

Toward Flexible Polymer and Paper-Based Energy Storage Devices

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All-polymer and paper-based energy storage devices have significant inherent advantages in comparison with many currently employed batteries and supercapacitors regarding environmental friendliness, flexibility, cost and versatility. The research within this field is currently undergoing an exciting development as new polymers, composites and paper-based devices are being developed. In this report, we review recent progress concerning the development of flexible energy storage devices based on electronically conducting polymers and cellulose containing composites with particular emphasis on paper-based batteries and supercapacitors. We discuss recent progress in the development of the most commonly used electronically conducting polymers used in flexible device prototypes, the advantages and disadvantages of this type of energy storage devices, as well as the two main approaches used in the manufacturing of paper-based charge storage devices.

1. Introduction

There is currently a strong demand for the development of new inexpensive, flexible, light-weight and environmentally friendly energy storage devices.^[1–5] An obvious reason for this is that energy storage materials represent a key technology in conjunction with energy-conversion materials. As a result of these needs, research is currently carried out to develop new versatile and flexible electrode materials as alternatives to the materials used in for example contemporary batteries and supercapacitors. In this process, electronically conducting polymers (ECPs), such as polypyrrole (PPy), polyaniline (PANI) and polythiophene (PTP) are particularly interesting since it has been shown that these materials can be used to manufacture polymer-based batteries and supercapacitors.^[6–10] During more than two decades, the relatively high theoretical capacities of these materials,

ranging from approximately 100 to 140 mAh g^{−1},^[9,11] have been the main reason for the significant research interest in this type of materials. In addition, it has also been shown,^[12–17] that thin layers of ECPs can be oxidized and reduced at very high rates indicating that these materials could be used in high power applications. The main problems with ECP based batteries and supercapacitors are generally considered to be their poor cycling stabilities,^[6,8,9,11,18] high self-discharge rates,^[6,19–26] and low capacities due to the low attainable doping degrees^[9,10] as well as mass transport limitations within thick polymer layers.^[9,14,27–30] The latter problem has been addressed by nanostructuring of ECP materials,^[31–39] manufacturing carbon nanotube (CNT) containing composites^[14,29,31,40–51] or by depositing the ECPs in the form of a thin

film on large surface area substrates.^[12,16,41,52,53] As certain ECP based supercapacitors have been found to be stable for thousands of cycles,^[16,17,37,46,54–60] recent work indicates significant progress in overcoming the cycling stability limitations. The problems with poor long time stability and self-discharge of conducting polymer-based charge storage devices are, however, still far from solved and there are, unfortunately, very few recent reports addressing the latter two critical questions. Other contemporary shortcomings related to the applicability of ECPs in flexible energy storage devices include their limited post-synthesis processability due to their poor solubility, infusibility, and mechanical brittleness. The possibility of armoring the conductive polymers with cellulose fibers to obtain better cycling stability, mechanical flexibility and robustness and to enable subsequent molding of the produced composites into paper sheets of desired shape is therefore highly appealing. The addition of cellulose to other electrode materials, such as CNTs, is similarly attractive both from a mechanical property- as well as from a manufacturing- point of view.

In the most recent development of flexible and versatile energy storage devices, several approaches have been adopted in which the electrode materials have been either conducting polymers^[12,13,27,28,52,61,62] or combinations of conducting polymers and various types of carbon materials,^[40] such as for example CNTs.^[42–51] There has also been a large interest in using only CNTs as the active material in such devices.^[63–72]

In the subsequent sections, we review the state of the art of conducting polymers as electrode materials for flexible charge storage devices and the development of polymer and

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DOI: 10.1002/adma.201004134

paper-based batteries and supercapacitors. A particular focus is also set on cellulose based devices with either CNTs or conducting polymers as the active material, given the large inherent potential of such devices with respect to novel and existing application areas. Since device data in the literature have been recorded using different types of setups (e.g. two or three electrodes) and calculations of capacitances and capacities often are performed with respect to an active electrode mass, a full prototype device, or without describing the normalization procedure, it is generally difficult to obtain an unambiguous comparison of all parameters of an electrode material or a device. In the present review, we therefore summarize the properties presented in the original reports and, when possible, highlight the method of measurement and calculation used to obtain these results.

2. Conducting Polymer Electrode Materials

This section highlights the most interesting recent studies of the electrode materials applicable in the development of flexible and versatile energy storage devices based on conducting polymers or composites of conducting polymers with CNTs as the active material. The development of composites containing cellulose and conducting polymers or CNTs is also discussed since these composites are the basis for the development of paper-based batteries and supercapacitors.

2.1. PPy-Based Electrode Materials

PPy is one of the most studied conducting polymers for energy storage applications. With a relatively small monomeric mass, PPy has a theoretical specific charge capacity of 100 mAh g^{-1} ,^[6] assuming a 25% degree of doping. This, in combination with a straightforward synthesis procedure based either on chemical or electrochemical polymerization, the possibility to employ both aqueous and non aqueous media as well as PPy's compatibility with a large variety of substrates,^[6,73,74] has led to a high interest for using PPy as an active material in conducting polymer-based electrodes.

Several early studies (reviewed in Refs. [6,73]) involving PPy were focused on using PPy as a cathode material in lithium ion batteries. Even if PPy electrodes have been shown to be non-competitive with respect to this application, PPy has recently found new use as a performance enhancing additive in lithium ion battery anodes and cathodes.^[75,76] A hybrid metal-conducting polymer (Sn-PPy), composite electrode was electrodeposited in a one-step process on a copper foil using an electrochemically generated oxidizing agent for subsequent chemical polymerization of PPy. When used as an anode versus lithium, this material showed^[75] an improved cycling performance compared to pure tin electrodes of comparable thickness. However, one potential problem with this one-step approach is that the generated oxidant may oxidize the metal layer. PPy can also be used to replace some of the conductive carbon and binder materials used in LiFePO_4 cathodes.^[76] The latter $\text{LiFePO}_4/\text{PPy}$ composite cathodes showed an improved capacity and rate capability compared to LiFePO_4 cathodes prepared with conventional conductive carbon and binder material. This suggests that conducting



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polymers may play a role in the development of new stable electrode materials.

The application of PPy as a capacitance increasing electrode material in supercapacitors has been in focus during the last 10 years. Below, nanostructuring and different activations of PPy^[35,58,75,77–80] will be discussed together with composites containing CNTs,^[49–51,59,60,81,82] other forms of carbon,^[14,83–85] as well as combinations with other polymers.^[53,79]

PPy supercapacitor electrodes, with a high porosity nanostructure, have been prepared by electrodeposition on Ti foils employing cyclic voltammetric scans at 200 mV s^{−1} in oxalic acid.^[35] A specific capacitance of 480 F g^{−1} was obtained from 3-electrode cyclic voltammetry experiments and a 9% decrease in the capacitance was seen after 1000 cycles. These results show that a high porosity of the material can be obtained during electrodeposition and that this facilitates fast cycling of the material.

Several strategies for “activating” PPy supercapacitor electrodes, including micellar deposition, self-doping by attached anions and the use of aryl sulfonates have also been studied.^[77] It was concluded that structural relaxations that facilitate solvent uptake and dopant ion access are essential and it was shown that 15–20 µm thick activated PPy films could be cycled reversibly at scan rates up to 300 mV s^{−1}. The indication that rather thick films can be reversibly cycled at relatively high rates is promising although it is not clear how much of the capacity of the film was used at these scan rates.

The morphology and structure of 60 to 100 µm thick PPy films doped with different anions have been characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD).^[80] It was demonstrated that the use of chloride doped films resulted in higher specific capacitances (up to 270 F g^{−1}) but also a more rapid drop in the capacitance with increased scan rate when compared with p-touluenesulfonate doped films. Nafion doped PPy has also been studied as a capacitor material^[58] yielding capacitances of up to 344 F g^{−1} which was lower than that for perchlorate doped PPy. The Nafion doped films, however, exhibited significantly better cycling performance, both at high scan rates (up to 1 V s^{−1}) and after 3000 cycles. The influence of different dopants on the capacitance, stability and rate capability of the PPy films show that the electrochemical properties of these polymers depend on the size and mobility of the anion dopants.

Composites of PPy with CNTs have been proposed as the most effective solution to improve the mechanical and electrochemical properties of electrodes based on pseudo-capacitance materials.^[81] Three-electrode capacitances of up to 192 F g^{−1} were reported^[86] for a nanoporous composite with PPy layers of up to 250 nm thickness. When using a PPy composite with single walled CNTs, a specific capacitance of 265 F g^{−1} was reported.^[50] A corresponding value of 131 F g^{−1} was reported^[87] for a 1:1 composite comprising single walled CNTs and PPy. Aligned multi-walled CNTs coated with electropolymerized PPy have also been found to yield high area specific capacitances of up to 2.55 F cm^{−2}.^[82] The inclusion of CNTs is likewise known to improve the cycling performance of PPy electrodes. Capacitance losses of up to 20% after 2000 cycles^[59] and 25% after 5000 cycles^[60] were found for electrodes containing multi-walled CNTs combined with electrodeposited PPy and

electrochemically co-deposited PPy and multi-walled CNTs, respectively. Although these capacity losses still are too large for many practical applications, it is clear that the PPy and CNT composite approach may lead to significantly better cycling stability than for PPy alone.

Other carbon materials than CNTs have also been considered for PPy composite electrodes although less frequently. An electrode based on activated carbon and electropolymerized PPy thus exhibited a specific capacitance of 354 F g^{−1} obtained from CV experiments at 1 mV s^{−1},^[83] while a chemically polymerized PPy coating on a matrix of graphite fibers yielded a specific capacitance of 400 F g^{−1} at a scan rate of 10 mV s^{−1}.^[84] A composite electrode composed of a layer of chemically polymerized PPy on a combination of vapor grown carbon fibers (VGCF) and activated carbon (AC) had a specific capacitance of 140 F g^{−1}.^[14] As the capacitances in the three above cited references were all calculated from cyclic voltammograms recorded in the three-electrode mode after normalization with respect to the total weight of the electrode, these values are not directly comparable to the specific capacitances for the CNT composites described in the above paragraph. Excellent rate capabilities were observed^[14] for 5 nm thin PPy layers on the above mentioned VGCF/AC electrode with practically constant specific capacitances for scan rates up to 200 mV s^{−1}. This can be ascribed to the thin films used which ensured a sufficiently fast mass transport of the ions within the PPy layers.

Bimodal porous carbon has also been used as a matrix, and a composite electrode was produced using electropolymerization of PPy inside the macropores of the carbon matrix. This electrode was evaluated versus a lithium electrode and a capacity of 78 mAh g^{−1} was reported^[85] in the potential range 2.0–4.0 V vs. Li/Li⁺. Reticulated vitreous carbon/PPy composites have likewise recently been tested^[88] as electrodes for lithium batteries. It was demonstrated that the electrodes could attain specific capacities up to 95 mAh g^{−1}. Although the latter value is promising, the capacities for porous carbon based PPy composites are still rather low when evaluating the capacity per weight of the composite.

Another fundamentally interesting concept is to use conducting polymer hydrogels as electrode materials in supercapacitors. In one study,^[53] PPy was electropolymerized on a cross-linked poly(3,4-ethylenedioxythiophene) (PEDOT)-poly(styrene sulfonate) (PSS) hydrogel surface on top of a gold surface giving rise to a three-dimensional all-polymer electrode material with a specific capacitance of up to 70 F g^{−1}. It was reported that the latter porous swollen hydrogel electrode exhibited very high power densities (i.e. up to 10 kW kg^{−1}) without drastic loss of energy density. Although this rate capability is impressing, the capacity of the material was rather low when evaluated with respect to the weight of the swollen hydrogel since the latter contained up to 90% water.

While PPy is a very popular and versatile electrode material, the major limitation of this material in supercapacitor applications is generally claimed^[11,18] to be its limited cycling stability. However, the improved cycling stability observed for PPy composites with CNTs,^[59,60] and MnO₂,^[89] certainly represent interesting progress towards acceptable cycle life. More work is, however, needed to reach a fundamental understanding of the processes involved in the

degradation of the material upon cycling as well as during storage. Table 1 summarizes the most recent literature data on PPy based electrodes for supercapacitors and battery devices.

2.2. PANI Based Electrode Materials

For more than 30 years, there has been a large interest in PANI based electrode materials^[6,8,90,91] for batteries and supercapacitor

Table 1. Literature data on PPy based electrodes for supercapacitor or battery applications.

Material	Capacitance [F g ⁻¹]	Capacity [mAh g ⁻¹]	Energy density [Wh kg ⁻¹]	Power Density [kW kg ⁻¹]	Remarks	Ref.
PPy on Ti foil ^{a)}	480 ^{c)}	—	—	—	PPy mass, capacitance from CV	[35]
PPy nanowires ^{b)}	282 ^{d)}	—	31.8 ^{d)}	—	PPy mass of one electrode, capacitance from charge-discharge measurement, 1 Ag ⁻¹	[79]
PPy on carbon fibers ^{a)}	—	23.9 ^{d)}	11 ^{d)}	—	PPy mass	[104]
PPy on carbon/ PtP on carbon ^{a)}	—	33.3 ^{d)}	27 ^{d)}	—	PPy mass	[104]
PPy/ PPy ^{a)}	—	—	2.38 ^{d)}	19.7 ^{d)}	PPy mass	[40]
PPy-Ni ^{a)} , PPy-ClO ₄ on Pt ^{a)}	240 ^{c)} , 210 ^{c)}	—	14.6, 12.3 ^{c)}	4.3, 3.7 ^{c)}	PPy mass of one electrode, capacitance from CV measurements, 1000 mV s ⁻¹	[58]
MWNT/PPy ^{b)}	163 ^{d)}	—	—	—	Mass of one electrode, capacitance from CV measurements, 1 mV s ⁻¹	[48]
MWNT/PPy ^{a)}	192 ^{c)}	—	—	—	Mass of one electrode, capacitance from CV measurements	[86]
SWNT/PPy ^{b)}	265 ^{d)}	—	—	—	Capacitance from charge-discharge measurements, unknown normalization	[50]
CNT/PPy ^{a)}	220 ^{d)}	—	—	—	Mass of one electrode, capacitance from charge-discharge at 2 mA, 0.8 V potential window	[40]
SWNT/PPy ^{b)}	131 ^{c)}	—	—	—	Mass of one electrode, capacitance from CV measurements, 10 mV s ⁻¹	[87]
MWNT/PPy ^{b)}	200 ^{d)}	—	—	—	Mass of one electrode, capacitance from charge-discharge measurements	[49]
MWNT/ACNF/ PPy ^{b)}	333 ^{d)}	—	—	—	Mass of active weight of one electrode, capacitance from charge-discharge measurements, 1 mA cm ⁻²	[51]
AC/PPy ^{a)}	354 ^{c)}	—	—	—	Capacitance from CV measurements, 1 mV s ⁻¹ , unknown normalization	[83]
Graphite fiber/ PPy ^{b)}	400 ^{c)}	—	—	—	Capacitance from CV, 10 mV s ⁻¹ , unknown normalization	[84]
VGCF/AC/PPy ^{b)}	140 ^{c)}	—	—	—	Total mass of one electrode, capacitance from CV, 30 mV s ⁻¹	[14]
Bimodal porous carbon/PPy ^{a)}	—	78 ^{c)}	—	—	Mass of carbon and PPy of one electrode, capacity from charge-discharge in the range 2.0 V–4.0 V vs. Li/Li ⁺ , 0.1 Ag ⁻¹	[85]
Reticulated vitreous carbon/ PPy ^{a)}	—	95 ^{c)}	—	—	Mass of PPy of one electrode, capacity from charge-discharge in the range 2.0V–3.8V vs. Li/Li ⁺	[88]
Graphene/fibrous PPy nanowires ^{b)}	165 ^{d)}	—	—	—	Capacitance from charge-discharge at 1 Ag ⁻¹ , unknown normalization	[164]
PPy/ poly(OC ₁₀ DASTT) on Ni/Cu-coated polyester ^{a,b)}	39.1 ^{d)}	—	—	—	Unknown normalization	[159]
Au/PEDOT-PSS/ PPy ^{a)}	70 ^{d)}	—	6	10	Mass of one electrode, capacitance from CV, 100 mV s ⁻¹	[53]

^{a)}Electrochemical polymerization; ^{b)}Chemical polymerization; ^{c)}3-electrode measurement; ^{d)}2-electrode measurement.

applications. The reasons for this stem mainly from the relatively high theoretical specific capacity of PANI (compared to those of e.g. PPy and PTP), its processability and chemical stability in air as well as its high conductivity and favorable electrochemical cycling characteristics.^[90–93] The electrochemistry of PANI is, on the other hand, more complex than that of e.g. PPy and PTP since at least two redox reactions and several oxidation states of PANI – including the fully reduced leucoemeraldine form, the intermediate emeraldine form and the fully oxidized pernigraniline form – need to be taken into account.^[90,91] In addition, at least, the former two oxidation states are both involved in protonation-deprotonation equilibria which further complicate the electrochemistry of PANI. While the protonated emeraldine salt form is conducting, all the other forms of PANI are non conducting which means that, unlike for PPy and PTP, the conductivity and thus the electroactivity of PANI films depends on the pH. It has, however, been pointed out^[94] that PANI films can be cycled even at pH values as high as 9 provided that the films are only switched between their leucoemeraldine and emeraldine states and that the loss of electroactivity, often reported for pH values above 3 to 4, hence is unlikely to be caused by a deprotonation of the emeraldine salt. The loss of the electroactivity is more likely to be due to a rapid degradation of the polymer at high pH values.

Several groups have investigated the possibilities of improving the electrochemical properties of PANI by controlling the morphology of the deposited films. A porous PANI material with a specific surface area of 211 m² g⁻¹ was prepared^[38] employing sodium dodecylsulfate as a soft template. Using a three-electrode setup, a specific capacitance of 1570 F g⁻¹ could be reached using a current density of 10 mA g⁻¹. A 20% loss of capacitance was found during 300 cycles at a current density of 100 mA g⁻¹ but the capacitance was still found to be 606 F g⁻¹ after 1000 cycles. It is thus clear that large surface-area PANI films can be made merely by controlling the electrodeposition conditions.

PANI nanofibers, obtained by a straightforward seeding process, were reported^[95] to yield capacitances of up to 122 F g⁻¹ for emeraldine HCl nanofibers. The latter PANI fibers had an average diameter ranging from 20 to 60 nm and it was proposed that the seeding resulted in PANI polymerization first on the surface of the nanofiber seed templates. The latter effect is very interesting as it may explain the well-known influence of the polymerization conditions on the properties of conducting polymers.

In an investigation of the theoretical and experimental capacitance of PANI nanofibers in H₂SO₄, yielding 2000 and up to 608 F g⁻¹, respectively, it was proposed^[96] that the too low experimental capacities for PANI were due to limited mass transport rates of anions and too low PANI conductivities. Since the theoretical value was based on a 100% oxidation of the PANI nanofibers, implying an oxidized state containing one counter ion for each nitrogen atom, the theoretical value is clearly unrealistic. The experimental results should therefore rather be compared with theoretical values, e.g. 750 F g⁻¹,^[9] based on more realistic doping levels. Nevertheless, as the specific capacitance was demonstrated to decrease significantly with increasing scan rates (between 20 and 200 mV s⁻¹), the results did indicate increasing problems with mass transport

limitations for increasing scan rates. The latter hence shows that this problem may be seen also with PANI nanofibers, most likely depending on the thickness, conductivity and porosity of the particular nanofibers.

PANI layers of different morphologies, from open to sponge-like structures to more compact and pebble-like surfaces have been compared^[97] as cathode materials together with a Zn anode in a NH₄Cl/ZnCl₂ electrolyte. It was concluded that the charging/discharging of the PANI layers was limited to a relatively thin layer at the polymer/solution interface. Specific charge capacities up to 170 mA h g⁻¹ could be reached for porous structures while specific capacitances of up to about 885 F g⁻¹ were obtained based on charge-discharge curves. In the battery mode, a 20% capacity loss was seen during the 20 first cycles which was ascribed to the release of low-molecular weight polymer chains trapped within the polymer matrix. The need for a good and reliable contact between the PANI layer and the substrate was also stressed based on the results of ac impedance measurements before and after cycling of the materials. This finding and the hypothesis regarding the release of low-molecular fragments are very interesting since these issues will affect the electrochemical stability of the material. The release of small polymer fragments may in fact explain some of the self-discharge problems observed for conducting polymers.

Ordered whisker-like PANI, grown on mesoporous carbon, with a specific capacitance of up to 940 F g⁻¹ for the composite and 1221 F g⁻¹ with respect to PANI have also been described.^[37] When increasing the current density from 0.5 to 5 A g⁻¹, the composite capacitance decreased from 940 to 770 F g⁻¹ and the loss of capacitance after 3000 cycles was about 5% employing 5 A g⁻¹. The high capacitance, rate capability and good cycling stability stress the importance of using sufficiently porous polymers in which the electrolyte is in good contact with the polymer.

Higher specific capacitances of up to 2200 F g⁻¹, recorded at a current density of 0.67 A g⁻¹, were reported^[16] for thin porous PANI layers deposited on a hierarchically porous carbon monolith which served both as the current collector and substrate. As is seen in **Figure 1**, showing the cyclic voltammograms, charge and discharge curves and the specific capacitances as a function of the specific current, the porous composite (denoted HPCM-1 in the figure) resulted in a significantly better performance than the corresponding composite based on a non-porous carbon monolith (denoted NPCM in the figure). The carbon monolith had a surface area of 277 m² g⁻¹ and a pore volume of 0.47 cm³ g⁻¹ while the diameters of the meso- and macropores were about 7 nm and 1–4 μm, respectively. A specific capacitance of 1270 F g⁻¹ was obtained even at a current density of 66.7 A g⁻¹ and at a specific power of 47 kW kg⁻¹, the specific energy was still as high as 173 Wh kg⁻¹. The results were explained based on the unique structure of the monolith facilitating fast penetration of the electrolyte to the PANI layer. Good cycling stability, i.e. a 10% loss in the specific capacitance over 1200 cycles were likewise demonstrated. Rather moderate capacitances of up to 35 F g⁻¹ were, however, obtained when the normalizations were carried out with respect to the weight of the composite rather than that of the active PANI layer. The fact that the a porous electrolyte filled structure was employed also means that the specific capacitance per weight of a complete

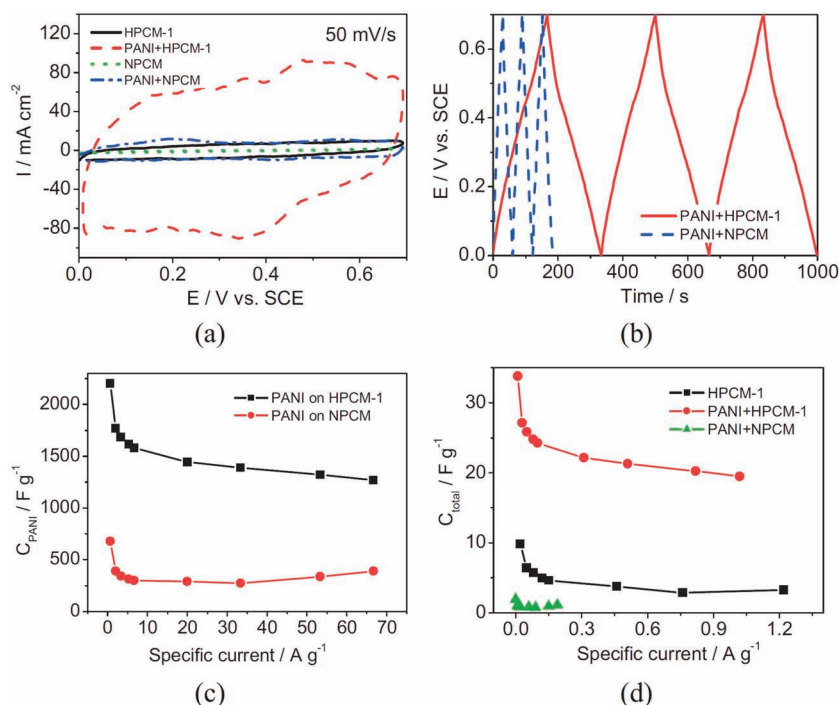


Figure 1. Comparisons of porous (PANI + HPCM-1) and nonporous (PANI + NPCM) PANI carbon monolith composites based on cyclic voltammograms recorded at a sweep rate of 50 mV s⁻¹ a), charge-discharge curves obtained with a current of 1 mA b), the PANI specific capacitance as a function of the specific current c) and the composite specific capacitance as a function of the specific current d). Reproduced with permission from [16].

device would be rather low. Nevertheless, the concept very nicely demonstrates that porous structures facilitate the rapid movements of ions required during fast charge and discharge reactions.

In a recent publication, a thin layer of PANI on the surface of a three-dimensionally ordered macroporous carbon was studied as an electrode material for supercapacitors.^[17] A specific capacitance of 1490 F g⁻¹ (at a current density of 0.5 A g⁻¹) was reported for the prepared composite although it was found that most of the pores of the carbon substrate were closed after the deposition of thick PANI layers. The latter also resulted in a loss of capacitance retention at increased rates. The power density was stated to be 3.0 kW kg⁻¹ and the specific energy density 182 Wh kg⁻¹ based on the PANI weight of one electrode. The capacitance for the composite was 352 F g⁻¹ employing a current density of 0.5 A g⁻¹ which corresponded to a specific energy density of 49 Wh kg⁻¹. It was found that 85% of the capacitance remained after cycling for 1000 cycles. It is thus clear that relatively high specific capacitances and promising stability can be reached with porous PANI materials although more work is needed to optimize the pore distributions of these materials.

Studies on PANI composites with single-walled CNTs have demonstrated^[54] that specific capacitances and specific power values of 485 F g⁻¹, and 2.25 kW kg⁻¹, respectively, can be realized. The latter results were found for a composite composed of 73 wt% PANI for which a loss of 5% of the specific capacitance was seen during the first 500 cycles. These results are consequently analogous to the results obtained for composites of PPy

with CNTs in that improved stability generally are seen for the CNT composites compared to for the pristine polymers.

In addition, composites composed of graphene and PANI have been prepared using a microwave-solvothermal approach.^[98] For a 50:50 wt% graphene PANI composite, a specific capacitance of 408 F g⁻¹ could be obtained as compared to 100 F g⁻¹ for pristine graphene. Composites with lower concentrations of PANI were also tested in Li-ion batteries in an attempt to improve the cycling stability of graphene anodes. A nanocomposite of graphene and PANI nanofibers prepared by chemical oxidation of aniline in the presence of graphene oxide was found^[99] to yield a specific capacitance of 480 F g⁻¹ at a current density of 0.1 A g⁻¹. As the work on composites containing graphene and conducting polymers still is in its development phase, significant improvements of the electrochemical properties can be expected. It also remains to be seen if graphene is a suitable and practical material for real devices.

PANI-based electrode materials are—due to their high specific capacitances and versatility—very interesting and recent research clearly shows that the stability and rate capability of these materials can be improved by using nanofibers or different carbon composites. Its drawbacks are analogous to those of PPy and PTP and mainly involve stability problems in addition to a complex pH dependent interplay between the different redox states. **Table 2** summarizes recent literature data on PANI based electrodes for supercapacitors and battery devices.

2.3. PTP Based Electrode Materials

PTP and its derivatives, discovered in the mid 1980s,^[6,74,100] constitute a group of sulfur-containing heterocyclic conductive polymers which, together with PPy and PANI, is among the most commonly investigated non-metal materials for energy storage. Apart from a high conductivity (≤ 500 S cm⁻¹),^[101,102] the greatest advantage of PTP stems from the possibility of utilizing not only p-doping/undoping but also n-doping/undoping to store charge, as this is not feasible either with PPy or PANI. **Figure 2** shows a typical cyclic voltammogram of PTP featuring both p- and n-doping.^[103] Whereas the p-doping relates to reversible intercalation of ions via oxidation of ECPs at anodic potentials, the n-doping concerns reversible intercalation of ions via reduction of ECPs at cathodic polarization. Thus, both the p- and n-doped states are conductive whereas the undoped state is non-conducting. The attainment of the n-doped state generally requires relatively high cathodic potentials and can therefore only be reached for very few types of ECPs, e.g. polyacetylene, poly-p-phenylene, and PTP. However, only the PTPs exhibit sufficient stability to be employed in industrial applications.^[103,104]

The choice of the electrolyte is crucial for obtaining high efficiencies for PTP energy storage devices. The most commonly used non-aqueous solvents include acetonitrile, propylene carbonate, or ethylene carbonate as well as methylene chloride. It, however, seems that acetonitrile is the preferred non-aqueous solvent due to its wide stable voltage window and high solution conductivities as compared to propylene carbonate.^[104] The type of cation used to achieve n-doping appears to have significant effect on the overall performance of PTP systems. For instance, systems based on tetraalkylammonium salts in a suitable solvent are generally preferred to other salts, especially those of alkali metals, e.g. Li^+ , because the latter ions have large solvation

shells which hamper n-doping.^[104] As for the anion, BF_4^- and PF_6^- are quite common even though other anions such as trifluoromethanesulfonate CF_3SO_3^- have been claimed^[104,105] to be advantageous for n-doping. It should, however, be stated that despite all improvements, the n-doped states are still extremely sensitive to overreduction and readily undergoes irreversible destruction during repeated cycling whereas the p-doped states generally are stable.^[106,107] Further, the stability of the n-doped states is also more dependent on the size of the counter ion and the solvent properties.^[21,108]

In analogy with most other conducting polymers PTP can be synthesized both chemically and electrochemically. It has

Table 2. Literature data on PANI-based electrodes for supercapacitor or battery applications.

Material	Capacitance [F g ⁻¹]	Capacity [mAh g ⁻¹]	Energy density [Wh kg ⁻¹]	Power Density [kW kg ⁻¹]	Remarks	Ref.
Nanofibrous PANI ^{a)}	609 ^{d)}	—	26.8 ^{d)}	—	Prepared by a pulsed galvanostatic method, capacitance and specific energy density w.r.t PANI mass	[36]
PANI nanofibers ^{b)}	122 ^{c)}	—	—	—	Mass of PANI	[95]
Whisker-like PANI, on mesoporous carbon ^{b)}	940 ^{c)}	—	—	—	Mass of PANI	[37]
PANI with single-walled CNTs ^{a)}	485 ^{c)}	—	228 ^{c)}	2.25 ^{c)}	Mass of PANI	[54]
Thin porous PANI on hierarchically porous carbon monolith ^{a)}	2200 ^{c)} , 1270 ^{c)}	—	173 ^{c)}	47 ^{c)}	Mass of PANI	[16]
PANI layers vs. Zn anode ^{a)}	885 ^{c)}	170 ^{c)}	170 ^{c)}	—	In $\text{NH}_4\text{Cl}/\text{ZnCl}_2$ electrolyte, capacitance based on charge-discharge curves. Unknown normalization method.	[97]
PANI nanofibers ^{a)}	608 ^{c)}	—	—	—	In sulfuric acid, mass of PANI	[96]
PANI on stainless steel ^{a)}	248 ^{d)}	—	—	—	Mass of PANI	[96]
PANI and graphene composites	408 ^{c)}	—	—	—	Prepared by a microwave-solvothermal approach. Mass of composite	[98]
PANI layer on three-dimensionally ordered macroporous carbon ^{a)}	1490 ^{c)}	—	182 ^{c)}	3 ^{c)}	Mass of PANI	[17]
PANI/graphene nanofibers ^{b)}	480 ^{c)}	—	—	—	Prepared by chem. ox. of aniline in presence of graphene oxide. Mass of PANI	[99]
Porous PANI ^{b)}	1570 ^{c)}	—	—	—	Mass of PANI	[38]
PANI anode on Pt, poly-1-naphthol cathode ^{a)}	—	150 ^{d)}	113 ^{d)}	9 ^{d)}	Non-aqueous device Mass of PANI and 1-naphthol	[20]
Polyindole and PANI ^{b)}	—	65 ^{d)}	—	—	Mixed with graphite or carbon black, normalized w.r.t. PANI mass	[160]
PANI nanofibers and nanotubes	—	75.7 ^{d)}	—	0.227 ^{d)}	Made by evaporation of a PANI solution Measured vs. Li electrode during discharge. Mass of PANI	[161]
PANI doped with dimethyl sulfate ^{b)}	115 ^{d)}	80 ^{d)}	—	—	In Li ion battery and in symmetric supercapacitor, 5000 cycles	[56]

Table 2. (Continued)

Material	Capacitance [F g ⁻¹]	Capacity [mAh g ⁻¹]	Energy density [Wh kg ⁻¹]	Power Density [kW kg ⁻¹]	Remarks	Ref.
Porous PANI nano-wires ^{a)}	700 ^{d)}	—	10 ^{d)}	—	Electrochemically grown in alumina templates, symmetric supercap, mass of PANI	[93]
PAA doped PANI ^{b)}	5.05 ^{d)}	—	—	—	Symmetric supercapacitor	[158]
Nafion encapsulated PANI nanofibers ^{b)}	175 ^{d)}	—	—	—	Fully flexible symmetric supercapacitor. From charge-discharge at 1 mA cm ⁻²	[55]
PANI on activated porous carbons ^{a)}	160 ^{d)}	—	—	—	Normalized using the PANI mass of one electrode	[57]
PANI composite with Bucky paper ^{b)}	424 ^{d)}	—	—	—	From charge-discharge curves in 1 M H ₂ SO ₄ in symmetrical setup, unknown normalization	[43]
PANI-CNT paper-like composite ^{b)}	31.4 ^{d)}	—	7.1 ^{d)}	1.0 ^{d)}	Values for device	[26]
PANI/PANI ^{a)}	—	—	3.13 ^{d)}	10.9 ^{d)}	Mass of PANI	[40]
PANI on graphene paper ^{a)}	233 ^{d)}	—	—	—	From CV in 1 M H ₂ SO ₄ Mass of paper electrodes used	[41]

^{a)}Electrochemical polymerization; ^{b)}Chemical polymerization; ^{c)}3-electrode measurement; ^{d)}2-electrode measurement.

been claimed^[109] that bithiophene monomers produce ECPs with better conductivity than both thiophene and terthiophene monomers. To overcome the meager cycling stability of PTP as well as improve some other properties such as the solubility in common solvents, infusibility, and compactability, various substituted PTP have received considerable interest. PEDOT is considered as one of the most stable PTP types and has been used in various designs of energy storage devices.^[110] It should be noted that the post-synthesis processability of PTP can be improved by using alkyl substituted PTP, e.g. poly-3-octyl TP, which is soluble (in CHCl₃) and fusible and therefore easily can be applied on the surface of various substrate materials.^[111–114] The use of other soluble PTPs have also been described.^[115] It has been suggested that weakly electron donating groups, such as alkyl ones, improve both the solubility and fusibility^[116–118]

while strongly electron donating groups, such as alkoxy moieties, greatly diminish the oxidation potential as well as lower the band gap energy.^[119–121] It was also shown^[122] that, by introducing cyanovinylene groups as well as alternating repeat of donor/acceptor units in PTP, an enhanced π -conjugation can be achieved. 5,5'-bis(methylthio)-2,2'-bithiophene, with a theoretical specific capacity of 209 mAh g⁻¹, has also been proposed^[123] as an electrode material for batteries and supercapacitors.

A porous poly(tris(4-(thiophen-2-yl)phenyl)amine) film on gold or alumina porous substrates has been noted^[39] to exhibit extremely high capacitances (i.e. 990 F g⁻¹), comparable with those for RuO₂, for 20 nm thick coatings of dendritic PTP.^[39] The power and energy densities were found to be 6.0 kW kg⁻¹ and 25 Wh kg⁻¹, respectively. This was ascribed to the presence of three polymerization sites present in the dendritic monomer which allowed formation of secondary structures with higher degree of order than those observed with linear polymers.

More recently, deposition of ultrathin coatings of PPy and PEDOT on electrospun nanofibers were demonstrated^[15] employing a vapor-phase polymerization technique. The thickness of the coating could be varied from 5 to 12 nm and the charge storage capacity was reported to be 32 mAh g⁻¹ with a 97% reversibility. This work is hence similar to the work on thin-layers of PPy and PANI previously discussed.

One important limitation of using p/n doped systems in electrochemical capacitors, besides the poor stability of the n-doped state, is the substantially lower capacitance of the latter state as compared to the p-doped state. The capacitance of the n-doped state is sometimes as low as 1/10 of that of the p-doped state.^[124] By introducing electron-withdrawing groups, such as 3,4,5-fluorophenyl groups, into the backbone of PTP, this effect can, however, be diminished. Further, by introducing groups with high electron affinity, e.g. fluorenone as well as oxadiazole, it has recently been reported^[123] that n-doping levels even somewhat higher than for the p-doping (1.8 e⁻ vs. 1.1–1.3 e⁻ per

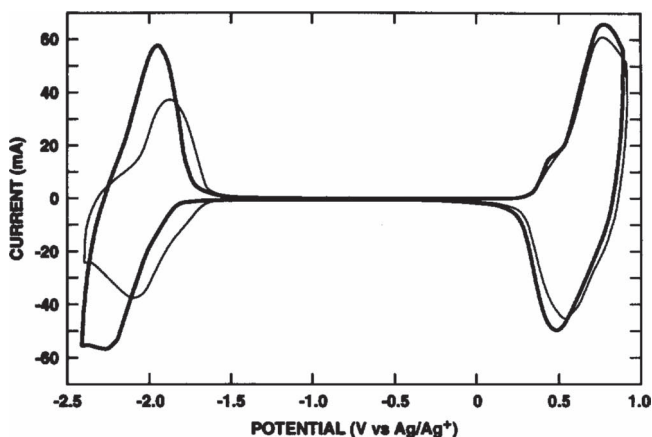


Figure 2. Typical cyclic voltammogram for PTP featuring both p- and n-doping. Adapted with permission from: [103] Copyright 1993 Pergamon Press Ltd.

repeat unit) can be reached. It was suggested that the presence of electron-withdrawing groups caused the onset of p-doping and n-doping to shift to higher positive potentials enabling open circuit voltages as high as 4.2 V.

To improve the electrochemical performance, many groups^[53] have tried to prepare PTPs with very large surface areas along the lines already discussed for PPy and PANI. One promising approach involves the use of a PEDOT-PSS polymer gel cross-linked with Mg^{2+} ions^[53] yielding a 25-fold increase of the capacitance in the swollen matrix as compared to the non-swollen system. However, as can be expected, the concept has the drawback that swollen systems accommodate large amounts of water which makes the electrodes heavier and therefore decreases their specific energy densities. Other groups have made PTP nanorods and nanotubes to enhance the charge storage capacity and the power density. Template based methods of making PmetTP was described already in 1994^[125] and recent publications in the field^[30,110] have corroborated this approach further. Template growth of nanotubes and nanorods due to solvophobic and electrostatic interactions has also been described.^[30,110] In this way, the growth of the conducting polymer is highly controlled and preferential along the pore walls of the template, and by varying the concentration and electropolymerization potential, both nanotubes and nanorods can be obtained. **Figure 3** shows the SEM and transmission electron microscopy (TEM) images of PEDOT nanotubes and nanorods as obtained by template-based growth mechanism at varying oxidation potentials.^[110] Nanotubes are typically obtained at high potentials and low concentrations while nanorods are obtained at low potentials and high EDOT monomer concentrations. For a conventional PEDOT film it usually takes 1–2 s to change the color from blue to transparent (as a result of its oxidation), whereas for nanotubes only about 10 ms is needed due to the short diffusion pathways for the counter ion.

It can be concluded that PTPs, thanks to their possibilities of n-/p-doping and great flexibilities with respect to their chemistry and optimization of properties, constitute promising electrode material alternatives to PPy and PANI as well as to activated carbons with high surface areas and possibly, but less likely, also to rare metal oxides. More work is still needed to stabilize the n-doped PTPs. An overview of the characteristics of various PTP electrode materials is given in **Table 3**.

2.4. Conducting Polymer Coatings on Cellulose

In the development of paper-based flexible energy storage devices, composites of conducting polymers with cellulose are particularly interesting chiefly as the procedures for manufacturing these composites are relatively straightforward and consequently should be relatively inexpensive. After discussing the most commonly used conducting polymer materials, we now focus on the reasons for using cellulose as a substrate for conducting polymers and the manufacturing of cellulose and conducting polymer composites suitable for use in flexible batteries and supercapacitors.

2.4.1. Cellulose as Substrate for Conducting Polymer

Due to the abundance of cellulose fibers in nature and ample variability of cellulose products, cellulose is a material of enormous industrial importance. There are several types of pure cellulose (I–VI), let alone various substituted cellulose types, i.e. cellulose esters, etc. In this section, only the native cellulose, i.e. cellulose I, will be discussed because it is this type of cellulose which is most commonly used in paper products. Whereas cellulose fibers are inherently non-conductive, they are widely known for their intrinsic mechanical strength and flexibility,

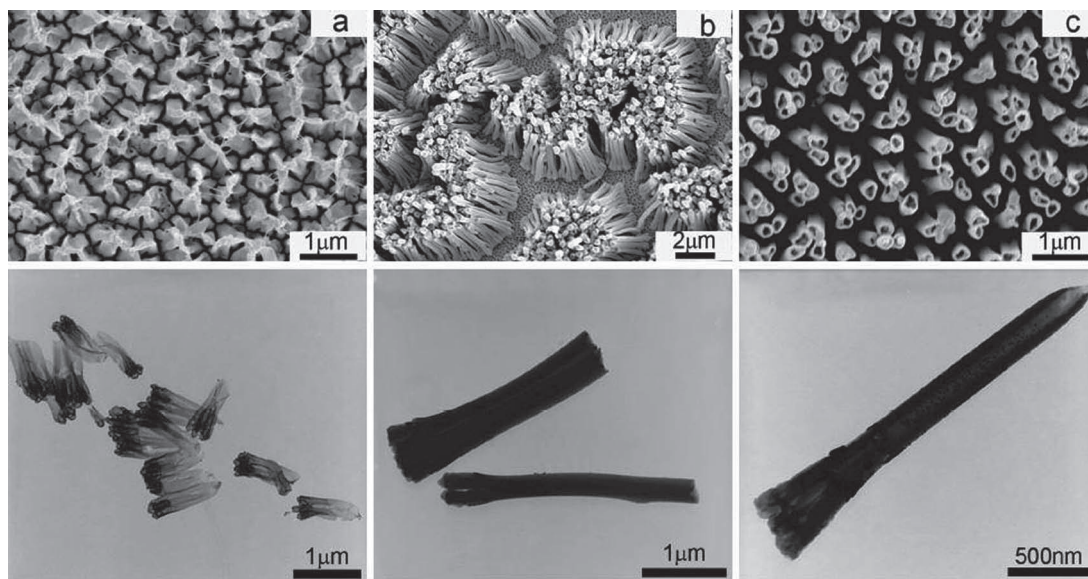


Figure 3. SEM (upper) and corresponding TEM (lower) images of PEDOT nanotubes and nanorods as obtained by template-based growth mechanism at varying oxidation potentials. Adapted with permission from [110]. Copyright 2008, American Chemical Society.

Table 3. Literature data on PTP based electrodes for supercapacitor or battery applications.

Material	Capacitance [F g ⁻¹]	Capacity [mAh g ⁻¹]	Energy density [Wh kg ⁻¹]	Power Density [kW kg ⁻¹]	Remarks	Ref.
PTP ^{b)}	260 ^{c)}	40 ^{c)}	—	—	From CV	[105]
PFTP ^{b)}	110 ^{c)}	7 ^{c)}	—	—	From CV, graphite additive	[105]
PTP ^{a)}	—	—	110 ^{d)}	—	Mass of active material	[151]
PTP ^{a)}	—	—	75 ^{d)}	300 ^{d)}	Mass of active material	[151]
PmetTP p-doped ^{a)}	220 ^{c)}	62 ^{c)}	—	—	From CV	[163]
PmetTP n-doped ^{a)}	165 ^{c)}	26 ^{c)}	—	—	From CV	[163]
PFTP p-doped ^{a)}	95 ^{c)}	19 ^{c)}	—	—	From CV	[163]
PFTP n-doped ^{a)}	80 ^{c)}	9 ^{c)}	—	—	From CV	[163]
PmetTP/PmetTP ^{a)}	37 ^{d)}	—	—	—	From charge-discharge curve of a device	[163]
PFTP ^{a)}	—	—	—	35 ^{d)}	From RC constant, Mass active material	[103]
PDTT ^{a)}	15 ^{d)}	—	18 ^{d)}	1.04 ^{d)}	From CV, mass of active material	[21]
PEDOT nanotubes ^{a)}	132 ^{c)}	—	27 ^{c)}	10.5 ^{c)}	Mass of PEDOT electrode material	[110]
PEDOT nanotubes ^{a)}	132 ^{d)}	—	5.6 ^{d)}	25 ^{d)}	Mass of PEDOT	[30]
PEDOT/PPy ^{a)}	230 ^{c)} , 276 ^{d)}	—	—	13 ^{c)}	From CV or charge-discharge curves, mass of active material	[101]
PEDOT nanofibers ^{b)}	—	30 ^{c)}	—	—	Mass of PEDOT	[166]
PEDOT on plastic film ^{b)}	—	—	4 ^{d)}	2.5 ^{d)}	Mass of active material	[156]
PFPT/PFTP on carbon fibers ^{a)}	—	14.4 ^{d)}	39 ^{d)}	—	Mass of active material	[104]
PEDOT/SWCNT ^{a)}	200 ^{c)}	—	—	—	from CV mass of one electrode composite	[102]
POC ₁₀ DASTT/PPy ^{a)}	—	45.2 ^{d)}	—	—	Mass of active material	[61]
POC ₁₀ STT/PPy ^{a)}	—	94.7 ^{d)}	—	—	Mass of active material	[61]
PMetTP/PMetTP ^{a)}	616 ^{d)}	—	—	9.3 ^{d)}	Mass of active material	[106]
PTP on graphite fibers ^{a)}	—	11.5 ^{d)}	28.5 ^{d)}	—	Mass of active material	[22, 23]

^{a)}Electrochemical polymerization; ^{b)}Chemical polymerization; ^{c)}3-electrode measurement; ^{d)}2-electrode measurement.

which makes them a suitable substrate material to reinforce brittle conductive polymers such as PPy, PANI, PTP and their likes. The inclusion of small amounts of cellulose whiskers was found advantageous for PPy^[126] since the reinforcement of the conductive polymer with cellulose whiskers resulted in a significant increase of the Young's modulus, reduced elongation at break, and increased tensile strength. Cellulose-ECP composites can be molded in different shapes to obtain conductive paper material which can be either directly used as a working electrode *per se* or function as an underlying conductive substrate material for electrochemical deposition of various metals, e.g. Cu or Ag.^[127]

ECPs generally have poor post-synthesis processabilities due to their infusible properties, brittleness, and low solubility in most solvents.^[128] Whereas a method of depositing PANI from toluene solution on cellulose aerogels was recently described,^[129] direct *in situ* chemical polymerization is still considered as the most attractive route of coating cellulose fibers. When direct *in situ* polymerization is of concern, three strategies can be employed: (i) mixing the cellulose with the monomer solution followed by addition of the oxidant^[130–132] (ii) soaking the cellulose in oxidant followed by adding the monomer solution^[133] and (iii) soaking the cellulose in oxidant

followed by deposition of the monomer from vapor.^[134,135] It, however, seems that the first approach is the most efficient and rapid method for obtaining cellulose composites with highest conductivities.

It is important to realize that the direct chemical polymerization of pyrrole on cellulose fibers employing the most commonly used oxidants such as iron (III) chloride, ammonium persulfate, etc, occurs at low pH (typically pH ~ 2), which is a strong limitation when for example employing inkjet printing technology due to the corrosive nature of oxidants.^[135] Furthermore, the aggressive acidic environment is potentially detrimental for cellulose fibers and has been suggested to cause degradation of cellulose and thus deterioration of the tensile strength of cellulose composites with ECP.^[136] After fully covering the individual cellulose fibers with ECP, the mechanical properties of the paper sheets usually become less favorable.^[52] Further, cellulose fiber length and fiber thickness as well as the degree of crystallinity of the cellulose are all anticipated to influence the tensile strength of the final conductive paper sheet. In order to improve the tensile strength of PPy-cellulose sheets, it has been suggested to blend a fraction of the bare cellulose fibers with those coated with PPy while still retaining the overall conductive properties of the composite.^[137,138]

2.4.2. Deposition of Thin Layers of Conducting Polymer on Cellulose Fibers

Several methods have been suggested in the literature to achieve layer-by-layer coating of cellulose fibers with ECP, which include (i) deposition from depleted bulk solution^[139–141] (ii) vapor polymerization^[135,142] and (iii) deposition from polymer solutions in organic solvents.^[129] The deposition from depleted bulk solution employs polymerization-induced adsorption of short soluble oligomers of PPy from a transparent supernatant solution formed following polymerization of pyrrole monomers in copper (II) chloride solution in isopropanol and removal of precipitated bulk polymer. The solution of soluble pyrrole oligomers is then brought in contact with cellulose substrate onto which the polymerization further proceeds to form a homogeneous and ultrathin coating of PPy on individual cellulose fibers.

It infers from above that, when employing direct chemical polymerization process, it is important that the polymerization occurs on the individual cellulose fibers rather than in the solution. As for the mechanism of coating different substrates with PPy, it was suggested that PPy oligomers adsorb to the substrate once their length makes them insoluble, with subsequent oligomers preferentially adsorbing to the PPy nucleation points.^[73] The latter mechanism is the foundation for coating cellulose fibers from depleted bulk solutions as discussed above. Therefore, the affinity of monomers and/or oligomers for the surface of cellulose fibers appears to be crucial. It is commonly conceived that there is a strong chemical interaction between the NH groups in pyrrole and available OH groups abundantly present at the surface of cellulose fibers.^[130] X-ray photoelectron spectroscopy studies conducted on cellulose fibers coated with PANI supported this hypothesis as manifested by a shift in the primary O1s peak relating to C–OH bonds, from 533.3 to 530.6 eV for cellulose and the PANI-coated analogue, which suggests the presence of chemical bonding between available OH groups in cellulose and NH groups in PANI.^[127]

The effect of the properties of the cellulose substrate—such as pulp type, fiber length, fines content, and fiber curl—on the conductivity of the PPy-fiber composite has been investigated.^[143] The type of cellulose pulp and degree of curl were found to only negligibly influence the conductivity of the composite, whereas the amount of fines and fiber length appeared to have a measurable effect. The latter effects were attributed to different propensity for monomer retention on cellulose fibers during polymerization. It was suggested that shortening of fiber length as well as increasing the fraction of fines were favorable for reducing the resistivity of the composite. However, it was also found that when too short fibers were employed, their ability to form continuous network was hampered.

By polymerizing PPy in the presence of cellulose nanofibers, a highly porous, mechanically robust conductive paper material of large charge capacity can be obtained.^[12,62,144–146] As a substrate, cellulose I extracted from *Cladophora* green algae was employed. The latter cellulose is a naturally occurring nanocellulose material with a high surface area ($\sim 100 \text{ m}^2 \text{ g}^{-1}$) and a high degree of crystallinity ($\sim 95\%$ as measured by XRD). The specific surface area of the obtained cellulose composite was up to $80 \text{ m}^2 \text{ g}^{-1}$ and the conductivity was $\sim 1 \text{ S cm}^{-1}$. **Figure 4**

shows SEM and TEM images of the obtained PPy coated cellulose fibers. As will be further described below, the composite exhibited good electrochemical properties including good cycling and rate capabilities. The high degree of crystallinity of the *Cladophora* cellulose substrate makes it more robust for processing and allows highly flexible black composite paper sheets to be obtained. Recently, high surface area composites of ECPs on cellulose aerogels of microfibrillated cellulose (MFC) were also reported (i) by deposition from PANI toluene solution^[129] and (ii) by direct polymerization of pyrrole monomers on MFC gels with good conductivities and charge capacities.^[52] The MFC based composite exhibited electrochemical properties similar to those of the *Cladophora* composite but the MFC composite was found to be less mechanically stable. PANI coated composites of freeze-dried cellulose nanofibers obtained by acidic hydrolysis with strong mineral acid have also been described.^[147]

In all, the high affinity between ECP monomers and cellulose fibers makes the latter an ideal coating substrate material and opens up for production of a unique class of non-metal based flexible electrode materials.

3. Batteries and Supercapacitors

In the present section we focus on the most recent work regarding the development of prototypes for batteries and supercapacitors based on conducting polymers, conducting polymers coated on carbon materials, as well as cellulose based composites containing CNTs or conducting polymers. Particular attention is paid to the latter two approaches given their potential application with respect to the manufacturing of flexible paper-based energy storage devices.

3.1. Conducting Polymer-Based Batteries and Supercapacitors

The concept of all-polymer based batteries and supercapacitors, which was introduced almost three decades ago,^[6] has recently gained a renewed interest mainly due to the possibilities of manufacturing flexible and environmentally friendly devices. To build an efficient electrochemical device using conducting polymers, three types of systems are usually considered:^[9,104] (i) symmetric p-doped/undoped systems wherein

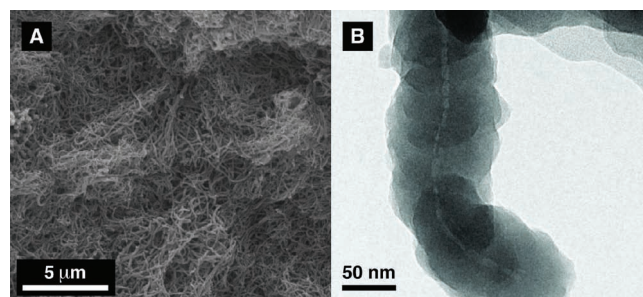


Figure 4. SEM (A) and TEM (B) images of PPy based conductive paper fibres. The back-bone structure in (B) is due to the cellulose fibre. Adapted with permission from: [12] Copyright 2009 American Chemical Society.

both electrodes are made of identical materials; (ii) asymmetric p-doped/undoped systems wherein the cathode and anode are made of different materials; and (iii) symmetric p-doped/n-doped systems. The p-doped/undoped systems typically give a cell voltage of about 1 V and aqueous electrolytes can be used. For the asymmetric designs cell voltages of up to about 1.5 V are possible to reach. Due to the relatively negative potentials needed to obtain the n-doped state, this state can generally only be achieved in non-aqueous electrolytes. However, the benefit of using p/n doped systems often surmounts the shortcomings associated with the increased resistance in non-aqueous electrolytes since a potential difference between the n-doped and p-doped states of PTP (which in contrast to, e.g., PANI and PPy can be utilized in a symmetric p-doped/n-doped system) of about 3 V can be achieved. The latter enables a substantial increase in the energy density of a supercapacitor, as the stored energy is proportional to the square of the cell voltage.^[9] The limited stability of the n-doped state^[9,148] and the lower charge capacity of this state^[9,124] as compared to the p-doped state are, however, still major limiting factors.

3.1.1. Early Prototype Development

The first prototype for a polymer battery was a PANI pellet electrode battery with a capacity of 13 mAh g⁻¹ described already in 1968.^[149] An all-polymeric solid state battery was described in 1981^[150] based on doped polyacetylene electrodes and a polyethylene oxide based electrolyte. Although an open circuit voltage of 2.8 to 3.5 V, a maximum power density of 0.25 kW kg⁻¹ and an energy density of approximately 20 Wh kg⁻¹ were obtained, the low conductivity of the solid electrolyte resulted in a too high internal resistance of the cell. The first battery with PTP as the active material, was described in 1983^[151] and featured an open cell voltage of 3.1 V, a calculated energy density of 75 Wh kg⁻¹ and a maximum power density of more than 300 kW kg⁻¹. The experimental support for these promising claimed values was, however rather weak. Batteries composed of PPy anodes and cathodes and an acetonitrile based electrolyte were described in 1986^[152] and it was concluded that secondary batteries with coulombic efficiencies of 75–90%, but with poor charge retention properties, could be manufactured. Better charge retention properties were subsequently obtained^[153] using dry cells comprising paper composite electrodes containing PPy or PANI. Thin film batteries obtained by sandwiching a Nafion layer between thin layers of PANI coated Nafion membranes,^[154] thin films of PPy and PANI,^[155] or two thin PANI layers^[19] were also demonstrated. High self-discharge rates, most likely due to reactions of the polymers with the electrolyte, were found to be a significant problem with the latter types of batteries.

Symmetric and asymmetric supercapacitors (i.e. type I, II and III capacitors) based on thiophenes were compared^[104] and it was found that energy densities of up to 39 Wh kg⁻¹ could be reached for type III devices while the corresponding values for type I and II devices were 11 and 27 Wh kg⁻¹, respectively. Symmetric PEDOT supercapacitors, obtained after chemical polymerization of the monomer on plastic substrates, were subsequently shown^[156] to have an energy density of up to 4 Wh kg⁻¹ and a power density of up to 2.5 kW kg⁻¹. Since the obtained cell voltage of 0.8 V was considered to be too low it was pro-

posed that asymmetric devices should be used to increase the energy density.

The initial studies on polymer-based batteries and supercapacitors thus indicated that promising energy densities could be obtained but that self-discharge of the systems was a major problem. It was also demonstrated that polymer-based supercapacitors can exhibit interesting power densities but that the realization of stable type III capacitors was difficult due to the instability and relative low specific capacitance of the n-doped polymers.

3.1.2. Recent Conducting Polymer-Based Prototypes

The recent work on the development of conducting polymer-based energy storage devices has involved development of both symmetrical^[30,36,55,79,93,96,106,157,158] and asymmetrical^[13,20,61,101,159,160] batteries and supercapacitors. Although flexible systems have been presented,^[13,27,28,55,61,157,159] very few of these^[61,159] may, however, be classified as prototypes for flexible all-polymer systems as electrodeposition of the polymers on metallic electrodes or metallic current collectors generally has been employed. While some of the most interesting prototypes will be discussed in more detail below, the reader is referred to Tables 1 to 3 for a more detailed summary of the energy storage characteristics of the prototypes discussed in this section.

In the development of flexible polymer fiber, non-aqueous batteries it has been shown^[157] that two PPy films polymerized on platinum wires and separated by a polymeric hollow membrane can yield capacities of about 10 mAh g⁻¹ over 30 cycles. In the latter case, the two PPy films used as the electroactive material contained different anions to increase the cell voltage. This approach is interesting although the cell voltages attainable with this method most likely are relatively small in comparison with those of asymmetric polymer systems. Another proposed method for the preparation of flexible supercapacitors involves encapsulation of PANI nanofibers in Nafion.^[55] The use of processable polyacrylic acid doped PANI composites as electrode materials for supercapacitors,^[158] as well as nucleophilic doping of PANI with dimethyl sulfate,^[56] have also been proposed as a means of facilitating the manufacturing of a flexible system. Since the processability of conducting polymers generally is relatively poor, the latter approaches constitute interesting recent attempts to circumvent this problem. In this context, it is interesting to note that recent work has demonstrated that freestanding flexible and paper-like films of PPy (and PPy films containing LiFePO₄ particles), can be prepared by electrochemical polymerization on stainless steel substrates.^[27,28] While the authors envisioned these as cathodes combined with CNT anodes in soft flexible batteries it is evident that more research is needed to fully characterize these materials in terms of flexibility and stability.

Efforts have been made to develop all-polymer based devices utilizing electropolymerized polypyrrole (PPy) containing two different redox active anions, indigo carmine and 3-ethylbenzothiazoline-6-sulfonate, as thin layer electrodes on gold/titanium coated PET substrates.^[13] An energy density of 8 Wh kg⁻¹ and a power density of up to 10 kW kg⁻¹ were reported. A 50% loss of capacity, ascribed to overoxidation of PPy was, however,

seen after 60 cycles indicating that the stability of the described system needs to be improved significantly. Similar stability problems were noted when using different functionalized poly-erthiophenes (poly(3'-styryl-4,4"-didecyloxyterthiophene) and poly(4,4"-didecyloxyterthiophene)) as anodes versus PPy cathodes.^[61] The polymers were in this case electropolymerized on conducting and flexible mesh substrates (stainless steel and Ni/Cu coated polyester, respectively) and the losses of capacity during cycling were ascribed to mechanical degradation of the polymer. This may have been due to the swelling and shrinking of the polymers during cycling as was proposed to explain the capacity loss seen for a battery consisting of a PANI anode and a poly-1-naphthol cathode.^[20] The latter cell lost 5% of its capacity during a week due to self-discharge which can be considered to be a relatively low rate for this type of devices. A more stable system has been obtained with a claimed all-polymer battery containing a functionalized PTP based anode, a PPy cathode electrode and carbon-fiber mats or Ni/Cu-coated nonwoven polyester current collectors.^[159] The reported discharge capacity was 35.4 mAh g⁻¹ and no loss of capacity was seen after 50 charge and discharge cycles employing a current of 0.05 mA cm⁻². These results are encouraging and represent significant progress toward a flexible polymer-based device.

As has been demonstrated by several groups,^[30,78,93,161] nanotubes and nanofibers of conducting polymers may be produced using deposition in porous alumina membranes. Since this approach results in thin polymer materials with large surface area, these polymers may be of significant importance in the development of flexible energy storage devices with high power densities. PANI nanotubes and nanofibers,^[161] nano-PPy supercapacitors^[78,79] as well as PEDOT nanotubes^[30] have thus been prepared with specific capacitances of up to 700 F g⁻¹.^[93] It was noted that the capacity depended on the morphology of the nanowires and that the morphology could be altered utilizing different electropolymerization potentials.^[93] Due to the limited thickness of the alumina membranes, defining the length of the nanowires, the total power and energy capacity of the capacitors was, however, very limited. A symmetrical supercapacitor-based on PEDOT nanotubes with a power density of 25 kW kg⁻¹ and energy density of 5.6 Wh kg⁻¹ was also obtained.^[30] The latter high power density can be ascribed to rapid charge and discharge of the PEDOT nanotubes made possible by fast transport of counter ions within the porous structure.

It can be concluded that conducting polymer-based materials for flexible batteries and supercapacitors generally should consist of relatively thin polymer films coated on a flexible and electrically conducting substrate with a large surface area. As some carbon materials indeed fit this description, there is currently a large interest in conducting polymer coated carbon materials. These type of materials will therefore be discussed in the next section.

3.2. Prototypes Based on Conducting Polymer Coated Carbon Materials

Energy storage devices comprising electrodes made of conducting polymers and various carbon materials, including for example CNTs, graphite, carbon fibers and graphene, have been

rather extensively studied recently.^[29,40–44] Below (and in Table 1 to Table 3), we present the most important results gained so far for such devices.

Deposition on single-^[43] or multiwalled ^[46,48,49,51] CNTs is by far the most popular approach when using carbon based materials as supports for conducting polymers. One reason for this is that a substrate with a high surface area is generally required to obtain a high specific capacitance. The influence of the macropore surface area of the substrate on the capacitance has consequently been discussed.^[45] In the latter study, the capacitances for PPy modified single wall CNT electrodes were correlated with the BET surface area of the electrode materials and although micropores yielded higher surface areas this did not always result in higher specific capacitances. The capacitance was, on the other hand, found to be proportional to the macropore surface area, which clearly shows that the porosity of the substrate has to be optimized and that a large BET value does not *per se* guarantee a high capacitance. This important conclusion is of course also valid for other types of substrates.

Another related and essential issue concerns the influence of the cell design on the determination of the specific capacitance of conducting polymer/nanotubes composite electrodes.^[49] It has very nicely been demonstrated^[49] that only two-electrode cells yield good estimates of the capacitance of a supercapacitor as the results for PPy composites with multiwalled CNTs in three- and two-electrode cell configurations were 495 and 200 F g⁻¹, respectively. This effect, most likely, explains much of the variation in the reported experimental capacitance values in the literature as the experimental conditions have not always been clearly stated.

Important work regarding the stability of conducting polymer-based supercapacitors has likewise been carried out^[40] involving the influence of the voltage cycling region on the stability of CNT and ECP-based symmetric capacitors. It was concluded that the cycling stability of PPy was good in the 0.4 V region but poor in the 0.6 and 0.8 V regions. Similar results were also obtained for capacitors based on PANI and PEDOT. The phenomenon was ascribed to a shift in the potential of one of the electrodes into a region of electrochemical instability. This effect is generally not seen in three-electrode cycling experiments in which the electrodes are working in a controlled potential range. In the symmetrical capacitor case, the loss of specific capacity was ascribed to an undoping of the negative PPy electrode rather than an ECP degradation process. This very interesting and important finding demonstrates that the potential of each electrode should be monitored during cycling stability investigations.

In addition, there has been research aiming at the development of paper-like materials composed of ECPs and CNTs.^[26,43,47] Thin paper-like films composed of PANI and CNT paper (buckypaper) were thus obtained through a chemical polymerization of PANI on the surface of the paper.^[43] Flexible paper-like PANI-CNT based supercapacitors containing a H₂SO₄ polyvinyl alcohol gel electrolyte have likewise been described.^[26] In the latter case, a specific capacitance of 350 F g⁻¹ was reported for the electrode material while the corresponding value for the entire device was 31.4 F g⁻¹. The latter demonstrates the significant drop in capacitance of a complete device compared to those of the electrode materials, particularly when the latter are

reported with respect to the mass of only the ECPs. The 113 μm thin device, which had a energy density of 7.1 Wh kg^{-1} and a power density of about 1 kW kg^{-1} , exhibited a 8.1% decay in specific capacitance during 1000 cycles. There was a drop in the leakage current from 1.0 mA to 52.1 μA during 15 minutes as well as a rapid drop in the open circuit voltage from about 0.8 V to 0.6 V during several minutes, and after four hours a stable voltage of approximately 0.5 V was reached, corresponding to about 58% of the initial potential. These effects were ascribed to self-discharge caused by impurities in the electrode materials. The open circuit voltage could subsequently be maintained for a day and the decay in the specific capacitance during two months was reported to be 11.4%, presumably due to water evaporation from the electrolyte. These findings, which are very interesting since there are very few other reports on the self-discharge of different devices, clearly show that self-discharge remains to be a serious problem and that more fundamental research is needed to reach an understanding of the reactions causing this effect.

Apart from the development of CNT-based systems, research has been focused on composites of ECPs with carbon fibers,^[14,84,162] activated carbon,^[29,57,83,163] carbon paper,^[21] and more recently graphene.^[41,164] In this process, an all-polymer battery system comprising electrodes made of PPy on graphite fiber substrates and an ionic conducting polymer gel electrolyte has been described^[162] as well as a graphite fibre/PPy symmetric supercapacitor,^[84] for which PPy was chemically polymerized onto a porous graphite fibre substrate. Although carbon fibres generally have a lower inherent capacitance, the use of carbon fibres may be advantageous from a conductivity point of view as the resistances of carbon fibres should be lower than for the CNTs due to the larger diameters of the carbon fibres. These aspects were partly addressed in a study in which several PTP and PTP derivatives were used together with various conductive additives (including activated carbon or graphite) in symmetrical and asymmetrical supercapacitors.^[163] It has also been proposed^[164] that aligned graphene nanosheets facilitate the electronic transport within a PPy and graphene multilayer composite material while the fibrous PPy network ensured good ionic accessibility within the electrodes. This emphasizes the previously mentioned need for porous electronically conducting electrode materials.

The significance of a proper balance between the masses of the positive and negative electrodes was likewise discussed. As the latter ratio will determine the absolute potentials reached by the individual electrodes, it should be possible to set this ratio so that overoxidation of the electrode undergoing oxidation is avoided. Studies involving polymer coatings of different thickness on carbon fibers^[14] have also indicated that some fraction of the PPy layer could not be accessed for larger film thicknesses than 10 nm when employing cyclic voltammetric scan rates up to 200 mV s^{-1} but that the capacitance was close to the theoretical value (i.e. 620 F g^{-1}) for the thinnest films studied. Since the structure of the polymer film depends significantly on the deposition conditions, this conclusion is, however, most likely not valid for other films or other deposition conditions. Other authors have, for instance, reported^[29] that sub-micrometer thin PPy films were required to obtain sufficiently short charging times.

It has been found^[22,23] that the rate of self-discharge of a cell containing PTP on graphite fiber substrates as electrodes and an ionic conducting polymer gel electrolyte depended on the cycling history of the system. Although no explanation was given for this effect, the phenomenon is certainly interesting as it suggest that the self-discharge processes depend on the history of the cell.

3.3. Prototypes Based on Composites Containing Cellulose

At present there is a significant interest in the development of flexible paper-based energy storage devices. In this development, composites containing cellulose and CNTs^[63,65,70,72] and composites containing cellulose and conducting polymers^[12,52,62] have emerged as two promising electrode materials. As the CNT-based composites mainly rely on the double layer capacitance of the carbon material, the theoretical capacitances of the conducting polymer containing composites are generally higher due to the presence of both faradaic reactions and double layer charging. This advantage should, however, be weighed against the higher cycling stability of the CNT-based composites and in the following sections we will therefore discuss the recent progress within both approaches.

3.3.1. Prototypes Based on Composites of CNTs and Cellulose

A bendable nanoporous cellulose paper embedded with aligned multiwalled CNTs has been proposed as the electrode material in supercapacitor and battery devices in which cellulose also serve as the separator and electrolyte carrying material.^[63] In the supercapacitor case, both aqueous and non-aqueous electrolytes were used and specific capacitances of up to 36 F g^{-1} (and energy and power densities of 13 Wh kg^{-1} and 1.5 kW kg^{-1} , respectively) were obtained for the devices. These results clearly demonstrate that the basic components of a supercapacitor can be made from cellulose and cellulose-based CNT composites and that these components can indeed be integrated into mechanically flexible devices. The composite was also employed in a Li-ion battery mode where a capacity of 110 mAh g^{-1} was found during 10 cycles employing a current of 10 mA g^{-1} and 1 M LiPF₆ in EC/DMC as the electrolyte. In the battery, a thin evaporated layer of lithium on the paper served as the anode while the nanocomposite paper was used as the cathode. A supercapacitor-battery hybrid device was also described in which the battery was used to charge the adjoining supercapacitor. These results are thus promising for the development of devices which combine high energy and power densities.

In another study,^[65] regular printer paper conformably coated with CNTs was used as a material for supercapacitors as well as for lightweight current collectors in lithium batteries. Impressive specific capacitances of 200 F g^{-1} , specific energy densities of 30–47 Wh kg^{-1} and specific powers of up to 200 kW kg^{-1} , when operated at 3 V in an organic solvent, were reported when only considering the mass of the CNTs, see Figure 5. A specific energy of 7.5 Wh kg^{-1} was, on the other hand, obtained when using the weight of the complete device which emphasizes the importance of being able to

reduce the weights of all other components than the active material in the devices. A 3% capacitance loss in sulfuric acid electrolyte after 40 000 charge-discharge cycles was found while the corresponding loss in an organic electrolyte was only 0.6% which indicate very good cycling stability. A similar CNT coating approach was also employed^[71] to make printable thin film supercapacitors on plastic (i.e. PET) substrates. Energy and power densities of 6 Wh kg⁻¹ and up to 70 kW kg⁻¹, respectively, were reported utilizing organic electrolytes. Stretchable, porous and conductive cotton and polyester fibers were analogously produced^[70] based on a “dipping and drying” process using single walled CNT ink. The latter process resulted in highly conductive textiles (with conductivities of up to 125 S cm⁻¹) which could be utilized to make supercapacitors both as the active electrode material and as current collectors. Specific capacitances of up to 140 F g⁻¹ were achieved which was stated to be 2–3 times better than with PET substrates. The devices, which were operated with an organic electrolyte, exhibited a cell voltage of about 3 V and could be cycled for 130 000 cycles (at 200 mA cm⁻²) with only a 2% change in the capacitance. The reported specific energy and power densities were approximately 20 Wh kg⁻¹ and 10 kW kg⁻¹, respectively. It was also pointed out that the contribution of single walled CNTs to the total weight of a supercapacitor device is normally only 4 to 10% but that the weight percentage in the cotton based device was up to about 30%. This very nicely shows that the use of cellulose composites can result in significant improvements on the device level.

The rapid recent development of promising composites containing CNTs and cellulose is indeed very interesting for the development of new flexible paper-based energy storage devices. To further increase the specific energy density of the supercapacitors an incorporation of materials such as metal oxides or conducting polymers has been proposed^[70]. This would enable charge to be stored also via surface confined faradaic reactions which would introduce a pseudocapacitance that would increase the total energy storage capacity of the device. There is consequently a clear potential overlap between this research and that involving flexible composites of cellulose and ECPs discussed in the next section.

3.3.2. Prototypes Based on Composites of Conducting Polymers and Cellulose

An alternative approach for the development of flexible cellulose based electrode materials involves the use of a composite

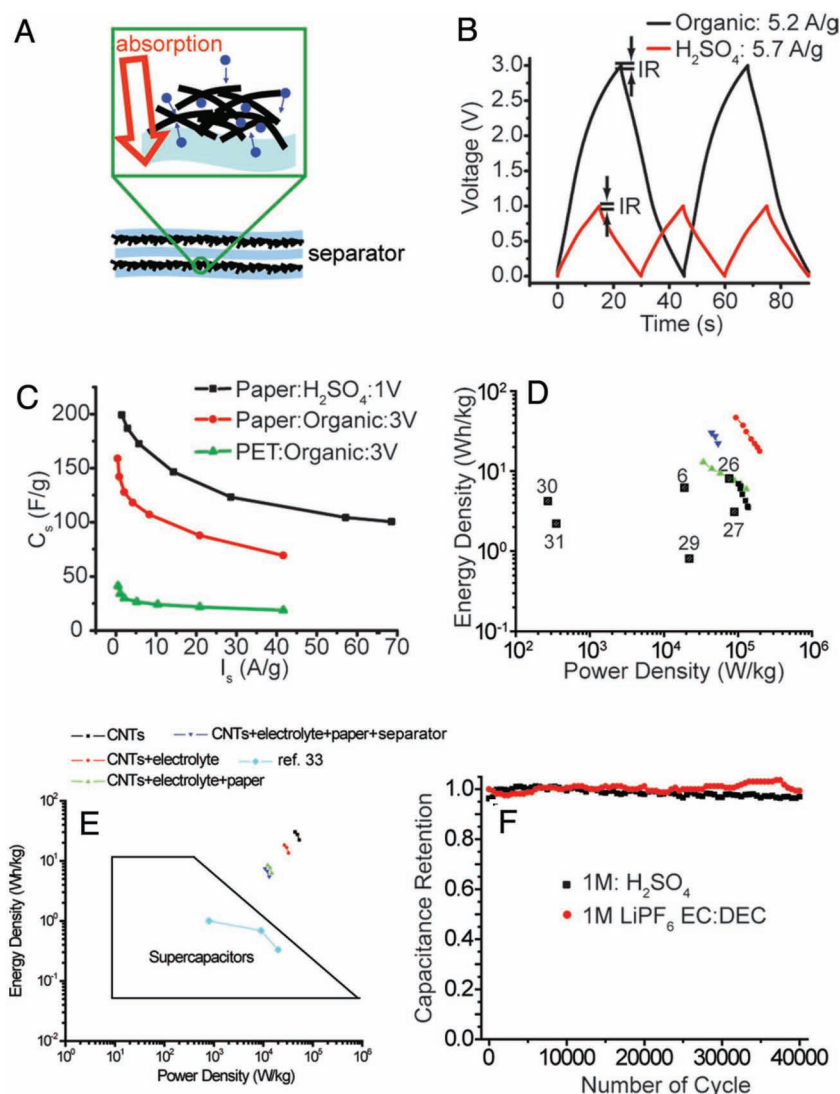


Figure 5. Schematic illustration of a paper-based CNT supercapacitor device a), charge-discharge curves in aqueous (lower curve) and non-aqueous (upper curve) electrolytes b), CNT weight normalized capacitance as a function of the charge-discharge current c), Ragone plot based on the active mass d), device specific Ragone plot e) and cycle life of the supercapacitor device f). Adapted with permission from [65]. Copyright 2009, Proceedings of the National Academy of Sciences of the United States of America (PNAS).

of nanostructured cellulose and PPy prepared by chemical oxidation of pyrrole in the presence of cellulose extracted from the *Cladophora* sp. green algae.^[62] It was demonstrated^[165] that the high BET surface area of the cellulose of about 100 m² g⁻¹ mainly was preserved in the composite which, as can be seen in Figure 4, consisted of cellulose fibers coated by a thin (i.e. 30–50 nm) layer of PPy. The fundamental idea behind this work was to employ the algae cellulose as a template for the generation of thin layers of PPy which would act as the electroactive material in a charge storage device. The porous structure of the composite (which was found to contain about 67% of PPy^[12]) and the thin PPy films would then ensure a rapid mass transport of the ions needed during the oxidation and reduction of the PPy while good overall flexibility of the material would be provided by the cellulose substrate.

A battery comprising two PPy-Cladophora cellulose composites as the two electrodes, and a cellulose separator containing 2 M NaCl as the electrolyte, see **Figure 6**, was found to yield charge capacities of up to 48 mAh g⁻¹ (or a device capacitance of 96 F g⁻¹) per total weight of the PPy active material when galvanostatically cycled between -1 and 1 V.^[12] The cell voltage was approximately 1 V and 94% of the capacity was maintained after 100 cycles employing a current density of 600 mA cm⁻². The fact that the battery was based on cellulose, PPy and salt water clearly shows that devices based on this concept can be made metal-free, provided that a suitable current collector and sealing materials can be found. As can be seen in **Figure 6**, the contacting problem can be solved with current collectors composed of carbon instead of the pieces of Pt employed in the original prototype. Another potential limiting factor for the concept is the access to the algae cellulose. Recently, it was, however, shown that the algae based cellulose matrix can be replaced with a nanostructured wood based nanocellulose^[52] while maintaining the high surface area and the electrochemical properties. The latter should open up new exciting possibilities given the more widespread availability of cellulose from land plants.

As the energy density of this type of cellulose-based charge storage system would be significantly lower than those of many metal-based systems, these paper-based devices will most likely be most interesting for applications where other devices cannot be used, e.g. due to demands for flexibility, conformability and environmental friendliness. Given the well-known problems with the stability and self-discharge of ECP-based batteries and supercapacitors, more fundamental research is, however, still needed before real devices can be manufactured.

4. Conclusions and Outlook

The research on conducting polymer-based charge storage devices is presently undergoing an exciting development as

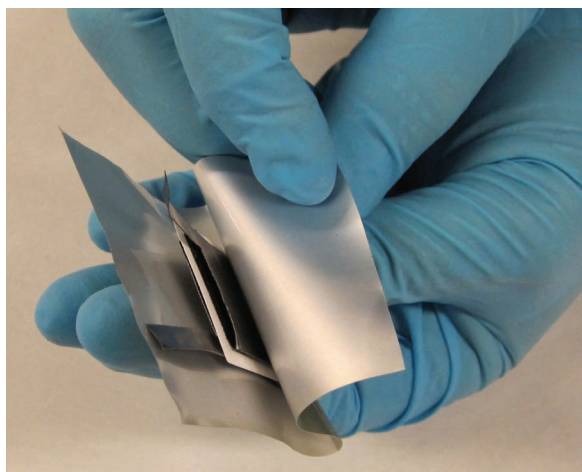


Figure 6. Photograph showing the assembly of a PPy based conductive paper cell with pieces of carbon cloth as current collectors.

new conducting polymer-based composites are being made with improved cycling and rate performances compared to devices based on conducting polymers alone. This suggests that the cycling stability problem, which long has been considered one of the major limitations of conducting polymer-based devices, may be possible to circumvent employing a proper design of the devices. Significant progress has also been made to design devices capable of delivering high power, mainly by the development of better methods for controlling the morphology and thickness of the conducting polymer layers. Surprisingly little attention has, however, been paid to the well-known self-discharge problems associated with conducting polymer-based batteries and supercapacitors. It is evident that more fundamental work is needed to fully understand the reasons for this important, albeit, complex phenomenon. Additional work is also needed to reach a full understanding of the overoxidation processes taking place in conducting polymer containing batteries or supercapacitors at sufficiently high positive potentials. At present, the latter effect and the relatively high self-discharge rates constitute major limiting factors for the application of conducting polymer-based batteries and supercapacitors.

As has been shown in this review, specific capacitances, specific capacities, energy densities and power densities up to about 600 F g⁻¹, 150 mAh g⁻¹, 110 Wh kg⁻¹ and 20 kW kg⁻¹, respectively, have been reported for prototype devices indicating that conducting polymer-based systems can indeed compete with many other charge storage devices, particularly with respect to high power applications. At present, there is also an interesting ongoing development involving the design of flexible cellulose-based charge storage devices, either containing carbon nanotubes or conducting polymers as the active materials. The latter types of devices hold great promise for a number of new applications which are incompatible with conventional contemporary battery and supercapacitor technologies.

Acknowledgements

Funding from the Swedish Foundation for Strategic Research (SSF) (grant RMA08-0025), the Swedish Research Council (VR) (grants 621-2008-3690 and 621-2009-4626) and the Nordic Innovation Centre (NICE) (project no 10014) is gratefully acknowledged. We are also grateful to Dr. Martin Sjödin, Henrik Olsson, Aamir Razaq, Daniel Carlsson and Christoffer Karlsson for valuable discussions regarding conducting polymer-based charge storage devices.

Received: November 8, 2010

Revised: December 9, 2010

Published online: February 10, 2011

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