

# Electrophoretic deposition of activated carbon YP-50 with ethyl cellulose binders for supercapacitor electrodes



Maheshwar Shrestha<sup>a</sup>, Ishop Amatya<sup>a</sup>, Keliang Wang<sup>a</sup>, Bocong Zheng<sup>a</sup>, Zhengrong Gu<sup>b</sup>, Qi Hua Fan<sup>a,\*</sup>

<sup>a</sup> Department of Electrical and Computer Engineering, Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, United States

<sup>b</sup> Agricultural and Biosystems Engineering Department, South Dakota State University, Brookings, SD 57007, United States

## ARTICLE INFO

### Article history:

Received 24 March 2016

Received in revised form 18 July 2017

Accepted 20 July 2017

Available online 1 August 2017

### Keywords:

Supercapacitors

Electrophoretic deposition

Biochar

## ABSTRACT

Activated carbon is widely used for electrodes in supercapacitors. Fabrication of supercapacitors is currently based on hydraulic pressing method, which is a lengthy process (several h) with challenges in controlling the layer thickness and mass. This work reports an electrophoresis method that can efficiently deposit activated biochar onto metal electrodes. The authors demonstrated that a suitable binder (ethyl cellulose) could ensure sufficient coating adhesion. Using commercial activated carbon (YP-50) as electrode material, supercapacitors were fabricated using electrophoretic deposition and the specific capacitance reached  $158.6 \text{ F g}^{-1}$ . The electrophoretic deposition was highly efficient as it only took about 3 min and enabled accurate control of the electrode mass by simply varying the deposition time. This work demonstrates that electrophoretic deposition has the potential to replace the conventional hydraulic press method in manufacturing supercapacitors that use sustainable and environmentally friendly biochar.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Supercapacitors also known as electric double layer capacitors (EDLCs) have the potential to become the leading energy-storage devices to meet the increasing demands for electrical energies [1–3]. Different from batteries, supercapacitors can provide high power density ( $>10 \text{ kW kg}^{-1}$ ) with fast charge/discharge and superior stability ( $>10^6$  cycles) [4,5]. Current supercapacitors are particularly suitable for applications that require high energy for a time range of  $10^{-2}$ – $10^2 \text{ s}$  [6–11]. A few examples are power grid stabilizing units, IC memories, engine starters, uninterruptible power supplies, and electrical automobiles [6,12]. The list of applications is expanding with the rapid increase in supercapacitor capacity. The main components of supercapacitors include electrodes that feature large surface areas, electrolyte that provides charged ions, and metal contact that is usually the casing. This along with a thin dielectric separator makes it possible to increase capacitance of several orders of magnitude higher than that of the conventional capacitors. EDLCs make use of the electric double layer formed at the electrode/electrolyte interface where

charges are accumulated on the electrode surfaces and ions of opposite charge compensate them by electrostatic attraction [13]. Among the variety of electrode materials tested [14], carbon materials meet the essential requirements for EDLCs electrodes: good electrical conductivity, excellent electrochemical stability, and abundance [2,15]. The state-of-the-art supercapacitors use synthesized carbon nanotubes, graphene, carbon aerogel and activated carbon for electrodes [7,16,17]. Graphene and carbon nanotubes have been reported with high specific capacitance due to pore size distribution, pore volume and average pore size [18]. However, fabrication of graphene and carbon nanotubes requires expensive techniques and is not sustainable [19]. Activated carbon is a low-cost alternative to graphene and carbon nanotubes. Therefore, many commercial supercapacitors use activated carbon, such as YP-50, which is derived from coconut shell. Such biomass-based activated carbon is sustainable and environmentally friendly [18,20]. Recent research has shown that activated biochar has surface areas comparable to that of other types of activated carbon after proper activation [21].

Supercapacitors made from activated carbon YP-50 have two essential limitations. First, the specific capacitance ( $\sim 100 \text{ F g}^{-1}$ ) still needs improvement. Second, the conventional method for fabricating the electrodes is based on hydraulic pressing of carbon slurry into porous metal contact. This process involves multiple

\* Corresponding author.

E-mail addresses: [qfan@egr.msu.edu](mailto:qfan@egr.msu.edu), [qihua\\_fan@yahoo.com](mailto:qihua_fan@yahoo.com) (Q.H. Fan).

steps that take ~60 min followed by a lengthy drying in oven for over 8 h. Furthermore, the fabrication requires sophisticated instrumentation to control the carbon thickness and mass [22]. Recently electrophoretic deposition of carbon nanotubes and graphene onto metal substrate was reported, showing the potential for efficient fabrication of supercapacitors [23–25]. Electrophoretic deposition uses an electric field to drive polarized particles suspended in a liquid to move towards a conductive substrate (electrode). This method has the advantage of short formation time, low-cost, simple setup, and high reproducibility for mass production [23,26–29]. However, it appeared very challenging to deposit activated carbon or biochar using electrophoresis method; the deposited layer generally had poor adhesion [30].

Electrophoretic deposition of carbon nanotubes was first investigated by Du et al. in 2002 [31]. Multi-walled carbon nanotubes were electrophoretically deposited by various research groups [27,32]. It was found that low electric field ( $<5\text{--}10\text{ V cm}^{-1}$ ) resulted in low density and non-uniform coating, and higher electric field ( $>20\text{ V cm}^{-1}$ ) or longer deposition time led to aggregation of carbon nanotubes, resulting in poor homogeneity of the carbon nanotube films [23,33]. One of the major issues of electrophoretic deposition of carbon nanotubes is adhesion. Kurnosov et al. in 2003 reported the improvement of adhesion of carbon nanotubes onto the metallic electrode by adding a resistive material on top of the conductive electrode using a suspension of carbon nanotubes in  $\text{NiCl}_2$ /isopropyl alcohol [34]. However, the film deposited was not uniform at the edges of the electrodes. An interesting work conducted by Wu et al. in 2010 demonstrated that electrophoretic deposition of nickel decorated activated carbon could promote the coating adhesion. They mixed Ni particles with activated carbon and deposited the mixture onto nickel foils for supercapacitors. They reported a specific capacitance of  $140\text{ F g}^{-1}$  using activated carbon, BlackPearls 2000 (Cabot Corp.) [35]. However, the cyclic voltammetry curve they obtained was not rectangular in shape and showed high peaks of oxidation and reduction. The reasons might be: (1) the raw Ni nanoparticles were oxidized, and (2) the polytetrafluoroethylene (PTFE) binder they added in the mixture during the electrophoretic deposition did not result in sufficient adhesion as it used to be in the conventional slurry process. It is worth noting that Black Pearls 2000 is synthesized from incomplete combustion of heavy petroleum products, such as coal tar, and is not sustainable. So far, no work was reported on electrophoretic fabrication of supercapacitors using biomass-based activated carbon.

In this work, we report electrophoretic deposition of activated biochar YP-50 for achieving high specific capacitance supercapacitors. We particularly compare ethyl cellulose with conventional binder PTFE in electrophoretic co-deposition of biochar onto electrodes in order to achieve sufficient adhesion. We demonstrate that electrophoretic deposition of activated carbon YP-50 with ethyl cellulose as binder and acetylene black as conductive carbon has the potential to become a scalable and cost-effective method to produce supercapacitors with better performance than conventional methods. We also show that the mass of the carbon materials deposited on the electrodes is reproducible and can be accurately controlled by varying the deposition time.

## 2. Experiment

Commercial YP-50 from Kuraray Chemicals was used as the activated carbon. The raw material used to derive the activated carbon was coconut and the activation was done by heating the coconut biochar in steam. YP-50 carbon powder, ethyl cellulose, and acetylene black were mixed in a weight ratio of 8:1:1 in 80 mL of isopropyl alcohol. This solution was ultrasonicated for 50 min

before starting the electrophoretic deposition. Nickel foil of  $50\text{ }\mu\text{m}$  thickness from Alfa Aesar was cut into  $\sim 2.5 \times 1.5\text{ cm}^2$  rectangular shape. The nickel foil and a copper foil (as counter-electrode) of the same size were clamped to two electrode holders and immersed in the carbon solution. The carbon solution was stirred throughout the electrophoretic deposition. The distance between the nickel and copper foils was 0.8 cm. The backside of the Ni substrate was covered with a 3 M scotch tape to avoid deposition. A DC voltage of 80 V was applied to the nickel and the copper electrode was connected to ground. The deposition time for all the samples was 3 min unless otherwise specified. All the samples were deposited at same voltage for same time to make the mass of the deposited carbon consistent. Increasing the deposition time yielded thicker film with higher mass of carbon.

The carbon coated Ni foils were dried in air for 10 min followed by annealing at  $120^\circ\text{C}$  for 12 h in atmosphere to evaporate the solvents in the film and improve the film adhesion. After the carbon deposition, the electrode thickness became  $\sim 200\text{ }\mu\text{m}$  with active mass  $\sim 4\text{ mg}$ . The supercapacitor electrodes were prepared by cutting the carbon-coated foil into a circular shape of 15 mm diameter using a MTI precision disc cutter (MSK-T-06). Two microporous separators (3501, Celgard) were dipped in  $6\text{ mol L}^{-1}$  KOH electrolyte and were set between two pieces of electrodes. These components were then sealed in a CR2032 coin cell using a hydraulic crimping machine (MSK-110, MTI Corp.). The fabricated cells were kept in room temperature overnight before the measurements in order to allow the electrolyte to disperse uniformly within the carbon electrodes.

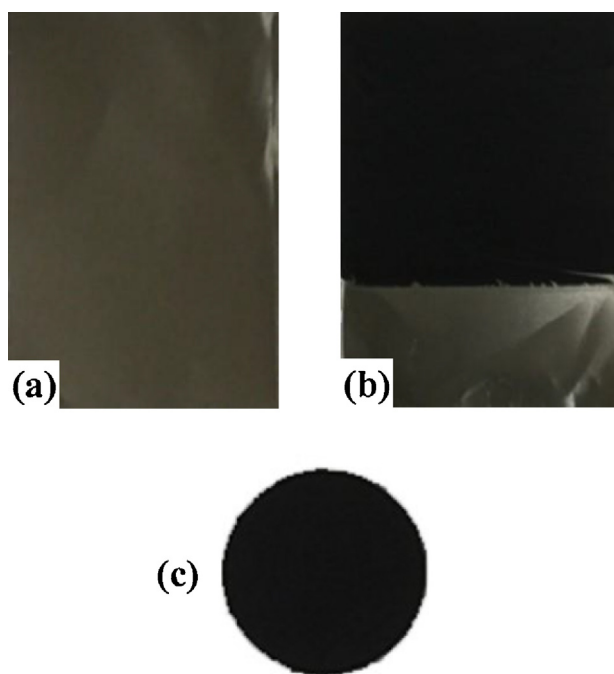
The surface morphology of the materials was analyzed using a Hitachi S3400-N scanning electron microscope (SEM) and the structure of the biochar was studied using a Horiba Raman spectrometer at room temperature. Cyclic voltammetry measurement was conducted using an Ametek VERSASTAT-450 Potentiostat in two-electrode configuration. Scan rate for the measurement was  $20\text{ mV s}^{-1}$ . The cyclic potential sweep was set from  $-1.0\text{ V}$  to  $1.0\text{ V}$ . The Ametek VERSASTAT-450 Potentiostat was also used to measure the impedance of the supercapacitors. Impedance was measured at frequencies ranging from 0.1 Hz to 100 kHz with potential amplitude of 10 mV. The specific capacitance of the capacitor is calculated from the following equation,

$$C = \frac{2I\Delta t}{m\Delta v}$$

where,  $C$  is the specific capacitance ( $\text{F g}^{-1}$ ),  $I$  is the charge or discharge current density,  $\Delta t$  is the charge or discharge time,  $m$  is the carbon electrode mass, and  $\Delta v$  is the total change in voltage. The capacitor performance was evaluated using galvanostatic charge/discharge cycling in the potential range 0.0–1.0 V at current density of  $100\text{ mA g}^{-1}$  using MTI Corporation 8 channels battery analyzer (BST8-3).

## 3. Result and discussion

Fig. 1 shows photograph images of the electrodes used to fabricate supercapacitors. Fig. 1(a) is the cleaned Ni foil before carbon deposition and Fig. 1(b) is the Ni foil with electrophoretic deposited YP-50 biochar film. The YP-50 film appeared highly uniform. Fig. 1(c) is the circular YP-50 biochar electrode used to assemble supercapacitors. We did standard tape adhesion tests on the electrodes with PTFE or ethyl cellulose binder. Classification of the adhesion was based on the amount of carbon left on the metal substrate. More than 65% of the carbon on the electrode with PTFE binder was removed by the tape, indicating poor adhesion strength of 0 B level. However, less than 5% of the carbon was removed from the electrode with ethyl cellulose binder, indicating good adhesion

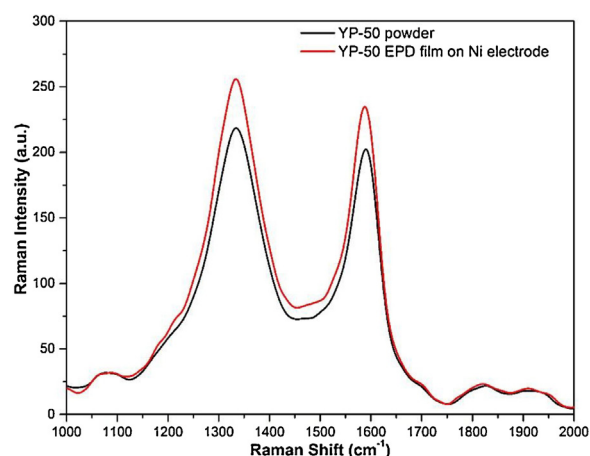


**Fig. 1.** Photograph images of electrodes: (a) cleaned Ni foil, (b) Electrophoretic deposited YP-50 film on Ni substrate, and (c) YP-50 electrode for supercapacitor ( $\Phi = 15$  mm).

strength of 4B level. Therefore, ethyl cellulose was used in the subsequent supercapacitor fabrication because it provided sufficient adhesion coating.

Fig. 2 shows SEM images of as-received YP-50 powder and the deposited electrode surface at 2500x magnification. The images clearly showed that the electrophoretic deposited film contained more small particles as compared to the as-received YP-50 powder. It appeared that the electrophoretic deposition favored the transport of smaller particles from the solution to the substrate surface. This effect was attributed to two factors: (1) smaller particles stayed in the suspension for longer time; and (2) smaller particles had higher mobility under an electric field. In addition, the electrophoretic deposited films appeared dense and uniform, which led to more surface areas accessible to the electrolyte. Therefore, increased specific capacitance was expected.

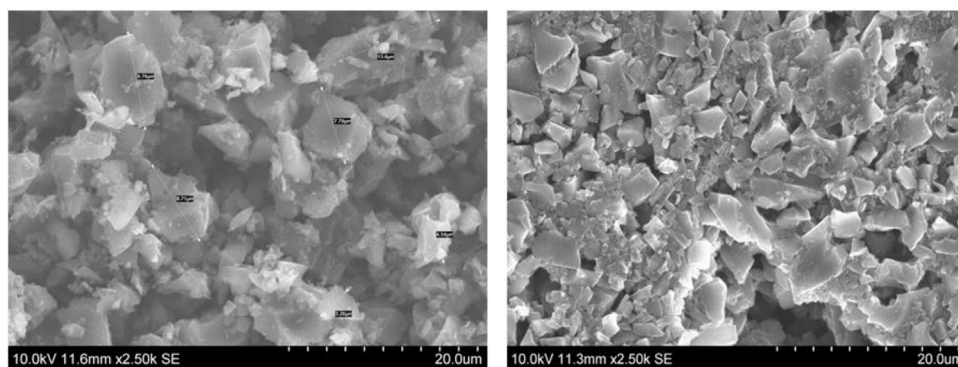
The large and small YP-50 particles had similar chemical properties and atomic structures as evidenced by the Raman spectra taken before and after the electrophoretic deposition (see Fig. 3). The characteristic peak around  $1320\text{--}1370\text{ cm}^{-1}$  (D-band)



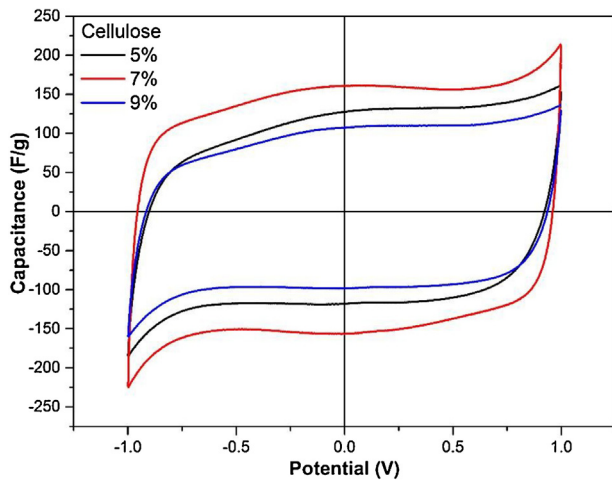
**Fig. 3.** Raman spectra of as-received YP-50 powder and electrophoretic deposited film YP-50 film on Ni substrate.

caused by disordered and imperfect structure of graphene, indicating disorder in  $sp^3$ -hybridized carbon system. Likewise, the peak around  $1530\text{--}1610\text{ cm}^{-1}$  (G-band) corresponded to graphite dominated by  $sp^2$ -bonded carbon, indicating stretching of the c-c bond in graphitic carbon [36]. The Raman intensity and Raman shift for both samples were similar. The intensity ratio of D to G bands ( $I_D/I_G$ ) provides information related to the degree of structural defects [37–39]. The  $I_D/I_G$  values for as-received YP-50 powder and YP-50 film on Ni electrode were 1.08 and 1.09, respectively, indicating no phase transformation due to electrophoretic deposition.

Fig. 4 shows the cyclic voltammetry (CV) curves of the supercapacitors made of YP-50 electrodes by electrophoretic deposition with different concentrations of ethyl cellulose. The CV curves were almost rectangular shape and symmetrical with respect to the zero-voltage line. The CV curves provided clear proof of near-ideal supercapacitor characteristics of the fabricated cells [10,13]. The specific capacitance was calculated to be  $122.8\text{ Fg}^{-1}$ ,  $158.6\text{ Fg}^{-1}$ , and  $102.7\text{ Fg}^{-1}$  for the cells fabricated with 5 wt%, 7 wt%, and 9 wt% cellulose in YP-50 biochar. The capacitance values were calculated for active carbon mass excluding the mass of acetylene black. The supercapacitor with 7 wt% cellulose had the highest specific capacitance of  $158.6\text{ Fg}^{-1}$ . This is the highest known specific capacitance for YP-50 activated carbon, indicating the promising potential of electrophoretic deposition as a simple and scalable method for fabricating supercapacitors. Note that the specific capacitance values presented in this report were calculated from a real two-electrode system, rather than from a



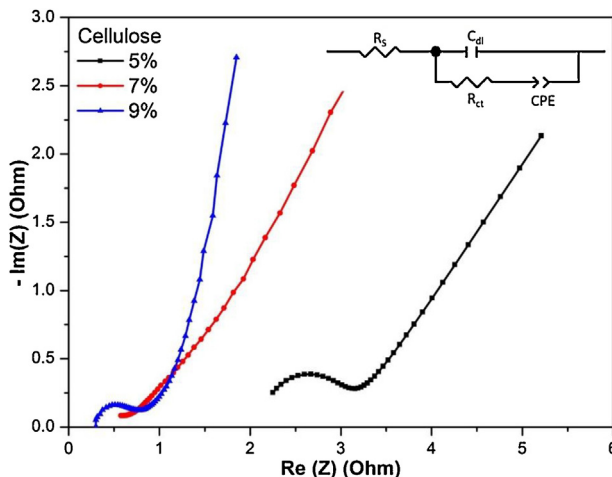
**Fig. 2.** SEM images at 2500x magnification of (a) as-received YP-50 powder, and (b) electrophoretic deposited film.



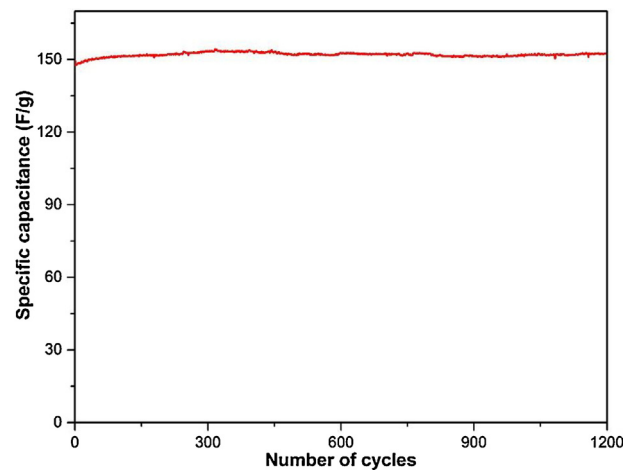
**Fig. 4.** Current vs. voltage of supercapacitors made of electrophoretically deposited YP-50 electrodes with different wt% of ethyl cellulose.

single electrode or a half-cell, as reported in some literatures [40–42]. When the cellulose concentration was lower than 5%, the adhesion between the carbon particles and metal substrate decreased, leading to lower specific capacitance and increased resistance. On the other hand, when the cellulose concentration was too high, the effective surface area of the activated carbon was reduced, leading to lower specific capacitance.

Fig. 5 shows the Nyquist plot, also known as electrochemical impedance spectroscopy (EIS), of YP-50 supercapacitors fabricated by electrophoretic deposition. These data were fitted with an equivalent circuit model consists of an equivalent series resistance ( $R_s$ ) accounting for transport resistance of biochar, a double layer capacitance ( $C_{dl}$ ), charge transfer resistance ( $R_{ct}$ ) at the carbon electrode/electrolyte interface, and constant phase element (CPE) representing pseudocapacitance. The applied voltage was 10 mV and frequency varied from 0.1 Hz to 10 kHz. The plot showed two distinct features: a high-frequency semicircle and a low frequency spike. The intercept of the high-frequency part with the real axis represents equivalent series resistance corresponding to the intrinsic resistance of active material, the resistance of the electrolyte solution and contact resistance of the active material/current collector interface [43–45]. The equivalent series resistances calculated from the X-intercept of the Nyquist plots were 0.85  $\Omega$ , 0.65  $\Omega$ , and 0.98  $\Omega$  for the cells fabricated with 5 wt%,



**Fig. 5.** EIS curves of supercapacitors made from electrophoretically deposited YP-50 with different wt% of ethyl cellulose.



**Fig. 6.** Specific capacitance vs. number of charge/discharge cycles of a supercapacitor made from electrophoretically deposited YP-50 with 7 wt% cellulose.

7 wt%, and 9 wt% ethyl cellulose, respectively. Similarly, charge transfer resistance were calculated as 1.5  $\Omega$ , 0.96  $\Omega$ , and 2.2  $\Omega$  respectively. The supercapacitor with 7 wt% cellulose in YP-50 biochar showed lowest equivalent series resistance of 0.65  $\Omega$ , which was small and would cause negligible energy loss upon charge and discharge.

Fig. 6 shows the specific capacitance vs. the number of charge/discharge cycles of a supercapacitor made from electrophoretically deposited YP-50 carbon. This test was done at a current density of 100 mA g<sup>-1</sup>. The specific capacitance remained about 153 F g<sup>-1</sup> throughout 1200 cycles. The cycling tests indicated excellent stability of the supercapacitors made of electrophoretically deposited YP-50 biochar.

#### 4. Conclusions

Electrophoretic deposition was a simple and efficient method for fabricating supercapacitor electrodes using activated coconut biochar YP-50. The PTFE binder used in conventional hydraulic-press supercapacitor fabrication gave poor biochar film adhesion on the Ni electrode. 6–8% ethyl cellulose played a critical role to provide sufficient adhesion for the coatings. Electrophoretic deposition of YP-50 carbon with 7 wt% of ethyl cellulose led to supercapacitors of 158.6 F g<sup>-1</sup>, which was the highest known value for supercapacitors made of this carbon materials. The resistance of the supercapacitors was found to be 0.65  $\Omega$ , indicating that the electrophoretic deposition led to densely packed carbon particles. The electrophoretic deposition allowed easy control of the deposited mass by simply varying the deposition time. Raman spectroscopy measurement showed no phase transformation of the carbon materials before and after electrophoretic deposition.

#### Acknowledgments

This work was supported by funding from the National Science Foundation, awards # 1700787. Also acknowledged is the Michigan Economic Development Corporation MTRAC Program: Grant CASE 179448 of the 21st Century Jobs Trust Fund received through the Michigan Strategic Fund from the State of Michigan.

#### References

- [1] I. Hadjipachalis, A. Poullikkas, V. Efthimiou, Overview of current and future energy storage technologies for electric power applications, *Renew. Sustain. Energy Rev.* 13 (2009) 1513–1522.



- [2] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors, *Chem. Soc. Rev.* 41 (2012) 797–828.
- [3] G. Lota, J. Tyczkowski, R. Kapica, K. Lota, E. Frackowiak, Carbon materials modified by plasma treatment as electrodes for supercapacitors, *J. Power Sources* 195 (2010) 7535–7539.
- [4] M. Vangari, T. Pryor, L. Jiang, Supercapacitors: review of materials and fabrication methods, *J. Energy Eng.* 139 (2012) 72–79.
- [5] M. Winter, R.J. Brodd, What are batteries, fuel cells, and supercapacitors? *Chem. Rev.* 104 (2004) 4245–4270.
- [6] R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors, *Electrochim. Acta* 45 (2000) 2483–2498.
- [7] L.L. Zhang, X. Zhao, Carbon-based materials as supercapacitor electrodes, *Chem. Soc. Rev.* 38 (2009) 2520–2531.
- [8] Z. Fan, J. Yan, T. Wei, L. Zhi, G. Ning, T. Li, F. Wei, Asymmetric supercapacitors based on graphene/MnO<sub>2</sub> and activated carbon nanofiber electrodes with high power and energy density, *Adv. Funct. Mater.* 21 (2011) 2366–2375.
- [9] M. Vangari, T. Pryor, L. Jiang, Supercapacitors: review of materials and fabrication methods, *J. Energy Eng.* 139 (2) (2012) 72–79.
- [10] A.G. Pandolfo, A.F. Hollenkamp, Carbon properties and their role in supercapacitors, *J. Power Sources* 157 (2006) 11–27.
- [11] L. Hu, M. Pasta, F.L. Mantia, L. Cui, S. Jeong, H.D. Deshazer, J.W. Choi, S.M. Han, Y. Cui, Stretchable, porous, and conductive energy textiles, *Nano Lett.* 10 (2010) 708–714.
- [12] R.G. Ardrian Schneuwly, Properties and application of supercapacitors from the state-of-the-art to future trends, *Proceeding PCIM* (2000).
- [13] B.E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Springer Science & Business Media, 2013.
- [14] M.S. Halper, J.C. Ellenbogen, *Supercapacitors A Brief Overview*, The MITRE Corporation, McLean, Virginia, USA, 2006, pp. 1–34.
- [15] J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan, X.W.D. Lou, Recent advances in metal oxide-based electrode architecture design for electrochemical energy storage, *Adv. Mater.* 24 (2012) 5166–5180.
- [16] Z. Fan, J. Yan, L. Zhi, Q. Zhang, T. Wei, J. Feng, M. Zhang, W. Qian, F. Wei, A three-dimensional carbon nanotube/graphene sandwich and its application as electrode in supercapacitors, *Adv. Mater.* 22 (2010) 3723–3728.
- [17] D. Yu, L. Dai, Self-assembled graphene/carbon nanotube hybrid films for supercapacitors, *J. Phys. Chem. Lett.* 1 (2009) 467–470.
- [18] M.D. Stoller, S. Park, Y. Zhu, J. An, R.S. Ruoff, Graphene-based ultracapacitors, *Nano Lett.* 8 (2008) 3498–3502.
- [19] M. Zhan, R.P. Wool, J.Q. Xiao, Electrical properties of chicken feather fiber reinforced epoxy composites, *Compos. Part A: Appl. Sci. Manuf.* 42 (2011) 229–233.
- [20] E. Frackowiak, F. Beguin, Carbon materials for the electrochemical storage of energy in capacitors, *Carbon* 39 (2001) 937–950.
- [21] A.M. Dehkoda, N. Ellis, E. Gyenge, Activated Biochar: a green and low-cost electrode material for capacitor applications, *Electrochem. Soc. Mtg. Abstr.* 9 (2013) 611.
- [22] J.H. Jang, A. Kato, K. Machida, K. Naoi, Supercapacitor performance of hydrous ruthenium oxide electrodes prepared by electrophoretic deposition, *J. Electrochem. Soc.* 153 (2006) A321–A328.
- [23] A.R. Boccaccini, J. Cho, J.A. Roether, B.J.C. Thomas, E.J. Minay, M.S.P. Shaffer, Electrophoretic deposition of carbon nanotubes, *Carbon* 44 (2006) 3149–3160.
- [24] P. Sarkar, P.S. Nicholson, Electrophoretic deposition (EPD): mechanisms, kinetics, and application to ceramics, *J. Am. Ceram. Soc.* 79 (1996) 1987–2002.
- [25] A.R. Boccaccini, I. Zhitomirsky, Application of electrophoretic and electrolytic deposition techniques in ceramics processing, *Curr. Opin. Solid State Mater. Sci.* 6 (2002) 251–260.
- [26] O.O. Van der Biest, L.J. Vandeperre, Electrophoretic deposition of materials, *Annu. Rev. Mater. Sci.* 29 (1999) 327–352.
- [27] C. Du, N. Pan, High power density supercapacitor electrodes of carbon nanotube films by electrophoretic deposition, *Nanotechnology* 17 (2006) 5314.
- [28] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna, P. Simon, Ultrahigh-power micrometre-sized supercapacitors based on onion-like carbon, *Nat. Nanotechnol.* 5 (2010) 651–654.
- [29] I. Corni, M.P. Ryan, A.R. Boccaccini, Electrophoretic deposition: from traditional ceramics to nanotechnology, *J. Eur. Ceram. Soc.* 28 (2008) 1353–1367.
- [30] R.L.D. Whitby, Chemical control of graphene architecture: tailoring shape and properties, *ACS Nano* 8 (2014) 9733–9754.
- [31] C. Du, D. Heldbrant, N. Pan, Preparation and preliminary property study of carbon nanotubes films by electrophoretic deposition, *Mater. Lett.* 57 (2002) 434–438.
- [32] B. Thomas, A. Boccaccini, M. Shaffer, Multi-walled carbon nanotube coatings using electrophoretic deposition (EPD), *J. Am. Ceram. Soc.* 88 (2005) 980–982.
- [33] B. Thomas, M. Shaffer, S. Freeman, M. Koopman, K.K. Chawla, A.R. Boccaccini, Key Engineering Materials, *Trans Tech Publ.* 2006, pp. 141–146.
- [34] D. Kurnosov, A. Baturin, A. Bugaev, K. Nikolski, R. Tchesov, E. Sheshin, Influence of the interelectrode distance in electrophoretic cold cathode fabrication on the emission uniformity, *Appl. Surf. Sci.* 215 (2003) 232–236.
- [35] M.-S. Wu, K.-H. Lin, One-step electrophoretic deposition of Ni-decorated activated-carbon film as an electrode material for supercapacitors, *J. Phys. Chem. C* 114 (2010) 6190–6196.
- [36] O. Paris, C. Zollfrank, G.A. Zickler, Decomposition and carbonisation of wood biopolymers—a microstructural study of softwood pyrolysis, *Carbon* 43 (2005) 53–66.
- [37] Y. Wang, Q. He, J. Guo, H. Wei, K. Ding, H. Lin, S. Bhana, X. Huang, Z. Luo, T. Shen, Carboxyl multiwalled carbon-nanotube-stabilized palladium nanocatalysts toward improved methanol oxidation reaction, *ChemElectroChem* 2 (2015) 559–570.
- [38] Y. Wang, Q. He, J. Guo, J. Wang, Z. Luo, T.D. Shen, K. Ding, A. Khasanov, S. Wei, Z. Guo, Ultrafine FePd nanoalloys decorated multiwalled carbon nanotubes toward enhanced ethanol oxidation reaction, *ACS Appl. Mater. Interfaces* 7 (2015) 23920–23931.
- [39] Y. Wang, H. Wei, J. Wang, J. Liu, J. Guo, X. Zhang, B.L. Weeks, T. Shen, S. Wei, Z. Guo, Electropolymerized polyaniline/manganese iron oxide hybrids with an enhanced color switching response and electrochemical energy storage, *J. Mater. Chem. A* 3 (2015) 20778–20790.
- [40] D. Qu, H. Shi, Studies of activated carbons used in double-layer capacitors, *J. Power Sources* 74 (1998) 99–107.
- [41] E. Raymundo-Pinero, V. Khomenko, E. Frackowiak, F. Beguin, Performance of manganese oxide/CNTs composites as electrode materials for electrochemical capacitors, *J. Electrochem. Soc.* 152 (2005) A229–A235.
- [42] S.T. Mayer, R.W. Pekala, J.L. Kaschmitter, The aerocapacitor: an electrochemical double-layer energy-storage device, *J. Electrochem. Soc.* 140 (1993) 446–451.
- [43] B. Dong, B.-L. He, C.-L. Xu, H.-L. Li, Preparation and electrochemical characterization of polyaniline/multi-walled carbon nanotubes composites for supercapacitor, *Mater. Sci. Eng.: B* 143 (2007) 7–13.
- [44] Q. Wang, Q. Cao, X. Wang, B. Jing, H. Kuang, L. Zhou, A high-capacity carbon prepared from renewable chicken feather biopolymer for supercapacitors, *J. Power Sources* 225 (2013) 101–107.
- [45] A. Jain, S.K. Tripathi, Nano-porous activated carbon from sugarcane waste for supercapacitor application, *Journal of Energy Storage* 4 (2015) 121–127.