



Review

Conducting-polymer-based supercapacitor devices and electrodes

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ARTICLE INFO

Article history:

Received 22 February 2010

Received in revised form 11 June 2010

Accepted 18 June 2010

Available online 15 July 2010

Keywords:

Supercapacitor

Ultracapacitor

Conducting polymer

Cycle-life

Specific energy

Specific power

ABSTRACT

Supercapacitor electrodes and devices that utilise conducting polymers are envisaged to bridge the gap between existing carbon-based supercapacitors and batteries to form units of intermediate specific energy. This review looks at the major conducting polymer materials, namely, polyaniline, polypyrrole, polythiophene and derivatives of polythiophene, as well as composites of these materials with carbon nanotubes and inorganic battery materials. Various treatments of the conducting polymer materials to improve their properties are considered and comparisons are made with other supercapacitor materials such as carbon and with inorganic battery materials. Conducting polymers are pseudo-capacitive materials, which means that the bulk of the material undergoes a fast redox reaction to provide the capacitive response and they exhibit superior specific energies to the carbon-based supercapacitors (double-layer capacitors). In general conducting polymers are more conductive than the inorganic battery materials and consequently have greater power capability. On the downside, conducting polymers swell and contract substantially on charge and discharge, respectively. Consequently, cycle-life is poor compared with carbon-based supercapacitors which generally only charge via adsorption and desorption of ions (giving typically a few thousand cycles for conducting polymers compared with >500 000 cycles for carbon-based devices).

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1. Introduction

Supercapacitors are designed to bridge the gap between batteries and capacitors to form fast charging energy-storage devices of intermediate specific energy. They are seen to have a potential

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market both in hybrid electric vehicles and pure electric vehicles to improve regenerative braking (through fast charge capability) and deliver larger acceleration (through fast discharge capability). Traditionally, capacitors have been constructed using a set of parallel conducting plates separated by an insulator. Capacitive charge of opposite sign builds up on the respective plates in response to a voltage difference between them. The capacitances are delivered in mF and μF quantities [1]. In more recent times, capacitors have been developed that give hundreds to thousands of Farads and these are usually known as supercapacitors, or ultracapacitors, and were initially constructed from carbons of high surface area [2]. These are in fact two capacitors connected in series with a conducting liquid media linking them. Such a supercapacitor device derives its performance from a so-called double-layer capacitance and is therefore often referred to as an (electric or) electrochemical double-layer capacitor (EDLC). The capacitance in these devices is stored as a build up of charge in the electrical double-layer in the solution interface close to the surface of the carbon to balance the charge in the carbon material.

Another type of supercapacitor, referred to as a pseudo-capacitor, derives its capacitance from the storage of charge in the bulk of a redox material in response to a redox reaction. This fast redox reaction [3–5] acts like capacitance (hence the name pseudo-capacitance). A pseudo-capacitor typically stores a greater amount of capacitance per gram than an EDLC, as the bulk of the material (not just the surface layer) reacts. On the other hand, an EDLC has faster kinetics as only the surface of the carbon is being accessed. An example of a pseudo-capacitive material is a conducting polymer (CP) (the conductivity of which was first reported in 1963 by Weiss and co-workers in Australia [6–8] and first utilised in supercapacitors in the mid 1990s [4]) and it is this material that will be the subject of this review. The review will focus on work done post-2000 but for a comprehensive description of work pre-2000 readers should consult Ref. [9]. The concept of 'bridging the gap' with batteries to form conducting-polymer-based supercapacitors with superior specific energy compared with carbon-based alternatives is illustrated in Fig. 1.

Conducting polymers are rendered conductive through a conjugated bond system along the polymer backbone. They are typically formed either through chemical oxidation of the monomer (for example with iron chloride) [5] or electrochemical oxidation of the monomer. Two oxidation reactions occur simultaneously – the oxidation of the monomer and the oxidation of the polymer [10] with the coincident insertion of a dopant/counter ion (e.g. Cl^-). The dopant or doping level (in this p-type conducting polymer) is typically below 1 dopant per polymer unit: approximately 0.3–0.5, i.e., 2–3 monomer units per dopant. This is limited by how closely the positive charges (so-called polarons) can be spaced along the polymer chain. The polymers that are most commonly studied for use in supercapacitor devices are polypyrrole, polyaniline, and derivatives of polythiophene [11]. The typical dopant level for these polymers, as well as their typical specific capacitances and voltage ranges, are given in Table 1.

The difference between EDLCs and conducting-polymer-based supercapacitors is shown schematically in Fig. 2. In general, carbon-

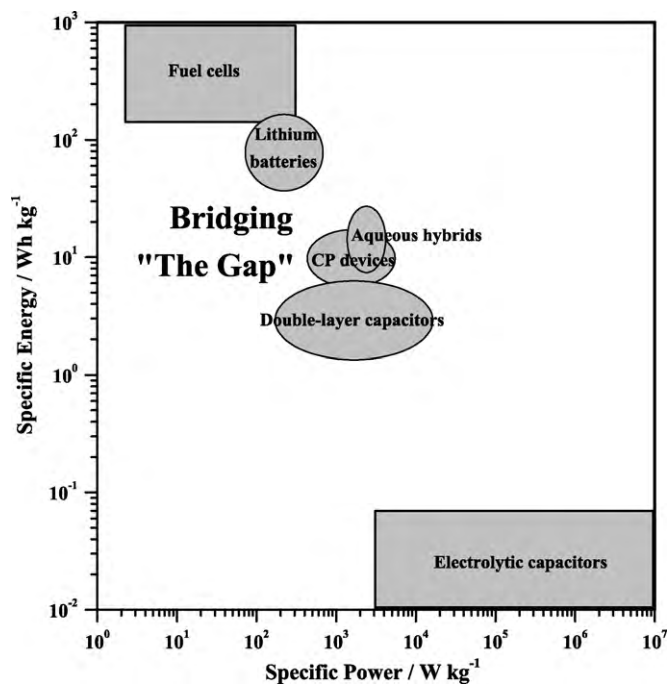


Fig. 1. Ragone plots for different types of energy-storage devices; where CP is conducting polymer.

based supercapacitors have high power capabilities, due to the fast sorption and desorption of ions, but a low specific energy [13]. Conducting polymers should improve the device as they undergo a redox reaction to store charge in the bulk of the material and thereby increase the energy stored and reduce self-discharge. One significant drawback of these materials is the relatively low power (or lower rate of charge–discharge) due to the slow diffusion of ions within the bulk of the electrode. Nevertheless, it is still proposed that conducting polymers can bridge the gap between batteries and double-layer supercapacitors as these electrodes have better kinetics than nearly all inorganic battery electrode materials (pseudo-capacitive materials) [13].

Conducting polymers are generally attractive as they have high charge density and low cost (compared with the relatively expensive metal oxides) [14,15]. It is possible to develop devices with low equivalent series resistance (ESR), high power, and high energy [16]. Polyaniline can exhibit a charge density of 140 mAh g^{-1} , which is slightly lower than that obtained with expensive metal oxides such as LiCoO_2 [17,18] but much higher than that given by carbon devices that often deliver less than 15 mAh g^{-1} (perhaps $\sim 40 \text{ mAh g}^{-1}$ for the individual electrode) [14]. Carbon–carbon symmetric supercapacitor devices can achieve a specific power of $3\text{--}4 \text{ kW kg}^{-1}$ and a specific energy of $3\text{--}5 \text{ Wh kg}^{-1}$ when fully packaged [13,19,20], while a conducting polymer supercapacitor, based on polyaniline, can achieve a slightly lower power at 2 kW kg^{-1} but double the specific energy (10 Wh kg^{-1}) [19]. As will be discussed in Section 3, the weight used for the calculation of specific energy

Table 1
Theoretical and experimental specific capacitances of conducting polymers.

Conducting polymer	Mw (g mol^{-1})	Dopant level	Potential range (V)	Theoretical specific capacitance (F g^{-1})	Measured specific capacitance (F g^{-1}) ^a
PAni	93	0.5	0.7	750	240
PPy	67	0.33	0.8	620	530
PTh	84	0.33	0.8	485	–
PEDOT	142	0.33	1.2	210	92

Cited from Ref. [5]. Mw is molecular weight per unit monomer (g mol^{-1}), PAni is polyaniline, PPy is polypyrrole, PTh is polythiophene and PEDOT is poly(3,4-ethylenedioxythiophene).

^a Cited from Ref. [12].

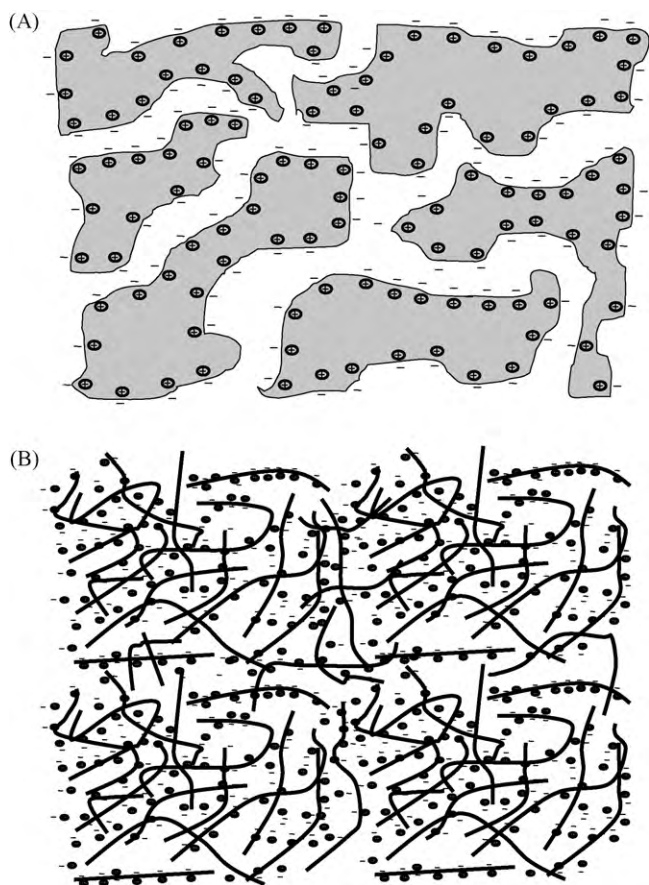


Fig. 2. Comparison of charging of (a) double-layer capacitor (carbon) and (b) pseudo-capacitor (conducting polymer).

and power is often not specified. That is whether it is the weight of device, packaged device, electrode or active material. This makes comparison of different supercapacitor performances difficult.

Double-layer capacitors are highly cycleable, namely, >0.5 million cycles [2] whereas conducting polymer pseudo-capacitors often begin to degrade under less than a thousand cycles due to changes in their physical structure that are caused by the doping/de-doping (intercalation/deintercalation) of ions [19]. Higher specific energies may be achieved with conducting polymer electrodes by increasing the doping level. This comes at a cost, due to a larger degree of counter ion insertion and de-insertion with an accompanying volume change [21]. This volume change, or swelling, causes mechanical failure of the electrode under prolonged cycling. Interestingly, results using conducting polymer electrodes with electrolytes based on ionic liquids [22,23] show that the electrodes perform better with greater life times, especially in actuators [24] where doping and undoping of ions into the polymer is required for the shape changes. The preparation of both conducting polymer electrodes and devices with ionic liquid electrolytes will be discussed later in more detail.

Table 3
p- and *n*-doping of various thiophene derivatives [16].

Polymer	<i>p</i> -Doping		<i>n</i> -Doping	
	Potential limits (V) vs. SCE	Capacitance (F g ⁻¹)	Potential limits (V) vs. SCE	Capacitance (F g ⁻¹)
PFPT	-0.2 to 1.0	95	-1.7/-1.0	80
PDIT	-0.2 to 1.0	110	-1.5/-0.2	75
PMeT	-0.2 to 1.15	220	-2.0/-1.0	165

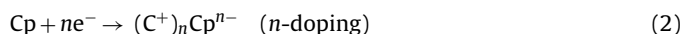
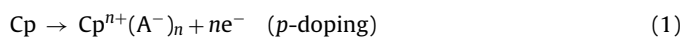
PFPT is poly(3-(4-fluorophenyl)thiophene), PDIT poly(ditheno(3,4-b:3',4'd) thiophene) is and PMeT is poly(3-methyl thiophene).

Table 2
Typical conductivities of various conducting polymers.

Polymer	Conductivity (S cm ⁻¹)	Reference
Polyaniline	0.1–5	[15,26,27]
Polypyrrole	10–50	[28]
PEDOT	300–500	[5]
Polythiophene	300–400	[5]

Conducting polymers are attractive because they have good intrinsic conductivity, namely, from a few S cm⁻¹ to 500 S cm⁻¹ in the doped state [5,25] as can be seen in Table 2. Conducting polymers have low band-gaps (1–3 eV) compared with conventional polymers (10 eV) [5]. They have relatively fast charge–discharge kinetics, suitable morphology, and fast doping and undoping processes [29]. Conducting polymers also have plastic properties [25] and are therefore easily manufactured, particularly as thin films.

Conducting polymers can be *p*-doped with (counter) anions when oxidised and *n*-doped with (counter) cations when reduced. The simplified equations for these two charging processes are as follows:



The discharge reactions are, of course, the reverse of the above equations. Complications can occur given that on oxidation a certain degree of cation inclusion (mixed doping) is possible under certain circumstances. Examples of *p*- and *n*-dopable thiophene-based conducting polymers are listed in Table 3, along with the voltage ranges in which these processes occur.

Supercapacitor devices made solely from conducting polymers can have three configurations [27,30–33]:

Type I (symmetric) using the same *p*-dopable polymer for both electrodes.

Type II (asymmetric) using two different *p*-dopable polymers with a different range of electroactivity.

Type III (symmetric) using the same polymer for both electrodes with the *p*-doped form used as the positive electrode and the *n*-doped form used as the negative electrode.

In addition, asymmetric (or hybrid) devices using a conducting polymer positive electrode and carbon or lithium-based negative electrode can be constructed [20,21,29,34].

A Type III device based entirely on conducting polymers is the most attractive. Theoretically, it should be highly conductive in the charged state as both electrodes will be doped (i.e. the negative is *n*-doped and the positive is *p*-doped) [14]. In addition the charge is released at higher potentials (up to at least 3 V) compared with Type I and Type II devices [14,21]. This higher potential range should result in high specific energy and power due to the $1/2CV^2$ relationship [34]. In reality, these types of conducting polymer supercapacitor devices do not perform as well as expected due to the difficulty of the *n*-doping process.

Early studies of *n*-doped materials were performed on polyacetylene (Fig. 3a–b) and later poly-*p*-phenylene [14] (Fig. 3c).

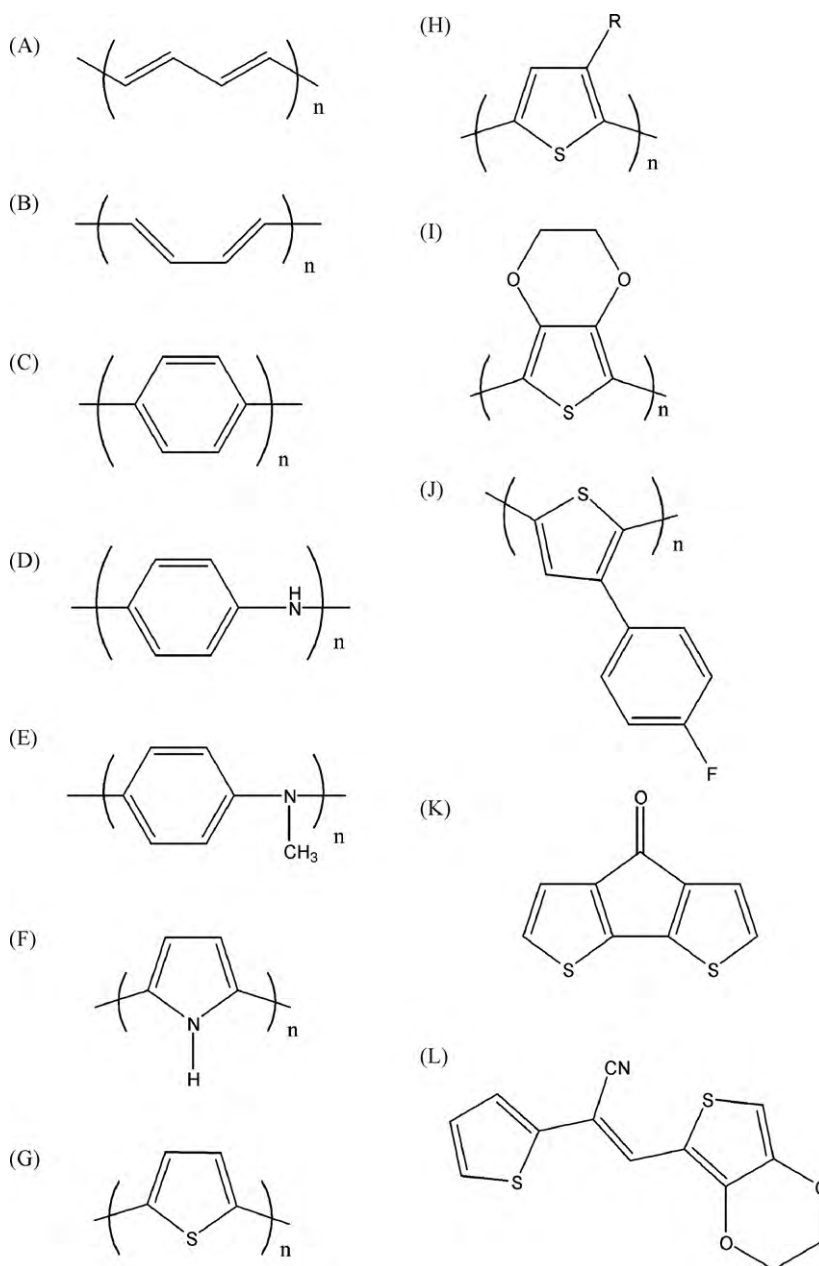


Fig. 3. Various conducting polymer structures. (A) *Trans*-poly(acetylene), (B) *cis*-poly(acetylene), (C) poly(*p*-phenylene), (D) polyaniline (PAni), (E) poly(*n*-methyl aniline) (PNMA), (F) polypyrrole (PPy), (G) polythiophene (PTh), (H) 3-substituted polythiophene, (I) poly(3,4-ethylenedioxythiophene) (PEDOT), (J) poly(3-(4-fluorophenyl)thiophene) (PFPT), (K) poly(cyclopenta[2,1-b;3,4-b'-dithiophen-4-one]) (PcDT), (L) 1-cyano-2-(2-[3,4-ethylenedioxythienyl])-1-(2-thienyl)vinylene (PThCNVEDT).

These polymers have high impedances upon *n*-doping and are therefore not suitable for use as negative electrodes. Many conducting polymers, such as polyaniline and polypyrrole, can only be *p*-doped due to the very negative potentials required for *n*-doping, when compared with the reduction potential limit of molecular solvent-based electrolytes [35]. A purified electrolyte or a room-temperature ionic liquid [36] with a wide electrochemical window, particularly at negative potentials, is required for *n*-doping [4]. An example of a promising *n*-dopable material is polythiophene and its derivatives. Polythiophene itself is not *n*-dopable in acetonitrile [14] as the potential for *n*-doping is more negative than the breakdown potential of the solvent at below -2.0V vs. Ag|Ag^+ [37,38]. Substitution at the 3-position with an aryl group results in more positive *n*-doping potentials. These polymers are not very conductive in the reduced state (at more negative potentials) and

have a low capacitance in this potential region. Consequently, they are usually only employed as the positive electrode with a negative electrode made from another material such as carbon [21,29].

The properties of conducting polymers can be greatly enhanced by forming composites between the conducting polymer and other materials such as carbon (including carbon nanotubes) [39], inorganic oxides and hydroxides [40,41], and other metal compounds [42–44]. Examples of some of these composites and their electrochemical properties are given in Table 4. These electrodes can allow the device to be made symmetric (Type I or Type III) with the same positive and negative electrode. The composite materials have improved conductivity (particularly at the more negative/reducing potentials) and better cycleability, mechanical stability, specific capacitance and processability [5].

Table 4
Specific capacitances of composite and treated materials.

Electrode material	Specific capacitance (F g^{-1})	Electrolyte	Reference
PPy-SWNTs	144	Aqueous	[45]
PPy-funct-SWNTs	200	Aqueous	[45]
PEDOT-on-PPy	230	1 M LiClO_4 (aq)	[46]
PEDOT-on-PPy	290	1 M KCl (aq)	[46]
PPy- Fe_2O_3	420	LiClO_4 (aq)	[41]
PPy	78–137	PVDF-HFD gel electrolyte	[47]
PEDOT- MoO_3	300	Non-aqueous Li^+	[48]
Non-irradiated HCl doped PANi	259	Gel polymer electrolyte	[49–51]
Non-irradiated HCl doped PANi	210 (10 000 cycles)	Gel polymer electrolyte	[49–51]
Irradiated HCl doped PANi	243	Gel polymer electrolyte	[49–51]
Irradiated HCl doped PANi	220 (10 000 cycles)	Gel polymer electrolyte	[49–51]
RuOx-PEDOT-PSS	1409		[40]
PPy-fast CV deposited	480	1 M KCl (aq)	[52]
ACP-PANi	273	1 M H_2SO_4	[53]
Non-treated PEDOT	72	1 M H_2SO_4	[54]
Ultrasonicated synthesis of PEDOT	100	1 M H_2SO_4	[54]
MWNT/PANI 20/80 wt%	360		[55]
MWNT/PPy 20/80 wt%	190		[55]
PANi coated CNF (20 nm)	264		[56]
PEDOT/MSP-20	56 (1000 cycles)	Et_4NBF_4 in PC, LiPF_6 in EC/DMC	[29]

CNF is carbon nanofibre, CNT is carbon nanotube, SWNT is single-walled carbon nanotube, MWNT is multiwalled carbon nanotube, RuOx is ruthenium oxide and MSP-20 is a type of activated carbon supplied by Kansai Coke & Chemicals Co.

This review will focus on the main conducting polymers used for supercapacitor devices, namely, polyaniline, polypyrrole and derivatives of polythiophene, together with the use of composites to improve the properties of these conducting polymer materials. Finally, a comparison with other types of supercapacitor materials will be made.

2. Discussion

The three main methods used for determining the capacitance of conducting polymer materials are illustrated in Fig. 4, namely, constant-current charge–discharge, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Ideally, the charge–discharge curve for a capacitor should be linear with a slope equal to the current divided by the capacitance. Calculation of capacitance from this data is given in Fig. 4a. In the absence of redox processes, the cyclic voltammogram of a capacitor should be rectangular with the capacitance roughly equal to half the value of the difference in plateau currents divided by the scan rate, see Fig. 4b. Finally, the low-frequency components of EIS data represent the capacitive region and a plot such as Fig. 4c can be used to determine the capacitance. There are, however, other ways of extracting capacitance from EIS measurements, e.g., modelling the data with equivalent circuits.

2.1. Polyaniline

Polyaniline has been studied extensively as a supercapacitor or battery electrode material [11,15,19,27,42,44,49,50,53,55–68]. The structure of polyaniline is illustrated in Fig. 3d. Polyaniline has many desirable properties for use in a supercapacitor device; it has high electroactivity, a high doping level (0.5 – see Table 1), excellent stability and a high specific capacitance (400–500 F g^{-1} in an acidic medium) [19]. In addition, it has good environmental stability, controllable electrical conductivity (around 0.1 S cm^{-1} in the doped state with a Li dopant, but can range from around 0.1 to 5 S cm^{-1} as shown in Table 2), and can be easily processed [15,27]. A major disadvantage of polyaniline is that it requires a proton to be properly charged and discharged; therefore a protic solvent, an acidic solution or a protic ionic liquid is required [58].

Polyaniline has been reported to have a wide capacity range from 44 to 270 mAh g^{-1} [11]. This variation in capacity is related to

many factors, including synthetic route used, polymer morphology, the amount and type of binders and additives, and the thickness of the electrode. Polyaniline has the most variable specific capacitance of all conducting polymers; the specific capacitance achievable is higher for electrodeposited than for chemically formed polyaniline.

It has been reported [27] that the cycle-life of polyaniline for a Li-doped positive electrode was over 5000 cycles, during which the specific capacitance dropped from 100 to 70 F g^{-1} . In another study [15], polyaniline doped with LiPF_6 achieved a specific capacitance of 107 F g^{-1} that decreased to 84 F g^{-1} after 9000 cycles.

A device has been constructed with polyaniline as the positive electrode and carbon as the negative [21], i.e., a so-called hybrid electrochemical capacitor. According to Park and Park [21] their device gives similar or higher values than recently reported Type III supercapacitors made from polythiophene derivatives. A constant-current charge–discharge (0.5 mA cm^{-2}) test yields 380 F g^{-1} , a specific energy of 18 Wh kg^{-1} and a specific power of 1.25 kW kg^{-1} (at 20 mA cm^{-2}). Using cyclic voltammetry, a cycle-life of 4000 cycles was observed. The device charges between 1.25 and 1.5 V and discharges between 1.4 and 1.0 V.

Polyaniline can be modified to make it more stable by forming poly(*n*-methyl aniline) (Fig. 3e) [11]. In this polymer, the proton exchange sites are blocked by the methyl groups, so that the polymer is stabilised against chemical degradation and made more redox active. A combination of this conducting polymer with a lithium negative electrode can achieve a capacity of 52 mAh g^{-1} .

2.2. Polypyrrole

Polypyrrole offers a greater degree of flexibility in electrochemical processing than most conducting polymers [69], and consequently the material has been the subject of much research as a supercapacitor or battery electrode [3,12,31,45–47,51,52,55,70–85]. On the downside, polypyrrole (Fig. 3f) cannot be *n*-doped like the thiophene derivatives, and thus it has only found use as a cathode material.

Due its greater density, polypyrrole has a high capacitance per unit volume (400–500 F cm^{-3}) [86]. One disadvantageous aspect of the dense growth is that it leads to limited access to the interior sites of the polymer for dopant ions. This reduces the capacitance per gram, especially for thicker coatings on electrodes [87]. Polypyrrole is typically doped with single-charged anions such as Cl^- ,

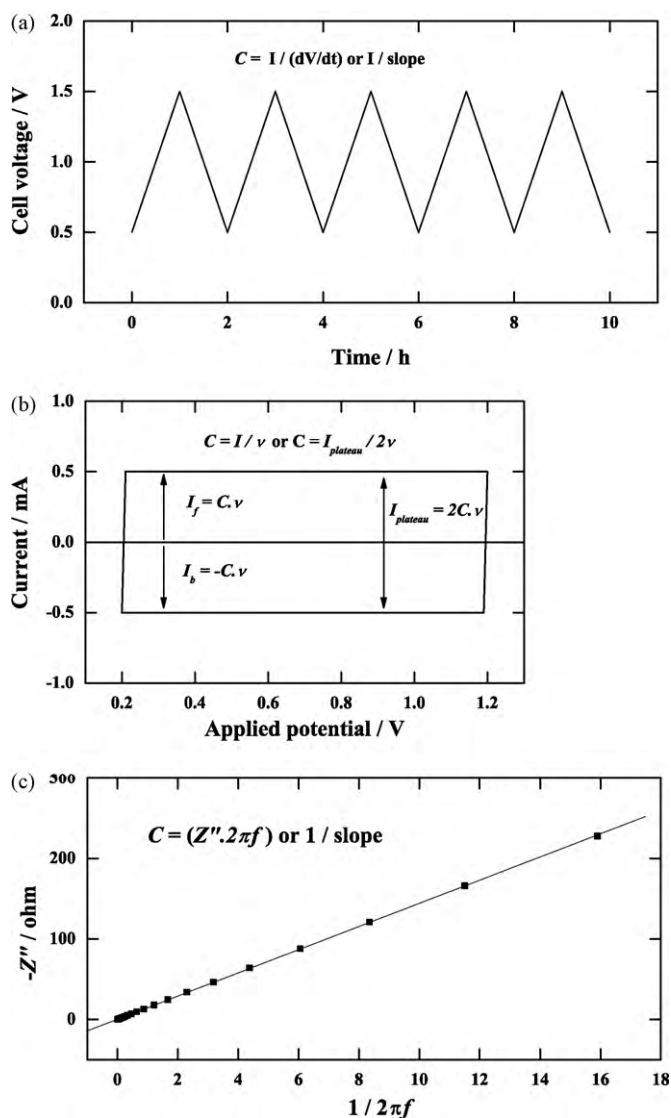


Fig. 4. Idealised schematic representation showing measurement of capacitance of supercapacitor devices and electrodes from (a) constant-current discharge curve; (b) cyclic voltammogram (rectangular component of response, ignoring redox peaks); (c) low-frequency component of imaginary impedance data from electrochemical impedance spectroscopy (EIS); where C is capacitance (F), I is current (A), v is scan rate (V s^{-1}), Z'' is imaginary impedance (ohm), f is frequency (Hz).

ClO_4^- and SO_3^- but if doped with multiple-charged anions, e.g. SO_4^{2-} , physical crosslinking of the polymer occurs [10]. According to Suematsu et al. [10], the cross-linked materials have high diffusivity and higher capacitance, presumably due to the greater porosity of the growth. Suematsu et al. [10] do not back up this statement by quoting the specific capacitance of the material; only capacitance per unit volume of material is quoted and is lower ($100\text{--}200 \text{ F cm}^{-3}$) than typically denser polypyrrole layers ($400\text{--}500 \text{ F cm}^{-3}$), as expected.

Combining polypyrrole with polyimide (a dopant of high molecular weight) is claimed to improve the charge storage properties [81], due to the polyimide matrix protecting the polypyrrole from oxidative degradation and the polyimide is cathodically electroactive (whereas polypyrrole is anodically electroactive). Polyimide has excellent thermal stability and very good mechanical properties. No details as to how the material performed as a supercapacitor electrode were given, except for EIS data that was used to examine the capacitive behaviour. Polyimide is generally considered an insulative material which may result in poor performance.

Polypyrrole has been used as an electrode to make a Type I supercapacitor, as well as combined with poly(3-methyl thiophene) or PMeT to form a Type II version [31]. The Type I device has a discharge capacitance of $8\text{--}15 \text{ mF cm}^{-2}$, which is similar to that for the Type II device. The voltage range is around $0.5\text{--}1.0 \text{ V}$ for the Type I device, but is extended to 1.2 V for the Type II. Polypyrrole has also been used to fabricate an all solid-state-supercapacitor with a PVA-based polymer electrolyte [88]. The design gave up to 84 F g^{-1} [88] with a stable capacitance after 1000 cycles, and delivered a specific energy of 12 Wh kg^{-1} .

2.3. Thiophene-based conducting polymers

A range of n -dopable thiophene (Fig. 3g) based conducting polymers is given in Table 3. The mass specific capacitance in the n -doped form is, in general, lower than that of the p -doped form. It is also found, in general, that the conductivity in the n -doped form is poor. This limits the use of these materials in the n -doped form as an anode material. Most polythiophene derivatives are stable in air and moisture in both the p -doped and undoped forms [5]. According to Ryu et al. [29] and Villers et al. [30], Type III devices made from polythiophene derivatives should achieve $30\text{--}40 \text{ Wh kg}^{-1}$ and $5\text{--}10 \text{ kW kg}^{-1}$ per active material mass. An example of this type of symmetric supercapacitor is made from poly(ditheno(3,4-b:3',4'd)thiophene) (PDTT) [89,90]; a p -doped PDTT electrode had a capacitance of 106.4 mF cm^{-2} while a n -doped PDTT electrode exhibited a capacitance of 43.2 mF cm^{-2} [89].

Polythiophene is n -doped at very low potentials (below -2.0 V vs. Ag|Ag^+) [37,38] and has low stability to oxygen and water, as well as lower conductivity, than in the p -doped state [20]. As a consequence, it has high self-discharge (i.e., it is easily oxidised back to the neutral form) and has low cycle-life in devices. To overcome these disadvantages, polythiophene derivatives with a lower band-gap (i.e., derivatives that are n -doped at less negative potentials) can be prepared [29,30,91]. By substituting at the 3-position of the thiophene ring with phenyl, ethyl and alkoxy groups stability to oxygen and water can be further improved [90]. A further approach is to add electron withdrawing groups to these substituents. The general structure of these substituted thiophene derivatives is presented in Fig. 3h. Some of these derivatives are poly(3,4-ethylenedioxythiophene) (PEDOT) (Fig. 3i), poly(3-(4-fluorophenyl)thiophene) (PFPT) (Fig. 3j), poly(3-(3,4-difluorophenyl)thiophene) (MPFT), and poly(1-cyano-2-(2-(3,4-ethylenedioxythienyl))-1-(2-thienyl)vinylene) (ThCNVEDT) [30]. There are few reports of n -doped thiophene derivatives being used as supercapacitor materials because of intrinsic difficulties in the n -doping process [89], which result in a strong dependence of the behaviour on the size of the counter ion and on the solvent.

A successful strategy to overcome the problem of the n -doped polymer is to use carbon as the negative electrode in an asymmetric configuration, with the p -doped polymer as the positive electrode. This results in a device with superior specific power (compared with carbon-carbon supercapacitors) and that can be cycled at least 10 000 times [20].

The potential range and specific capacitance of some polythiophene derivatives are in Tables 3 and 5. A popular thiophene derivative is poly(3,4-ethylenedioxythiophene) (PEDOT) and its structure is given in Fig. 3i. The polymer is highly conductive (see Table 2), as are many of the thiophene derivatives, and can be p -doped and n -doped. The polymer has a higher potential range of 1.4 V , but the smallest specific capacitance due to a combination of the large molecular weight of the monomer unit and the low doping level [12].

The literature on PEDOT has grown rapidly in recent years due to its extremely desirable properties [5,29–31,40,44,46,48,54,78,87,92–106]. This polymer is elec-

Table 5
Properties of derivatives of polythiophene in *p*-doped state [30].

Active material	Potential limits (V) vs. Ag/AgCl	Voltammetric charge (C g ⁻¹)	Specific capacitance (F g ⁻¹)
P-PFPT	0.3 to 0.9 (0.6)	146	244
P-MPFPT	0.3 to 0.9 (0.6)	127	212
PThCNVEDT	0 to 0.8 (0.8)	173	216
P-MeT	-0.16 to 1.18 (1.34)	-	220 [16]
PEDOT	-0.5 to 0.9 (1.4)	144	103
Carbon	-1.5 to 2.1	82	133

P-PFPT is poly(3-(4-fluorophenyl)thiophene), P-MPFPT is poly(3-(3,4-difluorophenyl)thiophene), PThCNVEDT is poly(1-cyano-2-(2-(3,4-ethylenedioxythienyl))-1-(2-thienyl)vinylene).

tron rich and consequently has a low oxidation potential [104] together with a wide potential window over which the capacitance is high (1.2–1.5 V wide) [30,87,99] (also see Tables 1 and 3). The polymer has a low band-gap of 1–3 eV, is highly conducting in the *p*-doped state (300–500 S cm⁻¹) [5], has good thermal and chemical stability and high charge mobility that results in fast electrochemical kinetics [5,29,99,107]. The main reason why PEDOT has very fast kinetics is its high surface area [99] coupled with high conductivity. The polymer has also been found to have good film-forming properties [107] and can be switched rapidly with a minimum of side reactions leading to a long cycle-life [104]. On the negative side, because of its large molecular weight and a doping level of around 0.33 [5], it has a relatively low specific capacitance of around 90 F g⁻¹ [12]. Lota et al. [5] claim a capacitance of 180 F g⁻¹ is possible with PEDOT, but the authors reported this value for a thin film that is impractical for energy-storage purposes. When the authors prepared a pellet (10–20 mg), the PEDOT gave a capacitance of 80–100 F g⁻¹, as expected. Another disadvantage of this polymer is that the monomer cannot be dissolved in aqueous solvents. Consequently, a volatile and toxic organic solvent, such as acetonitrile, is generally used to deposit the polymer.

PEDOT has been used in both symmetric supercapacitors (Type I device) and a hybrid device with a PEDOT cathode and an activated carbon anode [29]. After 1000 cycles (between 0 and 1 V), the symmetric supercapacitor has a capacity of 22 F g⁻¹ in Et₄NBF₄ in propylene carbonate (PC) and 27 F g⁻¹ in LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC), while the asymmetric supercapacitor, after 1000 cycles, has a capacity of 19 F g⁻¹ in PC and 50 F g⁻¹ in EC/DMC [29].

Many polythiophene derivatives have lower capacitances in the *n*-doped state relative to the *p*-doped state, as can be seen in Table 3. It has been found that poly(3-(4-trifluoromethylphenyl)thiophene) (PTFMPT) has the same charge for *n*- and *p*-doping [14] but exhibits 'charge trapping' where cycling of the material results in the formation of electronically isolated regions in the material. Consequently, less charge is released on discharge than on charge. Laforgue et al. [108] constructed a conducting polymer/carbon/binder electrode and observed charge trapping in initial cycles, but this decreased with continued cycling [108]. The best results were found using poly(3-(4-fluorophenyl)thiophene) (PFPT), where the *n*- to *p*-doping ratio is 60%. When using polythiophene as the conducting polymer, the specific capacitance of the electrode is 260 F g⁻¹, but with PFPT only 110 F g⁻¹ was achieved. For PFPT, cyclic voltammetry for over 500 cycles resulted in little loss in capacity. In other work on PFPT by Rudge et al. [14], it was found that *n*-doping was more facile at a higher electrolyte concentration with smaller ions, but the ability to *n*-dope was hindered when using highly solvated alkali metal salts in acetonitrile. Rudge et al. [14] suggested tetramethyl ammonium salts, in particular Me₄NCF₃SO₃, as the best results were achieved with this electrolyte.

PFPT has been made into a hybrid supercapacitor with an activated carbon negative electrode [109]. For 4 cm² cells, a specific

energy was 48 Wh kg⁻¹ and the specific power was 9 kW kg⁻¹, while for 60 cm² prototypes the specific energy was 7.5 Wh kg⁻¹ and the specific power was 250 W kg⁻¹. Industrial production of conducting polymer devices is difficult and therefore it was suggested that the use of composite electrodes would be advantageous [109].

Substituting other molecular groups on the polythiophene, to improve *n*-doping, results in higher molecular weight (hence lower specific capacitance), higher materials cost and the requirement for higher injected charge and greater mechanical strength. Poly(3-methyl thiophene) (PMeT) is a popular thiophene derivative that is employed in supercapacitor electrodes [79,110,111]. PMeT has a low cost, moderately low molecular weight (and consequently a reasonable specific capacitance of 220 F g⁻¹), and a low resistivity (2 Ω cm²) [20,111]. The charge is delivered at high potentials in a Type III device [14] and it can be cycled several thousand times without significant loss in capacity [112]. Laforgue et al. [20], prepared a hybrid device using PMeT with a cell ESR of approximately 12 Ω cm², most of which was attributed to the carbon electrode as the measured ESR of the positive electrode was less than 1 Ω cm². In the hybrid configuration, the specific capacitance is around 220 F g⁻¹ for the PMeT electrode and 35 F g⁻¹ for the final device. In another device made from PFPT the specific capacitance was 210 F g⁻¹ and 29 F g⁻¹ for the electrode and the final device respectively. The derivatised polythiophene electrodes are highly cycleable with 0.02% capacity loss in 2000 cycles in the case of PFPT and 0.004% loss in 10 000 cycles for PMeT [20].

Using PMeT, a hybrid device with a carbon negative have been constructed [111,112]. Arbizzani et al. [111] prepared a hybrid device and achieved a specific capacitance (per gram of active material) of 39 F g⁻¹ and a capacity of 19 mAh g⁻¹ at a discharge current of 5 mA cm⁻². This dropped to 28 F g⁻¹ and 8 mAh g⁻¹ at a substantially larger discharge current of 40 mA cm⁻². At 5 mA cm⁻², the specific energy is 30 Wh kg⁻¹ and the average specific power is 0.50 kW kg⁻¹, whereas at 20 mA cm⁻², the specific energy is 19 Wh kg⁻¹ and the average specific power is 1.8 kW kg⁻¹.

Poly(cyclopenta(2,1-b;3,4-b'-dithiophen-4-one)) (PcDT) is another interesting thiophene-based material (see Fig. 3k) which can be used in either the *p*- or *n*-doped state [113]. The doping level, as determined from cyclic voltammetry, was 0.19 dopants per monomer unit, significantly lower than polythiophene. The *p*- and *n*-doping states give 70 F g⁻¹ and the energy and power per mass of active material are around 6 Wh kg⁻¹ and 1 kW kg⁻¹ (at 18 s discharge), respectively. This device has a higher cell voltage of 2–3 V compared with polyaniline and polypyrrole (1 V), but the *n*-doped form is very unstable. After 20 cycles, the capacity decreases from 35 to 10 mC cm⁻² but remains constant for the next 80 cycles.

Other devices have been made using polythiophene derivatives and their specific energy and power has been calculated (per active material). Villers et al. [30] achieved for 1-cyano-2-(2-(3,4-ethylenedioxythienyl))-1-(2-thienyl)vinylene (PThCNVEDT, see Fig. 3l) a maximum specific energy and power of 40 Wh kg⁻¹ and 10 kW kg⁻¹. Ferraris et al. [96] quote values of 45 Wh kg⁻¹ and

11 kW kg⁻¹ for a poly-3-(4-cyanophenyl) thiophene (2.9 V) electrochemical capacitor in acetonitrile. Laforgue et al. [109] obtain values of 48 Wh kg⁻¹ and 9 kW kg⁻¹ for a carbon/P-PFPT hybrid capacitor in propylene carbonate. When constructing a prototype, Laforgue et al. [109] achieved device performance of 7 Wh kg⁻¹ and 250 W kg⁻¹.

When using carbon as the negative electrode [30] there was a linear charge–discharge curve when the carbon was the limiting electrode whereas there was a more battery-like curve when the carbon was in excess that suggested redox-type behaviour in the conducting polymer. Using the thiophene derivatives 3-(4-fluorophenyl)thiophene (PFPT), 3-(3,4-difluorophenyl)thiophene (P-MPFPT), poly(3,4-ethylenedioxythiophene) (PEDOT) and 1-cyano-2-(2-(3,4-ethylenedioxythienyl))-1-(2-thienyl)vinylene (PThCNVEDT) typically 50–70% of the capacitance remained after 1000 cycles [30].

2.4. Room-temperature ionic liquid electrolytes

In general, ionic liquids have desirable electrolyte properties as they usually have high ionic conductivity, low vapour pressure, non-flammability, a wide electrochemical window, and high thermal stability [114,115]. A number of electrodes and devices have been prepared using these electrolytes with conducting polymers. Balducci et al. [110] prepared a hybrid supercapacitor device based on an activated carbon negative with a PMeT positive electrode and an ionic liquid as the electrolyte, namely, N-butyl-N-methyl pyrrolidinium bis-(trifluoromethanesulfonyl)imide. This ionic liquid was chosen as it has a low melting temperature, and is hydrophobic and highly cycleable with a wide voltage window that allows hybrid supercapacitor operation between 3.43 and 1.5 V. The device exhibited a specific energy of 14 Wh kg⁻¹ and power of 1.9 kW kg⁻¹. This supercapacitor was cycled 16 000 times. After 1000 cycles, the coulombic efficiency was 99.3%, the capacitance was 15 F g⁻¹ and the capacity was 6 mAh g⁻¹. After 16 000 cycles, the average power was 90% of the initial value and the energy was 40–50% of the original value. The ESR with a large separation of electrodes of 0.5 mm was 17 Ω cm². Other recent work [116] has utilised PEDOT with the ionic liquid: 1-ethyl 3-methyl imidazolium bis-trifluoromethylsulfonyl imide as the electrolyte which is more fluid than the electrolyte used by Balducci et al. [110]. For an electrode with 19 mF cm⁻² capacitance, the ESR was approximately 5 Ω cm².

In the past, the deposition of the homo-polymers from ionic liquids has proven difficult and the resultant layers exhibit poor kinetics for both the charge and discharge reactions that are mainly due to dense growth. Snook and Best [117] combined two polymers (PPy and PEDOT) as one layer using electrodeposition from a mixed monomer solution in an ionic liquid, namely, 1-butyl-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (C₄mpyr TFSI). This creates a superior polymer layer with improved morphology and higher ionic transport, while maintaining a similar specific capacitance to the homo-polymer PPy. Less dense growth seems to occur due to the mismatch of growth between the two conducting polymers.

2.5. Thiophene/imidazolium

In work carried out by Naudin et al. [118], a thiophene monomer was covalently attached to an imidazolium counter ion. This is part of a class of conducting polymers which are self-doped where the counter ion is covalently attached. The polymer is *p*- and *n*-dopable at potentials centred at 0.65 V vs. Ag|Ag⁺ (*p*-doping) and –2.0 V vs. Ag|Ag⁺ (*n*-doping). Charge compensation for both oxidation and reduction is achieved via the anion. Thus, the presence of a permanent positive charge on the polymer backbone may be useful for the

development of supercapacitors where the charge compensation is solely by anions in the supporting electrolyte.

2.6. Redox conducting polymers

Typical conducting polymers have discharge capacities that are not much higher than 100 mAh g⁻¹. Performance can be increased by functionalising the polymer with electroactive moieties. Poly(1,5-diaminoanthraquinone) (pDAAQ) with the redox active anthraquinone moiety is an example of a redox conducting polymer [35,119]. Another example is poly(2-2'-dithiodianiline) (pDTDA) [119]. This polymer has a high conductivity (0.3–2 S cm⁻¹ from –2.0 to 0.8 V) [35], a specific capacity of 238 mAh g⁻¹, a wide potential window of approximately 2.3 V, fast redox kinetics, a high electrical conductivity, and the two redox reactions occur at the same potential. A symmetrical device was made from the polymer and achieved 25–46 Wh kg⁻¹ and 10.2–30.5 kW kg⁻¹ per active mass at discharge rates of 30–90 C. The specific power, however, seems high (it is quoted per active mass) and is unlikely to be translated to a device performance (as quoted per device mass).

2.7. Composites

A list of general composites and treatments of the conducting polymers and the specific capacitances achievable is given in Table 4. With the exception of mixing with ruthenium oxide, which is extremely costly, the specific capacitances are generally below 500 F g⁻¹. Combining polypyrrole with iron oxide to achieve a specific capacitance of around 400 F g⁻¹ is very promising [41]. This cheap metal oxide could produce a supercapacitor electrode of high specific energy.

It appears that the main advantage of compositing is not improved specific energy but, in fact, the improved stability of the materials (improved cycleability) and superior conductivity. Strategies for improving cycle-life that are often limited by the swelling and consequent breakage of the polymers, include compositing with carbon nanotubes to allow room for swelling as well as irradiation [49–51] or sonication [54] during production of the conducting polymer. Composite electrodes of polymers with other materials have been investigated mainly to extend cycle-life and improve conductivity, but many other benefits are seen to arise as outlined in the examples below.

2.7.1. PEDOT/PSS

When doped with a polyanion such as polystyrenesulfonate (PSS), PEDOT has good compatibility with polar group polymers and allows good device performance when using aqueous electrolytes. In order to achieve high specific power in a supercapacitor device, the fast kinetics of the electrochemical process are required. In organic media, the PEDOT/PSS material does not swell and this indicates a high ionic resistance and a slow electrochemical process [107]. Blending this composite material (PEDOT/PSS) with polyethyleneoxide (PEO), which is an ionic conductor, improves the ionic conductivity of PEDOT. The PEO phase swells in acetonitrile to allow easier ion motion. Using 50% PEDOT–PSS/PEO, a specific power of 100 W kg⁻¹ is achieved and appears to be a very small. Regardless, the authors claimed that the PEDOT–PSS formed a highly porous structure that results in very fast and efficient electrochemical reaction. Nonetheless, the power values measured here do not support this assertion.

In other work, the combination of PEDOT with the PSS dopant [120,121], provided low ionic resistance, but the kinetics were limited by a high electronic resistance. Ghosh and Inganas [120] claimed that when the electrode was put in pure water it swelled extensively and underwent cracking. High interfacial resistance arises [122] due to a low compatibility between the electrolyte

and polymer. The charge-transfer resistance was reduced [120,122] by crosslinking the conducting polymer with Mg^{2+} ions. Because electronic conductivity was now the limiting case, the pores are filled by electrodepositing polypyrrole [120,122]. This structure or morphology results in much better mechanical and electrical properties. In these studies [122], going from low power (100 W kg^{-1}) to high power (3 kW kg^{-1}) the pure polypyrrole specific energy reduces by one-fifth. On the other hand, for the PEDOT-PSS/PPy composite there is no loss in energy over this power range.

2.7.2. Composites with carbon nanotubes

Polypyrrole can be combined with CNTs [4,39,69,79,85,123–126] to form a composite for the positive electrode. Zhou et al. [123] used pyrrole combined with treated functionalised single-walled CNTs and claimed 350 F g^{-1} , 4.8 kW kg^{-1} and 3.3 kJ kg^{-1} for this positive electrode. A specific energy of 3.3 kJ kg^{-1} translates to a specific energy of 0.92 Wh kg^{-1} . This value appears to be low compared to the specific capacitance achieved. It also appears that the specific capacitance may have been reported on the basis of conducting polymer weight and not composite weight. CNTs are electron acceptors and PPy is an electron donor so the two form a charge-transfer complex. One of the electrodes gave a capacitance of 205 F g^{-1} at 0.4 A g^{-1} and 50 F g^{-1} at 2.5 A g^{-1} . This drop in capacity is due to the inaccessibility of the composite electrode material. Even though the composite structure is more open than PPy itself, it must not be sufficiently open to allow such high currents to be passed through the structure. The best electrode prepared by these authors gave a performance of 350 F g^{-1} at 0.4 A g^{-1} and 200 F g^{-1} at 30 A g^{-1} .

Polypyrrole can be co-deposited with carbon nanotubes by oxidising the monomer in the presence of negatively charged multi-walled carbon nanotubes (MWNT) [69]. In the absence of any other dopant, the polymer will be doped by these nanotubes [69]. The carbon nanotubes are made by treatment in an aqueous acid solution to form charged groups such as carboxylate, hydroxide and nitrous groups on the surface of the carbon. A monomer concentration of 0.5 M is used with a range of nanotube concentrations, namely, $0.025\text{--}0.4\text{ wt\% MWNTs}$. As the concentration of the MWNTs increases, the thickness of the polymer coating on the MWNT decreases. When combining with 0.4 wt\% MWNTs , the polymer layer gave a mass specific capacitance of 190 F g^{-1} with an electrode specific capacitance of 2.1 F cm^{-2} [69]. The mass specific capacitance is slightly lower than that for pure PPy, however, the electrode specific capacitance is quite high as generally PPy is limited to about 0.7 F cm^{-2} . This is due to a more open or porous structure resulting from the MWNT backbone.

Chen et al. [124], found that polypyrrole on its own exhibited a plateau in capacitance with increasing film thickness (at 10 C cm^{-2}) and thereby indicated limited access to the interior redox sites. Combining PPy with carbon nanotubes resulted in a linear capacitance versus deposition charge up to the same film thickness (10 C cm^{-2}). This suggests that the nanotubes open the structure and limit the thickness of the deposited PPy and thus allow the majority of internal sites to be accessed by ions.

Combining polythiophene with carbon nanotubes as a composite [5] results in improved cycleability and stability. This is due to the fact that the entangled mesoporous network of nanotubes, which supports the polymer structure, allows the material to adapt to volume changes, so that the open network structure does not need to expand and contract as much. The volume change, which can cause great stresses, is often the cause of poor cycleability.

Combining PEDOT with carbon means that there is no need for polymeric binders and that conductivity in the undoped state is improved [5,101]. The PEDOT, like most conducting polymers, is poorly conducting in the reduced state, so by combining with highly conductive carbon, the conductivity at these reducing potentials is

increased. Using carbon nanotubes can increase the cycle-life as the composite can adapt to volume changes upon insertion and removal of counter-ions [5]. In a study by Lota et al. [5], composite electrodes were prepared by three different methods: (i) direct polymerisation on ultrasonically dispersed CNTs (130 F g^{-1}), (ii) mixing of polymer with carbon nanotubes (composite capacitance of 120 F g^{-1}), and (iii) electrochemical deposition of polymer onto the CNTs (up to 150 F g^{-1}). In separate work [101], a fourth method was used where a negatively charged CNT suspension and the polymer were co-deposited [87] as in previous work by Chen et al. [69,85,124]. Successful co-deposition occurred with capacitances of at least 0.5 F cm^{-2} achieved. A symmetric supercapacitor [5] with electrodes made of $75\text{ wt\% PEDOT}/25\text{ wt\% CNT}$ degraded by only 5 F g^{-1} (from 85 F g^{-1}) in 3000 cycles, but the device had a limited operating potential of 0.8 V . An asymmetric device using $80\text{ wt\% PEDOT}/20\text{ wt\% acetylene black}$ as the positive electrode and activated carbon as the negative gave an extremely good cycle-life with little loss in capacitance after 20 000 cycles (160 F g^{-1}) [5].

2.7.3. Other composites

A porous structure of a carbonised polyacrylonitrile (PAN) aerogel support was coated with a thin film of polyaniline to give a foam like and highly reticulated composite structure [19]. The polyaniline is deposited in a thick coating so that the PAN aerogel capacitance contribution is no longer dominant. The electrochemical behaviour is now dominated by the polyaniline; however, the foam like carbon structure will provide a conductive backbone to provide high power. For a voltage range of 0.6 V , an energy of 4.25 Wh kg^{-1} and a power of 1.2 kW kg^{-1} (13 s discharge) were achieved. Over a wider cycling voltage range of 0.8 V , an energy of 5.8 Wh kg^{-1} and power of 1.5 kW kg^{-1} were possible [19].

Deposition of RuO_x on PEDOT, either by dip hydrolysis or electrochemical deposition, resulted in an electrode with a capacitance of 435 F g^{-1} [99]. The highest reported value for RuO_x is $720\text{--}768\text{ F g}^{-1}$ [99]. In the same study, a symmetric PEDOT unit [99] was able to deliver 12.4 mAh g^{-1} , whereas a symmetric version using the composite with the ruthenium oxide gave 27.5 mAh g^{-1} with a voltage of 1.0 V . Huang et al. [40] have claimed an impressive 1409 F g^{-1} for a composite with ruthenium oxide with PEDOT. While this device shows promise, the ruthenium starting materials are too expensive to produce commercially viable supercapacitors.

Polyaniline has been combined with a polyoxometallates to improve the stability, charge propagation and energy-storage capability [42]. An electrochemical co-deposition was found to be the most successful. This supercapacitor could be cycled for at least 2000 cycles while retaining around 115 F g^{-1} but only being cycled over a voltage range of $0\text{--}0.5\text{ V}$. Polyoxometallates have also been combined with conducting polymers in other work [42–44] but are more likely to find application based on the photoelectrochemical ability of polyoxometallate structures.

2.8. Prototypes

To date, prototypes with only small geometric areas have been made with conducting polymers and, in general, propylene carbonate rather than acetonitrile has been used as the host solvent for the electrolyte [33]. Hybrid supercapacitor modules/stacks have been made by Laforgue et al. [20] with PMeT as the positive electrode and activated carbon as the negative, and delivered 3 V and more than 1.5 kF capacitance and $2\text{--}3\text{ kW}$ of power. Such devices used carbon-coated aluminium current collectors and had a resistance of $33\text{ m}\Omega$. From capacitance and ESR data it was calculated that the device gave 5 Wh kg^{-1} and 2 kW kg^{-1} . The authors estimated with mass optimisation that a device with an energy of 13 Wh kg^{-1} and power of 5 kW kg^{-1} could be achievable.

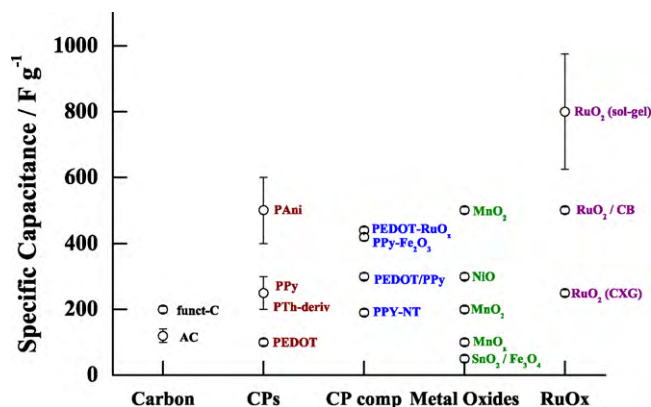


Fig. 5. Typical specific capacitances for different supercapacitor materials. Typical metal oxide values are taken from Ref. [128]; where CXG is carbon xerogel and CB is carbon black. Funct-C refers to functionalised carbons, AC refers to activated carbon, CPs refers to conducting polymers and CP comp refers to conducting polymer composites.

Du Pasquier et al. [13] have constructed an asymmetric device with a lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ or LTO) anode and a PFPT cathode. LTO has excellent stability and rate capability as it is a zero-strain material [127]. Supercapacitor devices based on LTO/C have the following performance, 20 Wh kg^{-1} , 90% utilisation, the ability to be charged at 10C charge rates, and a cycle-life of the order of 1000 cycles. On the downside, this system suffers from high self-discharge. The positive electrode (PFPT) delivers 270 F g^{-1} and a capacity of $40\text{--}45 \text{ mAh g}^{-1}$, while the negative electrode (LTO) achieves a capacity of around 160 mAh g^{-1} . Constructing a device with both these positive and negative electrodes and using 7 plates, a specific energy of 12 Wh kg^{-1} can be achieved based on device weight. This device can be charged at the 10C rate and discharged at the 100C rate. In one of these devices, 14% of the capacitance was lost after 1500 cycles.

Wang et al. [73] proposed a new anode for a flexible energy-storage device made entirely of conducting polymer electrodes (i.e., both the cathode and the anode). The cathode was polypyrrole and the anode was styryl-substituted dialkoxyterthiophene (poly(OC(10)DASTT)) on a Ni/Cu-coated nonwoven polyester. The discharge efficiency was measured at 94% and the capacity was 39.1 mAh g^{-1} .

2.9. Comparison with other types of supercapacitor materials

A comparison of the specific capacitances of conducting polymer and conducting polymer composites with other supercapacitor materials is given in Fig. 5. It is obvious that both conducting polymer and metal oxide materials (generally referred to as pseudo-capacitors) increase the amount of specific capacitance available for a device when compared with carbon-based supercapacitor materials, but this is generally at the sacrifice of cycle-life. The other notable point, at the opposite end of the scale, is that ruthenium oxide is capable of giving specific capacitances that are far superior to those of all other materials. In reality, however, ruthenium oxide is far too expensive to be a practical option for supercapacitors. Polyaniline is the most promising material when considering the specific capacitance of conducting polymer materials. The specific capacitance can, however, vary significantly depending on the method of production of the polymer. Moreover, utilisation of polyaniline as a supercapacitor material is complicated by the requirement for sufficient proton activity in the electrolyte solution to give satisfactory cycling. A variety of values for manganese oxide are given in Fig. 5 and this is because capacitance is dependent on the phase, morphology and form of

the oxide that vary according to the method of synthesis. Nevertheless, this material appears to be the greatest competitor to conducting polymers as a supercapacitor material. Specific capacitances comparable to that of polyaniline are possible with the other conducting polymer materials by making a composite with, for example, PEDOT and iron oxide. The advantages of such a composite is that the specific capacitance is high and the flexible nature of the film assists the production of devices. Other conducting polymer composites (for example with carbon materials) often do not result in greater specific capacitances, but have many other advantages such as increased cycle-lives and charge rates.

3. Conclusions

Conducting polymers offer many advantages as supercapacitor electrodes. They are flexible, highly conductive, easily processable and can be made into films. Many conducting polymers exhibit high specific capacities and capacitances, while being able to deliver energy at a relatively rapid rate. The major disadvantage of the conducting polymers when used as supercapacitor electrode is poor cycle-life. In general, symmetric supercapacitors based on conducting polymers will have a lower cycle-life than those based on carbon. This is unavoidable, because as anions or cations are doped or undoped into the conducting polymer, there is a corresponding volume change of the electrode when compared with carbon supercapacitors which involve only simple ion sorption and desorption. The literature tends to give vague reports of cycle-life of conducting polymer devices. Authors claim 'little' loss in capacitance over thousands of cycles but the depth of these cycles is usually not quoted. The main strategies for improving cycle-life include irradiation or sonication during production, or compositing the conducting polymer with carbon nanotubes to increase volume, improve porosity and allow room for swelling of the conducting polymer. A more recent method for increasing porosity and influencing the morphology of the conducting polymer electrode materials has involved co-deposition of different conducting polymers in an ionic liquid. It is anticipated that this should also increase cycle-life due to a greater degree of freedom to accommodate swelling of the electrode and a smaller amount of continuous thick conducting polymer material.

A degree of caution with over interpreting specific capacitance, energy and power data in the literature has to be applied. This is due to the fact that many numbers quoted are not device values and quite often relate only to the active material and do not include the mass of the binders, conductive carbon fillers, electrolyte and packaging. Again, this makes comparison of numbers in the literature often difficult.

Many investigations focus on mass specific properties and quote values per mass of active material. Often, however, the more important parameter is the area specific values for the devices. In other words, often (electrode) area specific capacitance (F cm^{-2}) can be just as important as mass specific capacitance (F g^{-1}). This means that the amount of capacitance for a given electrode geometric area will give an idea as to the device capacitance that is possible. In this respect, PEDOT is superior to many other conducting polymers due to its high porosity and deep accessibility of ions to the interior sites of the polymer layer. This means that while having a low mass specific capacitance (typically $90\text{--}100 \text{ F g}^{-1}$) it can still produce a large electrode specific capacitance (well in excess of 5 F cm^{-2}), which will translate to a large absolute device capacitance.

It should be noted, that the chemical method of deposition is limited in terms of how much polymer can be produced as a film. Consequently, this method is most often only suitable for thin films. If the capacitance of these thin films is converted to capacitance per area of electrode the value is lower when compared

to carbon-based supercapacitors. On the other hand, the use of electrochemical deposition methods yields thicker deposits of the conducting polymer that lead to broader peaks in the cyclic voltammograms and thereby suggesting slower kinetics. Consequently, only small geometrical area prototypes of supercapacitors have been made with conducting polymers and new strategies need to be devised to make both electrodes and devices with high specific capacitances. It is proposed that room-temperature ionic liquids (RTILs) will play an important part in harnessing the power of conducting polymers in supercapacitor devices. Furthermore, RTILs will most likely increase the cycle-life of the conducting polymer materials in supercapacitor devices.

Conducting polymers are most promising for supercapacitors with asymmetric configurations, i.e., with a conducting-polymer-based positive electrode and a carbon-based negative electrode. These devices appear to have much greater cycle-life as the conducting polymer electrode experiences a smaller voltage swing. Also, a range of composites, in particular with carbon-based materials, are promising in terms of improving the characteristics of the positive electrode. When comparing such materials with metal oxides, they can achieve comparable specific capacitance at an appreciably lower cost and with the added benefit of superior mechanical properties and often also superior conductive properties. For these reasons, conducting polymers are promising supercapacitor materials.

Acknowledgments

The authors would like to thank Drs Anthony G. Pandolfo and Seepalakottai Sivakkumar for constructive comments on the manuscript and Dr David A.J. Rand for assistance in the preparation of this manuscript.

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