Facile synthesis of polypyrrole nanofiber and its enhanced electrochemical performances in different electrolytes

S. Sahoo, S. Dhibar, C. K. Das*

Materials Science Centre, Indian Institute of Technology, 721302 Kharagpur, India

Received 10 May 2012; accepted in revised form 16 July 2012

Abstract. A porous nanocomposite based on polypyrrole (PPy) and sodium alginate (SA) has been synthesized by easy, inexpensive, eco-friendly method. As prepared nanocomposite showed fibrillar morphology in transmission electron microscopic (TEM) analysis. The average diameter of ~100 nm for the nanofibers was observed from scanning electron microscopic (SEM) analysis. As prepared nanofiber, was investigated as an electrode material for supercapacitor application in different aqueous electrolyte solutions. PPy nanofiber showed enhanced electrochemical performances in 1 M KCl solution as compared to 1 M Na₂SO₄ solution. Maximum specific capacitance of 284 F/g was found for this composite in 1 M KCl electrolyte. It showed 76% specific capacitance retention after 600 cycles in 1 M KCl solution. Electrochemical Impedance Spectra showed moderate capacitive behavior of the composite in both the electrolytes. Further PPy nanofiber demonstrated higher thermal stability as compared to pure PPy.

Keywords: nanocomposites, polypyrrole, sodium alginate, nanofiber, supercapacitor

1. Introduction

Among different nonstructural morphologies of conducting polymers (CP), one dimensional nanostructures have produced a great deal of research interest as these has offered various potential applications in different fields such as chemical sensor, gas-separation membranes, neuron devices etc. [1–3].

Among various CPs, PPys are well studied because of their good thermal stability, enhanced electrical as well as electrochemical properties, excellent environmental stability [4, 5]. Various approaches for the synthesis of PPy nanofiber have been reported. Several reports are available where PPy nanofibers were prepared by using templates like zeolites, alumina, various nanostructured templates [6, 7]. Some template free approaches for PPy nanofiber synthesis are also reported. Athawale *et al.* [8] has reported the synthesis of PPy nanofiber using ultrasonic wave at room temperature. It was also observed that

with increasing sonication time, the length of the fiber increases. PPy nano-network as well as nanofiber were also prepared by using interfacial and template polymerization technique and investigated as a promising material for device applications [9]. Zang *et al.* [10] has reported a template-free electrochemical one-step synthetic approach to prepare PPy nanofiber in aqueous solution using phosphate buffer solution, with unique chem-physical properties.

Among various energy storage devices of today's world, supercapacitors has been considered as the most widely investigated energy storage devices due to their low maintenance cost, fast charging ability as well as exceptionally high cyclic stability [11, 12]. Supercapacitors are mainly used in various high power equipments like hybrid electric vehicles, cellular phones, laptops etc., basically where fast charging is desirable. It has the ability to fulfill

*Corresponding author, e-mail: chapal12@yahoo.co.in

the gap between batteries and capacitors. However, supercapacitors are now mainly available in two types:

- (1) Electrochemical Double – Layer Capacitor (EDLC) – EDLCs store charges non-faradically. Mainly carbon based materials like activated carbon, carbon nanotube, graphene are used [13–15] as electrode for these type of supercapacitors. Due to high surface area, superior conductivity, high porosity graphene has been considered as an essential candidate for supercapacitor electrode materials. On the other hand, addition of carbon nanotubes can significantly enhance the performances of the EDLC due to its unique properties like nanoporosity, high surface area, and high conductivity [13–15]. In earlier research, activated carbon was also chosen as a part of electrode material because of its high surface area.
- (2) Pseudocapacitor – Pseudocapacitors has the capability to store charge faradically through various charge transfer reactions between electrode and electrolyte. Mainly metal oxides and CPs are used [16–18].

CPs are used as pseudocapacitive electrode materials mainly due to their high specific capacitance, high conductivity in charged state, low Equivalent Series Resistance (ESR). The charge – discharge process in these types of pseudocapacitive materials are basically associated with the insertion – deinsertion of counter ions, arises from the electrolyte [19]. Nanostructured materials are mainly used for energy devices because of their low scale dimension which increases the electrolyte transport rate and therefore enhances the electrochemical performances. The specific surface area and high porosity, which are the two significant properties of the nanostructured materials help to achieve superior electrochemical properties. Materials in nanometer size have the ability to improve electrochemical performances because of their unique conducting pathway, nanoscale dimension, high porosity etc. Gupta and Miura [20] prepared electrode material based on electrochemically deposited polyaniline nanowires on stainless steel and achieved a highest specific capacitance of 775 F/g at 10 mV/s scan rate. Li *et al.* [21] reported porous, mat-like polyaniline nanocomposite, which exhibited excellent specific capacitance of 2093 F/g with long cycle life and fast

charging/discharging. Kuila *et al.* [22] reported a simple approach to synthesize ordered arrays of polyaniline nanorods, which exhibited extraordinary electrochemical properties with an electrochemical capacitance value of 3407 F/g. They have suggested that the small dimension of the electrode material increases the utilization of conducting polymer as electrode material. Overall, nanostructured version of conducting polymer has been considered as an essential component for the preparation of electrode materials for supercapacitor applications.

In this work, we have synthesized PPy nanofiber through a facile chemical route using sodium alginate (SA) as template. Further, it's potential to be used as an electrode material for supercapacitor application has been investigated in two different aqueous electrolytes (1 M KCl and 1 M Na₂SO₄ solution).

2. Materials and experiment

2.1. Materials

Pyrrole (E. Merck Ltd, India) was used as a monomer for nanofiber preparation. Potassium chloride (KCl, E. Merck Ltd., India) and sodium sulfate (Na₂SO₄, E. Merck Ltd., India) were used as electrolytes for the electrochemical characterizations. Sodium alginate (SA, Food Grade, Loba Chemie Pvt. Ltd., Mumbai, India), sodium hydroxide (NaOH, Loba Chemie Pvt. Ltd. Mumbai, India) and ammonium persulfate (APS) [(NH₄)₂SO₄, Loba Chemie Pvt. Ltd., Mumbai, India] were also used for the preparation of PPy nanofiber. All the chemicals were used as received, without any further purification.

2.2. Characterization techniques

2.2.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of nanocomposites were recorded by IR spectrometer (NEXUS 870, Thermo Nicolet, USA). For the IR spectrum, little bit of sample was mixed with potassium bromide (KBr) in adequate level to make a disk and the disk was analyzed in order to get the spectrum.

2.2.2. Scanning Electron Microscopy (SEM)

The morphology of PPy nanofiber was analyzed through SEM instrument (Tescan VEGA LSU SEM, USA). Small amount of sample was adhered to the

sample holder by carbon tape and analyzed by SEM. However, before analysis the samples were sputtered with gold in order to make them conducting.

2.2.3. High Resolution Transmission Electron Microscopy (HR-TEM)

The bulk morphology of nanofiber was examined by high resolution transmission electron microscopy (HR-TEM, JEOL 2100, Japan). A small amount of the sample was dispersed in acetone through sonication and a drop of this dispersed solution was put on the copper grid for HRTEM analysis.

2.2.4. Electrochemical characterization

Electrochemical experiments such as Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) were carried out by three electrode system where platinum and saturated calomel electrode (SCE) were used as counter and reference electrodes respectively. Cyclic voltammetry (Gamry Instrument) measurements were performed in two different aqueous electrolytes – 1 M KCl and 1 M Na₂SO₄ solution at different scan rates from 10 to 200 mV/s within a potential window of –0.8 to 0.8 V. The electrodes were used for electrochemical characterization without any polymer binder. The impedance spectroscopy investigations of the nanofiber were performed in the frequency range of 100 mHz to 10 MHz.

2.2.5. Thermogravimetric analysis

Thermogravimetric analysis was carried out by Dupont 2100 Thermogravimetric analyzer (USA). The TGA measurements were conducted at a heating rate of 10°C/min under N₂ atmosphere from room temperature to 800°C.

2.3. Synthesis of PPy nanofiber

A simple facile method was carried out for the synthesis of PPy nanofiber. In this process, 300 mg of SA was stirred with 0.1 M NaOH (300 ml) at 60°C for 12 h. After that 1 mL of pyrrole was added to the above solution and further stirred for 1 h. The resulting solution was cooled at 0°C. 1 M H₂SO₄ was added drop wise to adjust the pH value of the solution to 7. 1 g of APS was poured into the solution and kept at 0°C for 24 h for the synthesis of nanofiber. The black colored precipitation was collected by filtration and washed with deionized water for sev-

eral times. Lastly the PPy nanofiber composite was dried at 60°C. For comparison, PPy without SA was prepared by an in-situ oxidative polymerization method [23].

3. Results and discussion

3.1. PPy nanofiber synthesis

SA is the sodium salt of alginic acid. It is a linear copolymer with homopolymeric blocks of (1-4)-linked β -D-mannuronate (M) and its C-5 epimer α -L-guluronate (G) residues (Figure 1) and can act as polyelectrolyte. This is a biomacromolecular polysaccharide, mainly used for different biomedical applications. The strong electrostatic repulsions among the carboxylate anions of SA (COO^-) allows it to form expanded network structure, which is the prime requirement for easy electrolyte accessibility and by this way it has become an important tool for the construction of electrode material for supercapacitor application [24]. However, in the typical synthetic procedure, addition of monomer allows the biomolecule to form biopolymer – monomer complexes through hydrogen bonding. The probable structure of the bio polymer-monomer complex has been proposed and shown in Figure 2. How-

Figure 1. Chemical structure of sodium alginate

Figure 2. Probable structure of bio polymer-monomer complex

ever, when the oxidant APS was added in the reaction mixture, polymerization occurred as well as PPy were initiated onto the biopolymer chains and also formed PPy Nanofiber composite [3]. The SEM image of PPy Nanofiber shows this fiber like network morphology. According to Zhang *et al.* [24] nanofibrillar morphology can be achieved only when the seed template also shows nanofibrillar morphology and has the capability to react with the monomer. Here, SA itself has the ability to exhibit nanofibrillar morphology and also can react with pyrrole. So, the choice of SA for nanofiber synthesis is reasonable and perfect.

3.2. FTIR analysis

FTIR analysis is generally carried out to identify the chemical environment of the composites. The FTIR spectrum of SA, pure PPy and PPy nanofiber are shown in Figure 3. The peaks at 1623, 1415, 1088 and 1034 cm^{-1} in the FTIR spectrum of SA correspond to the asymmetric COO^- , symmetric COO^- , C–O and C–O–C stretching respectively. The peaks at 1562, 1469 and 3410 cm^{-1} correspond to the C–C, C–N and N–H stretching vibrations of the pyrrole ring [23]. Whereas, the peaks at 2855 and 2962 cm^{-1} are associated with the symmetric and asymmetric vibrations of CH_2 of PPy [25]. However, it is noticed that the different peaks of SA are shifted to lower frequency region in the FTIR spectrum of PPy nanofiber. Such appearance of the bands at shifted positions in case of composite may be due to the result of the interaction between PPy and SA. Caykara *et al.* [26] successfully prepared the blend of poly (ethylene oxide) and SA by solution casting method and

established that the hydrogen bonding interaction between two polymers is responsible for the band shifting. Thus, FTIR spectrum of the composite confirms the formation of hydrogen bonding between PPy and SA. Similar type of spectrum was also observed by Ma *et al.* [27].

3.3. Morphological study

The morphology of as prepared PPy nanofiber was analyzed through SEM and TEM. The SEM image of PPy nanofiber (Figure 4a) shows the fiber like morphology. It shows a random network of nanostructured PPy with the diameter ~ 100 nm. This porous network is superior for easy and fast electrolyte transport, which is the essential requirement for enhanced electrochemical properties of the electrode materials. However, for better understanding of the morphological change, we have shown SEM image of PPy prepared by in-situ polymerization, without SA, which shows granular structure (Figure 4b) [23]. Thus SEM analysis of PPy nanofiber confirms that SA plays an important role for the synthesis of PPy nanofiber. For further analysis we have done the TEM analysis of PPy nanofiber. Figure 5 shows the TEM image of PPy nanofiber, which clearly indicates that the composite consists of nanofibers with diameter of ~ 100 nm. The uniform network of PPy nanofiber is further confirmed by TEM.

3.4. Electrochemical properties

The electrochemical performances of various electrode materials depend not only on the nature, porosity, conductivity of the electrode materials but also on the nature of the electrolytes. The choice of electrolyte depends on several factors like resistance, capacitance, electrochemically stable potential window, manufacturing cost etc. [28]. However, among organic and aqueous electrolytes, aqueous electrolytes are more superior for supercapacitors in terms of safety and cost. Further, aqueous electrolytes are environmentally benign. Here, we have chosen 1 M KCl and 1 M Na_2SO_4 solution as both are ecofriendly as well as cheaper and has the ability to serve as electrolytic solution for supercapacitors. Further, it is well established fact that the cycling behavior of the supercapacitors is superior in aqueous electrolyte as compared to organic electrolyte as it degrades in the electrode electrolyte interface in organic electrolyte [29]. Figure 6a, 6b

Figure 3. FTIR spectrum of PPy, SA, PPy nanofiber

Figure 4. SEM images of (a) PPy without SA (granular morphology) and (b) PPy nanofiber (fibrillar morphology)

Figure 5. TEM image of PPy nanofiber

shows the CV curves of PPy nanofiber in 1 M KCl and 1 M Na₂SO₄ solution respectively. The non-rectangular shape of CV curves designates the redox behavior due to broad pore size distribution. The wide area of the CV curves implies the pseudocapacitive performance of the PPy nanofiber. On the other hand, in case of Na₂SO₄, the CV curve deviates from the ideal rectangular shape with some redox peaks (in between –0.6 to –0.4), which is also

an indication of pseudocapacitance properties of the PPy nanofiber.

In order to find the prospect of the composites to be used as electrode materials for supercapacitors, constant current charging/discharging (CCD) analysis was performed at 1 A/g. CCD test is the common tool to compare the relative cycling efficiency among different capacitors. This test is an indicator of the quality of supercapacitors. The CCD curves of PPy nanofiber in different electrolytes are shown in Figure 7a, 7b. The curves are linear as well as symmetrical, which is a typical characteristic of ideal capacitor [30]. The specific capacitance of the composite was calculated from the discharge cycle of the typical voltage-time response curve in CC measurements using Equation (1) [31, 32]:

$$C_{cc} = \frac{I \cdot \Delta t}{\Delta V \cdot m} \quad (1)$$

where C_{cc} is the specific capacitance obtained from discharge cycle of constant current charge/discharge measurements, I is the constant current, Δt is the discharge time, ΔV denotes the potential range and m is the mass of the sample. PPy nanofiber shows maximum capacitance of 284 F/g in KCl electrolyte. This value is higher than that of pure PPy, synthesized by in-situ oxidative polymeriza-

Figure 6. Cyclic voltammograms of PPy nanofiber in (a) 1 M KCl and (b) 1 M Na₂SO₄ solution

Figure 7. CCD curves of PPy nanofiber in (a) 1 M KCl and (b) 1 M Na₂SO₄ electrolyte

tion method and reported earlier [23]. Further, as prepared composite shows enhanced capacitance value than several PPy based electrode materials for supercapacitors, reported in the literatures [33–35]. On the other hand, it shows lower specific capacitance of 148 F/g in Na₂SO₄ electrolyte. The enhanced specific capacitance of PPy nanofiber may be due to the network structure, which enhances the surface area of the redox reaction and shortens the distance of electrolyte ions transport [21]. Further, the improved capacitance properties of the electrode material in KCl electrolyte as compared to Na₂SO₄ electrolyte may be explained by the following way – the hydrated ionic radius of K⁺ (3.31 Å) is smaller than the hydrated ionic radius of Na⁺ (3.58 Å), which allows it's easier and faster accessibility into the inner surface of the electrode materials as compared to Na⁺ [36].

The cyclic stability test of PPy nanofiber in different electrolytes was conducted up to 600 cycles. The variation in specific capacitance with cycle

Figure 8. Specific capacitance vs. cycle number curve of PPy nanofiber in different electrolytes

number is shown in Figure 8. It shows 76% capacitance retention after 600 cycles in KCl electrolyte. Whereas this retention of capacitance decreases to 53%, when 1 M Na₂SO₄ was used as electrolyte. The variation in cyclic stability of composite material in different electrolytes may be caused by the doping

and de-doping of the electrode material, which allows the material to experience swelling and shrinkage and cause mechanical stress to the polymeric backbone. However, the enhanced cyclic stability may be due to the intermolecular interaction (Hydrogen Bonding) between SA and PPy chains, which restrict the change of regular network structure during the cyclic test and prevents the shrinkage and swelling of nanostructured polymer [21].

3.5. Electrochemical Impedance Spectroscopy (EIS)

EIS is one of the spectroscopic techniques, which measures the dielectric properties of any substance as a function of frequency. Basically, data obtained from EIS can be expressed through Bode plot or Nyquist plot. Nyquist plot is the plot of imaginary part of the impedance (Z'') versus real part of impedance (Z'). High frequency intercept of the real part of impedance gives the solution resistance (R_s) of the composite. Depressed semicircle in the higher frequency region indicates the charge transfer resistance (R_{ct}), which arises mainly due to the charge transfer processes of the electrode materials. On the other hand imperfectness of the supercapacitive materials can be expressed by Constant Phase Element (CPE). The CPE can be expressed by the Equation (2) [31, 32]:

$$Z_{CPE} = [Q^0(j\omega)^n]^{-1} \quad (2)$$

where Q^0 is the frequency independent constant related to the surface and electroactive substance, ω represents the angular frequency ($\omega = 2\pi f$). On the other hand, n value arises from the slope of $\log Z$

versus $\log f$. Depending on this n value, CPE shows different responses. If n value = 0 represents the resistance, whereas n value = 1 represents ideal capacitor response, which is impossible to obtain in real world. Further n value = 0.5 indicates the Warburg behavior. However, n value > 0.5 represents moderate capacitor behavior [31, 32, 37–39].

Figure 9a, 9b demonstrates the Nyquist plots (fitted) of PPy nanofiber in both the electrolytes. Generally ESR is determined from the x-intercept of the Nyquist plot. This data indicates the rate by which supercapacitor can be changed/discharged [40]. PPy nanofiber shows low ESR ($\sim 1 \Omega$) in both the electrolytes. Lower R_s value indicates the enhanced conductivity as well as improved capacitive properties. The interpretation of the impedance spectra mainly carried out by fitting the experimental impedance spectra with an equivalent electrical circuit. The appropriate equivalent circuit for fitting the impedance spectra of PPy nanofiber in different electrolytes is shown in Figure 10. The fitting data of the composite in two electrolytes are shown in Table 1. In both the electrolytes we found n value > 0.5 , which indicates moderate capacitor behavior. However, it is observed that, PPy nanofiber shows higher n value (0.714) in KCl electrolyte as compared to that in Na_2SO_4 electrolyte (0.556). The difference

Figure 10. Equivalent electrical circuit used in EIS fitting data

Figure 9. Nyquist plots of PPy nanofiber in (a) 1 M KCl and (b) 1 M Na_2SO_4 electrolyte

Table 1. Fitting data for equivalent circuit elements of PPy/SA composite

Electrolyte	R_s [Ω]	R_{ct} [Ω]	CPE (S-s ⁿ) · 10 ⁻³	n
1 M Na ₂ SO ₄	1.24	1.29	1.08	0.556
1 M KCl	1.002	0.82	0.66	0.714

in n value in different electrolytes may arise due to several factors like variation of porosity in different electrolytes, dynamic disorder and diffusion etc.

4. TGA analysis

The thermal behavior of the PPy nanofiber was analyzed by TGA analysis. Figure 11 shows the TGA curves of SA, PPy nanofiber and pure PPy (without SA). The initial mass loss of all the samples at around 100°C arises due to the deintercalation of water. For SA, a sharp weight loss is observed at 253°C, which is due to the decomposition of alginate. However, in case of PPy nanofiber, the decomposition of alginate arises at ~270°C. Hence, the decomposition temperature of alginate in PPy nanofiber is higher than that of SA, which clearly indicates the interaction between SA and PPy. On the other hand, 20% weight loss was observed at 322°C for PPy nanofiber, whereas pure PPy showed at 260°C. However the TGA curve clearly indicates higher thermal stability of PPy nanofiber as compared to PPy, without SA [23]. This enhanced thermal stability may be due to the formation of hydrogen bonds between SA and PPy chains. The enhanced thermal stability makes the nanofiber suitable for high temperature device applications.

Figure 11. TGA curves of PPy, SA, PPy nanofiber

5. Conclusions

We have proposed a simple ecofriendly synthetic procedure to prepare PPy nanofiber by using SA as template. The morphological study of the composite shows fiber like network. It demonstrates superior electrochemical performances in KCl electrolyte as compared to Na₂SO₄ electrolyte due to the formation of regular network structure between PPy and SA. Further enhanced thermal stability of the nanofiber allows it to be used in high temperature device application. Moreover, the nanofiber shows enhanced capacitance as well as improved cyclic stability due to the intermolecular interaction between SA and PPy. Overall this approach provides an inexpensive and facile way to prepare a supercapacitive electrode material using conducting polymer. Further Optimization of the experimental can improve the electrochemical performances of the electrode.

Acknowledgements

The first author would like to acknowledge CSIR, New Delhi [Grant No. 09/081(1018)/2010-EMR-I] of India for their financial support.

References

- [1] Gao J., Sansiñena J-M., Wang H-L.: Tunable polyaniline chemical actuators. *Chemistry of Materials*, **15**, 2411–2418 (2003). DOI: [10.1021/cm020329e](https://doi.org/10.1021/cm020329e)
- [2] Wu C-G., Bein T.: Conducting polyaniline filaments in a mesoporous channel host. *Science*, **264**, 1757–1759 (1994). DOI: [10.1126/science.264.5166.1757](https://doi.org/10.1126/science.264.5166.1757)
- [3] Yu Y., Zhihui S., Chen S., Bian C., Chen W., Xue G.: Facile synthesis of polyaniline–sodium alginate nanofibers. *Langmuir*, **22**, 3899–3905 (2006). DOI: [10.1021/la051911v](https://doi.org/10.1021/la051911v)
- [4] Wu T-M., Chang H-L., Lin Y-W.: Synthesis and characterization of conductive polypyrrole/multi-walled carbon nanotubes composites with improved solubility and conductivity. *Composites Science and Technology*, **69**, 639–644 (2009). DOI: [10.1016/j.compscitech.2008.12.010](https://doi.org/10.1016/j.compscitech.2008.12.010)
- [5] Wu T-M., Lin S-H.: Synthesis, characterization, and electrical properties of polypyrrole/multiwalled carbon nanotube composites. *Journal of Polymer Science Part A: Polymer Chemistry*, **44**, 6449–6457 (2006). DOI: [10.1002/pola.21724](https://doi.org/10.1002/pola.21724)

- [6] Ikegame M., Tajima K., Aida T.: Template synthesis of polypyrrole nanofibers insulated within one-dimensional silicate channels: Hexagonal versus lamellar for recombination of polarons into bipolarons. *Angewandte Chemie International Edition*, **42**, 2154–2157 (2003). DOI: [10.1002/anie.200250800](https://doi.org/10.1002/anie.200250800)
- [7] He J., Chen W., Xu N., Li L., Li X., Xue G.: SERS studies on the ordered structure of the surface of polypyrrole nanotubules. *Applied Surface Science*, **221**, 87–92 (2004). DOI: [10.1016/S0169-4332\(03\)00810-9](https://doi.org/10.1016/S0169-4332(03)00810-9)
- [8] Athawale A. A., Katre P. P., Bhagwat S. V., Dhamane A. H.: Synthesis of polypyrrole nanofibers by ultrasonic waves. *Journal Applied Polymer Science*, **108**, 2872–2875 (2008). DOI: [10.1002/app.27301](https://doi.org/10.1002/app.27301)
- [9] Burke A.: Ultracapacitors: Why, how, and where is the technology. *Journal of Power Sources*, **91**, 37–50 (2000). DOI: [10.1016/S0378-7753\(00\)00485-7](https://doi.org/10.1016/S0378-7753(00)00485-7)
- [10] Zang J., Li C. M., Bao S.-J., Cui X., Bao Q., Sun C. Q.: Template-free electrochemical synthesis of superhydrophilic polypyrrole nanofiber network. *Macromolecules*, **41**, 7053–7057 (2008). DOI: [10.1021/ma801345k](https://doi.org/10.1021/ma801345k)
- [11] Winter M., Brodd R. J.: What are batteries, fuel cells, and supercapacitors? *Chemical Reviews*, **104**, 4245–4269 (2004).
- [12] Kötzt R., Carlen M.: Principles and applications of electrochemical capacitors. *Electrochimica Acta*, **45**, 2483–2498 (2000). DOI: [10.1016/S0013-4686\(00\)00354-6](https://doi.org/10.1016/S0013-4686(00)00354-6)
- [13] Qu D., Shi H.: Studies of activated carbons used in double-layer capacitors. *Journal of Power Sources*, **74**, 99–107 (1998). DOI: [10.1016/S0378-7753\(98\)00038-X](https://doi.org/10.1016/S0378-7753(98)00038-X)
- [14] An K. H., Kim W. S., Park Y. S., Moon J.-M., Bae D. J., Lim S. C., Lee Y. S., Lee Y. H.: Electrochemical properties of high-power supercapacitors using single-walled carbon nanotube electrodes. *Advanced Functional Materials*, **11**, 387–392 (2001). DOI: [10.1002/1616-3028\(200110\)11:5<387::AID-ADFM387>3.0.CO;2-G](https://doi.org/10.1002/1616-3028(200110)11:5<387::AID-ADFM387>3.0.CO;2-G)
- [15] Li Y., van Zijl M., Chiang S., Pan N.: KOH modified graphene nanosheets for supercapacitor electrodes. *Journal of Power Sources*, **196**, 6003–6006 (2011). DOI: [10.1016/j.jpowsour.2011.02.092](https://doi.org/10.1016/j.jpowsour.2011.02.092)
- [16] Acik M., Baristiran C., Sonmez G.: Highly surfaced polypyrrole nano-networks and nano-fibers. *Journal of Materials Science*, **41**, 4678–4683 (2006). DOI: [10.1007/s10853-006-0034-7](https://doi.org/10.1007/s10853-006-0034-7)
- [17] Lang X., Hirata A., Fujita T., Chen M.: Nanoporous metal/oxide hybrid electrodes for electrochemical supercapacitors. *Nature Nanotechnology*, **6**, 232–236 (2011). DOI: [10.1038/nnano.2011.13](https://doi.org/10.1038/nnano.2011.13)
- [18] Aricò A. S., Bruce P., Scrosati B., Tarascon J.-M., van Schalkwijk W.: Nanostructured materials for advanced energy conversion and storage devices. *Nature Materials*, **4**, 366–377 (2005). DOI: [10.1038/nmat1368](https://doi.org/10.1038/nmat1368)
- [19] Mastragostino M., Arbizzani C., Soavi F.: Polymer-based supercapacitors. *Journal of Power Sources*, **97**, 812–815 (2001). DOI: [10.1016/S0378-7753\(01\)00613-9](https://doi.org/10.1016/S0378-7753(01)00613-9)
- [20] Gupta V., Miura N.: High performance electrochemical supercapacitor from electrochemically synthesized nanostructured polyaniline. *Materials Letters*, **60**, 1466–1469 (2006). DOI: [10.1016/j.matlet.2005.11.047](https://doi.org/10.1016/j.matlet.2005.11.047)
- [21] Li Y., Zhao X., Xu Q., Zhang Q., Chen D.: Facile preparation and enhanced capacitance of the polyaniline/sodium alginate nanofiber network for supercapacitors. *Langmuir*, **27**, 6458–6463 (2011). DOI: [10.1021/la2003063](https://doi.org/10.1021/la2003063)
- [22] Kuila B. K., Nandan B., Böhme M., Janke A., Stamm M.: Vertically oriented arrays of polyaniline nanorods and their super electrochemical properties. *Chemical Communication*, **2009**, 5749–5751 (2009). DOI: [10.1039/B912513B](https://doi.org/10.1039/B912513B)
- [23] Sahoo S., Karthikeyan G., Nayak G. C., Das C. K.: Electrochemical characterization of in situ polypyrrole coated graphene nanocomposites. *Synthetic Metals*, **161**, 1713–1719 (2011). DOI: [10.1016/j.synthmet.2011.06.011](https://doi.org/10.1016/j.synthmet.2011.06.011)
- [24] Zhang G. Q., Zha L. S., Zhou M. H., Ma J. H., Liang B. R.: Preparation and characterization of pH- and temperature-responsive semi-interpenetrating polymer network hydrogels based on linear sodium alginate and crosslinked poly(*N*-isopropylacrylamide). *Journal of Applied Polymer Science*, **97**, 1931–1940 (2005). DOI: [10.1002/app.21957](https://doi.org/10.1002/app.21957)
- [25] Bose S., Kuila T., Uddin M. E., Kim N. H., Lau A. K. T., Lee J. H.: In-situ synthesis and characterization of electrically conductive polypyrrole/graphene nanocomposites. *Polymer*, **51**, 5921–5928 (2010). DOI: [10.1016/j.polymer.2010.10.014](https://doi.org/10.1016/j.polymer.2010.10.014)
- [26] Çaykara T., Demirci S., Eroğlu M. S., Güven O.: Poly(ethylene oxide) and its blends with sodium alginate. *Polymer*, **46**, 10750–10757 (2005). DOI: [10.1016/j.polymer.2005.09.041](https://doi.org/10.1016/j.polymer.2005.09.041)
- [27] Ma G., Fang D., Liu Y., Zhu X., Nie J.: Electrospun sodium alginate/poly(ethylene oxide) core-shell nanofibers scaffolds potential for tissue engineering applications. *Carbohydrate Polymers*, **87**, 737–743 (2012). DOI: [10.1016/j.carbpol.2011.08.055](https://doi.org/10.1016/j.carbpol.2011.08.055)
- [28] Tanahashi I., Yoshida A., Nishino A.: Comparison of the electrochemical properties of electric double-layer capacitors with an aqueous electrolyte and with a non-aqueous electrolyte. *Bulletin of the Chemical Society of Japan*, **63**, 3611–3614 (1990). DOI: [10.1246/bcsj.63.3611](https://doi.org/10.1246/bcsj.63.3611)

- [29] Chen W., Rakhi R. B., Alshareef H. N.: High energy density supercapacitors using macroporous kitchen sponges. *Journal of Materials Chemistry*, **22**, 14394–14402 (2012).
DOI: [10.1039/C2JM32030D](https://doi.org/10.1039/C2JM32030D)
- [30] Yan J., Wei T., Shao B., Ma F., Fan Z., Zhang M., Zheng C., Shang Y., Qian W., Wei F.: Electrochemical properties of graphene nanosheet/carbon black composites as electrodes for supercapacitors. *Carbon*, **48**, 1731–1737 (2010).
DOI: [10.1016/j.carbon.2010.01.014](https://doi.org/10.1016/j.carbon.2010.01.014)
- [31] Chen W.-C., Wen T.-C.: Electrochemical and capacitive properties of polyaniline-implanted porous carbon electrode for supercapacitors. *Journal of Power Sources*, **117**, 273–282 (2003).
DOI: [10.1016/S0378-7753\(03\)00158-7](https://doi.org/10.1016/S0378-7753(03)00158-7)
- [32] Sahoo S., Karthikeyan G., Nayak G. C., Das C. K.: Modified graphene/polyaniline nanocomposites for supercapacitor application. *Macromolecular Research*, **20**, 415–421 (2012).
DOI: [10.1007/s13233-012-0042-1](https://doi.org/10.1007/s13233-012-0042-1)
- [33] Qu Q., Zhang P., Wang B., Chen Y., Tian S., Wu Y., Holze R.: Electrochemical performance of MnO₂ nanorods in neutral aqueous electrolytes as a cathode for asymmetric supercapacitors. *Journal of Physical Chemistry C*, **113**, 14020–14027 (2009).
DOI: [10.1021/jp8113094](https://doi.org/10.1021/jp8113094)
- [34] Hu C.-C., Chu C.-H.: Electrochemical impedance characterization of polyaniline-coated graphite electrodes for electrochemical capacitors – Effects of film coverage/thickness and anions. *Journal of Electroanalytical Chemistry*, **503**, 105–116 (2001).
DOI: [10.1016/S0022-0728\(01\)00385-0](https://doi.org/10.1016/S0022-0728(01)00385-0)
- [35] Piao T., Park S.-M., Doh C.-H., Moon S.-I.: Intercalation of lithium ions into graphite electrodes studied by AC impedance measurements. *Journal of the Electrochemical Society*, **146**, 2794–2798 (1999).
DOI: [10.1149/1.1392010](https://doi.org/10.1149/1.1392010)
- [36] Levi M. D., Aurbach D.: Simultaneous measurements and modeling of the electrochemical impedance and the cyclic voltammetric characteristics of graphite electrodes doped with lithium. *Journal of Physical Chemistry B*, **101**, 4630–4640 (1997).
DOI: [10.1021/jp9701909](https://doi.org/10.1021/jp9701909)
- [37] Ingram M. D., Staesche H., Ryder K. S.: ‘Activated’ polypyrrole electrodes for high-power supercapacitor applications. *Solid State Ionics*, **169**, 51–57 (2004).
DOI: [10.1016/j.ssi.2002.12.003](https://doi.org/10.1016/j.ssi.2002.12.003)
- [38] Jurewicz K., Delpeux S., Bertagna V., Béguin F., Frackowiak E.: Supercapacitors from nanotubes/polypyrrole composites. *Chemical Physics Letters*, **347**, 36–40 (2001).
DOI: [10.1016/S0009-2614\(01\)01037-5](https://doi.org/10.1016/S0009-2614(01)01037-5)
- [39] Sun W., San S., Duo Y., Chen Y.: Preparation and characterization of micro polypyrrole electrodes for supercapacitor. *Advanced Materials Research*, **60–61**, 375–379 (2009).
DOI: [10.4028/www.scientific.net/AMR.60-61.375](https://doi.org/10.4028/www.scientific.net/AMR.60-61.375)
- [40] Wang Y., Shi Z., Huang Y., Ma Y., Wang C., Chen M., Chen Y.: Supercapacitor devices based on graphene materials. *Journal of Physical Chemistry C*, **113**, 13103–13107 (2009).
DOI: [10.1021/jp902214f](https://doi.org/10.1021/jp902214f)