subsidiary role in charge storage.

It is possible that work with more inert solvent−electrolyte systems (such as those explored by Shacklette and co-workers)[222,475] will lead to further progress in genuine PPP battery electrodes. The PPP systems should be quite promising inasmuch as self-discharge has never been mentioned as a problem.

3.5.1. Specific Charge and Energy

Numbers for these parameters can be found in Table 3.1. Many of these values are somewhat theoretical in view of the lack of solvent stability. This is an important argument already put forward in the first PPP "battery" paper.[24] The doping levels actually seem to rise continuously with the doping voltage, both for PPP positive and for PPP negative electrodes.[215,220] The values of specific charge, but hardly ever of specific energy have been reported (Table 3.1). This is a reflection of potentials of the positives which are so high that no solvent can be found which resists at the same time the oxidizing effects of the PPP positives and the reducing effects of feasible negatives.

Formation cycles are beneficial (see section 2.5) for developing electrode structures with high, constant specific charge. For negative electrodes, phase transformations and staging have been seen during ion insertion and deinsertion.[222] For positives, solvent co-insertion has been noticed;[215] for positives in aqueous acids, two acid molecules per acid anion were found to be incorporated, as in the case of graphite.[216] Such phenomena imply a need for structural adjustment of the material.

Not only the alkali metal ions have been inserted,[222,475] but also a cation as large as $(C_4H_9)_4N^+$.[231] Moreover, *p*- and *n*-doping can be accomplished in a given electrolyte solution. However, different solvents should be used for positives and negatives in order to achieve optimum results with respect to specific charge.

For anodes, a doping "limit" of 0.5 was argued theoretically and nearly attained experimentally.[222]

3.5.2. Electrode Potential/Cell Voltage

The open-circuit voltage against Li/Li^+ is 4.4 to 4.5 V for anion-doped (about 10%) PPP, the precise value of course being a function of the doping level.[220] The threshold for anion doping is around 4.0 V.[220] These values are about 1 V higher than for PPy.[216]

Cation doping is associated with equilibrium voltages between 0.7 and 0.4 V[220] or working voltages between 0.9 and 0.6 V against Li/Li^+.[215]

The charge−discharge curves are sloping, like those for all polymer electrodes, although it has been claimed that they have more pronounced plateaus in the case of PPP positives prepared electrochemically.[230] The hysteresis for ion insertion and deinsertion was found to be minor in the case of PPP negatives, despite the structural adjustments required,[222] which implies better round-trip energy efficiency.

For the PPP−metal alloy composite electrodes, the electrode potential varies by about 0.5 V due to changes in alloy stoichiometry involving phase changes during charge and discharge.[224−226] Complete cells with PPP−alloy composite negatives and oxide positives exhibit a potential variation of distinctly more than 1 V with some rather pronounced steps.

3.5.3. Charging Rate/Specific Power

A rate capability of 50 mA cm^{-2} (for an undisclosed amount of PPP per square centimeter) was reported when the first PPP electrodes were tested.[24,219] Values of specific power have not been reported (in harmony with the lack of specific energy data), but Table 3.1 lists two discharge rates of the order of 10 kA kg^{-1} of PPP.[221,230]

High conductivity, high surface area, and high porosity are responsible for this positive feature.[220] Annealing (a day at 400 °C for example) has been recommended to preserve these physical characteristics.[221,230] It was pointed out that the last 20−30% of charge are not available at a high discharge rate: at this point slow ion diffusion in the polymer is assumed to become important.[220]

The high performance of PPP−alloy composite electrodes is attributed to PPP raising the rate capability by acting as a highly disperse, elastic conducting matrix and filler, mediating ion transfer to the alloy, and securing electrode porosity while providing structural integrity and offering a low impedance (high capacitance).[223] The lack of alkali metal dendrite formation, exfoliation, and shape change[59,224] and the high alkali metal utilization[415] can be attributed to these functions of PPP.

3.5.4. Coulombic Efficiency

There is a tendency in Coulombic efficiencies to be lower for higher doping levels (Table 3.1), which is not unusual for conducting polymer electrodes but is accentuated in the case of PPP by system instabilities arising on account of the high cell voltages or electrode potentials. Finding an upper potential limit for practical secondary batteries employing these polymers[220] is only part of the answer to this problem in the case of PPP.

In the aqueous systems of Beck and Pruss,[39,216,217] the relatively high Coulombic efficiencies actually occurred as rather narrow maxima at particular, very high acid concentrations.

No particular differences in the Coulombic efficiences appear to exist between *p*- and *n*-doped PPP.

Excellent Coulombic efficiences were found for the composite electrodes. The importance of PPP for this result can be seen from the arguments listed in the previous section. These efficiencies were also reported for complete cells with Na_xCoO_2 anode.[225]

3.5.5. Cycling Properties

Reported cycling properties of the pure PPP are not particularly impressive (Table 3.1). Impressive values (about 1000 cycles) have been recorded for the PPP−alloy composite anodes,[59,225,226,415] which according to morphological studies[225] is due to a particular synergy. After formation cycles, the composites assume the fibrillar structure of pure polymer electrodes. Distinct alloy (lead) particles could not be found in microprobe analyses after 350 cycles (when the specific charge had dropped by 5%). Thus, the alloy was uniformly distributed within the PPP fiber network. Electrolyte-swollen fibers provide the path for rapid charge transport (ions and electrons) within the electrode, while the redox behavior of the composite is alloy-governed (several flat sections are present in both the discharge and charging part of cycles).

In the best aqueous systems with PPP cathode, some degradation was noticed after 200 cycles.[39]

Many poor results for cycling properties are probably due to the notorious solvent instability mentioned earlier in connection with specific charge.

Very few cycling properties have been reported for the alkali metal-doped PPP anodes, so a comparison between pure polymer anodes and cathodes is not possible.

3.5.6. Chemical Stability/Self-discharge

In its chemical stability, PPP is superior to all other conducting, ion-inserting polymers (see section 2.5). Degradation has only been reported for PPP in aqueous systems,[39,320] where overoxidation produces −COOH groups after C−C cleavage,[216] *p*-quinone structures, and apparently a maleic acid derivative.[320] Self-discharge is minimal: 1 μA cm^{-2}.[216]

No degradation or sensitivity to overoxidation has been observed in nonaqueous systems.[18,215,475] Excellent charge retention (negligible self-discharge) was reported for the composite anodes:[225] in one example, 98% of the charge could be recovered from an $Li_{4.3}$-Pb-PPP film left fully charged for 40 days.

If self-discharge data have not been reported for any of the complete cells, then the reason once more is the lack of solvent stability: a solvent has not been found so far which is stable both against the *p*-doped PPP (about 4.5 V *vs* Li/Li$^+$) used as cathode and against the alkali metal or *n*-doped PPP used as anode.

3.6. Other Conducting Polymers

Among the materials considered in section 3.6, PAz and PCz are the two materials worth investigating further.

3.6.1. Poly(triphenylene) (PTP)

From cyclic voltammetry and potential-step coulometry,[234] it was concluded that PTP can attain a doping level of 0.5. In view of the number of benzene rings involved, and of the fact that the polymer is less regular in structure, the performance in a battery application would certainly be inferior to that of PPP.

3.6.2. Polyazulene (PAz)

The oxidation potential and, accordingly, the average discharge potential of polyazulene positive electrodes is more positive than that of PPy, and more negative than that of PT.[236] The films exhibit conductivities of up to 1 S cm^{-1} when fully doped, but their resistivity increases rather strongly during undoping.[238] The rough surface and highly porous morphology enable such films to exhibit high reversibility in voltammetry.[238]

The few performance data listed in Table 3.1 may not be overly impressive; however, it has been stated that Li/PAz batteries would outperform Li/PPy batteries.[239] In addition to a higher average discharge voltage (3.2 V *vs* Li/Li$^+$), the charge and discharge curves are flatter.[238] Very good cycling properties have been demonstrated for the optimized material.[239] Self-discharge was studied over a period of 48 h,[238] but unfortunately no results were reported for these tests.

In the PPy−PAz copolymers, the good rate capability of the azulene component becomes distinctly noticeable when its content exceeds 25%.[240,241] This feature is attributed to the bulkiness of the azulene molecule, which would open up the copolymer structure and cause a more columnar film growth, so diffusion of the dopant ions is facilitated. Larger values of specific charge are recorded when the azulene content exceeds 50%.[241] It appears from the results reported by Naoi *et al.*[240] that 100% PAz is the best positive electrode material.

3.6.3. Polyfluorene (PFl)

Within certain potential limits, according to CV, doping is reversible (charge introduced by *n*- or *p*-doping can be reextracted) but kinetic hindrance appears to occur within the polymer film.[245] The *n*-doping is faster, but some residual charge can only be reextracted in the anodic region. Destructive processes including cross-linking occur outside the potential limits mentioned.

It appears that PFl is not an interesting material for battery electrodes.

3.6.4. Polynaphthalene (PNap) and Polyanthracene (PAnt)

It appears that PNap and PAnt are not an interesting material for battery electrodes.

3.6.5. Polyfuran (PFu)

All polymer films (PPy, PT, PFu) prepared electrochemically by Tourillon and Garnier[166] exhibited the same dopability (one anion per four monomer units in the polymer), which would be encouraging for PFu as an ion-inserting polymer. However, other authors[80] were not successful in their attempts to dope or undope chemically prepared PFu. These results leave strong doubts as to the utility of PFu in batteries.

3.6.6. Polycarbazole (PCz)

Coulometric data indicate that the material prepared in aqueous media[248,249] has a doping charge of 15−40% upon preparation; the chemical analysis indicates a level of 50%. The unsubstituted material strongly resembles emeraldine in its stability and electrochemical behavior.[249]

Pellets of the chemical polymer produced[29] by oxidation with $NOBF_4$ were paired with Li electrodes in PC-$LiClO_4$ electrolyte. These cells showed satisfactory charge−discharge curves for relatively thin films: the curves were comparable to those of cells assembled likewise with polypyrrole and polythiophene. The curves were recorded somewhat arbitrarily with a depth of charge and discharge of 17 A h kg^{-1}. These Li/PCz cells exhibited 91% Coulombic efficiency. (At the doping level of 0.5 mentioned above, a theoretical specific charge of 80 A h kg^{-1} of the polymer could be expected.)

3.7. Redox Polymers

Redox polymers (for their definition as applied here, see section 2.6) have redox states determined by their pendant groups or other redox centers. Comparison has often been made with the redox behavior of solutes corresponding to these groups. The reduced and oxidized states involved are rather more definite than in the case of conjugate-chain conducting polymers.

3.7.1. A Tetrathiafulvalene-Substituted Polystyrene (PS-PTTF)

The TTF-functionalized polystyrene film used by Kaufman *et al.*[255] exhibited the same redox changes as TTF in solution. Limitations to the ion transport rate in the films are responsible for wave shifts which occur with increasing voltammetric scan rate.

Several charged species (mixed-valence dimers TTF_2^+, the isolated monocations TTF^+, the dimeric dications TTF_2^{2+}) could be identified. All TTF substituents were found to undergo oxidation/reduction. A film 0.5-μm thick stored 20 mC cm^{-2}, which translates to a charge density of 111 A h dm^{-3}. The 3.5 M $TTF^+ClO_4^-$ quoted by Kaufman *et al.* for their films is equivalent to 94 A h dm^{-3}. For the film material PS-PTTF, a specific charge of 67 A h kg^{-1} can be calculated on the assumption of 1 e^- per TTF group. This does not include the solvent and electrolyte incorporated during charging.

A formation (a number of charge−discharge cycles) is required for the films to attain their activity. Formation is "forgotten" by the films on long standing, and must be repeated. The film resistance decreases upon oxidation. Cycling behavior under CV conditions was found to be excellent.

3.7.2. Ferrocene-Substituted Polyethylene (PVFc)

This polymer is generally described, due to its preparation, as poly(vinylferrocene) or PVFc. Iwakura *et al.*[257] tested their film and pellet electrodes by cyclic voltammetry but also measured charge−discharge curves in half-cells. In AN solutions, Coulombic efficiencies of 99%, PVFc utilizations of 78−99% (at current drains of 500 to 25 A kg^{-1}), and a self-discharge rate of 1.4% per day were measured for the pellet-type electrodes containing 50% graphite powder. In aqueous solutions at 50 A kg^{-1}, the Coulombic efficiency was 96%, PVFc utilization 69%, and self-discharge 0.6 to 1.1% per day. While swelling and disintegration of the electrodes was a problem in the AN solutions, degradation was minimal after 50 cycles in aqueous solutions. A particular virtue of the PVFc electrodes is the flatness of the charging and discharge curves found, even at higher current densities. The specific charge values reported in Table 3.1 refer to the polymer alone and must be reduced according to the level of conductive filler in the electrodes.

Hunter *et al.*[258] were concerned with impedance measurements, but it should be reported that in their work the fraction of oxidized polymer sites ($PVFc^+$) could be raised from 0.05 to 0.80 when the potential was raised from 0.3 to 0.5 V against the saturated Ag/AgCl reference electrode.

The data reported by Naoi *et al.*[423,432] refer to calculations performed to demonstrate the high-power capabilities of polymer batteries in bipolar designs with Li anode. They compared designs with PAni, PPy, and PVFc positives. According to their postulates and estimates, polyaniline should provide the highest energy density, while poly(vinylferrocene) should give the highest pulse power. The two performance figures cannot simultaneously be optimized: very thin film batteries (1-μm electrode thickness) would provide high specific power but low specific energy. Even if the calculations are based on a highly idealized situation and lack considerations of heat transfer, it becomes evident that pulse power is by far the larger virtue of polymer batteries.

3.7.3. Carbazole-Substituted Polyethylene (PVCz)

This polymer is generally described, due to its preparation, as poly(vinylcarbazole) or PVCz. The poly(*N*-vinylcarbazole) produced electrochemically[259,260] was combined with Li in cells subjected to charge and discharge at rather low current densities. Relatively flat curves were recorded through up to 100 cycles. Considerable short-circuit currents could be drawn (6 mA cm^{-2}), which appears to be the chief virtue of these cells. For the superior films obtained recently,[261] quantitative information on charge storage properties was not supplied.

Oxidation and reduction occur in two steps. In formed films, dimers (assumed to bridge (cross-link) different polyethylene chains) are oxidized and reduced at the less positive potential, and isolated carbazole pendant groups are oxidized and reduced at the more positive potential.

Dimerization was estimated for steric reasons to only involve about 50% of the carbazole groups. Further oxidation (at less positive potentials) involves two electrons per dimer. The overall reaction of dimerizing carbazole groups thus involves two electrons per pendant carbazole group. This charge storage capacity would be of battery interest if a much larger percentage of the Cz groups incorporated were involved.

3.7.4. Polyoxyphenazine (POPh)

The polymer was discovered when studying electrodes modified with adsorbed 1-hydroxyphenazine.[263] The polymer offers a 2 e^-, 2 H^+ redox system operable in strongly acidic aqueous solutions (0.01 to 2 M H_2SO_4).[476] Because of its low potential, it can best function as a negative electrode material when combined with a positive material such as PbO_2. For POPh, the theoretical specific charge is 275 A h kg^{-1} of the undoped polymer; for the system with PbO_2, the theoretical energy density is 185 W h kg^{-1} of the active materials in the battery electrodes. In POPh/PbO_2 cells and in POPh half-cells, almost complete self-discharge occurred within 3 h, which may have been due to the high oxygen sensitivity of the reduced POPh.[264,476]

In studies combining cyclic voltammetry with probe-beam deflection,[264,265] it was revealed that the first one-electron oxidation step of reduced POPh is attended by anion insertion rather than proton expulsion, while the second oxidation step is attended by proton expulsion. Also, oxidation is attended by water loss from the film.

3.7.5. Polymer Adducts (PAm·I_2, PTHF·I_2)

Polyamide–iodine adducts (PAm·I_2) were used in the form of nylon–carbon composites by Yamamoto *et al.*[267,268] for battery electrodes sustaining 300 charge–discharge cycles. The Coulombic and energy efficiency were reported as 100% and 83%, respectively.[267] The charge and discharge curves are flatter than those of cells with conducting-polymer positive electrodes. The numbers reported in Table 3.1 do not include the electrolyte but account for polymer, carbon, iodine, and zinc.

Of particular interest are the rather high short-circuit currents (80–170 mA cm^{-2} for an electrode with 200 mg of nylon and 40 mg of carbon per cm^2).

Rechargeability was achieved when similar primary cells were equipped with an ion-exchange membrane as the separator. Some self-discharge still occurs (by the diffusion of I_3^-, supposedly), amounting to 50% per month.[268] It was pointed out that the nylon adduct/zinc system was comparable in its energy density to the nickel–cadmium storage cells.

The specific charge and energy were even higher for the poly(tetrahydrofuran) adduct, PTHF·I_2. However, nylon is more convenient to handle and more readily available.

3.7.6. A Polymer Complex (PVP-Ru)

The PVP-Ru$(bipy)_2$ complexes prepared by Haas and Vos[270,486] were studied voltammetrically and used to mediate heterogeneous redox reactions. The ruthenium ion in the pendant complex undergoes a very fast one-electron redox reaction. The specific charge involved is low on account of the system's bulk. Even in the 1:1 complex of Ru$(bipy)_2$Cl·PVP, the specific charge would merely be about 35 A h kg^{-1}. In an electrode with 4-fold PVP excess,[270] this value drops to about 20 A h kg^{-1}.

These values are reported here merely in order to provide a feeling for the orders of magnitude of charge storage capacity provided by such complexes, which could of course have a cheaper metal ion such as iron, and not in order to suggest an immediate battery application of such complexes. A capacitor-type application might be more realistic owing to the fast electron exchange properties of these materials.

3.8. Sulfur and Redox Polymerization Electrodes

Quite in contrast to the electrodes made of conducting polymers, data for the sulfur systems described in section 2.8 are often single-source and less systematic. Very few of the solid redox polymerization electrodes (SRPE) have been investigated by several groups, so that more complete performance data are not usually available.

3.8.1. Activation of Sulfur (–S–)

The room-temperature system of Cairns and coworkers[271] was described as an aqueous half-cell in which the redox reaction

$$S_4^{2-} + 4H_2O + 6\,e^- \rightleftharpoons 4\,HS^- + 4\,OH^-$$

gave current densities of 10–20 mA cm^{-2} at less than 50 mV "overpotential". The reaction is heterogeneous in the electrochemical sense and requires efficient catalysis. With the catalysts used, the design goal for a counter electrode in redox batteries for energy storage (or photoelectrochemical cells) was met. This system, where the active material of the positive electrode is present as a solution, must be operated as a flow cell. The data presented graphically for operation with Mo/MoS_2 expanded metal electrodes look perfectly symmetric between the anodic and cathodic current–overpotential plots for the optimized solution composition.

The system of Yamin and Peled[272] was tested in laboratory prototype button cells. Their nonaqueous Li/S cells represent a low specific power, high specific energy primary system which was said to be potentially secondary (rechargeable). In the polysulfide solution, a passivating layer forms on the lithium anode slowing self-discharge (2−5% per month at 60 °C). At room temperature, the cells gave 330 A h kg^{-1} or 730 W h kg^{-1} (400 A h dm^{-3} or 900 W h dm^{-3}); at 60 °C, they gave 430 A h kg^{-1} or 950 W h kg^{-1} (550 A h dm^{-3} or 1200 W h dm^{-3}). These figures were said to include all cell materials except the case. The cell OCV were between 2.15 and 2.38 V (depending on the precise solution composition). The discharge curves were said to be flat.

Since Li polysulfides are highly soluble, formation of the passivating layer[272] actually depends on a high solution concentration of polysulfide.

Kavan *et al.*[274] found that 29% S could be attached to the rather special carbon materials prepared. Acetylenic bonding of the C atoms in these carbons should enable formation of the dithiol structures formulated in Table 2.2 for $(CS)_n$. In voltammetric tests, 0.30 e^- per sulfur atom were found to be available when operating the cell in PC (1 M $LiClO_4$). The cycling performance was poor: from a solid-state cell with $P(EO)_8{\cdot}LiClO_4$ electrolyte (this material was also incorporated into the cathodes), 175 A h kg^{-1} of the C(S) active material were available in the first discharge. After recharging with 745 A h kg^{-1}, only 100 A h kg^{-1} were available in a second discharge, which corresponds to one-electron reduction of 25% of the sulfur present. The OCV in freshly prepared cells were 3.05−3.5 V, but lower values were obtained after the first discharge−charge cycle.

Degott's carbon−sulfur materials gave impressive performance figures corresponding to the insertion of about one Li^+ ion per sulfur atom,[275] which constitutes an improvement over polyacetylene as the conceptual ancestor of these materials. The electrodes were composites containing acetylene black as well as electrolyte. Important defects of the system were the high slope of the discharge curves (which dropped from 2.77 V OCV to about 1.0 V at 100% discharge of available capacity) and a sensitivity to overdischarge (splitting of C−S bonds below 1.5 V *vs* Li/Li^+), which would require appropriate control of the charge−discharge cycles. Also, the system is kinetically slow, since cross-linking interferes with lithium ion diffusion.

The polyacetylene-sulfur composites of Perichaud and Le Mehaute[276] were reported to yield as much as about 900 A h kg^{-1} or 1850 W h kg^{-1}, probably only in a primary-cell configuration. Stiehl and colleagues[277] two years later claimed a similar material for rechargeable batteries, mentioning the higher environmental stability and thus lower self-discharge of the sulfur-modified polyacetylene as compared to polyacetylene itself. The substituted polyacetylene materials of Stiehl *et al.*'s 1989 patent[278] having the structure of DATA (see Table 2.2) are claimed to offer stability, rechargeability, and cyclability for low-power applications.

Performance figures for the low molecular weight DTDT[279] (see Table 2.2), again for low specific power but high specific energy secondary cells, can be derived from the diagrams as exceeding 300 A h kg^{-1} for the electrode material in discharge, while cycling tests were conducted with 56 A h kg^{-1}. The same material dissolved in DME gave more than 500 A h kg^{-1}. A more sulfur-rich low molecular weight material, DT-TCA[280] (see Table 2.2), had even higher performance characteristics and was claimed to be, not merely high specific energy but high specific power. Chemically very good stability was claimed for MTBT (see Table 2.2), though apparently in primary cells.[281] Rechargeable cells were claimed as well for DTDT or DT-TCA containing between 40% and 90% S.[477]

These materials, which probably did not quite meet the practical stability criteria for applications, predate the developments at Berkeley, the Kubota patent,[297] and the Teo patent[282] (see section 3.8.2).

3.8.2. Thiol Dimerization Electrodes

The work of the group at Berkeley was quite systematic in the sense that conductivity of the disulfide−thiolate salt mixtures, the behavior of the β''-alumina electrolytes, and the requirements for PEO-based electrolytes were studied at the outset.[290,291,304] These investigations were aimed at applications such as electric vehicle or communications satellite (high specific energy, low specific power at room temperature, high specific power at moderately high temperatures). The work continues in the form of a developing venture company.[478]

The TETD-DEDC (for abbreviations and structures see Table 2.2) cathode coupled with a Na anode and β''-alumina separator was reported[286] to have a theoretical specific energy of 360 W h kg^{-1}, could be cycled at 5 mA cm^{-2} (130 °C), and provided peak currents of 100 mA cm^{-2} (1 V).

The generalized cell reactions of dimerization systems can be written as

$$RSSR + 2e^- \rightleftharpoons 2RS^- \qquad \text{(positive)}$$

$$2Na \rightleftharpoons 2Na^+ + 2e^- \qquad \text{(negative)}$$

$$RSSR + 2Na \rightleftharpoons 2NaRS \qquad \text{(cell)}$$

From theoretical specific energies calculated for these reactions with different, suitable R (between CH_3 and DEDC), Visco and DeJonghe concluded that practical specific energies of 100 to 150 W h kg^{-1} will readily be achieved with these electrodes.[287] Their Na/HEDS cell provided stable voltage efficiencies of 90−95% at a current density of 10 mA cm^{-2} (the surface area being that of the electrolyte) and a rate capability of up to 50 mA cm^{-2} for 20 min, but buildup of internal pressure unfortunately was indicative of problems arising from the polymerization of HEDS (by an autocondensation reaction liberating steam, presumably). This problem did not arise in the Na/EEDS cell, but some parasitic reactions still occurred,[287] possibly related to solvent instability.

Continued efforts[288] led to prototype Na/TETD cells which, at weights of 50−53 g, contained 13 g of TETD and provided a capacity of 2−2.5 A h, a peak power of 2 W for more than 1 min (2 A, 1 V) which translates to 40−60 W kg^{-1}, an output during cycling

Table 3.3. Theoretical Specific Energy of Redox Polymerization Electrodes (ref 283)

						specific energy			
		specific charge		nom. voltage (V)		*vs* Li		*vs* Na	
electrode	equiv wt	A h kg^{-1}	A h L^{-1}	*vs* Li	*vs* Na	W h kg^{-1}	W h L^{-1}	W h kg^{-1}	W h L^{-1}
X0	68	390	630	2.0	1.7	720	960	500	690
X1	74	360	580	3.0	2.7	990	1350	750	1030
X5	58	460	740	3.0	2.7	1240	1630	890	1210
X8	46	580	930	2.0	1.7	1010	1280	660	870

(between 10% and 90% of capacity) of 6 W kg^{-1}, a specific energy of 80 W h kg^{-1} and an energy efficiency of 75%. At zero drain, the specific energy was over 110 W h kg^{-1}.

A prototype Na/HEDS cell (for which the theoretical specific energy is 560 W h kg^{-1} when the OCV is 2.1 V) had a capacity of 4.5 Ah and a specific energy of 200 W h kg^{-1} at zero current drain, half of which could be realized, and 90% of which could be recharged. The HEDS is a liquid, so a solvent is not needed and the system is very attractive on principle, but it does not seem to be possible to prevent polymerization.[288]

Dimethyl disulfide, which has the highest theoretical specific energy among materials for Na/RSSR cells (780 W h kg^{-1}), requires solvents (40% DMSO) in order to dissolve the sodium methylthiolate produced upon discharge. A cell which could be discharged to the extent of about 70% and completely recharged (at 10 mA cm^{-2} and 105 °C) was built,[288] cycling between 10 and 20 mA cm^{-2} was possible to the extent of 80% of the DMS present.[288]

All sodium cells operate above 100 °C. Ambient temperature cells with disulfide positives were built using lithium anodes and a microporous separator.[292] The lithium salt LiDEDC is soluble in TETD-DMSO as a liquid cathode. Of the theoretical specific energy of 470 W h kg^{-1}, 156 W h kg^{-1} were reported as the "practical energy density at zero current drain", and 82 W h kg^{-1} as the practical energy density at 16 mA cm^{-2} (current collectors and cell case disregarded). The cell weighed 182 mg (125 μm of Li foil, Celgard separator, 1.6 mm of graphite felt). During early cycles performance improved; 135 cycles were performed at 3.4 mA cm^{-2}. The Li electrode (the size of which has little influence on the specific energy figures of the cell) was generously oversized in these cells. Self-discharge data were not determined, but a passivating layer forms on the Li electrode.[292,293]

For the cyclodisulfides of Kubota,[297] probably used in cells operating between 40 and 80 °C, cycle lives of 500 cycles were cited. The cell voltages reported are between 3.0 and 3.8 V at open circuit, between 2.2 and 2.4 V during discharge in cells with polymers, carbon black, and PTFE in the positives and Li as the negative.

Teo[282] does not provide any numbers for performance of his tetrathio compounds (see section 2.8.1), except for a cell voltage of 0.7 V in a cell with [Ni(TTT)]$_x$ negative and PVP·(x/2)Br$_2$ positive, and one of 1.8 V for a cell with [Ni(TTT)]$_x$ positive and Li negative.

3.8.3. Thiol Polymerization Electrodes

From Visco *et al.*,[283] who use the term of "solid redox polymerization electrodes" (SRPE) for their materials, Table 3.3 provides theoretical specific energies for four of the series-X polymers. The generalized cell reactions of polymerization systems can be written as

$$(-\mathrm{SRS}-)_n + 2ne^- \rightleftharpoons n\mathrm{RS_2}^{2-} \qquad \text{(positive)}$$

$$2n\mathrm{Na} \rightleftharpoons 2n\mathrm{Na}^+ + 2ne^- \qquad \text{(negative)}$$

$$(-\mathrm{SRS}-)_n + 2n\mathrm{Na} \rightleftharpoons n\mathrm{RS_2Na_2} \qquad \text{(cell)}$$

(The S−S bonds are present in polymers $(-\mathrm{SRS}-)_n$ but not in dianions $\mathrm{RS_2}^{2-}$ or molecules $\mathrm{RS_2Na_2}$.) Practical Li cells with PEO-based electrolytes operating between ambient temperature and 100 °C were described in a 1989 symposium.[304] To the performance data given in Table 3.1, it should be added that in the Li/PEO/X1 cell studied, cathode utilization was a strong function of temperature (38% at 50 °C, 75% at 93 °C, and 96% at 100 °C). At ambient temperature, the cell still delivered 250 μA cm^{-2}: a merit of the $\mathrm{LiN(CF_3SO_2)_2}$ used as a plasticizing electrolyte in the PEO, which was also present in the cathode. Apparent insensitivity to overcharge and overdischarge is another interesting feature of these systems.[307]

Results for Li/X cells with $\mathrm{P(EO)_{20}{\cdot}LiCF_3SO_3}$ electrolyte where the positive electrodes consisted of cast films with 30 or 45% (by weight) of the active material were reported in 1992.[308] The figures refer to the weight of the cathode films. For high specific energy and fast kinetics, X1 is the preferred polymer: several milliamps per square centimeter can be drawn at 100 °C, and even at room temperature the cells still provide practical values of specific power. A conspicuous feature are steps in the discharge curves of Li/X1 cells, which have been ascribed to two stages of discharge: polymer to dimer, and dimer to dithiolate monomer.[306] For polymer X8, the outstanding feature is a high utilization of the material in thick cathode films, which translates into high specific energies for practical cells. Again, two steps can be seen in the discharge curve.[308] Utilization during discharge is poorest for X7 and X0.[308]

Polymer X8 was said to be highly insensitive to overcharging, perhaps because of a shuttle mechanism provided by some intermediate existing in the partly discharged state of the cell.

Recent work on laboratory-type Li/PEO/X1 cells from Berkeley describes thin-film solid-state batteries with PEO of the amorphous type.[298] These cells can either be made paper-thin (storing 1 C cm^{-2} in 18-μm thickness) or stacked to obtain thicker battery structures. An 80% utilization of the active material is possible, 140 W h kg^{-1} (150 W h dm^{-3}) were demonstrated, up to 300 W h dm^{-3} were said to be possible by design optimization. A 30 W dm^{-3} power density was demonstrated in continuous discharge, up to 200 W dm^{-3} were said to be possible. During cycling, some conditioning was observed. The systems proved to be quite insensitive to accidental overcharge or overdischarge (they exhibit recovery effects) and sustained 100 cycles.

Work on Li/X1 cells with liquid electrolyte (1 M $LiClO_4$, $LiN(CF_3SO_2)_2$, or $LiCF_3SO_3$ in 1:1 PC-DME) published by the Berkeley group[479] showed that their cycling compares very unfavorably with the solid-state cells (here $PEO{\cdot}LiN(CF_3SO_2)_2$ solvent swollen with acetonitrile). Other limitations of the liquid-electrolyte cells relate to loading (% X1 in the carbon mats) and utilization of the active material. Preference is therefore given to solid-state cells with suitably modified polymer electrolyte, notably an amorphous polyethylene glycol with oxymethylene links, which is superior to solvent-swollen PEO.[298]

Prototype Li/X1 cells were assembled and tested in work reported in 1993.[306] The corresponding data of Table 3.1 refer to C/2 discharge (average discharge voltage 2.5 V); they disregard the current collector weight. It was concluded that these cells are superior to Li/TiS_2 cells in voltage and have a flatter discharge curve. For Li/X5 cells with $P(EO)_8{\cdot}LiCF_3SO_3$ electrolyte, performance data were slightly inferior at 100 °C and much inferior at lower temperatures[304] for structural reasons (hindered Li^+ ion diffusion).

Practical Na/X cells with β''-alumina electrolyte operating at 130 °C were described in the 1989 symposium.[294] The open-cell voltages are given in Table 3.1 for six of the series-X polymers. Cycling results were reported for a Na/X1 cell operated between 80 and 130 °C (80% cathode utilization) and for a Na/X5 cell (50% cathode utilization). Polymer X5 can also be utilized more fully when working at lower current drain.[309]

Polymers where the sulfur atom in the disulfide group is bonded to nitrogen (X2, X3, X4, X6) were also tested, and said to offer very good rate capability, but degraded after a few cycles, presumably due to impurities.[294]

From the results illustrated in Gauthier's patent,[311] which refer to polymers X1 (DMcT polymer) and X7 (dithiouracil polymer), cycle lives of 100 cycles at 60 °C can be deduced. His discharge curves also reveal voltage steps in the discharge of X1: OCV 3.05 V, first plateau 2.8 V, second plateau 2.5 V. Steps are not present in the curves for X7. Other numbers given in this patent refer to theoretical quantities only.

From the Japanese work[105] on composite cathodes (X1 + 25% polyaniline), a figure of 303 W h kg^{-1} can be quoted as "cathode energy density" (against Li) for a cell where a gel electrolyte was used (20:1 acrylonitrile−methacrylate copolymer with $LiCF_3SO_3$). The gel electrolyte was also present at a level of 230% relative to X1 in the composite cathode. When carbon was used instead of polyaniline, the "cathode energy density" was only 235 W h kg^{-1}. Referred to the complete cells, "expected" values of 220 and 172 W h kg^{-1} were quoted for X1 with PAni and C, respectively. All these values refer to discharge with 0.1 mA cm^{-2}. The discharge curves are rather sloping, and much more so at even slightly higher current densities.

Work toward electrolyte optimization[106,302,303] showed that $LiBF_4$ as salt in the gel electrolyte affords higher discharge current densities and longer cycle lives. Higher contents of PAni and C slowed degradation during extended cycling. An interesting observation was made during the first few cycles: The discharge curves appeared to be a simple combination of the corresponding curves for X1 and PAni in cycles no. 1 and no. 2, but in subsequent cycles they fused into a single, monotonic and rather sloping curve.[106] Addition of a substituted pyrrole polymer to the X1-PAni composite enabled it to be more rapidly charged, but did not improve the discharge rate capability.[303] A large improvement in specific energy was obtained when the X1-PAni cathode was made by film casting from *N*-methyl-2-pyrrolidone, which was partly retained in the active material constituting an X1-PAni mixture at the molecular level.[107] Geniès and Picart[108] have discussed the merits of PAni-X1 combinations. They found experimental evidence for PAni catalysis of X1 reduction and predicted that an energy density of 700 W h kg^{-1} could be attained in batteries with Li anode.

Concerning PAni-X1 or other, analogous combinations, it should be added that the conducting polymer might fill a number of functions in addition to being a catalyst:[283,301] It could contribute electronic conductivity (which necessitates a redox potential of the thiol [solid redox] polymerization material to be in the region where the conducting polymer is in its well-conducting, doped state); it could contribute ionic conductivity (which requires counterions); it is likely to provide a porous structure; and it may function as an additional active material. (Compare these features with properties of the PPP-alloy composites discussed in section 3.5.) The family of patents from Matsushita Electric[109] reflects efforts to find optimum combinations of this type (and the corresponding electrolytes).

Recent papers by Naoi and colleagues[480,481] introduce a bit of uncertainty into the promising picture of disulfide polymers. They found that X1 is obtained by polymerization at 0.8 V *vs* Ag/AgCl with an induction time, and at 1.4 V without an induction time. Islands of the 1.4 V material were found to disappear when left at open circuit. Also, polymerization consumed more charge than depolymerization, so that side reactions such as overoxidation or a degradation process cannot be ruled out. The degree of polymerization was found to be low (five to nine), while dimers and oligomers exhibited solubility. These observations may indicate that depending on operating conditions in cells containing X1, a degradation of capacity may occur, amounting to self-discharge if the decomposition reaction is depolymerization.

Another comment should be made in concluding this section: *viz.*, that self-discharge data have not been published for the redox dimerization and polymerization electrodes. The promise of redox polymerization electrodes is large, if their performance figures as reported by the Berkeley group are compared with those of the lead–acid system:[482]

performance figure	lead–acid	SRPE
W kg^{-1}	94	120–1800
W dm^{-3}	220	140–2200
W h kg^{-1}	36	140
W h dm^{-3}	92	170
η/%	91	≤96
cycles	370	about 350

Therefore, if self-discharge proves to be no more important than in the lead–acid system, the redox polymerization electrodes could become competitive in power applications, at least where operation somewhat above ambient temperature is not an obstacle (such as EV propulsion).

Considering the known disadvantages of Li electrodes, it is surprising that results on Na/β''-alumina/X batteries have not been reported for some time now. Thinner ceramic electrolyte membranes could become available owing to progress in ceramic electrolytes for solid-oxide fuel cells.[283] First efforts to make sodium/X1 cells with PEO electrolyte have been reported.[483] Their cycling and capacity performance figures fall short of those from Li/X1 cells even at 90 °C.

Current efforts go into improving the X1–polyaniline adducts or bringing about a covalent bonding between the thiol groups and a conducting polymer having the appropriate functional groups.[283,301]

3.9. Polyacenes and Carbons

Most of the results presented in this chapter for carbon-based electrodes are recent. Complete systems have been studied quite rarely in the work cited. Most of the cells used in research work had a lithium counter electrode, so effectively the carbon materials were studied as positive electrodes in lithium/carbon cells. Their cell voltages are much too low to be of practical interest.

Lithium/carbon cells are a laboratory device to study the carbons. The term "discharge" used in lithium/carbon cell studies[332,351,361] gives rise to confusion, which should be mentioned before describing in more detail the corresponding results.

The interest of carbon materials is in their use as negative electrode materials (anodes) in practical lithium ion cells such as carbon/$LiNiO_2$, carbon/$LiCoO_2$, or carbon/$Li_xV_3O_8$. In these cells, Li^+ intercalation corresponds to charging. In the lithium/carbon cells, Li^+ intercalation corresponds to cell discharge.

Intercalation of lithium leads to compositions somewhere between $Li_{0.5}C_6$ and $Li_{1.0}C_6$. To achieve this, the charging of the carbon negative may be driven, *e.g.*, to 10 mV *vs* Li/Li$^+$, whereupon the carbon material is fully loaded with lithium. Charging further (*e.g.*, by driving the carbon electrode to potentials negative to Li/Li$^+$) may lead to the deposition of metallic lithium on the carbon. This could occur inadvertently when using inappropriately high charging rates.

An important parameter determined experimentally is the value of x in the (idealized) formula Li_xC_6. The limiting formula LiC_6 reflects the sites available for Li in the hexagonal graphite lattice and was confirmed most convincingly in the studies of staging.[317,318] The parameter x in Li_xC_6 is reported in the place of y in the column of "doping level" in Table 3.1, together with information on the systems tested and with other results of interest.

Table 3.4. Carbon Materials: Values of Specific Charge (Ref 321)

carbon material (abbrev.)	specific charge (A h kg^{-1})	initial Coulombic efficiency (%)
natural graphite (NG)	320	92
graphite whiskers (GW)	363	83
mesocarbon microbeads (MCMB)	280–290	88
pitch-based carbon fiber (PCF)	290	93

Table 3.1 confirms that intercalation in graphitic materials approaches the limit of $x = 1.0$,[318,327,328,330–332,335,341] while in materials on the basis of petroleum coke not subjected to thorough graphitization it approaches a limit of $x = 0.5$.[331,339] A number of materials have been prepared or found where $x > 1.0$.[329] Boron or silicon doping appear particularly helpful in achieving such values.[361,363] A small table from the review of Iijima[321] is reproduced as Table 3.4. The initial efficiencies listed reflect the irreversibility of the first cycle discussed in section 2.9.

While cycle lives may not seem particularly impressive, it should be realized that cycles of deep discharge–complete charging are the rule when testing carbons, so direct numerical comparison with the results for conducting polymers is of limited relevance. In fact, Howard[323] mentioned six companies as being active in the lithium ion battery field, not counting Varta,[322] which implies highly satisfactory performance of the systems used.

3.9.1. Graphite, Pitch-Based Carbons (C)

Recall at the outset the specific charge reported for graphite sulfate,[216] of 37.0 A h kg^{-1}, for a compound with $x = 0.17$ and co-insertion of two molecules of sulfuric acid for each hydrogen sulfate ion HSO_4^-. This material would constitute a positive electrode (cathode). At these low degrees of anion intercalation or doping ($y = 0.02–0.04$, corresponding to $x = 0.12–0.24$), reversibility was reported to be very good,[39,216] but the specific charge is too low for a practical application. On the contrary, in practical (commercial) lithium ion cells the carbon materials intercalating Li^+ ions and constituting negative electrodes (anodes) have achieved a specific charge of over 300 A h kg^{-1} (see below).

Excellent results for the intercalation of Li^+ into carbon were already available in 1989: Mohri *et al.*[327] reported 350 A h kg^{-1}, >99% Coulombic efficiency, and about 500 cycles to 80% of the initial capacity when a pyrolytic graphite prepared from benzene in the gas phase was tested in combination with chromium dioxide or vanadium oxide cathodes. Slightly higher in specific charge is the graphite whiskers material reported five years later,[348,349,355] which exhibits 100% Coulombic efficiency. For the mesocarbon microbeads,[329] for which a reversible capacity of 410 A h kg^{-1} was reported, the Coulombic efficiency and cycle lives were not reported; first-cycle

Coulombic efficiency was low. The behavior of this material strongly depends on the heat treatment temperature.[484]

The voltage limits of charge and discharge are a point of concern for specific energy (as opposed to specific charge) performance. For highly graphitic materials, the reversible capacity is associated with potentials not very far from Li/Li^+ (say, 10 to 200 mV *vs* Li/Li^+). For the specific energy of complete cells, this is important. (Note that just a single value of specific energy was available in the papers included in the review.)

Flat discharge curves (and the corresponding charging curves) in which the potential remains relatively close to the Li/Li^+ value have been reported for graphitized pitch-based carbon fibers,[321,344,345,347,358,374] vapor-grown graphite fibers,[355] natural graphite,[318,328] synthetic graphites,[316,330,340] high-temperature heat-treated petroleum coke,[316] mesocarbon microbeads heat-treated at 2800 °C,[484] also for graphite in polymer electrolyte cells.[332] On the other hand, highly sloping curves have been found in a number of other systems. They are a mixed blessing. First, sloping discharge curves constitute a disadvantage in applications: electronic gear for voltage stabilization may be required. Second, the specific energy of such a cell will be lower than that of a cell with flat discharge curve. But a discharge voltage further away from Li/Li^+ also implies a charging voltage further away from lithium deposition. This is important in high-rate charging, where anodes with a flat curve may readily be driven to potentials negative of Li/Li^+. Lithium may then deposit on the carbon (rather than be intercalated in it), and consequently the carbon cell's safety feature is lost and its reversibility impaired.

Such sloping characteristics have been reported by Iijima[321] from a Japanese conference paper for pitch coke heat treated to 600 °C (its specific charge: 450 A h kg^{-1} for discharge to 1.2 V *vs* Li/Li^+). They have also been reported for a petroleum coke heat treated to 1300 °C,[331] where the capacity corresponds to $x = 0.5$; for heat-treated petroleum pitches (900−1200 °C);[316] for pitch-based carbon powder (1400 °C);[346] for mesophase pitch carbon fibers (900, 1500 °C);[341] and for mesocarbon microbeads heat treated at different temperatures.[354,484] Strongly sloping characteristics are exhibited by the highly disordered pyrolytic carbons of Sandí *et al.*[351] which gave a record 825 A h kg^{-1} reversible capacity. The curves for sodium intercalation into carbons also exhibit relatively high slopes.[336]

The OCV values, when plotted as a function of x, mirror the sloping nature of the discharge curve.[346] The potentials recorded during electrochemical intercalation were shown to be determined by the surface stage of graphite intercalation.[317] This is important for an interpretation of sloping curves, since for kinetic reasons (slow Li diffusion in the bulk of the carbon material), the surface stage may differ from the bulk stage.

A sloping section (plateau or bulge) in the curve for first charging (reduction)[316,318,331,333] of the carbon anode is indicative of the phenomena discussed in section 2.9. The solution composition and electrode pretreatment are important in the efforts to reduce the associated irreversible capacity.

When the reversible capacities (values of specific charge after the first cycle) of "soft" carbons were studied for different heat treatment temperatures,[316] high values were found (together with strongly sloping curves) at low heat treatment temperatures (900−1300 °C), a minimum in the values of specific charge was seen for intermediate heat treatment temperatures (between 1300 and 1900 °C), and high values of specific charge were again recorded (together with flat discharge curves) as the heat treatment temperature was raised from 1900 to 3000 °C. Over this temperature range, the disorder parameter P (fraction of adjacent layers having turbostratic shifts between them) remains constant ($P = 1$) until $T > 2000$ °C, then drops steeply with increasing temperature to $P = 0.2$ at 3000 °C. A plot of x against P extrapolates to $x = 1$ for $P = 0$. These findings indicate a possible approach to higher values of specific charge, but do not yet indicate how the cycle life will be affected.

Cycle life was studied by Iijima *et al.*,[339] whose work confirms the findings concerning the values of specific charge as a function of heat treatment temperature, but also reveals that the cycle life is distinctly improved in a monotonic fashion with increasing heat treatment temperature. The high values of specific charge found for low heat treatment temperatures are lost during cycling. Those found at high heat treatment temperatures (2900 °C for carbon fibers and pitch cokes: 260 A h kg^{-1}) are preserved (50 cycles were reported). For pitch coke or fibers treated at intermediate temperatures, the values of specific charge are stabilized at about 120−140 A h kg^{-1}, which is 50% of the values found for the materials treated at high temperatures.

The cycling properties also depend on the carbon material. Aurbach *et al.*[333] concluded that "the choice of carbon as the anode material should be the result of a compromise between highly ordered, graphitic materials which intercalate Li at low potentials and optimal stoichiometry and much less ordered carbons of worse performance but which are more stable than graphite in prolonged charge−discharge cycling". They went on to show, however, that solution composition is important for cycle life, and can be manipulated to improve the cycle life of graphite.

Ishikawa *et al.*[344,345] had found that in systems with 1 M $LiCF_3SO_3$, the Coulombic efficiencies were closest to 100% and the discharge capacity exhibited the best stability during cycling with EC-DMC (1:1) as a solvent; however, only 20 cycles were performed. Aurbach *et al.*[333,335] showed that for 1 M $LiAsF_6$ in the presence of CO_2 (6 atm), EC-DEC and MF-EC (1:1) were the best solvents. Good results were also obtained in THF-MF and, at a lower level, in BL-MF. Other workers[332] had found that $LiAsF_6$ is reactive. This, and the favorable results obtained with CO_2, may be taken as evidence that a mechanism of passive-layer formation is involved. Other rather interesting findings of the Israeli group[335] were the dramatic improvement of cycle life at ordinary temperature resulting when the first charging was carried out at −80 °C, and the beneficial effects of modest amounts of water (about 500 ppm). All these factors are attributed to surface chemistry producing a film with more or less passivating properties. It is curious, with respect to the temperature effect, that at −80 °C, the amount of irreversible capacity (charge consumed for film buildup) was found to be negligible. It is not quite clear then how a passivating film develops, unless this occurs purely chemically (rather than electrochemically, with the consumption of charge).

Even binders were found to affect the lithium storage capacity of lithium intercalation anodes.[340] Theoretical $x = 1$ capacity (a specific charge of 372 A h kg^{-1} based on the carbon alone, or of 340 A h kg^{-1} based on LiC_6) and the lowest irreversible capacity loss in the first cycle were attained for a synthetic graphite when a polymer-derived carbon binder was used. (It is not clear whether this binder material could itself contribute to capacity, but at any rate the irreversible first-cycle capacities were distinctly higher when PVDF, and particularly so when PTFE was used as a binder material.)

The effect of overcharging was studied at the Toshiba R&D Center.[341] Their mesophase pitch carbon fibers belong to the high-slope materials. Coulombic efficiencies were found to decrease from 100% to 94.5% and to 88.7% when the charging was performed with 200, 300, and 400 A h kg^{-1}, at the same time the voltage hysteresis between charging and discharge became much larger, the discharge curves became even more sloping. The high slopes of these curves and the strong hysteresis also exist for the mesocarbon microbeads of Osaka Gas studied at Grenoble (410 A h kg^{-1}).[329]

Among the surface treatments proposed by Takamura *et al.*[347] for mesophase carbon fibers, heating to 700 °C with acetylene black (partial oxidation) was found to bring about the largest improvement, supposedly by removing surface hydroxyl groups or water and enlarging the effective surface area (the fiber sample used to show this effect was the 3000 K material).

Mild oxidation (slight burn-off) was found to improve the performance of graphite material:[338] the reversible capacity was higher, while the irreversible capacity required for SEI (solid electrolyte interface) formation was lower.

For the rate capability, a small particle size of graphite[353] and accessibility of individual carbon fibers in an electrode[485] will be important. Prior potassium intercalation was found to produce a lattice spacing enabling faster kinetics.[352]

The rate capabilities of carbon anodes are sometimes hidden by plots which only show the cell voltage (or half-cell potential) against capacity (specific charge, in mA h g^{-1}). For record specific charge values, low charge−discharge rates have been preferred (typically a 50-h rate may have been used in order to obtain many of the performance data shown in Table 3.1). Rate capabilities of the C/1 type (1 h) and higher have been demonstrated, for instance in the case of graphitized mesophase pitch-based carbon fiber anodes.[358] The A-size cells built with these anodes and $LiCoO_2$ exhibited a discharge capacity of 0.95 A h, a drain capability of up to 3 A, and high energy density (see Table 3.1).

3.9.2. Heteroelement-Substituted Carbons (CHet)

The boron compound BC_2N has a graphitelike layer structure. The material heat treated at 1500 °C had a first-cycle specific charge of 300 A h kg^{-1}, but this parameter rapidly fell to values below 100 A h kg^{-1} after only five cycles.[360] Very highly sloping curves, but also higher values of specific charge, *viz.*, 437 A h kg^{-1}, were found for $Li_{1.16}(B_{0.17}C_{0.83})_6$.[361] For reasons already discussed, this material would be favorable in cells designed for high-rate charging, but its specific energy will be much less than expected from the high value of specific charge.

The data obtained for the nitrogen-substituted carbon[362] are not poor, but they are distinctly lower than the corresponding pure-carbon values, hence nitrogen substitution is not an advisable way of improving carbon anodes. Also, the irreversible (first-cycle) capacities are large. Here, too, very sloping curves are recorded.

Silicon substitution was the most successful improvement so far for CVD-type carbon materials.[363] The silicon-free carbon exhibited 300 A h kg^{-1}, while the materials with 1.8, 3.1, 5.9 and 11 atom % of Si gave 363, 433, 478 and 493 A h kg^{-1} of reversible specific charge. The curves are sloping, and the (first-cycle) irreversible capacity strongly increases with increasing silicon content. The constancy of specific charge during cycling (35 cycles were shown) was excellent.

3.9.3. Polyacenes (PAS)

For the polyacenes and similar materials with condensed-ring structures, doping levels have been reported, not as x in Li_xC_6 but as ions (incorporated or expelled) per carbon atom. Thus, a factor of 6 should be applied for comparison with the materials of sections 3.9.1 and 3.9.2. For comparison with ordinary ion-inserting, conducting polymers, a factor of 8−10 should be applied when reading the corresponding data in Table 3.1. No such obstacle to comparison exists for the values of specific charge, which exhibit an unusually wide spread, considering the modest chemical disparity. Again, specific energies have been reported rather less frequently than values of specific charge.

Polyacenes ("polyacenic semiconductors", PAS) often have a "zero-doping potential" somewhere between 2.0 and 3.0 V *vs* Li/Li^+, and thus can readily be *p*- and *n*-doped.[364,365,368,370,371] The related charge−potential curves pass smoothly, even symmetrically, through the zero-doping potential. PAS/PAS cells are readily assembled and operated.[365,368,371] However, contrary to assertions made,[371] such systems cannot offer an interesting energy density, since their discharge ends at zero voltage.

Very attractive power densities or rate capabilities together with very long deep-discharge cycle life[368] rather predestine such systems as capacitors.[364,365,368,371] Some capacity values are given in Table 3.1. Most authors claim that such systems can also be regarded as batteries; they may well fill the demands of load leveling and backup power where constant voltage is not a requirement. Their low-temperature performance is remarkable (for example, 36 A h kg^{-1} at −30 °C, as compared to 41.5 A h kg^{-1} at room temperature, always with a current drain of 19 A kg^{-1}).[368]

Li/PAS systems where PAS is the cathode have interesting values of specific charge and energy when discharge is performed over a very wide voltage range; see the values of Yata *et al.*[368,371] in Table 3.1. Here rechargeability (cycling performance) would depend on the (lithium) counter electrode.

For complete systems, both of the PAS/PAS type[368,371] and of the PAS/metal oxide type,[40,377] cycle lives are very satisfactory. The PAS/Li(Ni,Co)O_2 system is a true lithium ion battery and has been commercialized.[40] (According to the review[40] describing the Sony system, the carbon was prepared by thermal decomposition of a furan-based polymer. It was not called a PAS by Sony or the reviewers.[40]) Separate discussion would be required to decide whether "hard" carbons such as the pyrolyzed polymer of the Sony battery or pyrolyzed PFA can actually be called a PAS. A nomenclature has not been established. It is suggested here that the ACF of the workers at Osaka University[364,365] and the pyrolyzed products of furan and benzene polymers, PPFA and PPPP, like the materials with heteroatoms of section 3.9.4, be regarded as PAS.

The ACF/ACF system when assembled from felt electrodes separated by a glass fiber filter has been called an organic-electrolyte double-layer capacitor, the reasoning being that $(C_4H_9)_4N^+$ ions are too large for intercalation.[364] Depending on microporosity, this reasoning may or may not be entirely correct. If all of the surface area of 2000 m^2 g^{-1} is accessible, a double-layer capacitance of 100−400 F g^{-1} is expected, which is more than the 27 F g^{-1} reported.

Self-discharge data for the ACF-based systems were reported as 60% in 4 days for the battery and 40−50% per day for the capacitor.[365] The self-discharge rate appears to be much less important in the PAS of Yata *et al.*[371]

For the phenol−formaldehyde-based PAS material, Yata *et al.*[370] found that the charge-storing capacity is highest when the residual hydrogen content is between 0.15 and 0.30 H atoms per C atom. This implies that for these particular materials, the HTT ought to be between 500 and 700 °C. Materials prepared[371] at 510 °C exhibited excellent cycle lives, satisfactory function between −40 and +70 °C, very good rate capability (90% charging in 10 min), and low self-discharge. The latter parameter, however, was only evaluated in terms of the drop in OCV (from 4.0 to 3.2 V after 20 days at 60 °C). A considerable increase in specific charge could be attained by predoping of PAS anodes:[373] record values of specific charge (530 A h kg^{-1} corresponding to $Li_{1.42}C_6$ or 0.24 Li^+ ions per C atom) and a maximum intercalation corresponding to $LiC_{2.2}$ (or $Li_{2.7}C_6$) were reported very recently by Yata *et al.*[373] It is important to note that, while these values are far in excess of the maximum doping level in the carbon materials of section 3.9.1, and more particularly even of graphite, the structural stability of the present PAS is also much higher.[373]

The best of the carbons prepared by Dahn *et al.*[383] exhibited a specific charge of 560 A h kg^{-1}, including 350 A h kg^{-1} in the low-voltage plateau.

Curves showing plots of the electrode potential against the state of charging have been reported rather recently.[373] They are sloping, with a downward curvature and starting at 1.0 V *vs* Li/Li^+. The material with the highest specific charge also exhibited the largest hysteresis between the charge and discharge curves. Therefore, even though the values of specific charge are extremely interesting, more data concerning the specific energy and the voltage of complete cells are needed before such values can be regarded as realistic. Zhang *et al.*[372] reported that their polyacene/polyaniline cell had a reversible capacity (specific charge) of 35 A h kg^{-1} when cycled between 2.0 and 4.0 V, which would translate to about 100 W h kg^{-1}, but they refer to the polyacene weight only.

Further, it should not be overlooked that like other carbon materials, the PAS materials of the present section, when used as lithium-inserting anodes, exhibit the familiar capacity loss on first charging. In the materials of Yata *et al.*,[373] the first-cycle capacity loss increases considerably with increasing reversible capacity (reversible specific charge). In the materials of Sony Corporation,[378] capacity loss and discharge capacity were found to decrease with increasing HTT, concurrently with a decrease in the (002) lattice spacing. According to the compromise between the (undesired) loss of reversible capacity and a (desirable) reduced capacity loss, the optimum HTT was 1100 °C in this case. This HTT also led to the materials with longest cycle life. Low crystallinity (high disorder) is preserved at this HTT in pyrolyzed poly(furfuryl alcohol) (PPFA).

For Sony's lithium ion battery, performance values were quoted[40] as attaining more than 1200 cycles when charging and discharging at the 2-h rate. The negative in this battery is a pyrolyzed polymer like the PPFA just described, while the positive consists of a lithium-inserting metal oxide, Li(Ni,Co)O_2. The charge−discharge curves reported for PPFA are strongly sloping and exhibit a good deal of hysteresis.[316]

The highest specific charge was reported for pyrolyzed PPP in a liquid electrolyte.[379] It was already mentioned that this material offers sites for lithium. This lithium replenishes Li^+ sites in the disordered lattice emptied during discharge, providing extra capacity. Very high values of specific charge (up to 610 A h kg^{-1} with $LiClO_4$) were also reported for the same material in cells with PAN-based solid electrolyte.[380] However, rather pronounced plateaus of irreversible capacity are seen during first charging. Charging curves of subsequent cycles are rather smooth and much closer to the Li/Li^+ potential. The discharge curves again are strongly sloping.

Concerning the fullerene (F) data (see Table 3.1), it should be added that the charging curves are located at potentials more than 2.0 V more positive than Li/Li^+, the discharge curves are highly sloping, and the values of specific charge are rather low. This would disqualify C_{60}-F or C_{70}-F for use in batteries.

It will be instructive at the end to briefly consider the model carbons prepared by workers at Osaka Gas.[382] Carbons prepared from acenaphthylene carbonized at 800 or 1000 °C, or graphitized at 2780 °C, exhibited values of specific charge of 497, 264, and 316 A h kg^{-1}, respectively. Acenaphthylene is actually graphitizable, and the 2780 °C value reflects the possibility of graphitic intercalation of the Li^+ ions. Carbons prepared at the same temperature from phenolphthalein had values of specific charge of 386, 282, and 134 A h kg^{-1}, which can be rationalized by noting that phenolphthalein is not graphitizable but forms a highly cross-linked material unfavorable for intercalation.

Summarizing, it can be stated that the polyacenes or pyrolyzed polymers of section 3.9.3 offer the highest values of specific charge found thus far in anode materials, but it will be necessary to verify the values of specific energy, improve the discharge curves, and reduce the irreversible capacity lost on first charging. Realistic performance data accounting for all battery components are needed as well. But even now, these materials already appear to be the most practically useful ion-inserting material.

3.9.4. Poly(heteroacenes) (PHAS)

The data for the poly(heteroacenes) or poly(heteroacenic) semiconductors (PHAS) are presented in the same way as those for polyacenes (Table 3.1). The doping levels are assumed to be ions per carbon atom, although they were usually given less explicitly in mole %.[386] No relation has been established between doping levels and the levels of heteroatoms in the materials. This does not imply that these atoms were unimportant. Lithium ion insertion was said to be favored by polyacenic nitrogen atoms,[375] although this substitution appears to cause some increase in the reaction resistance during charge and discharge.[375]

For the PAN-derived products (thermally structured PAN, TSPAN), properties have been reported which are highly reminiscent of those for the PAS products of section 3.9.3. They are stable, insensitive to the presence of oxygen, and can be reversibly *p*- and *n*-doped. Again, *p*-doping appears to be less efficient than *n*-doping. Interesting values of charge and energy density can only be obtained when using them as a positive electrode in lithium batteries and working over a wide potential range encompassing both doping modes.[375,386−388] This leads to highly sloping curves of voltage against the state of charge for the Li/TSPAN battery. For its use as a negative electrode, TSPAN appears to be much too positive in its potential: its zero-doping potential is around 3.2 V *vs* Li/Li^+.[386] When passing through this potential one smoothly changes over from the range of *p*-doping to that of *n*-doping or *vice versa* (zero band gap).

Very good cycling results have been obtained for the TSPAN/TSPAN combination,[388] which again functions more like a capacitor than like a battery.

The highest values of specific charge have been reported for pyrolyzed PAN[389] (a cathode material similar to TSPAN) and for PAN-derived foam carbon[340] (an anode material).

Data for self-discharge of TSPAN materials have been reported in terms of the change in electrode potential at open circuit. The percentage values given appear to refer to potentials *vs* Li/Li^+. Complete self-discharge of Li/TSPAN cells was reported to lead to the “open-circuit”, more precisely the zero-doping, potential,[386] although rather slowly (15% after 3 months).[388] The cycling performance of Li/TSPAN batteries and TSPAN/TSPAN capacitors which were assembled in commercial R 2032 coin-type cases was rather impressive and would provide backup power, according to Jobst *et al.*, for CMOS-RAM.[388]

Electrochemical data for the polyacenic structures made from *o*-aminophenol[392] and *o*-phenylenediamine[393] are available only in the form of voltammograms, which are too complex to derive any performance figures. It should be stressed, though, that the films produced proved to be very stable in acidic solutions.

Prototype CR 2016 cells were assembled from anodes of pyrolyzed modified aromatic polyimide (PAPI) and cathodes of PAni. The carbon itself exhibited 500 A h kg^{-1}, the PAni without dopant ions 118 A h kg^{-1}. The cell gave up to 5.9 mA h or 17 mW h. This cell was claimed to be the first rechargeable lithium ion battery in which both electrodes were derived from synthetic organic polymers.[102]

The boron-substituted materials[395] yield results not much different from those reported for similar anode materials in section 3.9.2.[360] They include interesting values of the specific charge; however, the discharge curves (potential *vs* Li/Li^+ as a function of time) are very steep. The charging curves are rather sloping, too, so that it would not be possible, according to data published, to attain similary high values of specific energy.

In contrast, the discharge curve reported for $P_{0.04}C_{0.96}$ (“phosphorus-containing PFA-C”) runs close to the Li/Li^+ potential for about 250 A h kg^{-1} and then rises to about 1 V *vs* Li/Li^+ during discharge to 450 A h kg^{-1}.[396] The corresponding charging curve is not given in the conference paper, nor is it clear whether the value of specific charge is a truly reversible value. Still, in view of the discharge curve, it can be assumed that this interesting electrode is much more likely to offer a high value of specific energy than electrodes with sloping curves. Its cycling properties remain to be seen.

The data for Si_zC_{1-z} made from poly(methylphenylsiloxane), which is Dow Chemical’s DOW 710 Fluid, imply a very high reversible specific charge,[363] but again the discharge curve is strongly sloping (rising from 0 to about 1.5 V), while the charging curve is also sloping (descending from about 1 to 0 V), and the two curves together exhibit hysteresis. Hence, the values of specific energy and energy efficiency may be much less sensational.

In summary, certain data for PAS and PHAS are exciting and promising, and as an educated guess, the expectation could be offered that with an optimized combination of starting polymer and pyrolysis conditions, and also with a more appropriate physical form (whiskers or fibers?), a near-perfect anode material and a cathode material comparable to the best materials presently available can be created. This task has not been completed, and it cannot at present be concluded that any of the carbons derived from known polymers or other precursors will be able to outperform existing cathode materials. It can be concluded, although on a meager data base, that ion-inserting carbon or polyacene anodes are superior to others at this time.

4. Concluding Remarks

We remark before arriving at some judgment and outlook that a few years ago in Japan a commercialization of a Li/PAni cell was attempted, and in Germany a Li/PPy cell was prepared for commercialization. The Japanese design[78] was of the coin-type, its operating voltage fell from 3 to 2 V during discharge; the batteries offered 0.5 to 3 mAh of capacity. The German (Varta/BASF) battery, according to descriptive publications,[124,126,459] offered a choice between a cylindrical, bobbin-type design with rolled-up sheets of Li and PPy, and a rectangular sandwich-type stack of alternating Li and PPy films in bipolar configuration. Certainly, the latter principle of assembling bipolar stacks will provide the only practical solution to the problem of contacting relatively thin films and of providing a means for tapping the high pulse-power discharge capability of polymer electrodes. Rolled designs will be favorable for lower drain rates.

In ion-transfer battery designs, for instance with cells with cation-inserting anode and cathode, the salt concentration changes in the solution are avoided and the electrolyte volume required can be minimized. Obviously, the highest specific energy and energy density may be achieved in an ion-transfer battery having a lithium-inserting carbon negative (or metallic lithium) combined with a polymer, metal oxide, or metal sulfide positive which is able to insert Li^+ ions during discharge and give them off during charging. For this reason, conducting (ion-inserting) polymers still constitute interesting electrode (chiefly cathode) materials for battery applications. Their specific charge is comparable to that of metal oxide electrodes, and it could even be higher.

Negative electrode materials to be considered more generally will include metals such as Li, Na, Mg, and Zn, as well as metal hydrides. Lithium electrodes have been reviewed in detail.[40] Some conducting polymers have also been tested as negative electrodes, as pointed out in the present review (see Table 3.1). Polymer/polymer systems offer promise as supercapacitor devices to be used as secondary power sources in electric vehicle propulsion.[472]

It is not too early to comment on the materials discussed in sections 2.9/3.9. Today they already appear to provide a viable solution for anodes in rechargeable batteries for portable devices (camcorders, laptops) and electric vehicles. Up to now these batteries have positive electrodes selected from the inorganic oxide and chalcogenide materials, not from the conducting polymers and redox polymerization electrodes described in the present review.

Not long after the market introduction of lithium ion batteries (with a C anode and $LiCoO_2$ cathode, see section 3.9), Sony came out with an EV battery which has a specific energy of 100 W h kg^{-1} and a specific power of 300 W kg^{-1}.[487] In a Ragone plot of specific power (W kg^{-1}) against specific energy (W h kg^{-1}), lithium ion systems of this type beat all other technically mature rechargeable systems (lead–acid, nickel–cadmium, nickel/metal hydride, sodium/sulfur).[487,488] The driving range would be 200 km with a lithium ion, as against 70 km with a lead-acid battery.

The system is mature enough to be the target of advertising for fully automatic winding machines.[489] Even before the Sony EV battery became known, United States authors came to optimistic conclusions when comparing the specific energy, peak specific power, and cycle life between different systems competing to meet the US ABC goals, in that lithium ion is at the top in all three parameters.[325]

Note that, if lithium ion is mentioned for those applications just discussed, then this system has a carbon insertion material from section 3.9 as the negative electrode, and inorganic material ($LiNiO_2$ or $LiCoO_2$, for instance) as the positive electrode, rather than any ion-inserting polymer.

Still, among the ion-inserting polymers prepared, many already meet requirements as to specific charge. Fewer meet requirements as to cycling, Coulombic efficiency, or flatness of the discharge curves. Specifically for this reason, polymers other than PAni and PPy merit optimization and development efforts. Despite much work, PAc today appears to be a poor candidate (see section 3.1). It has poor charge retention, lacks ease of processing, and is insufficiently stable in battery environments. Despite its near commercialization, the specific energy of PPy has remained too far below the theoretical value, and PPy is not kinetically as fast as other polymers. More promising polymers could be among those recommended below for further work.

Considering the results discussed, it appears that further systematic work on ion-inserting conducting polymers should be carried out along the following lines:

– *An optimization of electrolyte compositions* (probably mixed solvent or complex organic polymer; in the past, frequently a “default” system such as PC-$LiClO_4$ was used without any optimization)

– *A proper balancing of the anode and cathode in complete cells* (in most cases in the past Li was present in excess)

– *An interlaboratory comparison* for polymers other than PAc, PAni, PPy (certainly some *polythiophenes,*[184] *PPP, PCz, PAz, and also the PPP-alloy composites* merit attempts at reproduction of the best results available so far, the same holds true for redox polymerization electrodes)

– The *integration of electrolytes into cathode materials* (developments in ion-conducting polymers useful as battery electrolytes have been reviewed in a book[491] and in reviews)[492–498]

– *Studies of self-discharge* (loss of charge on open circuit in optimized systems and comparison to performance requirements)

– *A search for optimum applications* (it is unlikely that polymer batteries will be very universal but, depending on design, they could offer high pulse power, specific low-temperature capability, or advantages related to shape versatility, such as extremely flat design)

– *Studies of* Coulombic *efficiency under realistic boundary conditions* (such as the time of rest in the charged state typically found in the applications envisaged)

– Inquiries into the heat management of stacked bipolar designs undergoing high-rate discharge[499,500]

– *Work with polymers obtained with industrial production methods* (such as the electrolytic preparation known from the Varta/BASF work,[124] from work involving rotating cylinder electrodes,[501] or from Battelle's PML technology.[502]

Considering the long and important list of topics for further or more systematic work, the full set of interesting properties of ion-inserting polymers, the many interesting uses of these high-tech materials, and unexplored energy-storage principles such as bonds involving phosphorus, the authors of the current review are optimistic as to future success of ion-inserting polymers and related materials. They do acknowledge that early, high expectations of light, high-specific-energy polymer batteries have not been met as yet, but they share the optimism of McBreen[503] and Matsuda.[504]

5. Abbreviations

A^-	anion
A:	anode material
(A+C)	anode and cathode
AB	acetylene black
ABC	advanced battery consortium
ABS	acrylonitrile–butadiene–styrene copolymer
ACF	activated carbon fibers
AN	acetonitrile
AS	acrylonitrile–styrene copolymer
Az	azulene
bipy	bipyridine
BL	γ-butyrolactone
BN	benzonitrile
BP	biphenyl
BT	bithiophene
C	carbon
C, $C_{\max}$	capacity (in cycle lives)
C/n	n hour discharge rate in battery testing
(C)	cathode
CA	chemical analysis
cat.	catalytic; catalyst
CB	carbon black
CCV	constant cell voltage
CE	counter electrode
CFP	carbon fiber plate
CH	cyclohexanone
CHet	heteroelement-substituted carbon
Ck	coke
CMOS	complementary metal oxide semiconductor
CPE	constant potential electrolysis
CV	cyclic voltammetry
CVD	chemical vapor deposition
Cz	carbazole
DATA	dialkylthioacetylene polymer
DBS	dodecylbenzenesulfonate
DEC	diethyl carbonate
DEDC	diethyldithiocarbamate
DL	doping level
DMC	dimethyl carbonate
DMcT	2,5-dimercapto-1,3,4-thiadiazole
DME	dimethoxyethane
DMF	*N*,*N*-dimethylformamide
DMS	dimethyl disulfide
DMSO	dimethyl sulfoxide
DMSU	dimethyl sulfite
DOD	depth of discharge
DTDT	dithiolodithiol
DT-TCA	thioxodithiolyldithiocarbonic acid alkyl ester
EC	ethylene carbonate
EEDS	bis(ethoxyethyl) disulfide
EPDM	ethylene–propylene diene monomer (terpolymer precursor)
EV	electric vehicle
F	fullerene
Fc	ferrocene
FC	foam carbon
FCP	fibrous carbon paper
FPDS	bis(fluorophenyl) disulfide
GC	glassy carbon
GE	gel electrolyte
Gr	graphite
GS	galvanostatic
GW	graphite whiskers
HC	hard carbon
HEDS	bis(hydroxyethyl) disulfide
HOPG	highly oriented pyrolytic graphite
HT	heat treatment
HTT	HT temperature
ITO	indium-tin oxide
M	metal
M^+	cation
MCMB	mesocarbon microbeads
MeH_x	metal hydride
MF	methyl formate
MOEGA	methoxy-oligo(ethylene glycol) acrylate
MP	*N*-methyl-2-pyrrolidone
MPC	matrix-pyrolysis carbon
MS	molten salt
MTBT	tetramethylthiobis(dithiol)
MTHF	2-methyltetrahydrofuran
MU	monomer unit
MW	molecular weight
n	number of electrons
NB	nitrobenzene
NBR	nitrile butadiene rubber
NESA	transparent conducting substrate
NG	natural graphite
OCV	open-circuit voltage
opt.	optionally
OS	organic solvent
P	polymer
P	disorder parameter
PAc	polyacetylene
PAm	polyamide (example: nylon 6)
PAN	polyacrylonitrile
PAN-FC	PAN-derived foam carbon
PAni	polyaniline
PAnt	polyanthracene
PAPI	polymerized modified aromatic polyimide
PAQ	poly[*p*-(9,10-anthraquinone-2-carbonyl)styrene]-*co*-styrene
PAS	polyacenic semiconductor
PAT	poly(3-alkylthiophene)
PAz	polyazulene
PBT	poly(bithiophene)
PBTI	poly(benzothienoindole)
Pc	phthalocyanine
PC	propylenecarbonate
PCF	pitch-based carbon fiber
PCk	petroleum coke, pitch coke
PCP	pitch-based carbon powder
PCz	polycarbazole

PD	polymeric dopant
PDS	diphenyl disulfide
PDTT	poly(dithienothiophene)
PE	polyethylene
PECz	poly(*N*-ethylcarbazole)
PEDOT	poly(3,4-(ethylenedioxy)thiophene)
PEO	polyethylene oxide
PF	phenol−formaldehyde
PFA	poly(furfuryl alcohol)
PFAK	poly[(fluoro-3-alkyl)thiophene]
PFl	polyfluorene
PFPT	poly[3-(4-fluorophenyl)thiophene]
PFu	polyfuran
PG	pyrolytic graphite
PHAS	poly(heteroacenic) semiconductor
PIBT	poly(isobenzo[*c*]thiophene)
PIn	polyindole
PMOT	poly(4,4′-dimethoxybithiophene)
PMT	poly(3-methylthiophene)
PM$_2$T	poly(3,4-dimethylthiophene)
PNap	polynaphthalene
POAP	poly(*o*-aminophenol)
POPDA	poly(*o*-phenylenediamine)
POPh	polyoxyphenazine
POT	poly(3-*n*-octylthiophene)
PP	pyropolymer
PPAN	pyrolyzed PAN
PPCNAc	pyrolyzed poly(cyanoacetylene)
PPCz	poly(*N*-phenylcarbazole)
PPFA	pyrolyzed PFA
PPP	poly(*p*-phenylene)
PPPP	pyrolyzed PPP
PPT	poly(3-phenylthiophene)
PPy	polypyrrole
PS	polystyrene; polystyryl; potentiostatic
PSS	poly(*p*-styrenesulfonate)
PSSA	poly(*p*-styrenesulfonic acid)
PSw	potential sweep
PT	polythiophene
PTB	poly[1,4-di(2-thienyl)-1,3-butadiene]
PTE	poly[1,2-di(2-thienyl)ethylene]
PTFE	polytetrafluoroethylene
PTHF	poly(tetrahydrofuran)
PTP	poly(triphenylene)
PTT	poly(thienothiophene)
PTTF	phenoxytetrathiafulvalene
PTV	poly(thienylene vinylene)
PV	polyvinyl
PVC	poly(vinyl chloride)
PVCz	poly(vinylcarbazole)
P(V)Cz	poly(*N*-vinylcarbazole)
PVDF	poly(vinylidene fluoride)
PVFc	poly(vinylferrocene)
PVP	poly(vinylpyridine)
Py	pyrrole
P3T	poly(terthiophene)
R	organic residue
RAM	random-access memory
ref	reference
RT	room temperature
SB	Shawinigan black
SC	soft carbon
SCE	saturated calomel electrode
SD	styrene−divinylbenzene
SE	synthesis electrolyte
SEI	solid electrolyte interface
SEO	styryl-substituted PEO
SG	synthetic graphite
SL	sulfolane
SRPE	solid redox polymerization electrodes
SS	stainless steel
T	thiophene
TCA	thiocarbonic acid
TCTTN	tetrachlorotetrathionaphthalene
TETD	tetraethylthiuram disulfide
THF	tetrahydrofuran
Tl	toluene
TMTD	tetramethylthiuram disulfide
Tos	tosylate
TP	triphenylene
TS	thermally structured
TSPAN	thermally structured PAN
TTF	tetrathiafulvalene
TTN	tetrathionaphthalene
TTP	tetrathiaporphyrin
TTT	tetrathiotetracene
UD	undoping
VCz	*N*-vinylcarbazole
VFc	vinylferrocene
VP	vapor phase
WE	working electrolyte
x	degree of polymerization; number of Li atoms in Li_xC_6
X0, X1...	see Table 2.2
y	degree of doping/doping level

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7. References

(1) Heinze, J. *Top. Curr. Chem.* **1990**, *152*, 1.
(2) Scrosati, B., Ed. *Application of Electroactive Polymers*; Chapman & Hall: London, 1993.
(3) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578.
(4) Passiniemi, P.; Österholm, J.-E. *Synth. Met.* **1987**, *18*, 637.
(5) Caja, J.; Kaner, R. B.; MacDiarmid, A. G. *J. Electrochem. Soc.* **1984**, *131*, 2744.
(6) Armand, M. B. In *Solid State Batteries*; Sequeira, C. A. C., Hooper, A., Eds.; Martinus Nijhoff Publ.: Dordrecht, 1985; p 363.
(7) Walker, C. W., Jr. *J. Electrochem. Soc.* **1991**, *138*, 1559.
(8) Calvert, J. M.; Weiner, B.; Smith, J. J.; Nowak, R. J. *J. Electrochem. Soc.* **1989**, *136*, 593.
(9) Gabano, J.-P. Ed. *Lithium Batteries*; Academic Press: London, 1983.
(10) Pistoia, G. Ed. *Lithium Batteries: New Materials, Developments and Perspectives*; Elsevier: Amsterdam, 1994.
(11) Chiang, C. K. *Polymer* **1981**, *22*, 1454.
(12) MacDiarmid, A. G.; Kaner, R. B. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, p 689.
(13) Wegner, G. *Makromol. Chem., Macromol. Symp.* **1986**, *1*, 151.
(14) Wieners, G.; Monkenbusch, M.; Wegner, G. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 935.
(15) Shimidzu, T.; Ohtani, A.; Iyoda, T.; Honda, K. *J. Chem. Soc., Chem. Commun.* **1987**, 327.
(16) MacDiarmid, A. G. Eur. Pat. 0 210 023 B1, 1986.
(17) Wolf, J. F.; Forbes, C. E.; Gould, S.; Shacklette, L. W. *J. Electrochem. Soc.* **1989**, *136*, 2887.
(18) Dietrich, M.; Mortensen, J.; Heinze, J. *J. Chem. Soc., Chem. Commun.* **1986**, 1131.
(19) Scrosati, B.; Panero, S.; Prosperi, P.; Corradini, A.; Mastragostino, M. *J. Power Sources* **1987**, *19*, 27.
(20) MacDiarmid, A. G.; Chiang, J.-C.; Halpern, M.; Huang, W. S.; Krawczyk, J. R.; Mammone, R. J.; Mu, S. L.; Somasiri, N. L. D.; Wu, W. *Polym. Prep., Am. Chem. Soc., Div. Polym. Chem.* **1984**, *25*, 248.
(21) Nigrey, P. J.; MacInnes, D., Jr.; Nairns, D. P.; MacDiarmid, A. G.; Heeger, A. J. *J. Electrochem. Soc.* **1981**, *128*, 1651.
(22) MacDiarmid, A. G.; Nigrey, P. J.; MacInnes, D. F., Jr.; Nairns, D. P.; Heeger, A. J. *Org. Coat. Plast. Chem.* **1981**, *44*, 372.
(23) Kaner, R. B.; MacDiarmid, A. G.; Mammone, R. J. Polymers in Electronics. *ACS Symp. Ser.* **1984**, *242*, 575.

(24) Elsenbaumer, R. L.; Shacklette, L. W.; Sowa, J. M.; Chance, R. R.; Ivory, D. M.; Miller, G. G.; Baughman, R. H. *Polym. Prep., Am. Chem. Soc., Div. Polym. Chem.* **1982**, *23*, 132.
(25) Dalas, E. *Solid State Commun.* **1991**, *77*, 63.
(26) Huang, W.-S.; Humphrey, B. D.; MacDiarmid, A. J. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2385.
(27) Nakajima, T.; Kawagoe, T. *Synth. Met.* **1989**, *28*, C629.
(28) Beck, F.; Boinowitz, T.; Tormin, U. *DECHEMA Monogr.* **1993**, *128*, 287.
(29) Nishio, K.; Fujimoto, M.; Yoshinaga, N.; Furukawa, N.; Ando, O.; Ono, H.; Suzuki, T. *J. Power Sources* **1991**, *34*, 153.
(30) Chattaraj, A. P.; Basumallick, I. N. *J. Power Sources* **1993**, *45*, 237.
(31) Tanaka, K.; Shichiri, T.; Yamabe, T. *Synth. Met.* **1986**, *16*, 207.
(32) Satoh, M.; Kaneto, K.; Yoshino, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1629.
(33) Beck, F. *Electrochim. Acta* **1988**, *33*, 839.
(34) Heinze, J. *Synth. Met.* **1991**, *41*−*43*, 2805.
(35) Bidan, G. *Proc. Int. Autumn School of Conductive Polymers*; Kazimierz nad Wisla: Poland, 1986; p 1.
(36) Geniès, E. M.; Hany, P.; Santier, Ch. *J. Appl. Electrochem.* **1988**, *18*, 751.
(37) Mermilliod, N.; Tanguy, J.; Petiot, F. *J. Electrochem. Soc.* **1986**, *133*, 1073.
(38) Yamamoto, T.; Zama, M.; Yamamoto, A. *Chem. Lett.* **1985**, No. 5, 563.
(39) Beck, F.; Pruss, A. *Electrochim. Acta* **1983**, *28*, 1847.
(40) Fauteux, D.; Koksbang, R. *J. Appl. Electrochem.* **1993**, *23*, 1.
(41) Shirakawa, H.; Ikeda, S. *Polym. J.* **1971**, *2*, 231.
(42) Shirakawa, H.; Ito, T.; Ikeda, S. *Polym. J.* **1973**, *4*, 460.
(43) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.
(44) Nagatomo, T.; Honma, T.; Yamamoto, C.; Negishi, K.; Omoto, O. *Jpn. J. Appl. Phys.* **1983**, *22*, L275.
(45) Farrington, G. C.; Huq, R. *J. Power Sources* **1985**, *14*, 3.
(46) Edwards, J. H.; Feast, W. J. *Polymer* **1980**, *21*, 595.
(47) Takehara, Z.; Kanamura, K.; Hanawa, H. *J. Power Sources* **1987**, *20*, 231.
(48) Chien, J. C. W.; Schlenoff, J. B. *Nature* (*London*) **1984**, *311*, 362.
(49) MacDiarmid, A. G.; Heeger, A. J. *Polym. Prep., Am. Chem. Soc., Div. Polym. Chem.* **1982**, *23*, 241.
(50) MacInnes, D., Jr.; Druy, M. A.; Nigrey, P. J.; Nairns, D. P.; MacDiarmid, A. G.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 317.
(51) Osaka, T.; Kitai, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3386.
(52) Broich, B.; Hocker, J. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 497.
(53) Scrosati, B.; Padula, A.; Patriarca, M.; Schwarz, M.; Lugli, G. Proc. Symp. "Lithium Batteries". *Electrochem. Soc. Proc.* **1984**; *84*−*1*, 422.
(54) Nagatomo, T.; Kakehata, H.; Ichikawa, C.; Omoto, O. *J. Electrochem. Soc.* **1985**, *132*, 1380.
(55) Nagatomo, T.; Ichikawa, C.; Omoto, O. *J. Electrochem. Soc.* **1987**, *134*, 305.
(56) Farrington, G. C.; Scrosati, B.; Frydrych, D.; DeNuzzio, J. *J. Electrochem. Soc.* **1984**, *131*, 7.
(57) Nigrey, P. J.; MacDiarmid, A. G.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1979**, 594.
(58) MacDiarmid, A. G. *Prog. Batteries Sol. Cells* **1984**, *5*, 31.
(59) Maxfield, M.; Jow, T. R.; Gould, S.; Sewchok, M. G.; Shacklette, L. W. *J. Electrochem. Soc.* **1988**, *135*, 299.
(60) Changzhi, L.; Borong, Z.; Baochen, W. *J. Power Sources* **1993**, *43*−*44*, 669.
(61) Taguchi, S.; Tanaka, T. *J. Power Sources* **1987**, *20*, 249.
(62) Goto, F.; Abe, K.; Okabayashi, K.; Yoshida, T.; Morimoto, H. *J. Power Sources* **1987**, *20*, 243.
(63) Goto, F.; Asaoka, T.; Okabayashi, K.; Abe, K.; Yoshida, T. *Denki Kagaku* **1989**, *57*, 798.
(64) Daifuku, H.; Kawagoe, T.; Yamamoto, N.; Ohsaka, T.; Oyama, N. *J. Electroanal. Chem.* **1989**, *274*, 313.
(65) Miyazaki, K.; Sawaura, M.; Nishihama, H. *Proc. Symp. "Primary and Secondary Ambient Temperature Lithium Batteries", Electrochem. Soc. Proc.* **1988**, *88*−*6*, 762.
(66) Kanamura, K.; Kawai, Y.; Yonezawa, S.; Takehara, Z. *J. Electrochem. Soc.* **1995**, *142*, 2894.
(67) Maeda, Y.; Katsuta, A.; Nagasaki, K.; Kamiyama, M. *J. Electrochem. Soc.* **1995**, *142*, 2261.
(68) Wang, B.; Li, G.; Wang, F. *J. Power Sources* **1988**, *24*, 115.
(69) Mengoli, G.; Musiani, M. M.; Pletcher, D.; Valcher, S. *J. Appl. Electrochem.* **1987**, *17*, 525.
(70) Mengoli, G.; Musiani, M. M.; Pletcher, D.; Valcher, S. *J. Appl. Electrochem.* **1987**, *17*, 515.
(71) Lee, J. Y.; Ong, L. H.; Chuah, G. K. *J. Appl. Electrochem.* **1992**, *22*, 738.
(72) Mailhe-Randolph, C.; Desilvestro, J. *J. Electroanal. Chem.* **1989**, *262*, 289.
(73) Kitani, A.; Kaya, M.; Sasaki, K. *J. Electrochem. Soc.* **1986**, *133*, 1069.
(74) LaCroix, J.-C.; Diaz, A. F. *Makromol. Chem., Macromol. Symp.* **1987**, *8*, 17.
(75) Boschi, T.; Di Vona, M. L.; Tagliatesta, P.; Pistoia, G. *J. Power Sources* **1988**, *24*, 185.
(76) Diaz, A. F.; Logan, J. A. *J. Electroanal. Chem.* **1980**, *111*, 111.
(77) Barbero, C.; Miras, M. C.; Haas, O.; Kötz, R. *J. Electrochem. Soc.* **1991**, *138*, 669.
(78) Matsunaga, T.; Daifuku, H.; Nakajima, T.; Kawagoe, T. *Polymers for Advanced Technologies*; VCH Publishers, Inc.: New York, 1990; Vol. 1, p 33.
(79) Doubova, L.; Mengoli, G.; Musiani, M. M.; Valcher, S. *Electrochim. Acta.* **1989**, *34*, 337.
(80) Desilvestro, J.; Scheifele, W. *J. Mater. Chem.* **1993**, *3*, 263.
(81) Rishpon, J.; Redondo, A.; Derouin, C.; Gottesfeld, S. *J. Electroanal. Chem.* **1990**, *294*, 73.
(82) Michaelson, J. C.; McEvoy, A. J.; Kuramoto, N. *J. Electroanal. Chem.* **1990**, *287*, 191.
(83) Somasiri, N. L. D.; MacDiarmid, A. G. *J. Appl. Electrochem.* **1988**, *18*, 92.
(84) MacDiarmid, A. G.; Yang, L. S.; Huang, W. S.; Humphrey, B. D. *Synth. Met.* **1987**, *18*, 393.
(85) Cameron, R. E.; Clement, S. K. U.S. Patent No. 5,008,041, 1991.
(86) Chiang, J. C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193.
(87) Nishio, K.; Fujimoto, M.; Yoshinaga, N.; Ando, O.; Ono, H.; Murayama, T. *J. Power Sources* **1995**, *56*, 189.
(88) Osaka, T.; Nakajima, T.; Naoi, K.; Owens, B. B. *J. Electrochem. Soc.* **1990**, *137*, 2139.
(89) Osaka, T.; Ogano, S.; Naoi, K. *J. Electrochem. Soc.* **1988**, *135*, 539.
(90) Osaka, T.; Nakajima, T.; Shiota, K.; Owens, B. B. Office of Naval Research Technical Report 6, Contract No. N00014-88K-0360, 1989.
(91) Osaka, T.; Nakajima, T.; Shiota, K.; Owens, B. B. *Proc. Symp. "Rechargeable Lithium Batteries", Electrochem. Soc. Proc.* **1990**, *90*−*5*, 170.
(92) Miras, M. C.; Barbero, C.; Kötz, R.; Haas, O. *J. Electrochem. Soc.* **1991**, *138*, 335.
(93) Yonezawa, S.; Kanamura, K.; Takehara, Z. *J. Electrochem. Soc.* **1995**, *142*, 3309.
(94) Yue, J.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 2800.
(95) Barbero, C.; Miras, M. C.; Kötz, R.; Haas, O. *Synth. Met.* **1993**, *55*−*57*, 1539.
(96) Barbero, C.; Miras, M. C.; Schnyder, B.; Haas, O.; Kötz, R. *J. Mater. Chem.* **1994**, *4*, 1775.
(97) Wei, X.; Epstein, A. J. *Synth. Met.* **1995**, *74*, 123.
(98) Barbero, C.; Kötz, R. *Adv. Mater.* **1994**, *6*, 577.
(99) Tsutsumi, H.; Fukuzawa, S.; Ishikawa, M.; Morita, M.; Matsuda, Y. *J. Electrochem. Soc.* **1995**, *142*, L168.
(100) Morita, M.; Miyazaki, S.; Ishikawa, M.; Matsuda, Y.; Tajima, H.; Adachi, K.; Anan, F. *J. Electrochem. Soc.* **1995**, *142*, L3.
(101) Morita, M.; Miyazaki, S.; Ishikawa, M.; Matsuda, Y.; Tajima, H.; Adachi, K.; Anan, F. *J. Power Sources* **1995**, *54*, 214.
(102) Echigo, Y.; Asami, K.; Takahashi, H.; Inoue, K.; Kabata, T.; Kimura, O.; Ohsawa, T. *Synth. Met.* **1993**, *55*−57, 3611.
(103) Hwang, K. S.; Kim, J. S.; Kong, M. J. *Synth. Met.* **1995**, *71*, 2201.
(104) Kahata, T.; Ohsawa, T.; Fujii, T.; Kimura, O. (Ricoh) JP 6-163 047, 1994; *Chem. Abstr.* **1994**, *121*, 209 233.
(105) Sotomura, T.; Uemachi, H.; Takeyama, K.; Naoi, K.; Oyama, N. *Electrochim. Acta* **1992**, *37*, 1851.
(106) Sotomura, T.; Uemachi, H.; Miyamoto, Y.; Kaminaga, A.; Oyama, N. *Denki Kagaku* **1993**, *61*, 1366.
(107) Oyama, N.; Tatsuma, T.; Sato, T.; Sotomura, T. *Nature (London)* **1995**, *373*, 598.
(108) Geniès, E. M.; Picart, S. *Synth. Met.* **1995**, *69* 165.
(109) Matsushita Electric Ltd., JP 6-231 752, JP 6-310 173, JP 6-314 568, 1994; JP 7-45 271, JP 7-57 723, JP 7-57 781, JP 7-57 782, 1995.
(110) Naoi, K.; Sakai, H.; Ogano, S.; Osaka, T. *J. Power Sources* **1987**, *20*, 237.
(111) Osaka, T.; Naoi, K.; Ogano, S. *J. Electrochem. Soc.* **1988**, *135*, 1071.
(112) Osaka, T.; Naoi, K.; Ogano, S.; Nakamura, S. *J. Electrochem. Soc.* **1987**, *134*, 2096.
(113) Mohammadi, A.; Inganäs, O.; Lundström, I. *J. Electrochem. Soc.* **1986**, *133*, 947.
(114) Panero, S.; Prosperi, P.; Scrosati, B. *Electrochim. Acta* **1987**, *32*, 1465.
(115) Osaka, T.; Naoi, K.; Ogano, S.; Nakamura, S. *Chem. Lett.* **1986**, 1687.
(116) John, R.; Wallace, G. G. *J. Electroanal. Chem.* **1991**, *306*, 157.
(117) Novák, P.; Rasch, B.; Vielstich, W. *J. Electrochem. Soc.* **1991**, *138*, 3300.
(118) Beck, F.; Oberst, M. *J. Appl. Electrochem.* **1992**, *22*, 332.
(119) Panero, S.; Prosperi, P.; Bonino, F.; Scrosati, B. *Electrochim. Acta* **1987**, *32*, 1007.
(120) Holdcroft, S.; Funt, B. L. *J. Appl. Electrochem.* **1988**, *18*, 619.
(121) Trinidad, F.; Alonso-Lopez, J.; Nebot, M. *J. Appl. Electrochem.* **1987**, *17*, 215.
(122) Matsuda, Y.; Morita, M.; Miyake, R. 41st ISE Meeting, Prague, 1990; Abstr. Mo-179.
(123) O'Brien, R. N.; Santhanam, K. S. V. *J. Electrochem. Soc.* **1983**, *130*, 1114.

(124) Bittihn, R.; Ely, G.; Woeffler, F.; Münstedt, H.; Naarmann, H.; Naegele, D. *Makromol. Chem., Macromol. Symp.* **1987**, *8*, 51.
(125) Novák, P.; Vielstich, W. *J. Electrochem. Soc.* **1990**, *137*, 1036.
(126) Naegele, D.; Bittihn, R. *Solid State Ionics* **1988**, *28−30*, 983.
(127) Yamamoto, T.; Zama, M.; Hishinuma, M.; Yamamoto, A. *J. Appl. Electrochem.* **1987**, *17*, 607.
(128) Christensen, P. A.; Hamnett, A. *Electrochim. Acta* **1991**, *36*, 1263.
(129) West, K.; Jacobsen, T.; Zachau-Christiansen, B.; Careem, M. A.; Skaarup, S. *Synth. Met.* **1993**, *55−57*, 1412.
(130) Naarmann, H. *Makromol. Chem., Macromol. Symp.* **1987**, *8*, 1.
(131) Wu, H.-M.; Shy, H.-J.; Ko, H.-W. *J. Power Sources* **1989**, *27*, 59.
(132) Novák, P.; Inganäs, O.; Bjorklund, R. *J. Power Sources* **1987**, *21*, 17.
(133) Novák, P.; Inganäs, O.; Bjorklund, R. *J. Electrochem. Soc.* **1987**, *134*, 1341.
(134) Novák, P. *Electrochim. Acta* **1992**, *37*, 1227.
(135) Nishio, K.; Fujimoto, M.; Ando, O.; Ono, H.; Murayama, T. *J. Appl. Electrochem.* **1996**, *26*, 425.
(136) Novák, P.; Vielstich, W. *J. Electrochem. Soc.* **1990**, *137*, 1681.
(137) Novák, P.; Vielstich, W. *Collect. Czech. Chem. Commun.* **1992**, *57*, 339.
(138) Boinowitz, T.; tom Suden, G.; Tormin, U.; Krohn, H.; Beck, F. *J. Power Sources* **1995**, *56*, 179.
(139) Raymond, D. E.; Harrison, D. J. *J. Electroanal. Chem.* **1993**, *355*, 115.
(140) Beck, F.; Oberst, M. *Makromol. Chem., Macromol. Symp.* **1987**, *8*, 97.
(141) Naoi, K.; Ishijima, A.; Osaka, T. *J. Electroanal. Chem.* **1987**, *217*, 203.
(142) Osaka, T.; Naoi, K.; Maeda, M.; Nakamura, S. *J. Electrochem. Soc.* **1989**, *136*, 1385.
(143) Naoi, K.; Osaka, T.; Owens, B. B. *Electrochem. Soc. Ext. Abstr.* **1988**, *88−2*, 38.
(144) Shimizu, A.; Yamataka, K.; Kohno, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4401.
(145) Momma, T.; Nishimura, K.; Osaka, T.; Kondo, N.; Nakamura, S. *J. Electrochem. Soc.* **1994**, *141*, 2326.
(146) Ren, X.; Pickup, P. G. *J. Phys. Chem.* **1993**, *97*, 5356.
(147) Killian, J. G.; Coffey, B. M.; Gao, F.; Poehler, T. O.; Searson, P. C. *J. Electrochem. Soc.* **1996**, *143*, 936.
(148) Bjorklund, R.; Liedberg, B. *J. Chem. Soc., Chem. Commun.* **1986**, 1293.
(149) Novák, P.; Inganäs, O. *J. Electrochem. Soc.* **1988**, *135*, 2485.
(150) Nagashima, M.; Mine, T.; Ikezawa, Y.; Takamura, T. *Denki Kagaku* **1992**, *60*, 1021.
(151) Wampler, W. A.; Wei, C.; Rajeshwar, K. *J. Electrochem. Soc.* **1994**, *141*, L13.
(152) Gemeay, A. H.; Nishiyama, H.; Kuwabata, S.; Yoneyama, H. *J. Electrochem. Soc.* **1995**, *142*, 4190.
(153) Kuwabata, S.; Kishimoto, A.; Tanaka, T.; Yoneyama, H. *J. Electrochem. Soc.* **1994**, *141*, 10.
(154) Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W.-Y. *J. Electroanal. Chem.* **1981**, *129*, 115.
(155) Diaz, A. F.; Bargon, J. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, p 81.
(156) Naoi, K.; Hirabayashi, T.; Tsubota, I.; Osaka, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1213.
(157) Novák, P.; Vielstich, W. *J. Electroanal. Chem.* **1991**, *300*, 99.
(158) Jackowska, K.; Kudelski, A.; Bukowska, J. *Electrochim. Acta* **1994**, *39*, 1365.
(159) Tölgyesi, M.; Szücs, A.; Visy, C.; Novák, M. *Electrochim. Acta* **1995**, *40*, 1127.
(160) Schlenoff, J. B.; Xu, H. *J. Electrochem. Soc.* **1992**, *139*, 2397.
(161) Peres, R. C. D.; De Paoli, M.-A.; Panero, S.; Scrosati, B. *J. Power Sources* **1992**, *40*, 299.
(162) Nagasubramanian, G.; Di Stefano, D.; Moacanin, J. *J. Phys. Chem.* **1986**, *90*, 4447.
(163) Choi, K. M.; Kim, C. Y.; Kim, K. H. *J. Phys. Chem.* **1992**, *96*, 3782.
(164) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
(165) Yoshino, K.; Hayashi, S.; Sugimoto, R. *Jpn. J. Appl. Phys. Part 2 Lett.* **1984**, *23*, L899.
(166) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173.
(167) Kaneto, K.; Yoshino, K.; Inuishi, Y. *Jpn. J. Appl. Phys.* **1983**, *22*, L567.
(168) Kaneto, K.; Kohno, Y.; Yoshino, K.; Inuishi, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 382.
(169) Kaufman, J. H.; Chung, T.-C.; Heeger, A. J.; Wudl, F. *J. Electrochem. Soc.* **1984**, *131*, 2092.
(170) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1985**, 713.
(171) Panero, S.; Prosperi, P.; Klapste, B.; Scrosati, B. *Electrochim. Acta* **1986**, *31*, 1597.
(172) Arbizzani, C.; Mastragostino, M. *Electrochim. Acta* **1990**, *35*, 251.
(173) Rasch, B.; Novák, P.; Vielstich, W. *Synth. Met.* **1991**, *41*−43, 2963.
(174) Corradini, A.; Mastragostino, M.; Panero, A. S.; Prosperi, P.; Scrosati, B. *Synth. Met.* **1987**, *18*, 625.
(175) Mastragostino, M.; Marinangeli, A. M.; Corradini, A.; Arbizzani, C. *Electrochim. Acta* **1987**, *32*, 1589.
(176) Rasch, B. Inaugural-Dissertation, Universität Bonn, 1992.
(177) Osterholm, J. E.; Passiniemi, P. *Chem. Eng. News* **1986**, *64*, No. 6, 2.
(178) Bandey, H. L.; Cremins, P.; Garner, S. E.; Hillman, A. R.; Raynor, J. B.; Workman, A. D. *J. Electrochem. Soc.* **1995**, *142*, 2111.
(179) Tourillon, G.; Garnier, F. *J. Electrochem. Soc.* **1983**, *130*, 2042.
(180) Chowdhury, A.-N.; Harima, Y.; Kunugi, Y.; Yamashita, K. *Electrochim. Acta* **1996**, *41*, 1993.
(181) Nagatomo, T.; Mitsui, M.; Matsutani, K.; Omoto, O. *Electrochem. Soc. Ext. Abstr.* **1987**, *87−2*, 252.
(182) Nagatomo, T.; Mitsui, M.; Matsutani, K.; Omoto, O. *Trans. IEICE* **1987**, *E70*, 346.
(183) Sato, M.; Tanaka, S.; Kaeriyama, K. *Synth. Met.* **1986**, *14*, 279.
(184) Barsch, U.; Beck, F.; Hambitzer, G.; Holze, R.; Lippe, J.; Stassen, I. *J. Electroanal. Chem.* **1994**, *369*, 97.
(185) Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706.
(186) Kawai, T.; Kuwabara, T.; Wang, S.; Yoshino, K. *J. Electrochem. Soc.* **1990**, *137*, 3793.
(187) Heinze, J.; Dietrich, M. *Werkstoffe in der Elektrochemie*; Sturm, F. v., Ed. *DECHEMA Monogr.* **1990**, *121* 125.
(188) Dietrich, M.; Heinze, J. *Synth. Met.* **1991**, *41−43*, 503.
(189) Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, F. *J. Electroanal. Chem.* **1994**, *369*, 87.
(190) Krylov, V. A.; Konoshchuk, N. V.; Pokhodenko, V. D. *Russ. J. Electrochem.* **1993**, *29*, 1013.
(191) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc. Chem. Commun.* **1987**, 1725.
(192) Rudge, A.; Raistrick, I.; Gottesfeld, S.; Ferraris, J. P. *Electrochim. Acta* **1994**, *39*, 273.
(193) Onoda, M.; Morita, S.; Iwasa, T.; Nakayama, H.; Yoshino, K. *J. Chem. Phys.* **1991**, *95*, 8584.
(194) Kawai, T.; Iwasa, T.; Onoda, M.; Sakamoto, T.; Yoshino, K. *J. Electrochem. Soc.* **1992**, *139*, 3404.
(195) Onoda, M.; Iwasa, T.; Kawai, T.; Yoshino, K. *J. Phys. D Appl. Phys.* **1991**, *24*, 2076.
(196) Kawai, T.; Iwasa, T.; Onoda, M.; Ohsawa, T.; Nakazono, M.; Yoshino, K. *Synth. Met.* **1993**, *55*−57, 1608.
(197) Vogel, E.; Röhrig, P.; Sicken, M.; Knipp, B.; Herrmann, A.; Pohl, M.; Schmickler, H.; Lex, J. *Angew. Chem.* **1989**, *101*, 1683.
(198) Jow, T. R.; Jen, K. Y.; Elsenbaumer, R. L.; Shacklette, L. W.; Angelopoulos, M.; Cava, M. P. *Synth. Met.* **1986**, *14*, 53.
(199) Biserni, M.; Marinangeli, A.; Mastragostino, M. *J. Electrochem. Soc.* **1985**, *132*, 1597.
(200) Buttol, P.; Mastragostino, M.; Panero, S.; Scrosati, B. *Electrochim. Acta* **1986**, *31*, 783.
(201) Biserni, M.; Marinangeli, A.; Mastragostino, M. *Electrochim. Acta* **1986**, *31*, 1193.
(202) Arbizzani, C.; Catellani, M.; Mastragostino, M.; Mingazzini, C. *Electrochim. Acta* **1995**, *40*, 1871.
(203) Onoda, M.; Morita, S.; Nakayama, H.; Yoshino, K. *Jpn. J. Appl. Phys. Part 1* **1993**, *32*, 3534.
(204) Onoda, M.; Nakayama, H.; Morita, S.; Yoshino, K. *J. Electrochem. Soc.* **1994**, *141*, 339.
(205) Casalbore-Miceli, G.; Beggiato, G.; Daolio, S.; DiMarco, P. G.; Emmi, S. S.; Giro, G. *J. Appl. Electrochem.* **1987**, *17*, 1111.
(206) Capuano, F.; Casalbore-Miceli, G.; Giro, G.; Scrosati, B. *J. Appl. Electrochem.* **1994**, *24*, 114.
(207) Mastragostino, M.; Scrosati, B. *J. Electrochem. Soc.* **1985**, *132*, 1259.
(208) Panero, S.; Prosperi, P.; Zane, D.; Scrosati, B. *J. Appl. Electrochem.* **1992**, *22*, 189.
(209) Tanguy, C.; Baudoin, J. L.; Chao, F.; Costa, M. *Electrochim. Acta* **1992**, *37*, 1417.
(210) Walker, C. W. *J. Appl. Electrochem.* **1992**, *22*, 817.
(211) Büchner, W.; Garreau, R.; Lemaire, M.; Roncali, J.; Garnier, F. *J. Electroanal. Chem.* **1990**, *277*, 355.
(212) Speight, J. G.; Kovacic, P.; Koch, F. W. *J. Macromol. Sci.* **1971**, *C5*, 295.
(213) Kovacic, P.; Oziomek, J. *J. Org. Chem.* **1964**, *29*, 100.
(214) Kovacic, P.; Kyriakis, A. *J. Am. Chem. Soc.* **1963**, *85*, 454.
(215) Shacklette, L. W.; Elsenbaumer, R. L.; Baughman, R. H. *J. Phys. Colloq.* **1983**, *C3* (Suppl. to *J. Phys. 44*, no. 6), 559.
(216) Pruss, A.; Beck, F. *J. Power Sources* **1985**, *16*, 179.
(217) Pruss, A.; Beck, F. *J. Electroanal. Chem.* **1984**, *172*, 281.
(218) Shacklette, L. W.; Eckhardt, H.; Chance, R. R.; Miller, G. G.; Ivory, D. M.; Baughman, R. H. *J. Chem. Phys.* **1980**, *73*, 4098.
(219) Shacklette, L. W.; Elsenbaumer, R. L.; Chance, R. R.; Sowa, J. M.; Ivory, D. M.; Miller, G. G.; Baughman, R. H. *J. Chem. Soc. Chem. Commun.* **1982**, 361.
(220) Shacklette, L. W.; Chance, R. R.; Elsenbaumer, R. L.; Baughman, R. H. *Proc. Power Sources Symp.* **1982**, *30*, 66.
(221) Maurice, F.; Froyer, G.; Pelous, Y. *J. Phys. Colloq.* **1983**, *C3* (Suppl. to *J. Phys. 44*, no. 6), 587.
(222) Shacklette, L. W.; Toth, J. E.; Murthy, N. S.; Baughman, R. H. *J. Electrochem. Soc.* **1985**, *132*, 1529.

(223) Jow, T. R.; Shacklette, L. W.; Maxfield, M.; Vernick, D. *J. Electrochem. Soc.* **1987**, *134*, 1730.
(224) Jow, T. R.; Shacklette, L. W. Proc. Symp. Primary and Secondary Ambient Temperature Lithium Batteries. *Electrochem. Soc. Proc.* **1988**, *88−6*, 589.
(225) Maxfield, M.; Jow, T. R.; Sewchok, M. G.; Shacklette, L. W. *J. Power Sources* **1989**, *26*, 93.
(226) Jow, T. R.; Shacklette, L. W. *J. Electrochem. Soc.* **1989**, *136*, 1.
(227) Kaeriyama, K.; Sato, M.; Someno, K.; Tanaka, S. *J. Chem. Soc. Chem. Commun.* **1984**, 1199.
(228) Satoh, M.; Tabata, M.; Kaneto, K.; Yoshino, K. *J. Electroanal. Chem.* **1985**, *195*, 203.
(229) Satoh, M.; Tabata, M.; Takiguchi, T.; Kaneto, K.; Yoshino, K. *Technol. Rep. Osaka Univ.* **1986**, *36*, No. 1835, 133.
(230) Satoh, M.; Tabata, M.; Kaneto, K.; Yoshino, K. *Jpn. J. Appl. Phys. Part 2 Lett.* **1986**, *25*, L73.
(231) Tabata, M.; Satoh, M.; Kaneto, K.; Yoshino, K. *J. Phys. C Solid State Phys.* **1986**, *19*, L101.
(232) Morita, M.; Komaguchi, K.; Tsutsumi, H.; Matsuda, Y. *Electrochim. Acta*. **1992**, *37*, 1093.
(233) Bidar, H.; Fabre, C.; Geniès, E. M.; Syed, A. A. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 241.
(234) Schiavon, G.; Zecchin, S.; Zotti, G.; Cattarin, S. *J. Electroanal. Chem.* **1986**, *213*, 53.
(235) Meerholz, K.; Heinze, J. *Electrochim. Acta* **1996**, *41*, 1839.
(236) Waltman, R. J.; Diaz, A. F.; Bargon, J. *J. Electrochem. Soc.* **1984**, *131*, 740, 1452.
(237) Hirabayashi, T.; Naoi, K.; Osaka, T. *J. Electrochem. Soc.* **1987**, *134*, 758.
(238) Osaka, T.; Naoi, K.; Hirabayashi, T. *J. Electrochem. Soc.* **1987**, *134*, 2645.
(239) Naoi, K.; Ueyama, K.; Osaka, T. *J. Electrochem. Soc.* **1989**, *136*, 2444.
(240) Naoi, K.; Ueyama, K.; Osaka, T.; Smyrl, W. H. *J. Electrochem. Soc.* **1990**, *137*, 494.
(241) Osaka, T.; Momma, T. *Electrochim. Acta* **1993**, *38*, 2011.
(242) Bargon, J.; Mohmand, S.; Waltman, R. J. *Mol. Cryst. Liq. Cryst.* **1983**, *93*, 279.
(243) Rault-Berthelot, J.; Simonet, J. *J. Electroanal. Chem.* **1985**, *182*, 187.
(244) Rault-Berthelot, J.; Simonet, J. *Nouv. J. Chim.* **1986**, *10*, 169.
(245) Rault-Berthelot, J.; Angely, L.; Delaunay, J.; Simonet, J. *New J. Chem.* **1987**, *11*, 487.
(246) Janiszewska, L.; Osteryoung, R. A. *J. Electrochem. Soc.* **1988**, *135*, 116.
(247) Satoh, M.; Uesugi, F.; Tabata, M.; Kaneto, K.; Yoshino, K. *J. Chem. Soc., Chem. Commun.* **1986**, 979.
(248) Mengoli, G.; Musiani, M. M.; Schreck, B.; Zecchin, S. *J. Electroanal. Chem.* **1988**, *246*, 73.
(249) Cattarin, S.; Mengoli, G.; Musiani, M. M.; Schreck, B. *J. Electroanal. Chem.* **1988**, *246*, 87.
(250) O'Brien, R. N.; Sundaresan, N. S.; Santhanam, K. S. V. *J. Electrochem. Soc.* **1984**, *131*, 2028.
(251) Santhanam, K. S. V.; O'Brien, R. N. In *Techniques for Characterization of Electrodes and Electrochemical Processes*; Varma, R., Selman, J. R., Eds.; Wiley: New York, 1991; p 447.
(252) O'Brien, R. N.; Santhanam, K. S. V. *J. Electrochem. Soc.* **1985**, *132*, 2613.
(253) Papez, V.; Novák, P.; Mrha, J. *Z. Phys. Chem. N.F.* **1988**, *160*, 99.
(254) Geissler, U.; Hallensleben, M. L.; Toppare, L. *Synth. Met.* **1991**, *40*, 239.
(255) Kaufman, F. B.; Schroeder, A. H.; Engler, E. M.; Kramer, S. R.; Chambers, J. Q. *J. Am. Chem. Soc.* **1990**, *102*, 483.
(256) Shirota, Y.; Kakuta, T.; Mikawa, H. *Makromol. Chem. Rapid Commun.* **1984**, *5*, 337.
(257) Iwakura, C.; Kawai, T.; Nojima, M.; Yoneyama, H. *J. Electrochem. Soc.* **1987**, *134*, 791.
(258) Hunter, T. B.; Tyler, P. S.; Smyrl, W. H.; White, H. S. *J. Electrochem. Soc.* **1987**, *134*, 2198.
(259) Shirota, Y.; Noma, N.; Kanega, H.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* **1984**, 470.
(260) Kakuta, T.; Shirota, Y.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* **1985**, 553.
(261) Skompska, M.; Peter, L. M. *J. Electroanal. Chem.* **1995**, *383*, 43.
(262) Compton, R. G.; Davis, F. J.; Grant, S. C. *J. Appl. Electrochem.* **1986**, *16*, 239.
(263) Haas, O.; Zumbrunnen, H.-R. *Helv. Chim. Acta* **1981**, *64*, 854.
(264) Haas, O.; Rudnicki, J.; McLarnon, F. R.; Cairns, E. J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 939.
(265) Miras, M. C.; Barbero, C.; Kötz, R.; Haas, O. *J. Electroanal. Chem.* **1992**, *338*, 279.
(266) Miras, M. C. Unpublished results, Paul Scherrer Institute, 1992.
(267) Yamamoto, T.; Hishinuma, M.; Yamamoto, A. *Inorg. Chim. Acta* **1984**, *86*, L47.
(268) Yamamoto, T.; Hishinuma, M.; Sugimoto, H.; Yamamoto, A.; Sukawa, H. *J. Electroanal. Chem.* **1985**, *194*, 197.
(269) Otsu, T.; Goto, K.; Aoki, S.; Imoto, M. *Makromol. Chem.* **1964**, *71*, 150.
(270) Haas, O.; Vos, J. G. *J. Electroanal. Chem.* **1980**, *113*, 139.
(271) Lessner, P. M.; McLarnon, F. R.; Winnick, J.; Cairns, E. J. *J. Appl. Electrochem.* **1992**, *22*, 927.
(272) Yamin, H.; Peled, E. *J. Power Sources* **1983**, *9*, 281.
(273) LeGuillanton, G.; Elothmani, D.; Do, Q. T.; Simonet, J. *J. Electrochem. Soc.* **1994**, *141*, 316.
(274) Kavan, L.; Novák, P.; Dousek, F. P. *Electrochim. Acta* **1988**, *33*, 1605.
(275) Degott, P. Carbon-Sulfur Polymer, Synthesis and Electrochemical Properties. Dissertation; National Polytechnic Institute, Grenoble, 1986.
(276) Perichaud, A.; Le Mehaute, A. (CGE). EU Patent Appl. 0 176 877, 1986.
(277) Stiehl, K.-P.; Viola, H.; Wiesener, K. (TU Dresden). DD Patent 262 735, 1988.
(278) Stiehl, K.-P.; Richter, A. M.; Fanghänel, E.; Wiesener, K. (TU Dresden). DD Patent 274 709, 1989.
(279) Stiehl, K.-P.; Viola, H.; Wiesener, K.; Mayer, R.; Brückner, H.; Schneider, W. DD Patent 241 978, 1987.
(280) Stiehl, K.-P.; Viola, H.; Wiesener, K.; Mayer, R.; Brückner, H.; Schneider, W. DD Patent 242 909, 1987.
(281) Stiehl, K.-P.; Viola, H.; Brückner, H. DD Patent 245 525, 1987.
(282) Teo, B. K. (Bell). U.S. Patent 4 181 779, 1980.
(283) Visco, S. J.; DeJonghe, L. C.; Ue, M. *Denki Kagaku* **1994**, *62*, 300.
(284) Naoi, K. *Denki Kagaku* **1993**, *61*, 135.
(285) Zagal, J. H.; Herrera, P. *Electrochim. Acta* **1985**, *30*, 449.
(286) Mailhe, C. C. A Novel Class of Positive Electrodes for Rechargeable Batteries, Dissertation: Berkeley, 1987.
(287) Visco, S. J.; DeJonghe, L. C. *Mater. Res. Soc. Symp. Proc.* **1989**, *135*, 553.
(288) Visco, S. J.; Mailhe, C. C.; DeJonghe, L. C.; Armand, M. B. *J. Electrochem. Soc.* **1989**, *136*, 661.
(289) DeJonghe, L. C.; Visco, S. J.; Mailhe, C. C.; Armand, M. B. (U.S.D.O.E.). U.S. Patent 4 833 048, 1989.
(290) Visco, S. J.; DeJonghe, L. C. *J. Electrochem. Soc.* **1988**, *135*, 2905.
(291) Mailhe, C.; Visco, S.; DeJonghe, L. *J. Electrochem. Soc.* **1987**, *134*, 1121.
(292) Visco, S. J.; Liu, M.; DeJonghe, L. C. *J. Electrochem. Soc.* **1990**, *137*, 1191.
(293) DeJonghe, L. C.; Liu, M.; Mailhe, C. C.; Visco, S. J. (U.S.D.O.E.). U.S. Patent 4 917 974, 1990.
(294) Liu, M.; Visco, S. J.; DeJonghe, L. C. Proc. Symp. Rechargeable Lithium Batteries. *Electrochem. Soc. Proc.* **1990**, *90−5*, 233.
(295) Liu, M.; Visco, S. J.; DeJonghe, L. C. *J. Electrochem. Soc.* **1989**, *136*, 2570.
(296) Liu, M.; Visco, S. J.; DeJonghe, L. C. *J. Electrochem. Soc.* **1990**, *137*, 750.
(297) Kubota, T. (Fuji Photo Film). JP Patent 04-155 766, 1992.
(298) Doeff, M. M.; Visco, S. J.; DeJonghe, L. C. *J. Electrochem. Soc.* **1992**, *139*, 1808.
(299) Visco, S. J.; Liu, M.; Doeff, M. M.; Ma, Y. P.; Lampert, C.; DeJonghe, L. C. *Solid State Ionics* **1993**, *60*, 175.
(300) Visco, S. J.; Doeff, M. M.; DeJonghe, L. C. *Annu. Tech. Conf. Proc. Soc. Vac. Coaters* **1991**, *34*, 89.
(301) Oyama, N.; Naoi, K.; Sotomura, T.; Uemachi, H.; Sato, Y.; Kanbara, T.; Takeyama, K. (Matsushita Electric). EU Patent Appl. 0 497 308, 1992.
(302) Sotomura, T.; Sato, T.; Tatsuma, T.; Oyama, N. *Ext. Abstr., Annu. Meet. ISE* **1995**, *46* (Xiamen), Vol. 11, Abstract I-5-04. Vol. II, Abstr. I-5-04.
(303) Tatsuma, T.; Sotomura, T.; Sato, T.; Buttry, D. A.; Oyama, N. *J. Electrochem. Soc.* **1995**, *142*, L182.
(304) Liu, M.; Visco, S. J.; DeJonghe, L. C. Proc. Symp. Rechargeable Lithium Batteries. *Electrochem. Soc. Proc.* **1990**, *90−5*, 220.
(305) Visco, S. J.; Liu, M.; DeJonghe, L. C. (Univ. Calif. Berkeley), WO Patent 91/06132, 1991.
(306) Ue, M.; Visco, S. J.; DeJonghe, L. C. *Denki Kagaku* **1993**, *61*, 1409.
(307) Liu, M.; Visco, S. J.; De Jonghe, L. C. *J. Electrochem. Soc.* **1991**, *138*, 1891.
(308) Doeff, M. M.; Lerner, M. M.; Visco, S. J.; DeJonghe, L. C. *J. Electrochem. Soc.* **1992**, *139*, 2077.
(309) Liu, M.; Visco, S. J.; De Jonghe, L. C. *J. Electrochem. Soc.* **1991**, *138*, 1896.
(310) DeJonghe, L. C.; Doeff, M. M. Personal communication, April, 1995.
(311) Gauthier, M. (Hydroquebec), EU Patent 0 415 856, 1991.
(312) Naoi, K.; Menda, M.; Ooike, H.; Oyama, N. *J. Electroanal. Chem.* **1991**, *318*, 395.
(313) Oyama, N.; Sato, T.; Tatsuma, T.; Sotomura, T.; Uemachi, H. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *171* (Fall), Abstract 108.
(314) Ye, S.; Bélanger, D. *J. Electrochem. Soc.* **1994**, *141*, L49.
(315) Todres, Z. V. *Electrochim. Acta* **1991**, *36*, 2171.
(316) Dahn, J. R.; Sleigh, A.; Shi, H.; Reimers, J. N.; Zhong, Q.; Way, B. M. *Electrochim. Acta* **1993**, *38*, 1179.
(317) Inaba, M.; Yoshida, H.; Ogumi, Z.; Abe, T.; Mizutani, Y.; Asano, M. *J. Electrochem. Soc.* **1995**, *142*, 20.

(318) Ohzuku, T.; Iwakoshi, Y.; Sawai, K. *J. Electrochem. Soc.* **1993**, *140*, 2490.
(319) Arnold, B. B.; Murphy, G. W. *J. Phys. Chem.* **1961**, *65*, 135.
(320) Beck, F.; Pruss, A. *J. Electroanal. Chem.* **1987**, *216*, 157.
(321) Iijima, T. *Denki Kagaku* **1994**, *62*, 1029.
(322) Brandt, D. K.; Krüger, F. J. *Batteries International* **1993**, No. 16, 24.
(323) Howard, W. F. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *198* (Fall), Abstract 126.
(324) Megahed, S.; Scrosati, B. *Interface* **1995**, *4*, No. 4, 34.
(325) Kalhammer, F. R.; Kozawa, A.; Moyer, C. B.; Owens, B. B. *Interface* **1996**, *5*, No. 1, 32.
(326) Coffey, B.; Madsen, P. V.; Poehler, T. O.; Searson, P. C. *J. Electrochem. Soc.* **1995**, *142*, 321.
(327) Mohri, M.; Yanagisawa, N.; Tajima, Y.; Tanaka, H.; Mitate, T.; Nagajima, S.; Yoshida, M.; Yoshimoto, Y.; Suzuki, T.; Wada, H. *J. Power Sources* **1989**, *26*, 545.
(328) Sawai, K.; Ueda, A.; Nagayama, M.; Iwakoshi, Y.; Ohzuku, T. *Denki Kagaku* **1993**, *61*, 715.
(329) Yazami, R.; Deschamps, M. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *148* (Fall), Abstract 94.
(330) Takami, N.; Satoh, A.; Hara, M.; Ohsaki, T. *J. Electrochem. Soc.* **1995**, *142*, 371.
(331) Fong, R.; Sacken, U. v.; Dahn, J. R. *J. Electrochem. Soc.* **1990**, *137*, 2009.
(332) Jiang, Z.; Alamgir, M.; Abraham, K. M. *J. Electrochem. Soc.* **1995**, *142*, 333.
(333) Aurbach, D.; Ein-Eli, Y.; Chusid (Youngman), O.; Carmeli, Y.; Babai, M.; Yamin, H. *J. Electrochem. Soc.* **1994**, *141*, 603.
(334) Aurbach, D.; Ein-Eli, Y.; Markovsky, B.; Zaban, A.; Abramson, O. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *118* (Fall), Abstract 75.
(335) Ein-Eli, Y.; Markovsky, B.; Aurbach, D.; Carmeli, Y.; Yamin, H.; Luski, S. *Electrochim. Acta* **1994**, *39*, 2559.
(336) Doeff, M. M.; Ma, Y.; Visco, S. J.; DeJonghe, L. C. *J. Electrochem. Soc.* **1993**, *140*, L169.
(337) Morita, M.; Ichimura, T.; Ishikawa, M.; Matsuda, Y. *J. Electrochem. Soc.* **1996**, *143*, L26.
(338) Peled, E.; Menachem, C.; Bar-Tow, D.; Melman, A. *J. Electrochem. Soc.* **1996**, *143*, L4.
(339) Iijima, T.; Suzuki, K.; Matsuda, Y. *Denki Kagaku* **1993**, *61*, 1383.
(340) Tran, T.; Feikert, J.; Mayer, S.; Song, X.; Kinoshita, K. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *136* (Fall), Abstract 88.
(341) Satoh, A.; Takami, N.; Ohsaki, T.; Kanda, M. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *142* (Fall), Abstract 91.
(342) Jean, M.; Tranchant, A.; Messina, R. *J. Electrochem. Soc.* **1996**, *143*, 391.
(343) Morita, M.; Nishimura, N.; Matsuda, Y. *Electrochim. Acta* **1993**, *38*, 1721.
(344) Ishikawa, M.; Asao, M.; Morita, M.; Matsuka, Y.; Iijima, T.; Suzuki, K. *Denki Kagaku* **1993**, *62*, 1317.
(345) Ishikawa, M.; Morita, M.; Asao, M.; Matsuda, Y. *J. Electrochem. Soc.* **1994**, *141*, 1105.
(346) Uchida, T.; Itoh, T.; Morikawa, Y.; Ikuta, H.; Wakihara, M. *Denki Kagaku* **1993**, *61*, 1390.
(347) Takamura, T.; Kikuchi, M.; Ikezawa, Y. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *154* (Fall), Abstract 97.
(348) Tatsumi, K.; Zaghib, K.; Abe, H.; Ohsaki, T.; Sawada, Y. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *134* (Fall), Abstract 87.
(349) Zaghib, K.; Tatsumi, K.; Abe, H.; Ohsaki, T.; Sawada, Y.; Higuchi, S. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *138* (Fall), Abstract 89.
(350) Chu, X.; Schmidt, L. D.; Smyrl, W. H. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, 150 (Fall), Abstract 95.
(351) Sandí, G.; Winans, R. E.; Carrado, K. A. *J. Electrochem. Soc.* **1996**, *143*, L95.
(352) Tossici, R.; Berrettoni, M.; Nalimova, V.; Marassi, R.; Scrosati, B. *J. Electrochem. Soc.* **1996**, *143*, L64.
(353) Winter, M.; Besenhard, J. O.; Novák, P. *DECHEMA Monogr.*, in press.
(354) Mabuchi, A.; Tokumitsu, K.; Fujimoto, H.; Kasuh, T. *J. Electrochem. Soc.* **1995**, *142*, 1041.
(355) Tatsumi, K.; Zaghib, K.; Sawada, Y.; Abe, H.; Ohsaki, T. *J. Electrochem. Soc.* **1995**, *142*, 1090.
(356) Jean, M.; Desnoyer, C.; Tranchant, A.; Messina, R. *J. Electrochem. Soc.* **1995**, *142*, 2122.
(357) Zheng, T.; Liu, Y.; Fuller, E. W.; Tseng, S.; Sacken, U. v.; Dahn, J. R. *J. Electrochem. Soc.* **1995**, *142*, 2581.
(358) Takami, N.; Satoh, A.; Hara, M.; Ohsaki, T. *J. Electrochem. Soc.* **1995**, *142*, 2564.
(359) Shu, Z. X.; McMillan, R. S.; Murray, J. J.; Davidson, I. J. *J. Electrochem. Soc.* **1995**, *142*, L161.
(360) Ishikawa, M.; Morita, M.; Hanada, T.; Matsuda, Y.; Kawaguchi, M. *Denki Kagaku* **1993**, *61*, 1395.
(361) Way, B. M.; Dahn, J. R. *J. Electrochem. Soc.* **1994**, *141*, 907.
(362) Weydanz, W. J.; Way, B. M.; van Buuren, T.; Dahn, J. R. *J. Electrochem. Soc.* **1994**, *141*, 900.
(363) Wilson, A. M.; Dahn, J. R. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *144* (Fall), Abstract 92.
(364) Nogami, T.; Mikawa, H.; Nawa, M. *J. Phys. Colloq.* **1983**, *C3* (Suppl. to *J. Phys. 44*, no. 6), 573.
(365) Nawa, M.; Nogami, T.; Mikawa, H. *J. Electrochem. Soc.* **1984**, *131*, 1457.
(366) Yamabe, T.; Tanaka, K.; Ohzeki, K.; Yata, S. *J. Phys. Colloq.* **1983**, *C3* (Suppl. to *J. Phys. 44*, no. 6), 645.
(367) Tanaka, K.; Ohzeki, K.; Yamabe, T.; Yata, S. *Synth. Met.* **1984**, *9*, 41.
(368) Yata, S.; Hato, Y.; Sakurai, K.; Osaki, T.; Tanaka, K.; Yamabe, T. *Synth. Met.* **1987**, *18*, 645.
(369) Yata, S.; Hato, Y.; Sakurai, K.; Satake, H.; Mukai, K.; Tanaka, K.; Yamabe, T. *Synth. Met.* **1990**, *38*, 169.
(370) Yata, S.; Osaki, T.; Hato, Y.; Takehara, N.; Kinoshita, H.; Tanaka, K.; Yamabe, T. *Synth. Met.* **1990**, *38*, 177.
(371) Yata, S.; Sakurai, K.; Osaki, T.; Inoue, Y.; Yamaguchi, K.; Tanaka, K.; Yamabe, T. *Synth. Met.* **1990**, *38*, 185.
(372) Zhang, S. S.; Liu, Q. G.; Yang, L. L. *J. Electrochem. Soc.* **1993**, *140*, L107.
(373) Yata, S.; Kinoshita, H.; Komori, M.; Ando, N.; Kashiwamura, T.; Harada, T.; Tanaka, K.; Yamabe, T. *Synth. Met.* **1994**, *62*, 153.
(374) Jobst, K.; Sawtschenko, L.; Wuckel, L.; Doge, H. G.; Schwarzenberg, M. (Academy of Sciences of the DDR). DD Patent 240 285, 1986.
(375) Schwarzenberg, M.; Jobst, K.; Sawtschenko, L.; Novák, P. *Electrochim. Acta* **1990**, *35*, 403.
(376) Jobst, K.; Sawtschenko, L.; Schwarzenberg, M. (Academy of Sciences of the DDR). DD Patent 281 609, 1990.
(377) Nishi, Y.; Azuma, H.; Omaru, A. (Sony). EU Patent 0 357 001, 1994.
(378) Imoto, H.; Omaru, A.; Azuma, H.; Nishi, Y. Proc. Symp. Lithium Batteries 1992. *Electrochem. Soc. Proc.* **1993**, *93−24*, 9.
(379) Sato, K.; Noguchi, M.; Demachi, A.; Oki, N.; Endo, M. *Science* **1994**, *264*, 556.
(380) Alamgir, M.; Zuo, Q.; Abraham, K. M. *J. Electrochem. Soc.* **1994**, *141*, L143.
(381) Seger, L.; Wen, L.-Q.; Schlenoff, J. B. *J. Electrochem. Soc.* **1991**, *138*, L81.
(382) Tokumitsu, K.; Mabuchi, A.; Fujimoto, H.; Kasuh, T. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *140* (Fall), Abstract 90.
(383) Zheng, T.; Zhong, Q.; Dahn, J. R. *J. Electrochem. Soc.* **1995**, *142*, L211.
(384) Xue, J. S.; Dahn, J. R. *J. Electrochem. Soc.* **1995**, *142*, 3668.
(385) Jobst, K.; Sawtschenko, L.; Schwarzenberg, M.; Wuckel, L. *Synth. Met.* **1992**, *47*, 279.
(386) Sawtschenko, L.; Jobst, K.; Schwarzenberg, M.; Paasch, G. *Synth. Met.* **1992**, *47*, 287.
(387) Jobst, K.; Sawtschenko, L.; Wuckel, L.; Doge, H. G.; Schwarzenberg, M. (Academy of Sciences of the DDR). DD Patent 240 286, 1986.
(388) Jobst, K.; Sawtschenko, L.; Schwarzenberg, M.; Paasch, G. *Synth. Met.* **1992**, *47*, 297.
(389) Levy, S. C.; Cieslak, W. R.; Lagasse, R. R. *Ext. Abstr. Electrochem. Soc. Battery Div.* **1994**, *152* (Fall), Abstract 96.
(390) Matsumura, K.; Tsukamoto, J.; Takahashi, A.; Sakoda, K. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 329.
(391) Jobst, K.; Sawtschenko, L.; Schwarzenberg, M. (Academy of Sciences of the DDR). DD Patent 252 710, 1987.
(392) Barbero, C.; Silber, J. J.; Sereno, L. *J. Electroanal. Chem.* **1989**, *263*, 333.
(393) Chiba, K.; Ohsaka, T.; Ohnuki, Y.; Oyama, N. *J. Electroanal. Chem.* **1987**, *219*, 117.
(394) Kawaguchi, M.; Kawashima, T.; Nakajima, T. *Denki Kagaku* **1993**, *61*, 1403.
(395) Ishikawa, M.; Nakamura, T.; Morita, M.; Matsuda, Y.; Kawaguchi, M. *Denki Kagaku* **1994**, *62*, 897.
(396) Omaru, A.; Azuma, H.; Aoki, M.; Kita, A.; Nishi, Y. Proc. Symp. Lithium Batteries 1992. *Electrochem. Soc. Proc.* **1993**, *93−24*, 21.
(397) Xue, J. S.; Myrtle, K.; Dahn, J. R. *J. Electrochem. Soc.* **1995**, *142*, 2927.
(398) Tarascon, J. M.; Guyomard, D. *Electrochim. Acta* **1993**, *38*, 1221.
(399) Abraham, K. M. *Electrochim. Acta* **1993**, *38*, 1233.
(400) Shinozaki, K.; Tomizuka, Y.; Nojiri, A. *Jpn. J. Appl. Phys.* **1984**, *23*, L892.
(401) Papez, V.; Novák, P.; Pfleger, J.; Kminek, I.; Nespurek, S. *Electrochim. Acta* **1987**, *32*, 1087.
(402) Pfleger, J.; Kminek, I.; Nespurek, S.; Papez, V.; Novák, P. *Collect. Czech. Chem. Commun.* **1989**, *54*, 1482.
(403) Tuck, C. D. S.; Gilmour, A. In *Modern Battery Technology*; Tuck, C. D. S., Ed.; Ellis Horwood: Chichester, 1991; p 35.
(404) Bénière, F.; Boils, D.; Cánepa, H.; Franco, J.; Le Corre, A.; Louboutin, J. P. *J. Phys. C3* **1983**, *44*, 567.
(405) Rasch, B.; Cattaneo, E.; Novák, P.; Vielstich, W. *Electrochim. Acta* **1991**, *36*, 1397.
(406) Will, F. G. *J. Electrochem. Soc.* **1985**, *132*, 2093.
(407) Will, F. G. *J. Electrochem. Soc.* **1985**, *132*, 2351.
(408) Morzilli, S.; Patriarca, M.; Scrosati, B. *J. Electroanal. Chem.* **1985**, *191*, 147.
(409) Will, F. G. *J. Electrochem. Soc.* **1985**, *132*, 743.

(410) Kaufman, J. H.; Mele, E. J.; Heeger, A. J.; Kaner, R.; MacDiarmid, A. G. *J. Electrochem. Soc.* **1983**, *130*, 571.
(411) Takehara, Z.-I.; Kanamura, K.; Yonezawa, S.-I.; Hanawa, T. *J. Power Sources* **1989**, *25*, 277.
(412) Schlenoff, J. B.; Chien, J. C. W. *Synth. Met.* **1988**, *22*, 349.
(413) Novák, P.; Christensen, P. A.; Iwasita, T.; Vielstich, W. *J. Electroanal. Chem.* **1989**, *263*, 37.
(414) Furukawa, N.; Nishio, K. In *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman & Hall: London, 1993; p 150.
(415) Shacklette, L. W.; Jow, T. R.; Maxfield, M.; Hatami, R. *Synth. Met.* **1989**, *28*, C655.
(416) Osaka, T.; Shiota, K.; Momma, T.; Nakamura, S. *Proc. ISE Meet.* **1991** *42* (Montreux), Abstract 3-52.
(417) Gao, Z.; Bobacka, J.; Ivaska, A. *J. Electroanal. Chem.* **1994**, *364*, 127.
(418) Desilvestro, J.; Scheifele, W.; Haas, O. *J. Electrochem. Soc.* **1992**, *139*, 2727.
(419) Wan, M. *Synth. Met.* **1989**, *31*, 51.
(420) Osaka, T.; Nakajima, T.; Shiota, K.; Momma, T. *J. Electrochem. Soc.* **1991**, *138*, 2853.
(421) Kitani, A.; Kaya, M.; Hiromoto, Y.; Sasaki, K. *Denki Kagaku* **1985**, *53*, 592.
(422) Slama, M.; Tanguy, J. *Synth. Met.* **1989**, *28*, C139.
(423) Naoi, K.; Owens, B. B.; Smyrl, W. H. Office of Naval Research Technical Report 20, Contract No. N00014-88-K-0360, 1989. Naoi, K.; Smyrl, W. H.; Owens, B. B. Proc. Symp. Rechargeable Lithium Batteries. *Proc. Electrochem. Soc.* **1990**, *90*−*5*, 194.
(424) Li, C.; Peng, X.; Zhang, B.; Wang, B. *J. Power Sources* **1992**, *39*, 255.
(425) Lang-sheng, Y.; Zhong-qiang, S.; Pei-min, H.; Wei-xiang, C.; Li, L. *J. Power Sources* **1993**, *43*−*44*, 499.
(426) Li, C.; Zhang, B.; Wang, B. *J. Power Sources* **1992**, *39*, 259.
(427) Koura, N.; Kijima, T. *Denki Kagaku* **1987**, *55*, 386.
(428) Sarkar, S.; Basumallick, I. N. *J. Electrochem. Soc. India* **1989**, *38*, 153.
(429) Trinidad, F.; Montemayor, M. C.; Fatás, E. *J. Electrochem. Soc.* **1991**, *138*, 3186.
(430) Li, C.; Zhang, B.; Wang, B. *J. Power Sources* **1993**, *43*−*44*, 669.
(431) Barbero, C.; Miras, M. C.; Haas, O.; Kötz, R. *J. Electroanal. Chem.* **1991**, *310*, 437.
(432) Naoi, K.; Owens, B. B.; Smyrl, W. H. *Ext. Abstr. Electrochem. Soc.* **1989**, *89-2*, 92 (Fall), Abstract 63.
(433) Visco, S. J.; Doeff, M. M.; DeJonghe, L. C. *Annu. Tech. Conf. Soc. Plast. Eng.* **1994**, *52* (ANTEC '94), 1406.
(434) Horányi, G.; Inzelt, G. *J. Electroanal. Chem.* **1989**, *264*, 259.
(435) Mizumoto, M.; Namba, M.; Nishimura, S.; Miyadera, H.; Koseki, M.; Kobayashi, Y. *Synth. Met.* **1989**, *28*, C639.
(436) Armand, M.; Sanchez, J. Y.; Gauthier, M.; Choquette, Y. In *The Electrochemistry of Novel Materials*; Lipkowski, J., Ross, P. N., Ed.; VCH: New York, 1994; p 65.
(437) Li, N.; Lee, J. Y.; Ong, L. H. *J. Appl. Electrochem.* **1992**, *22*, 512.
(438) Beck, F.; Boinowitz, T. *Proc. ISE Meet.* **1993**, *44* (Berlin), Abstr. P:III.1.41.
(439) Nicholson, M. A.; Van Dyke, L. S.; Martin, C. R. *Ext. Abstr. Electrochem. Soc.* **1990**, *90-1*, 14.
(440) Shinohara, H.; Kojima, J.; Aizawa, M. *J. Electroanal. Chem.* **1989**, *266*, 297.
(441) Krtil, P.; Kavan, L.; Novák, P. *J. Electrochem. Soc.* **1993**, *140*, 3390.
(442) Feldberg, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 4671.
(443) Deiss, E.; Haas, O.; Schlenoff, J. B. *J. Electrochem. Soc.* **1995**, *142*, 3256.
(444) Barsukov, V.; Chivikov, S. *Electrochim. Acta* **1996**, *41*, 1773.
(445) Okabayashi, K.; Goto, F.; Abe, K.; Yoshida, T. *J. Electrochem. Soc.* **1989**, *136*, 1986.
(446) Novák, P.; Kötz, R.; Haas, O. *J. Electrochem. Soc.* **1993**, *140*, 37.
(447) Slama, M.; Tanguy, J. In *Accumulateurs electrochimiques. Evolution et techniques récentes* (*Electrochemical Storage Batteries: Their Evolution and Recent Technology*); Gif-sur-Yvette 1989; p 73.
(448) Slama, M.; Tanguy, J. *Synth. Met.* **1989**, *28*, C171.
(449) Bittihn, R. In *Electronic Properties of Polymers and Related Compounds*; Kuzmany, H., Mehring, M., Roth, S., Eds.; Springer: Berlin, 1985; p 206.
(450) Gosch, J. *Electronics* **1987**, July 9, 41.
(451) Lee, C.; Kwak, J.; Bard, A. J. *J. Electrochem. Soc.* **1989**, *136*, 3720.
(452) Tezuka, Y.; Kimura, T.; Ishii, T.; Aoki, K. *J. Electroanal. Chem.* **1995**, *395*, 51.
(453) Panero, S.; Prosperi, P.; Passerini, S.; Scrosati, B.; Perlmuter, D. D. *J. Electrochem. Soc.* **1989**, *136*, 3729.
(454) Bennett, H.; Porter, S. J. *Synth. Met.* **1989**, *28*, C103.
(455) Geniès, E. M.; Pernaut, J. M. *Synth. Met.* **1984/85**, *10*, 117.
(456) Momma, T.; Kakuda, S.; Yarimizu, H.; Osaka, T. *J. Electrochem. Soc.* **1995**, *142*, 1766.
(457) Novák, P.; Vielstich, W. *Mater. Sci. Forum* **1990**, *62*−*64*, 471.
(458) Novák, P.; Vielstich, W. *Dechema Monogr.* **1990**, *121*, 311.
(459) Münstedt, H.; Voss, E. *Progr. Batt. Sol. Cells* **1987**, *6*, 250.
(460) Osaka, T.; Momma, T.; Nishimura, K.; Kakuda, S.; Ishii, T. *J. Electrochem. Soc.* **1994**, *141*, 1994.
(461) Beck, F.; Braun, P.; Oberst, M. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 967.
(462) Park, D.-S.; Shim, Y.-B.; Park, S.-M. *J. Electrochem. Soc.* **1993**, *140*, 2749.
(463) Yatsuda, Y.; Sakai, H.; Osaka, T. *J. Chem. Soc. Jpn.* **1985**, 1331.
(464) Münstedt, H.; Köhler, G.; Möhwald, H.; Naegele, D.; Bittihn, R.; Ely, G.; Meissner, E. *Synth. Met.* **1987**, *18*, 259.
(465) Thiéblemont, J. C.; Gabelle, J. L.; Planche, M. F. *Synth. Met.* **1994**, *66*, 243.
(466) Ossola, F.; Pistoia, G.; Seeber, R.; Ugo, P. *Electrochim. Acta* **1988**, *33*, 47.
(467) Thomas, M. G. S. R.; Bruce, P. G.; Goodenough, J. B. *J. Electrochem. Soc.* **1985**, *132*, 1521.
(468) Pasquali, M.; Pistoia, G.; Manev, V.; Moshtev, R. V. *J. Electrochem. Soc.* **1986**, *133*, 2454.
(469) Kakuda, S.; Momma, T.; Osaka, T.; Appetecchi, G. B.; Scrosati, B. *J. Electrochem. Soc.* **1995**, *142*, L1.
(470) Arbizzani, C.; Mastragostino, M.; Meneghello, L.; Hamaide, T.; Guyot, A. *Electrochim. Acta* **1992**, *37*, 1631.
(471) Rasch, B.; Vielstich, W. *J. Electroanal. Chem.* **1994**, *370*, 109.
(472) Arbizzani, C.; Mastragostino, M.; Meneghello, L. *Electrochim. Acta* **1996**, *41*, 21.
(473) Nagatomo, T.; Omoto, O. *J. Electrochem. Soc.* **1988**, *135*, 2124.
(474) Novák, P. *Chem. Listy* **1991**, *85*, 1005.
(475) Shacklette, L. W.; Maxfield, M.; Gould, S. *Proc. Intersoc. Energy Convers. Eng. Conf.* **1986**, *21*, Vol. 1, 28.
(476) Equey, J.-F.; Hartmann, J.; Wullschleger, D. Report TM-51-89-19, Paul Scherrer Institute, Villigen, Switzerland, 1989.
(477) Stiehl, K.-P.; Viola, H.; Schneider, W.; Lonnecke, K. DD Patent 258 107, 1988.
(478) DeJonghe, L. J. Personal communication, 1994.
(479) Doeff, M. M.; Visco, S. J.; DeJonghe, L. C. *J. Appl. Electrochem.* **1992**, *22*, 307.
(480) Naoi, K.; Ooike, H.; Oura, Y. *Denki Kagaku* **1994**, *62*, 534.
(481) Naoi, K.; Oura, Y.; Iwamizu, Y.; Oyama, N. *J. Electrochem. Soc.* **1995**, *142*, 354.
(482) *Electric Vehicle Progress* **1993**, January (Sonnenschein 1991−1992 data).
(483) Visco, S. J.; Liu, M.; Doeff, M. M.; Ma, Y. P.; Lampert, C.; DeJonghe, L. C. *Solid State Ionics* **1993**, *60*, 175.
(484) Tatsumi, K.; Iwashita, N.; Sakaebe, H.; Shioyama, H.; Higuchi, S.; Mabuchi, A.; Fujimoto, H. *J. Electrochem. Soc.* **1995**, *142*, 716, 100C.
(485) Verbrugge, M. W.; Koch, B. J. *J. Electrochem. Soc.* **1996**, *143*, 24.
(486) Andrieux, C. P.; Haas, O.; Savéant, J.-M. *J. Am. Chem. Soc.* **1996**, *108*, 8175.
(487) Holt, D. *Automot. Eng.* **1995**, *103* (No. 12, Dec) 12.
(488) Scrosati, B. *Nature London* **1995**, *373*, 557.
(489) Hohsen Corporation, Osaka. *Denki Kagaku* **1996**, *64*, No. 5 (May).
(490) Feast, W. J. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, p 1.
(491) Gray, F. M. *Solid Polymer Electrolytes*; VCH: New York, 1991.
(492) Abraham, K. M. In *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman & Hall: London, 1993; p 75.
(493) Croce, F.; Panero, S.; Passerini, S.; Scrosati, B. *Electrochim. Acta* **1994**, *39*, 255.
(494) Linford, R. G. In *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman & Hall: London, 1993; p 1.
(495) Scrosati, B.; Neat, R. J. In *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman & Hall: London, 1993; p 182.
(496) Watanabe, M. *Denki Kagaku* **1994**, *62*, 304.
(497) Murata, K. *Electrochim. Acta* **1995**, *40*, 2177.
(498) Fauteux, D.; Massucco, A.; McLin, M.; van Buren, M.; Shi, J. *Electrochim. Acta* **1995**, *40*, 2185. (The entire double issue, No. 13/14, is dedicated to new developments in polymer electrolytes.)
(499) Pals, C. R.; Newman, J. *J. Electrochem. Soc.* **1995**, *142*, 3274.
(500) Pals, C. R.; Newman, J. *J. Electrochem. Soc.* **1995**, *142*, 3282.
(501) Kathirgamanathan, P.; Qayyum, M. M. B. *J. Electrochem. Soc.* **1994**, *141*, 147.
(502) Affinato, J. D. (Battelle). U.S. Patent 5 260 095, 1993. Affinato, J.; Silva, L. Polymer multilayer vacuum-deposited thin films. Battelle PNL, 1994.
(503) McBreen, J. *Denki Kagaku* **1993**, *61*, 1337.
(504) Matsuda, Y. *Denki Kagaku* **1993**, *61*, 1338.

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