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Rechargeable lithium battery anodes: alternatives to metallic lithium

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This review is concerned with alternatives to metallic lithium for use in rechargeable lithium batteries. Emphasis is placed on the use of various materials and combinations of materials in different types of electrodes rather than on the properties of the materials themselves. The review includes carbon based electrodes, alloys, conducting polymers and transition metal compounds. Special consideration is given to electrodes and materials used in organic liquid and polymer electrolytes, whereas liquid cathode and molten salt systems are excluded.

1. Introduction

The development of rechargeable lithium batteries based on organic electrolytes, has proved to be difficult, particularly because of the inefficient cyclability of metallic lithium in these electrolytes. This lack of cyclability is related to the passivating layer at the electrode–electrolyte interface [1], which modifies the charge transfer reaction mechanism, decreases the overall ionic diffusion coefficient and imposes a cathodic overpotential, which further increases the reactivity of the lithium anode, promoting further growth of the passivating layer. These effects are responsible for the increased interface impedance of the lithium electrode, both during storage and cycling. A further consequence of the presence of the passivating layer is an increased tendency for growth of dendrites during the lithium plating, which is related to the nonuniform current density distribution at the electrolyte–electrode interface. Accumulation of dendrites, followed by subsequent lithium passivation and electrical insulation, progressively reduces the amount of lithium metal available for cycling, and increases the probability of cell failure through internal shorting. The dendrite formation and passivation of the dendrites gradually convert the lithium foil anode to a high surface area powder with a high reactivity towards organic compounds and thus reduces the safety of the battery concept significantly [2–10].

A variety of materials and electrode concepts, which are supposed to substitute the metallic lithium foil anode, have been under investigation for more than a decade. In this review, the materials are primarily described in connection with electrode configurations or battery concepts because it is intended to focus on systems rather than on materials properties. The cycling performance is related to both mat-

erials properties, electrode concepts and test conditions, but is often limited by the chosen concept. However, the remaining paper is divided into sections according to the primary material used in the electrode concept for practical reasons.

2. Metallic alloys

Alloys have been under examination as alternative anode materials since Dey [11] in 1971 demonstrated the possibility of electrochemical formation of lithium alloys in organic electrolytes. The utilization of metals and alloys as negative electrode materials is based on reversible insertion of lithium in the metal/alloy which acts as a host for the lithium metal. Examples of binary alloys for rechargeable lithium batteries are given in Table 1. Except for Li_4Sb and Li_4Bi (about 1 V against Li), the penalty in voltage reduction is acceptable. For most of the alloys, the gravimetric energy density ($Ah\,kg^{-1}$) is reduced significantly compared to metallic lithium, but the corresponding volumetric energy density ($Ah\,dm^{-3}$) is preserved to an acceptable level, especially in the case of $Li_{4.4}Si$, which only looses about 15% capacity relative to metallic lithium. It should be noted that the data in Table 1 refer to the maximum theoretical energy density, based on the stoichiometry of the alloy, and that the value could be significantly lower in a real application. The limitations imposed by the kinetic and thermodynamic properties of the materials and the limitations of electrode and cell design are not taken into account. On the other hand, the energy density of metallic lithium should be reduced by a factor of two to three (to $1290\,Ah\,kg^{-1}$), in order to take into account the usual two or three fold excess lithium metal used in rechargeable lithium batteries.

Kinetic properties have been investigated for some of these alloys at room temperature, by determination

Table 1. Comparison of the capacity of different alternative electrode materials with metallic lithium

No.	Material	$Ah\,kg^{-1}$	$Ah\,dm^{-3}$	Average voltage, V (relative to Li)	$Ah\,kg^{-1}$ (relative to Li)	$Ah\,dm^{-3}$ (relative to Li)	Reference
1	Li	3860	2061	0	1	1	–
Alloys							
2	LiAl	790	1280	0.36	0.20	0.62	31
3	$Li_{4.4}Si$	2010	1749	0.2	0.54	0.85	31
4	$Li_{4.4}Pb$	500	1270	0.45	0.13	0.62	31
5	$Li_{4.4}Sn$	790	1003	0.5	0.20	0.49	31
6	$Li_y Sn$ $(0.7 < y < 2.53)$	350	444	0.53	0.09	0.22	17
7	$Li_4 Sb$	715	–	0.95	0.19	–	17
8	$Li_4 Bi$	453	–	0.83	0.12	–	17
9	LiZn	371	–	0.2	0.10	–	36
10	$Li_3 Cd$	604	–	0.08	0.16	–	36
Dimensionally stable electrodes							
11	Li–B: $Li_7 B_6 \cdot 17Li$	1920	–	0.02	0.50	–	29, 30
12	β-LiAl/Cu 80/20 w/o	632	–	0.36	0.16	–	26
13	$Li_3 Cd/Li_{4.4} Sn$ Cd/Sn = 1	285	–	0.80	0.14	–	32, 33
Wood's alloy type							
14	Bi/Cd 60/40 w/o	–	1761	0.3	–	0.85	38
15	Pb/Cd 60/40 w/o	–	1489	0.3	–	0.72	38
16	Cd/Sn 70/30 w/o	–	1479	0.3	–	0.72	38
17	Bi/Cd/Pb 50/30/20 w/o	–	1963	0.3	–	0.95	38
18	Pb/Cd/Sn 60/30/10 w/o	–	1720	0.3	–	0.84	38
Insertion compounds							
19	$Li_6 Fe_2 O_3$	800	–	0.75	0.21	–	97
20	$LiWO_2$	120	–	0.75	0.03	–	101
21	WO_2	125	–	0.75	0.03	–	101
22	MoO_2	210	–	1.5	0.05	–	101
Carbon based anodes							
23	Graphite	340	–	0.5	0.09	–	50
24	Pyr. carbon*	350	–	0.5	0.08	–	58
25	PPCA†, 1st cyc.	600	–	< 1	0.16	–	56, 57
	PPCA, 5th cyc.	140	–	< 1	0.04	–	56, 57
26	PVdF†, 1st cyc.	580	–	< 1	0.15	–	56, 57
	PVdF‡, 5th cyc.	14	–	< 1	0.004	–	56, 57
27	Carbon fibres, 1st cyc.	180	–	< 1	0.05	–	57
	Carbon fibres, 5th cyc.	80	–	< 1	0.02	–	57
Redox polyers§							
28	PPq	94	140	1.5	0.02	0.07	79
29	PPP	190	240	0.7	0.05	0.12	79
30	PAc	340	410	1.0	0.09	0.20	79
Alloy/polymer electrolyte composites							
31	$LiAl/PEO/LiClO_4$ 50/33/17 w/o	386	–	0.36	0.10	–	48
32	$LiSi/PEO/LiClO_4$ 57/29/14 w/o	1117	–	–	0.29	–	48
33	$LiSi/PEO/LiClO_4/C$ 45/13/30/13 w/o	860	–	–	0.22	–	48
Alloy/redox polymer composites							
34	$(Li_{4.3}Pb)_{0.8}(PPP)_{0.18}$	230	450	0.4	0.06	0.22	81
35	$(Li_{4.3}Pb)_{0.24}(PAc)_{0.69}$	280	370	0.3	0.07	0.18	81
36	$(LiAl)_{0.11}(PAc)_{0.89}$	220	130	0.3	0.06	0.06	81
Linode							
37	$Li_5(Li_3 N)$	3400	–	0	0.88	–	45–47

*Prepared by thermal decomposition of benzene.
† PPCA = Poly-2-chloro-1-phenylacetylene.
‡ PVdF = Poly-vinylidenefluoride.
§ PPq = Poly(phenylquinoline), PPP = Poly(paraphenylene), PAc = polyacetylene.

Table 2. Volume change of alloy anode materials during cycling of the full capacity [35]

Unlithiated compound	Lithiated compound	Volume change %
Al	LiAl	97
Bi	Li_3Bi	177
Cd	Li_3Cd	268
Pb	$Li_{4.4}Pb$	234
Sn	$Li_{4.4}Sn$	676
Si	Li_4Si	323
Zn	LiZn	71
C	LiC_6	6

of the lithium diffusion coefficient, for example, β-LiAl: $7 \times 10^{-9}\,cm^2\,s^{-1}$ [12], $5 \times 10^{-11}\,cm^2\,s^{-1}$ [13], $8 \times 10^{-8}\,cm\,s^{-1}$ [14], $Li_{4.4}Sn$: $2 \times 10^{-9}\,cm^2\,s^{-1}$ [15–17], LiCd and LiZn: about $10^{-10}\,cm^2\,s^{-1}$ [15, 16]. The wide range covered for LiAl only serves to illustrate the difficulties involved in determination of reliable diffusion coefficients. The corresponding limiting current densities are in the $mA\,cm^{-2}$ range. At current densities exceeding the limiting current, metallic lithium is plated on the electrode surface, and thus dendrite formation is possible. Assuming all the lithium is removed from the anode during discharge, the α-Al phase is formed. The lithium diffusion coefficient is estimated to be $10^{-22}\,cm^2\,s^{-1}$ by extrapolation from high temperature data [18], but determined to be $2 \times 10^{-11}\,cm^2\,s^{-1}$ by Gernov et al. [19]. Thus, the limiting current is even lower during recharge and, therefore, the possibility for dendrite formation is correspondingly greater.

Cycling of LiAl foil electrodes in liquid electrolytes has been reported frequently during the last decade [18, 20–25] as well as in polymer electrolyte based cells at temperatures around 100 °C [18, 21]. In general, the cyclability of the LiAl electrode appears to be dependent of the current density and the amount of charge cycled, similarly to the lithium electrode. Also, a capacity decay is observed during cycling and the cycle life is likewise restricted to 100–200 cycles. The limited cycling capability is related to the mechanical degradation of the electrode. SEM pictures of electrodes, before and after cycling, clearly show cracks and powdering of the electrode material [18, 23, 26, 27]. Similar results are achieved with PEO based cells at temperatures around 100 °C [12, 21, 28]. The crumbling of the electrodes is caused by the drastic volume changes associated with the lithium insertion processes (Table 2).

Chemical corrosion of the negative electrode is less pronounced, though not completely avoided, than on pure lithium. This is partly because the alloys are less reactive and partly because a protective surface film is formed on the electrode surface [18, 21]. Addition of highly reactive compounds (H_2O, SO_2 and I_2) to the electrolyte also has a less pronounced negative effect on the LiAl electrode [23].

3. Dimensionally stable electrodes

As the major problems with cycling of alloys appear to be mechanical in nature, research has been directed towards 'dimensionally stable' electrodes, i.e. electrodes which are able to accommodate the volume changes of the electrochemically active alloy during cycling.

One such material, is the Li–B alloy with the approximate composition LiB, which has the peculiar property that it acts as a porous matrix which can contain large amounts of lithium metal (Table 1) [29–31]. The voltage is very close to that of metallic lithium and the capacity is high, but the cycle life is inferior compared to metallic lithium. This is partly because the reactivity is similar to metallic lithium and partly because lithium is unable to reach the inner cavities in the LiB matrix during recharge [29].

Another approach is to encapsulate the active alloy phase in another alloy: for example Li–Cd alloy as the active material in an 'inactive' Li–Sn matrix [32, 33]. The latter is inactive provided the voltage window is restricted to a narrow range, in which the Li–Sn phases remain stable. Alternatively, the inert alloy can be substituted by a metal matrix: LiAl/Si [34] and, especially, LiAl/Cu [34, 35]. Both electrode types are made by mixing of powder followed by tablet pressing and sintering of the electrodes. In both cases, a severe loss of capacity compared to metallic lithium is observed (Table 1), and no extensive cycling data are available in the literature. Comparison of SEM pictures of LiAl and LiAl/Cu electrodes show that the latter retains its morphology, whereas the former crumbles during cycling [35].

LiAl is hard and brittle, as is also Li_xPB. Li_xSn is brittle for $0.4 < x < 0.67$ and soft for $x = 1$. A similar behaviour is observed for Li_xCd [36]. Woods alloys (Table 1) are soft and malleable alloys which are able to accommodate rather large amounts of lithium on a volumetric basis and have acceptable low voltages vs lithium [37, 38]. These alloys are made by pyrometallurgical techniques and electrodes are either rolled or pressed. These alloys have been tested in cells containing Cr_2O_5 and Cr_3O_8 active cathode materials. The cycle life of a Cr_2O_5 based cell exceeded 400 cycles with a capacity retention of more than 50% of the initial capacity [37] but the available initial capacity of the electrodes is unclear.

The method of preparation of the alloy electrodes and the influence on the electrode behaviour has not been considered so far. In general, similar results have been obtained with electrochemically and pyrometallurgically prepared alloys. In the latter case a higher impedance is sometimes observed when lithiated alloys are prepared. This is ascribed to impurities present on the grain surface and can be avoided by a preparation technique which excludes powdering of the alloy. Apart from these procedures, a number of different methods are described in the patent literature [39–44].

4. Lithium nitride anode

Desjardins *et al.* have described an anode system consisting of lithium–lithium nitride [45–47], which they called a linode. The material is prepared, for example, by reaction between lithium and nitrogen or between lithium and lithium nitride. The linode contains about 11 mol% Li_3N [46]. The materials fabrication is similar to the methods used for manufacture of lithium foil, i.e. extrusion under similar environmental conditions. The two major advantages of the material are: (i) the potential is identical to that of lithium, i.e. no reduction of the cell voltage and (ii) the capacity is close to the capacity of metallic lithium (90% corresponding to about 3400 Ah kg^{-1}) [45].

As the lithium reactivity of the electrode is assumed to be reduced compared to metallic lithium, the stability of electrolytes in common use, whether liquid or solid, organic or inorganic, is expected to be better. The electrolyte/electrode interface impedance in a 2-MeTHF/LiAsF$_6$ electrolyte is slightly higher than the corresponding interface impedance of metallic lithium due to the different nature of the interface films formed [45]. Polarization curves show that the polarization is greater for metallic lithium. Furthermore, the polarization curves for the linode are similar in both plating and stripping, contrary to metallic lithium. It was also shown that formation of a passivating layer on the electrode surface takes place at a lower rate on the linode [45].

Comparison between cycling experiments, using lithium anodes and linodes, carried out with small laboratory cells using TiS$_2$ as the positive electrode material, showed the linode to have superior cycling properties as the charge retention is better. A similar comparison betwen AA cells revealed no significant difference in charge retention capability during cycling [45].

5. Composite carbon-alloy electrodes

A recent patent [48] describes a composite anode for rechargeable lithium batteries employing polymer electrolytes. The electrode is based on a mixture of lithium alloy and lithiated carbon (Li$_x$C, $0 \leqslant x \leqslant 0.3$) embedded in a polymer electrolyte. The carbon compound is optional but improves the utilization of the active material significantly. The preferred composition is in the range of 35–55 v/o alloy, 15–20 v/o Li$_x$C, and the remaining part being the polymer electrolyte. The electrodes are prepared by either hot pressing or by solvent casting.

Advantages of the electrode, compared to pure alloy powder electrodes, are claimed to be improved electronic conductivity, higher utilization of the lithium present in the electrode due to the larger active area and that the polymer content helps to maintain the flexibility and integrity of the electrode during cycling, in spite of the variation of the volume of the electrode materials.

Examples given in the patent include an electrode containing carbon (10 w/o Shawinigan black), LiAl (68 w/o) and PEO (22 w/o of M.W. 900 000). The electrolyte was (PEO)$_8$ LiClO$_4$ and composite cathodes containing either TiS$_2$ or V$_6$O$_{13}$. Cells were discharged at a current density of 25 μA cm^{-2} at a temperature of 110 °C and comparison was made between electrodes with and without carbon. Inferior results were realized with electrodes without carbon and electrodes containing graphite as replacement of the acetylene black. Under the given conditions about 57% of the lithium was utilized with the carbon containing electrode. No results concerning the cyclability were reported.

6. Carbon based electrodes

Extensive work has been carried out on the characterization of alkali metal intercalation in graphite and graphite type carbons. The basic properties of carbon intercalation compounds will therefore not be considered in detail in this review and the reader is referred to [49].

The lamellar structure of graphite allows intercalation of molecules, ions and atoms between the layers without major structural changes, which is considered to be an advantage for the reversibility of the reaction. Intercalation of lithium corresponding to LiC$_6$ (max. intercalation degree) results in only about 10% increase in the layer distance [50]. Lithiated graphite is, therefore, in principle suitable as an anode alternative to metallic lithium. Using LiC$_6$ as the negative electrode, the electrode reaction is:

$$LiC_6 \longrightarrow Li_xC_6 + (1 - x)e^- + (1 - x)Li^+$$
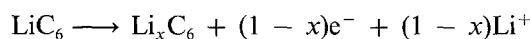
The reaction has been investigated at temperatures around 100 °C, using (PEO)$_8$ LiClO$_4$ as the electrolyte and metallic lithium as the counter electrode [50]. In this study electrochemically lithiated graphite was used, whereas chemically lithiated graphite was investigated in earlier studies [51–53]. The variation of the potential against the intercalation degree show three intercalation plateaux, corresponding to condensation of three different lithium stoichiometries, LiC$_{36}$, LiC$_{18}$ and LiC$_6$. The overall average voltage was about 0.5 V against lithium and the reversibility of the insertion reaction was proven by cyclic voltammetry [50]. Testing of the electrode was performed in a cell of configuration:

$$LiC_6 \mid (PEO)_8 LiClO_4 \mid C_7NiCl_2$$

in which the positive electrode consisted of graphite intercalated with NiCl$_2$ [54, 55]. The couple was claimed to be reversible.

Other carbonaceous materials have been reported to be promising negative electrode materials for rechargeable lithium batteries [56–58]. The materials were prepared by thermal decomposition (600–1200 °C in N$_2$) of different organic polymers. High capacities (Table 1) were obtained in the first discharge in Li/LiClO$_4$, PC–DME/carbon cells, i.e. more than 500 Ah kg^{-1} active material. The capacity is dependent on the surface area (which is more than 100

times greater than graphite) but does not seem to be influenced by the electronic conductivity. The shape of the first discharge curve depends on the polymer used for the electrode preparation, and is, in general, lower than 0.5 V against lithium in the major part of the intercalation range. The reversible capacity is rather low (Table 1), in general less than 10% of the initial capacity after five cycles, except for the PPCA based material which retains about 25% of its initial capacity. Extended cycling is only possible in a narrow composition range. The polymer dependency of the capacity and the rapid capacity decline suggest that the majority of the capacity is related to high amounts of incompletely decomposed polymer or intermediates between polymer and carbonaceous material which are electrochemically reducible by lithium. This is also supported by similar investigations on carbon fibers by the same research group [57], and the fact that the shape of the discharge curve of carbon, prepared from PPCA for example, is dependent on the decomposition temperature. It is also noteworthy that the potential of a new cell is rather high, about 3 V against lithium, in a relatively broad capacity range. Note that evolution of gas is observed during lithium insertion in both graphite [59], petroleum coke and acetylene black [60, 61] in propylene carbonate based electrolytes. Especially in the latter case, large amounts of propene were evolved in the first discharge. Usually, the capacity loss after the first cycle appeared to stabilize, and a capacity corresponding to that of graphite can be cycled [61, 62]. The stabilization of the reversible insertion range also seems to be related to formation of a surface film on the carbon particles. The film is ion conducting, thus allowing reversible insertion of lithium in the electrode material [62].

A number of carbon fibers have been investigated [57, 58, 63]. The carbon fibre materials appear to have a capacity and a voltage dependency of intercalation degree similar to that of graphite. Although the capacity increases as a function of the surface area during the first discharge, it appears to be virtually independent after a few cycles, indicating that the larger sized particles are reduced in size during cycling due to the volume changes (Table 2) associated with the intercalation reaction. The reversibility is fairly good, though not as good as that of graphite [57].

The best carbon material investigated so far seems to be pyrolytic graphite prepared by thermal decomposition of benzene vapour at about 1000 °C [58], which provide about 350 Ah kg^{-1}, mainly at potentials below 1 V against lithium. The rechargeability appears to be excellent, as the coulombic efficiency exceeds 99%. Small laboratory cells containing chromium or vanadium oxide based positive electrodes and lithiated carbon have been tested [58]. Using these cathode materials, a high average voltage was realized (close to 3 V against lithium). The capacity retention is reported to be around 80% up to about 500 cycles. In addition to preventing dendrite growth and the morphological changes associated with the use of metallic lithium, the lower capacity allows construction of

anode limited cells, whereby overdischarge, detrimental to most reversible positive electrode materials, is avoided. Based on LiC$_6$, the capacity is 340 Ah kg^{-1} active material, which is significantly lower than for metallic lithium, but exceeds the capacity of most transition metal chalcogenide cathode materials. Combined with the low average voltage of graphite and the high lithium ion diffusion coefficient (about 10^{-8} cm^2 s^{-1} in graphite [50]) which is promising for the rate capability, these materials are promising alternatives to metallic lithium.

Recently, Sony revealed data on a 'lithium ion battery' claimed to be completely without metallic lithium [64]. The battery has a high capacity, identical to the corresponding NiCd's, a voltage, and thus an energy, which is three times higher than a corresponding NiCd, and the safety problem related to metallic lithium is eliminated. More than 1200 cycles (2 h discharge and charge) was claimed. This concept utilizes a carbon negative electrode, prepared by thermal decomposition of a furan-based polymer, and LiCoO$_2$ (for example) as the positive electrode [65]. Apart from the lithium present in the electrolyte, the lithium for the electrochemical reaction is provided solely from the cathode. The carbonaceous material prepared according to [65] is claimed to have a higher useable capacity than graphite type carbons.

Publication of the Sony technology has prompted an increased research activity in this area. A number of papers describing the properties of LiMO$_2$/carbon cells have been published [60, 62, 66]. Although different carbons were used, none of the materials appear to have higher capacities than graphite but only 50% of the theoretical capacity of the carbon electrode was cycled in a cell employing LiNiO$_2$ in the cathode [66]. The rechargeability also appears to be good (> 100 cycles) after an initial capacity loss of about 20% during the first 5–10 cycles.
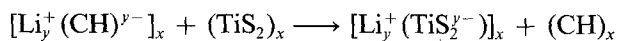
7. Redox polymer electrodes

The general properties of redox active polymers, have been reviewed by Scrosati [67] and only properties related to batteries will be considered in the following.

Caja et al. [68] suggested in 1984 the use of n-doped polyacetylene as negative electrode. TiS$_2$ was used as the positive electrode material, in a cell with the following configuration:

$$[Li_y^+(CH^{y-})]_x \,|\, THF\text{–}LiClO_4 \,|\, TiS_2$$

The electrode reaction can be described as:

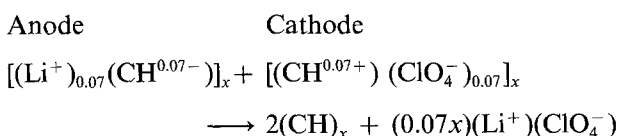$$[Li_y^+(CH)^{y-}]_x + (TiS_2)_x \longrightarrow [Li_y^+(TiS_2^{y-})]_x + (CH)_x$$

During cycling of an Li/[Li$_y^+$(CH)$^{y-}$)]$_x$ cell, to a potential corresponding to $y = 0.1$, it was observed that the capacity declined to about 60% of the initial capacity after 100 cycles [69]. It is therefore reasonable to assume that the degradation of the polyacetylene electrode is less pronounced than that of the metallic lithium electrode. Data for a few polymers are given in Table 1.

At doping levels in excess of $y = 0.1$, the ClO^{4-} ion is prone to reduction by the polyacetylene electrode material [70]. Although the use of other electrolytes such as organoborate salts ($Li^+ BR_4^-$, $R =$ phenyl, n-butyl), which are sufficiently stable up to doping levels corresponding to $y = 0.18$ [70], to some extent alleviates the problem, the achievable capacities are rather low (at the $y = 0.1$ doping level, the specific energy is limited to ca. $110\,Wh\,kg^{-1}$ [71]). Higher doping levels are likewise possible by chemical attachment of a thin layer of a different polymer to the polyacetylene fibrils. The attached polymer separates the reducing species from the electrolyte. The latter approach involves a reaction between reduced polyacetylene and either ethylene oxide, resulting in a PEO type polymer, or 1,4-butane sulphone which forms a layer of butyl sulphonate salt on the surface of the fibrils [71]. A reduction of the charge and discharge rates was, however, observed.

Cells employing conducting polymers as both positive and negative electrodes have also been described in the literature [72, 73]. A cell such as:

$$[Li^+_{0.07}(CH^{0.07-})]_x\,|\,THF-LiClO_4\,|\,(CH)_x$$

has an open circuit voltage (o.c.v.) of about $1\,V$ against lithium [73] and a charge retention of several months at this voltage. A higher voltage is achieved by replacement of the neutral $(CH)_x$ electrode by p-doped polyacetylene. Such a cell is exemplified by:

Anode   Cathode

$[(Li^+)_{0.07}(CH^{0.07-})]_x +$ $[(CH^{0.07+})\,(ClO_4^-)_{0.07}]_x$

$\longrightarrow 2(CH)_x + (0.07x)(Li^+)(ClO_4^-)$

in which the electrolyte is again $THF/LiClO_4$. The o.c.v. of the cell is close to $2.5\,V$ against lithium [73].

All-plastic batteries with a similar cell configuration using polymeric electrolytes are viable, as described by Nagatomo et al. [74–76] and Chiang [77]. In the former case, a polymeric electrolyte consisting of polyvinylidene flouride doped with a $PC/LiClO_4$ electrolyte was used. The electrolyte has sufficient conductivity to be useful at room temperature. Constant current cycling between $2.5\,V$ and about $4\,V$ against lithium, corresponding to a $10\,min$ charge time ($0.1\,mA\,cm^{-2}$) [75], was possible. The voltage curve is rather flat resulting in an average voltage of about $3\,V$ against lithium. The coulombic efficiency remained at about 80% within the first 300 cycles, though dependent of the charge rate. At lower current densities the efficiency decreased because at the lower charge current, the ClO_4^- ions have time to diffuse into the bulk of the polyacetylene fibrils. As a result it is difficult to reverse the process at higher rates. Short circuit currents of $7.5\,mA\,cm^{-2}$ were possible. This is a factor of 10 lower than the corresponding current densities obtained with identical electrodes and a liquid $LiClO_4/PC/EC$ electrolyte [75]. The self discharge rate was reported to be fast as the reaction took place spontaneously [75].

With the exception of polyparaphenylene (PPP), other polymers, such as polyquinolines, which can be n-doped, have been excluded from serious consideration for negative lithium electrode alternatives on the basis of too low capacities [78, 79].

Polyparaphenylene has only been tested in cells employing lithium as one electrode and PPP as the positive electrode [70]. Compared to polyacetylene, the capacity is far lower (50%), but a higher fraction of the capacity is available for anode use because of the more narrow voltage range (between 0 and $1\,V$ against lithium in the major insertion range). Other attractive characteristics are the good electrical properties, no electronic conducting additive is necessary, and that it is potentially inexpensive. Presently it is unavailable in the form of foils, as synthesis is only possible in the form of powder.

It is a major disadvantage of intrinsically conducting polymers that the electrolyte is consumed during operation of cells based on these materials [80] as this limits the available energy density, and therefore also requires careful optimization of the cell design.

8. Composite anodes containing redox polymers

In contrast to ionically conducting polymers, the polymers used in these electrodes contribute to the electric capacity of the electrode. In a series of papers and patents, researchers at Allied Signal have described an anode system for rechargeable alkali metal based batteries, which comprise a redox active polymer such as polyacetylene (PA) or polyparaphenylene (PPP), an alloy such as Li_xPb or LiAl, carbon and a binder [81–87]. Properties of some of the more promising systems are given in Table 1.

A typical anode contains, for example, $80\,w/o$ $Li_{4.3}Pb$, $18\,w/o$ Li–PPP and $2\,w/o$ EPDM rubber as inert binder [77, 81] and, for some PPP-based systems, also carbon as electronic conducting additive in order to enhance the kinetic properties of the composite electrode. Anodes are prepared by mixing of the powder constituents followed by pressing into an expanded nickel grid. To improve the performance, the alloy powder can be surface treated with a polymerization catalyst and mixed with an appropriate monomer whereby polymerization takes place on the powder surface. This technique facilitates adhesion between the alloy and polymer constituents and allows fabrication of flexible films containing up to $77\,w/o$ $Li_{4.3}Pb$ powder (in PA) and addition of binder and conductive diluent was unnecessary [81].

Electrochemical characterization of these systems involved potential step voltammetry, a.c. impedance spectroscopy, constant current cycling of half cells and complete asymmetrical cells containing different active cathode materials. Comparison of potential step voltammetry measurements on PPP-Pb and PPP–$Li_{4.3}Pb$ in which the Li–Pb alloy was formed metallurgically, shows that no significant differences in electrochemical properties were apparent as the shape of the potential curves and capacities were essentially identical. In the latter case, delithiation of the $Li_{4.3}Pb$ phase took place by lithium injection in PPP until a stable

potential, indicating equilibrium, was reached. Measurements of the cell resistance during a potential step cycle of this cell showed that the resistance was low (minimum) when a composition corresponding to a plateau was reached, while the resistance increased significantly at potentials above 0.8 V against Li when the PPP matrix was undoped and, therefore, nonconducting [81].

Constant current cycling revealed that the composition of the composite alloy/polymer electrodes, and the inclusion of an electronic conducting diluent such as carbon, influences the capacity and cycling properties. The best performance, in terms of capacity, was obtained with Li_yAl:PPP:inert (No. 1) in the weight ratio 65:25:10, but only 12 cycles were demonstrated in the voltage range 0.1–1 V against Li. In terms of cyclability, Li_yPb:PPP:inert (No. 2) in the weight ratio 80:18:2 is the superior composition as 350 cycles was demonstrated, again in the voltage range as above. The initial and final capacities of the two systems were $330/280\,Ah\,kg^{-1}$ and $230/220\,Ah\,kg^{-1}$, respectively, corresponding to a capacity loss per cycle of 1.36 and $< 0.2\%$. Comparison with pure polymer and pure alloy electrodes showed that the charge retention of the composite electrodes is superior to that of pure alloy and comparable to that of pure polymer electrodes. The charge retention during cycling of both systems is thus very good. The theoretical capacities are $500\,Wh\,kg^{-1}$ for No. 1 and $330\,Wh\,kg^{-1}$ for No. 2. The cells described above therefore only cycled 60–70% of the available capacity [81]. Also, the theoretical capacities are only about 10% of that of metallic lithium.

The morphology changes during cycling, were followed by SEM and XRD [77]. In the case of $Li_yPb/$ PPP, the SEM pictures showed that the alloy (2–20 μm diameter) and PPP particles form a porous electrode with lead present only in the alloy phase. After 350 cycles, the morphology of the electrode resembled the fibrillar structure typical for pure polymer electrodes without discrete lead (Pb) containing particles. The XRD analysis showed the alloy phases to be different from the initial alloys but no line broadening associated with decreasing particle size was observed [77].
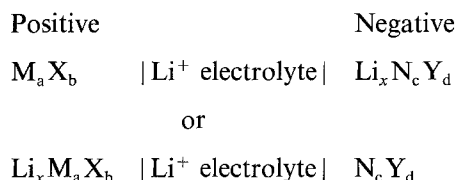
A.c. impedance measurements on a composite electrode containing 66 w/o $Na_{3.75}Pb$, 25 w/o PPP and 9 w/o PE binder has been compared with similar measurements on pure PPP and pure $Na_{3.75}Pb$ electrodes [87]. The impedance of the composite electrode appears to be intermediate between that of the pure polymer and that of the pure alloy electrodes. The PPP electrodes are characterized by a low frequency capacitive spur, and that of $Na_{3.75}Pb$ is characterized by a large semi circle, presumably related to formation of a surface film on the alloy due to reaction between alloy and electrolyte because it is growing in time. Similar results are expected for Li/polymer systems.

This electrode type also consumes electrolyte when a current is applied, though to a lower extent, as the amount of redox polymer present in the electrode is lower.

It is noteworthy that the best results were achieved with lead-containing alloys, i.e. an element which introduces an environmental problem which is otherwise eliminated in lithium battery systems.

9. Transiton metal oxide and sulphide electrodes

Another anode concept frequently described in the literature [88–99], takes advantage of the vast experience on composite cathodes and employs an insertion compound in the anode as well as in the cathode. One of the electrodes contains either a lithiated insertion compound or a ternary lithium compound able to extracalate lithium, providing the lithium ions in the cell:

Positive		Negative
M_aX_b	$\mid Li^+$ electrolyte $\mid$	$Li_xN_cY_d$
	or	
$Li_xM_aX_b$	$\mid Li^+$ electrolyte $\mid$	N_cY_d

in which M, N are transition metals and X, Y are oxygen or sulphur. During discharge, the cathode extracts lithium while lithium is inserted into the negative electrode, and vice versa during charge. The cell potential vs lithium is expected to have a value in between that of the two host materials. The concept has been described as a rocking chair battery by Armand [88] and is based on similar concentration cells employing identical electrode materials containing different amounts of the electroactive species in each electrode [89].

Examples of such systems, employing either lithiated positives or lithiated negatives are given in Table 1.

The use of anodes prepared both chemically and electrochemically has been demonstrated. Electrochemically formed anodes are made by insertion of lithium in the host material by the use of a liquid electrolyte cell utilizing a lithium metal anode. The cell is discharged to a potential corresponding to the desired insertion degree followed by replacement of the lithium foil with a cathode containing the desired positive electrode material [90–92]. For chemical lithiation, lithium naphthalide solutions (Li concentration corresponding to about 0.5 V against Li) have been used [93]. The anode is then manufactured by the methods also used for the composite cathode. In contrast to these configurations, the cells described by Auborn et al. [94, 95] employ a cathode, in which the pristine material, $LiCoO_2$, contains the lithium providing the lithium ions for the cell reaction when it is prepared by conventional high temperature synthesis.

Upon lithium insertion in Fe_2O_3, the major part of the insertion reaction takes place at potentials below 1 V against Li, thus providing a possibility for a high cell potential if matched with a suitable cathode material. Fe_2O_3 is of especial interest because it is inexpensive, abundant and has a high capacity (6 Li/Fe_2O_3). Both α-Fe_2O_3 and γ-Fe_2O_3 have been investigated [100]. Apart from the structural differences, the electronic conductivities are 10^{-13} and about 3×10^{-5}

$(\Omega\,cm)^{-1}$, respectively, increasing significantly during lithium insertion, reaching about $0.5\,(\Omega\,cm)^{-1}$ for $3 < x < 6$ in $Li_xFe_2O_3$ [100]. The reversibility was shown by both chemical and electrochemical methods to be poor as only $1\,Li/Fe_2O_3$ was inserted reversibly. The lithiated Fe_2O_3 (3–6 Li), is X-ray amorphous, an indication of major structural changes. Another drawback is the observation that propylene carbonate is reduced on the electrode at potentials between 0.5 and 0.8 V against Li.

Lithium is inserted in WO_2 at potentials in the range 1.1 to 0.5 V against Li, while the potential/composition curve of the Li/MoO_2 couple is situated at higher potentials, i.e. 1 to 2 V against Li. Although this material also becomes X-ray amorphous during lithium insertion, the crystallinity is recovered upon lithium extraction and about $1\,Li/WO_2$ can be cycled with only a minor loss of capacity [101].

The potential of a cell based on TiS_2 as positive and $Li_6Fe_2O_3$ as negative electrodes, varies between 2 and 0.5 V against Li, with the major part of the capacity below 1 V against Li [100]. It is obviously desirable to construct cells with a larger potential difference between the two half cells. Of the materials currently investigated, $LiCoO_2$ has the highest potential and it is possible to extracalate about $0.5\,Li/formula$ unit at potentials up to about 4.5 V against Li. With this material it is therefore possible to construct rocking chair batteries with an average voltage exceeding 3 V against Li. Detailed data have only been reported for the $LiCoO_2/MoO_2$ system which operates at potentials between 2 and 3 V against Li, and the cell potential varies almost linearly with the charge level. The $LiWO_2/TiS_2$ system, with an average potential around 1.5 V, has been tested in both liquid electrolyte [90, 91] and polymer electrolyte [92, 96] based cells. In the latter case, a polyphosphazene/$LiCF_3SO_3$ electrolyte was used at 90 °C. In general, results similar to those obtained at room temperature were obtained but no results on cycling were reported.

The Li_xWO_2/V_6O_{13} couple together with a polymer electrolyte, $(PEO)_8\,LiCF_3SO_3$, has also been suggested but no details on the electrochemical behaviour, except the current/voltage characteristic (o.c.v. $= 2.55$ V against Li), have been published [96].

10. Conclusion

It appears that composite electrodes containing lithium alloys or lithium insertion compounds, having high electronic conductivity and small volume changes during the insertion reaction, provide the best performance.

The use of carbon based electrodes is one of the most promising concepts. Although the electrode capacity decrease initially, the capacity remains at a suitable level for extended cycling. Their lower tendency to form electronic insulating passivation layers, coupled with the large surface area, allow high rate discharge and charge. The relatively small volume

changes provide dimensional stability to the composite electrode.

The alternatives to metallic lithium all seem to avoid formation of metallic lithium under controlled charge conditions and the compounds used are inherently more stable towards organic compounds than is metallic lithium, and the safety of rechargeable lithium batteries is, therefore, significantly improved. However, very little work has been directed towards safety investigation on the alternative concepts or other areas, such as overcharge and discharge, abuse, self discharge etc., which are of interest from an application point of view.

The current trend is towards carbon based anodes combined with a lithium manganese oxide containing cathode as described for example, by Guyomard et al. [102]. Since this article was finished, the technology has advanced and the reader is referred to the proceedings of the ECS 1991 Fall Meeting [103] and the 6th International Meeting on Lithium Batteries [104] for information on the latest developments.

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