

Impact of Different-2 Electrode Materials to the Performance of Electrochemical Super Capacitors

Amarendra Chaudhary¹, Pragati Singh²

¹M.Tech scholar, Department of Electronics Engineering, Buddha Institute of Technology

²M.Tech scholar, Department of Electrical Engineering Azad Institute of Technology

Abstract - Supercapacitors are the ideal electrochemical energy storage devices that bridge the gap between conventional capacitors and batteries tolerating the applications for various powers and energy requirements. Supercapacitor shares the same fundamental equations as conventional capacitors; to attain higher capacitances, supercapacitor uses electrodes having high specific surface area and thinner dielectrics. With these properties it makes them have power densities greater than those of batteries and energy density greater than those of conventional capacitors. Researches being carried out now are on how to improve the energy density so that they can be used in wider range of applications. The performance of supercapacitor relies on factors such as electrochemical properties of electrode materials used, electrolyte and voltage range. However, most researches are focused on the development of new electrode materials that will yield better performances. In this review paper, storage principle and characteristics of electrode materials such as carbon based materials in supercapacitors have been reported.

Key Words: carbon based Materials, EDLC, high specific surface area, power densities, energy densities, Columbic efficiency (η)

1. INTRODUCTION

Increasing demand in the need of global-energy drives the development of alternative or nonconventional energy sources with high power and energy densities. Batteries, fuel cells and supercapacitors are typical non-conventional energy devices which are based on the principle of electrochemical energy conversion. They find widespread applications in consumer electronics ranging from mobile phones, laptops, digital cameras, emergency doors and hybrid vehicles etc. In these devices, chemical energy is converted in to electrical energy by means of electrochemical reactions. As far the fuel cells are concerned, as long as the fuel is fed, electrical energy can be obtained. In case of batteries, the stored energy can be drawn at the time of need. Supercapacitor is a typical energy storage device (similar to secondary battery) which possess high specific capacitance, high power density and long cycle life. Supercapacitors can be used in combination with batteries to meet the start-up power, usually high power

density Depending on the mode of energy storage in supercapacitors.

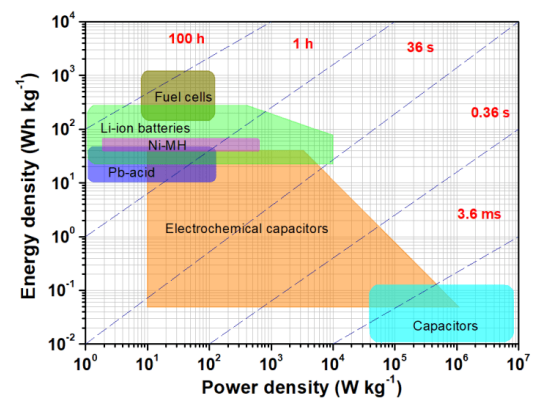


Figure 1. Ragone plot of the power-energy density range for different electrochemical energy storage devices.

1.1 Electrochemical Supercapacitors

Electrochemical supercapacitors (ESs) differ from traditional capacitors because they have lower power densities, greater charge storage densities, and different material requirements. Electrical double-layer capacitors (EDLCs) incorporate an electrolyte that allows charged ions to assemble on porous electrode surfaces with much higher areas than traditional capacitors. The charge is separated by a solvent cage layer at the interface of only 5 to 10 angstroms. A combination of high surface area and small charge separation enables the generation of high energy density compared to traditional static capacitors. Optimizing ES design involves the selection of appropriate electrodes, electrolytes, separators, and sealants. Electrode materials must be conductive and highly porous to increase charge storage ability. Non-metal porous electrodes are used in ECs rather than the metal plates of traditional capacitors; this creates a need for current collector plates to enhance the conduction of electrons in the capacitor. Collectors must be in strong contact with the electrode layer, remain stable during charge and discharge, and be highly conductive to enhance electron transport.

Overall, careful selection and matching of ES materials can minimize resistances, avoid short circuits, reduce

safety issues, support high ion mobility, increase operating voltage, and enhance the charge storage capacity of future ES devices.

Electrode materials in ESs fall into two categories based on storage mechanism: EDLC and pseudo capacitive materials. Each material in these categories presents its own benefits and challenges as this technology moves toward the next generation of ES devices. EDLC materials are carbons that provide physical charge storage at the interface between electrode and electrolyte.

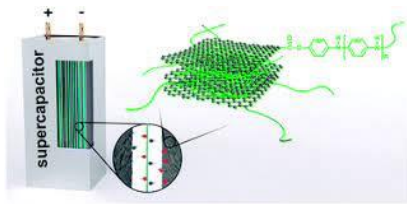


Figure1.1 Electrochemical Super capacitors for Energy Storage

2. Future Applications

As always, talk about super capacitor technology isn't without discussing plans for the future. We're getting very close to standalone super capacitor batteries. Researchers at the University of Central Florida successfully created a prototype super capacitor battery that takes up a fraction of the space of lithium-ion cells, charges more quickly, and can recharge 30,000 times while still working like new. Other innovations set to change the capacitor business include designing ECs with graphene to create lightweight super capacitors with energy-storage capabilities between 150 F/g and 550 F/g, at a fraction of the price of current EC designs. Still, it's a concept still being explored.

2.1 Realistic Applications

The most promising future of super capacitors is the combination of a double-layer charging interface with existing energy-storage technologies. By adding EC technology to fuel-cell applications, companies have been successful in rapidly improving the charge/discharge cycle performance of hybrid- and electric-vehicle applications. Many cities using hybrid technologies for public transit have also seen an improvement in overall energy storage and charge cycles when coupling their energy systems with things like super capacitor-based engine starters and charging stations. The closest future application for super capacitors is in energy storage and rapid charging.

3. PARAMETERS IN SUPERCAPACITORS

3.1 Columbic efficiency (η)

It is defined as the ratio of discharging time and charging time and it can be calculated by the following equation (1)

$$\eta = \frac{t_D}{t_C} \cdot 100\% \dots \dots \dots (1)$$

Where η is columbic efficiency, t_D is discharging time(s), t_C is charging time (s). The columbic efficiency is calculated by cyclic stability method; by comparing the first and the end cycle here, as the specific capacitance value increases, the columbic efficiency decreases up to applied higher voltage (2V).

3.2 Power density (P) and Energy density (E)

Charge-discharge method is one of the well known methods to analyze the power density and energy density values of the supercapacitors. Notably, the energy density of supercapacitor decreases with increase in power density and therefore both of them have inverse relationship with each others. The energy density and power densities two parameters are very important tools for the investigation of electrochemical performance and its electrochemical cells. These kinds of parameters have been used to estimate the performance of working electrode materials. Energy density and power density were calculated from the following equations (2) and (3).

$$E = \frac{1}{2} C (\Delta v)^2 \dots \dots \dots (2)$$

$$P = \frac{E}{t} \dots \dots \dots (3)$$

Where C is specific capacitance ($F g^{-1}$), ΔV is potential window (V), t is discharge time (s), E is energy density (Wh kg^{-1}) and P is power density (KW kg^{-1}).

4. TYPES OF ELECTRODE MATERIALS FOR SUPERCAPACITORS

The selection of electrode materials and their fabrication play a crucial role in enhancing the capacitive performance of SCs. Electrodes of SCs must provide thermal stability, high SSA, corrosion resistance, high electrical conductivity, appropriate chemical stability, and suitable surface wet ability. They should also be low-cost and environmentally benign. Besides, their capability of transferring the faradic charge is important to enhance the capacitance performance.

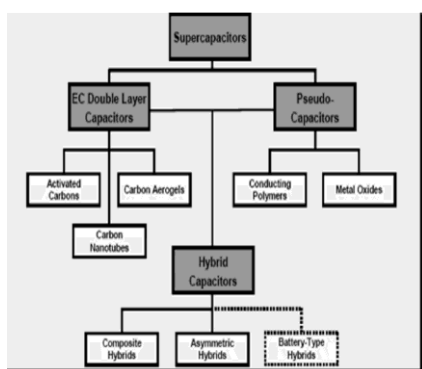


Figure 1.2 TYPES OF ELECTRODE MATERIALS FOR SUPERCAPACITORS

5. EDLC Electrode Materials

5.1 Activated Carbons

Carbons act as excellent conductors, are chemically stable, and have high surface areas, making them the preferred materials for double-layer electrodes in modern ESs. Activated carbons can often achieve capacitances as high as 100 to 200 F.g⁻¹ in aqueous electrolyte systems and 50 to 150 F.g⁻¹ in organic media. An AC material prepared by Gryglewicz et al. showed 160 F.g⁻¹ in aqueous electrolyte for a material made from coal and activated by steam (SA = 1270 m².g⁻¹). Prepared AC's from firewood using steam activation resulting in a maximum capacitance of 120 F.g⁻¹ in acidic electrolyte. KOH activation was used on petroleum coke by Wang et al. to produce material with 1180 m².g⁻¹ and maximum capacitance of 160 F.g⁻¹ in aqueous electrolyte. Kierzek et al. illustrated that high surface area carbon (3000 m².g⁻¹) produced with KOH activation showed improved capacitance of 300 F.g⁻¹ in aqueous electrolyte. Table 4.2 shows performances in organic electrolytes and illustrates that

- (1) High surface area AC does not directly correlate to higher performance and
- (2) Precursor materials and activation mechanisms are important to electrochemical performance.

Carbon	Activation Process	BET SA (m ² /g)	Average Pore Size (nm)	Capacitance (F/g)
Grade 1 Cloth	None	402	4.14	28
RP-15	Steam	1318	1.94	90
NK-260	KOH	2040	1.92	154
Nuchar RGC	Chemical	1622	2.99	82
Supra 50	Steam	1989	2.05	81
TDA-1	Carbon dioxide	2053	2.04	86
Generation 1	Carbon dioxide	1907	2.46	88

TABLE 1 Various Activated Carbon Powders and Their Performances in Organic Solvent

The Maxsorb commercial carbon made in Kansai, Japan is produced by KOH activation of petroleum coke at 700°C and achieves over 3100 m².g⁻¹. Wan et al. demonstrated that Maxsorb carbon can produce capacitance in aqueous electrolyte of 225 F.g⁻¹ at 1 A.g⁻¹ current density. In the same test, they showed that polymeric-activated carbon derived from KOH activation of resorcinol-formaldehyde exhibited only 1673 m².g⁻¹ surface area but was able to reach 325 F.g⁻¹ in aqueous electrolyte.

5.2 Templated Active Carbons

As carbon electrode technology moves forward, researchers have room to play with advanced carbon structures that have higher pore orders and increased conductivities. Closed pores produced by the activated carbon process reduce charge rate capabilities and overall storage capacities. Template systems offer to improve this deficiency by creating long range orders within carbon structures. The process commonly involves mesoporous silica or zeolite templates as seen in Figure 3 Results of studies of template systems have shown performance exceeding 300 F.g⁻¹. The costs of templates currently limit their use for building a theoretical understanding of the effects of pore size on capacitance and ion kinetics. With improved production methods and lower costs, these methods may become accessible to commercial energy storage applications over time.

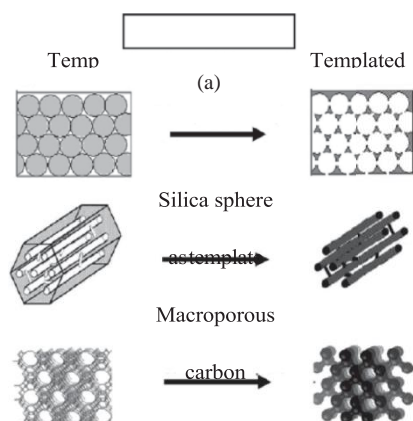


FIGURE 3 Templating for pore types. (Source: Zhang, L. L. and X. S. Zhao. 2009. *Chemical Society Reviews* 38, 2520–2531. With permission.)

Zeolite templated carbons exhibit high performance without extensive activation due to the high surface areas and long range orders of their porous structures. Wang et al. [37] used zeolite X ($670 \text{ m}^2.\text{g}^{-1}$, 1.4 nm pore size) and 8 hr of chemical vapor deposition (CVD) to introduce carbon into the template. The resulting template CNX-2 ($2700 \text{ m}^2.\text{g}^{-1}$) had capacitance of 158 F.g^{-1} (at 0.25 A.g^{-1}) and energy density of 25 Wh.g^{-1} , respectively, in aqueous electro-lyte. Due to the ordered nature of the pore structure, over 97% of the capacitance was retained at rates of 2 A.g^{-1} . The zeolite could produce dense carbon pore structure ($1.07 \text{ cm}^3.\text{g}^{-1}$) and improved volumetric capacitance versus most activated carbon materials.

5.3 Carbon Nanotubes

More advanced carbons are being heavily studied for their potential in controlling structures and enhanced properties compared to activated carbon. Carbon nanotubes (CNTs; Figure 4) are cylindrical nanostructures that exhibit a near-1-dimensional structures. The cylinders are composed of graphitic carbon walls in the forms: single wall (SWNTs), double wall (DWNTs), and multiwall nanotubes (MWNTs). Their cylindrical radii are on the order

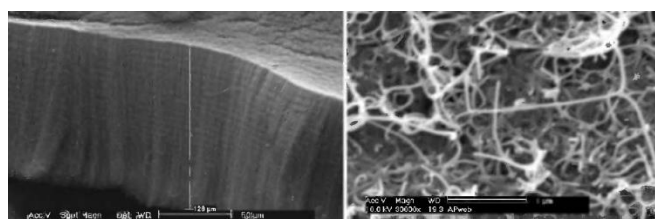


FIGURE 4 Comparison of (a) aligned CNT electrode array and (b) entangled CNT matrix.

of nanometers and length can reach millimeter scales. The graphitic planes in a CNT produce electrically conductive carbon tubes (conductivities as high as 1000 S.cm^{-1}) depending on CNT type. An ordered array or a loosely entangled layer of CNTs has high surface accessibility, leading to high ionic conductivity. The combination of rapid ion diffusion and high electrical conductivity produces devices of higher power than AC electrodes. demonstrated the power density of paper-based CNT electrodes. CNTs were brushed onto paper and through strong Vander Waals forces adsorbed to the cellulose fibers in the paper, forming a strong, porous, and conductive electrode. Considering only the weight of active CNT material, the device showed an exceptional maximum power density of 200 kW.kg^{-1} and a maximum energy density of 30 Wh.kg^{-1} . Yoon et al. shows that aligned CNT films can maintain a near rectangular CV curve at high scan rates of 1 V.s^{-1} . At the same rate, the AC material ($1800 \text{ m}^2.\text{g}^{-1}$) tested showed high levels of resistance. However, the combination of very low electrode equivalent series resistance (ESR, $1.9 \Omega.\text{cm}^2$) and high ionic conductivity could enable the MWNT electrode to retain 12 F.g^{-1} or 2.2 Wh.kg^{-1} for high current density of 200 A.g^{-1} , corresponding to power density of 125 kW.kg^{-1} . When the AC cloth was charged at rates above 10 A.g^{-1} , large resistance prevented the development of any energy or capacitance on the electrode. Maximum power of the device is calculated to be 3.2 MW.kg^{-1} . An optimized process was utilized to create a CNT device with intimate contact to the metal collector and surface area beyond $2000 \text{ m}^2.\text{g}^{-1}$. Minimization of bundling could lead to 80% availability of the area to electrolyte ions. The resulting CNT electrode showed high capacitance of 115 F.g^{-1} (24.7 Wh.kg^{-1}) in organic electrolyte at a current density of 1 A.g^{-1} . The maximum power density was calculated to be 98.9 kW.kg^{-1} and due to the dense CNT packing, maximum volumetric power density was determined to be 60.1 kW.L^{-1} .

5.3 Graphene

Graphene is a new advanced carbon material with unique morphology that distinguishes it from other materials in the EDLC market. Graphite is a highly ordered carbon structure consisting of many tightly stacked sheets that exhibit angstrom level interspacing due to strong $\pi-\pi$ bonding between the basal lattice planes of the graphene. A graphene sheet consists of many carbon atoms arranged into a large two-dimensional crystal lattice (Figure 4.15a). When separated into fewer layers through the application of some physical or chemical energy (single- or few-layer

graphene), the material takes on very different properties from its bulk graphite state. Graphene is mechanically robust, exhibiting a quantum Hall effect at room temperature and undergoing ballistic conduction of charge carriers along the basal planes, resulting in good conductivity in the material that the conductivity of chemically reduced graphene along its basal plane, on the order of 200 S.m^{-1} , was close to that of bulk graphite. The high conductivity helps reduce internal resistance in the materials and provides power gains similar to those exhibited by CNTs. The most important properties for the ES market include the ability of graphene to reach the high theoretical surface area of $2630 \text{ m}^2.\text{g}^{-1}$ of its parent graphite and the highly regular pore spacing across the crystal lattice. Due to the atomic thickness, negligible diffusion transport distances result in low ionic resistance. The high theoretical surface area of the fully exposed graphene sheets could provide a maximum theoretical capacitance of 550 F.g^{-1} . The combination of good electrical conductivity, low internal resistance, and high surface area makes graphene a competitive material for EDLCs. However, as with CNTs, aggregation and poor macroscale controls still limit the full potential of graphene materials. Restacking of graphene sheets can occur in solution over time during annealing and during drying procedures, leading to reduced surface area. Stoller et al. were one of the first groups to utilize chemically reduced graphene (CMG) for ES applications. They produced a CMG graphene that exhibited an area of $705 \text{ m}^2.\text{g}^{-1}$ and capacitances reaching to 107 F.g^{-1} in KOH and 100 F.g^{-1} in acetonitrile using cyclic voltammetry with a 20 mV.s^{-1} scan rate. Many graphene-based materials report 100 to 200 F.g^{-1} , outperforming CNT devices in an aqueous electrolyte. Most EDLC electrodes used in ESS use thick material layers that are opaque and fairly brittle. For example, Yu et al. produced flexible, uniform, 25 nm thick layers of graphene that offered up to 70% optical transparency and capacitance of 135 F.g^{-1} . At 1 A.g^{-1} the capacitance of the wet film reached $\sim 190 \text{ F.g}^{-1}$. Thermally dried graphene shows a complete voltage drop due to resistance that prevents the development of capacitance beyond a current density of 10 A.g^{-1} . Freeze-dried graphene fares better by restricting the pathways for pore collapse during the drying phase, but neither sample exhibited the same high power, high energy performance of the wet graphene electrode. Due to the high ionic conductivity of the graphene and short transport distances between solvated sheets, the electrode was also tested in an ionic liquid electrolyte that had a stable operation window of 4 V. By utilizing ionic liquid, the maximum energy and peak power densities were calculated at 150 Wh.kg^{-1} and 770 kW.kg^{-1} respectively. Figure 4.18 shows that energy density remains above 100 Wh.kg^{-1} for average power as high as 50 kW.kg^{-1} and with energy density approaching

that of a modern battery system. The high power and energy stability indicate the importance of keeping graphene samples wet between synthesis steps to maintain porosity and performance.

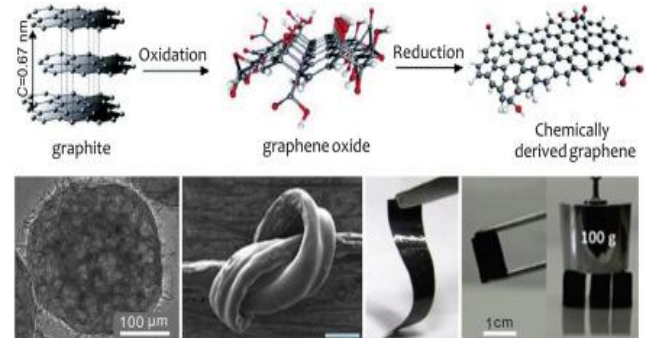


Figure 4. PIC Graphene-based materials for supercapacitor electrodes

5.4 Carbon Nanofibers

Carbon nanofibers (CNFs) are long hollow fibers composed of ordered arrangements of graphene sheets. Electrospun polymers exhibit low levels of molecular defects, thus optimizing strength and creating order that leads to higher conductivity of 700 to 900 mS.cm^{-1} after carbonization at temperatures between 700 and 800°C . The amorphous character of the CNFs allows effective functionalization and activation of the lowly graphitic form. Lowly graphitic PAN-based CNFs synthesized by Kim et al. with steam activation ($1100 \text{ m}^2.\text{g}^{-1}$) at 750°C showed 120 F.g^{-1} at 1 A.g^{-1} in KOH electrolyte. They also showed that polyamic acid (PAA) fibers steam activated at 750°C ($1400 \text{ m}^2.\text{g}^{-1}$), produced 160 F.g^{-1} at 1 A.g^{-1} in KOH electrolyte. electrospun CNF fibers by using a polymer blend containing a phenolic resin and a high density polyethylene (PE). The blend was carbonized at 800°C producing CNFs of $450 \text{ m}^2.\text{g}^{-1}$ (700 mS.cm^{-1}) and then KOH activated at 750°C to increase surface area to $1500 \text{ m}^2.\text{g}^{-1}$. The KOH activation reduced conductivity to 400 mS.cm^{-1} but boosted capacitance to 180 F.g^{-1} (from 50 F.g^{-1} not activated) at 1 A.g^{-1} (20 mA.cm^{-2}) in KOH electrolyte. utilized the accessible webs created by the long fibers to derive a CNF composite with PANI (Figure 4.19). The base capacitance of the CNFs inactivated managed 310 F.g^{-1} in H_2SO_4 at 2 A.g^{-1} and electrical conductivity was 950 mS.cm^{-1}

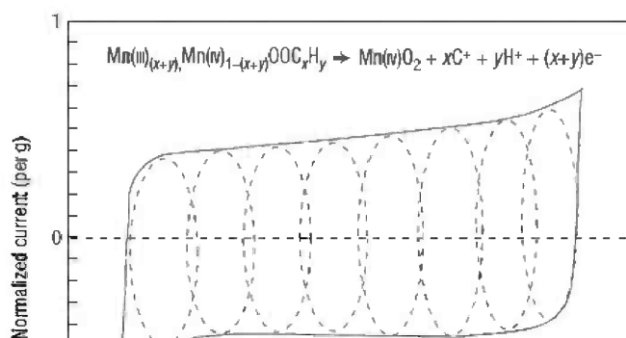


FIGURE 4.19 SEM images of: (a) PANI CNF composite web and (b) CNF web support (50,000× magnification). (Source: Yan, X. et al. 2011. *Nanoscale*, 3, 212–216. With permission.

6. CONCLUSIONS

On the whole, supercapacitors have emerged as an important alternative energy technology with superior electrochemical properties, high energy density and good cyclic stability. Due to the high surface area, low porosity, high thermal and electrochemical conductivity, carbon materials (CNT, MWCNT, carbon nanofibres and activated carbon) have shown greatly improved supercapacitance performances. The highest specific capacitance value of activated nanoporous carbon is about 240 F g^{-1} . Though some of the carbon materials exhibited low specific capacitance and high energy density, their specific capacitance can be enhanced by the incorporation of metal oxides or conducting polymers in the activated carbon electrode materials. Polyaniline/multi-walled carbon nanotubes exhibited the highest specific capacitance value of 560 F g^{-1} among all the polymers based supercapacitors. In conclusion, future efforts should focus on cheap electrode materials obtained using simple fabrication processes.

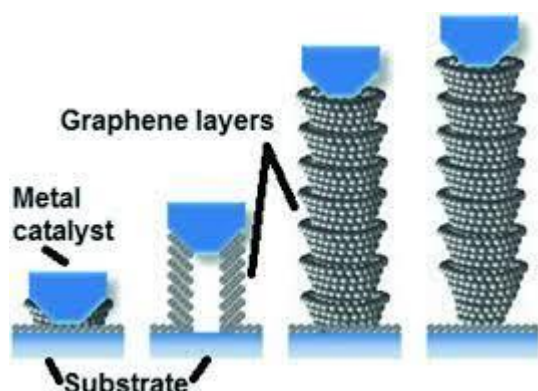


Figure.5 Graphene layer

7. REFERENCES

1. Simon, P. and Y. Gogotsi. 2008. Materials for electrochemical capacitors. *Nature: Materials*, 7, 845–854.
2. Kötz, R. 2000. Principles and applications of electrochemical capacitors. *Electrochimica Acta*, 45, 2483–2498.
3. Linden, D. and T. Reddy, *Handbook of Batteries*, 4th ed. New York: McGraw Hill.
4. Burke, A. and M. Miller. 2011. The power capability of ultracapacitors and lithium batteries for electric and hybrid vehicle applications. *Journal of Power Sources*, 196, 514–522.
5. Winter, M. and R. J. Brodd. 2004. What are batteries, fuel cells, and supercapacitors? *Chemical Reviews*, 104, 4245–4269.
6. Worlds of David Darling Encyclopedia (online). Lead–acid battery. http://www.daviddarling.info/encyclopedia/L/AE_lead-acid_battery.html [accessed April 4, 2012].
7. Georgia State University. 2012. Lead–acid battery: hyperphysics (online). <http://hyperphysics.phy-astr.gsu.edu/hbase/electric/leadacid.html> [accessed April 9, 2012].
8. Davies, A. and A. Yu. 2011. Material advancements in supercapacitors: From activated carbon to carbon nanotube and graphene. *Canadian Journal of Chemical Engineering*, 89, 1342–1357.
9. Qu, D. and H. Shi. 1998. Studies of activated carbons used in double-layer capacitors. *Journal of Power Sources*, 74, 99–107.
10. Kim, Y. et al. 2004. Correlation between the pore and solvated ion size on capacitance uptake of PVDC-based carbons. *Carbon*, 42, 1491–1500.