

Nanocomposite Electrodes for High-Performance Supercapacitors

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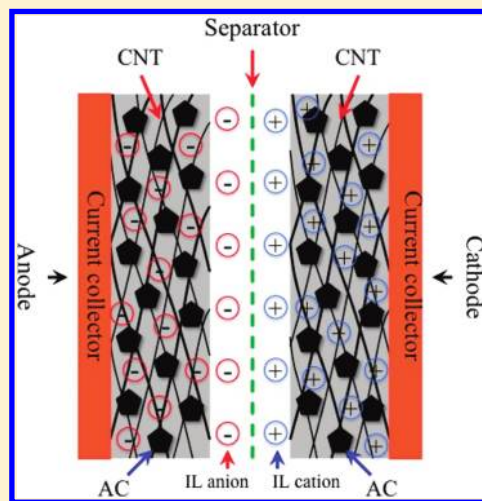
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ABSTRACT: We report a new class of nanocomposite electrodes for the development of high-performance supercapacitors with environmentally friendly ionic liquid electrolytes. Having the high-surface-area activated carbons, carbon nanotubes, and ionic liquids as integrated constituent components, the resultant composites show significantly improved charge storage and delivery capabilities. In an ionic liquid electrolyte, the composites possess a superior capacitance (188 F/g) over a pure carbon nanotube electrode (20 F/g) and a conventional activated carbon electrode (90 F/g). On the basis of these nanocomposite electrodes and an ionic liquid electrolyte, we have further developed prototype supercapacitors with a high cell voltage (4 V) and superior energy and power densities (50 Wh/kg and 22 kW/kg, respectively, in terms of the mass of the active electrode material). The nanocomposite supercapacitors developed in the present study clearly outperform the current supercapacitor technology, providing a new approach in fabricating advanced supercapacitors with a high-performance, inherently safe operation and long lifetime.

SECTION: Energy Conversion and Storage



Supercapacitors are a unique type of high-power electrochemical energy storage devices being developed for a wide range of applications, including consumer electronics, medical electronics, electrical utilities, transportation, and military defense systems. However, the energy and power densities, safety, and cycle life of currently available supercapacitors need to be significantly improved to satisfy the rapidly increasing performance demands for the aforementioned and many other applications. Therefore, the development of new electrodes and new electrolytes with superior properties is essential.

High-surface-area activated carbons (ACs) are predominant electrode materials for commercial supercapacitors.¹ However, ACs have a limited capacitance largely because of their low mesoporosity and poor electrolyte accessibility,² although they possess a high specific surface area (1000–2000 m²/g). A balanced surface area and mesoporosity is thus highly desirable for carbon electrode materials to be used in high-performance supercapacitors.^{3–5} In this regard, carbon nanotubes (CNTs) with a high specific surface area (albeit relatively lower than that of ACs) and well-defined hollow core are attractive electrode materials for supercapacitors.⁶ Indeed, CNTs have been used as either electrodes^{7,8} or conductive additives in composite electrodes with ACs,^{9,10} conjugated polymers,^{11–13} or metal oxides.^{14–16} Compared with ACs, CNTs have an excellent electrical conductivity, mesoporosity, and electrolyte-accessibility. Unlike the microporosity of ACs (pore size: <2 nm), the mesoporosity of CNTs (pore size: 2–50 nm) provides them

with a highly electrolyte accessible network and thus a high charging/discharging rate capability.^{6,7} It is then desirable to combine the high surface area of ACs with the high mesoporosity of CNTs to achieve a balanced surface area and mesoporosity and hence an enhanced capacitive performance for the resultant composites. Indeed, the combination of ACs with CNTs has allowed for the fabrication of composite electrode materials of an enhanced capacitive performance with synergistic effects, even in supercapacitors using conventional organic electrolytes.^{9,10} Recently, ionic liquids (ILs) have been explored as electrolytes in certain advanced supercapacitors with improved energy and power densities, operation safety, and lifetime.¹⁷ This is because ILs have a large electrochemical window, wide liquid phase range, nonvolatility, nonflammability, nontoxicity, and environmental compatibility with respect to conventional aqueous and organic electrolytes. However, initial study showed a limited capacitance for CNTs in IL electrolytes, even with the large potential window.^{18,19} The limited specific surface area of these CNT materials is believed to be responsible for their poor capacitance in IL electrolytes. Supercapacitors have also been fabricated from ACs in IL electrolytes, and only slightly improved energy and power densities were observed due to the poor compatibility between ACs and IL electrolytes.²⁰

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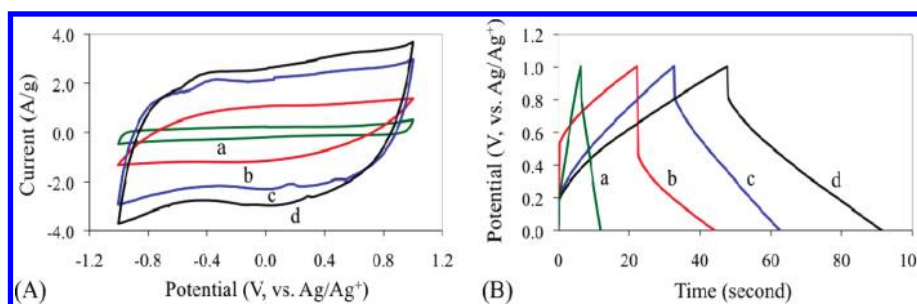


Figure 1. (A) CVs and (B) galvanostatic charge/discharge curves obtained in [EMIM][Tf₂N] for a (a) CNT paper electrode, (b) a conventional AC electrode, (c) an AC/CNT binary composite electrode, and (d) an AC/CNT/IL ternary composite electrode. Scan rate for CV: 20 mV/s. Current density for galvanostatic charging/discharging: 10 mA/cm².

In this study, we combined high-surface-area ACs, commercially available CNTs, and environmentally benign ILs to develop a novel class of nanocomposite electrodes (denoted as: AC/CNT/IL). Owing to the improved surface area and enhanced electrolyte accessibility, the AC/CNT/IL composites are highly capacitive in the IL electrolytes. In conjunction with large-electrochemical-window IL electrolytes, supercapacitors based on the AC/CNT/IL composite electrodes showed a high cell voltage (4 V) with superior energy and power densities (50 Wh/kg and 22 kW/kg, respectively, in terms of the mass of the active electrode materials), significantly outperforming the current supercapacitor technology.¹

In a typical experiment, a mixed single-walled/multiwalled CNT paper product with long tube length (10–100 μm) and high electrical conductivity (1000 S/cm) from Nanocomp Technologies was used directly as the CNT electrode and also as the CNT source for synthesizing composite electrodes. The composite electrodes were prepared by a slurry procedure. For AC/CNT composite (AC/CNT/PVdF (wt %): 61.5/20.5/18.0), predetermined amounts of ACs (specific surface area: ~2000 m²/g, from Maxwell Technologies) and CNTs were mixed with a PVdF (poly(vinylidene fluoride))/NMP (1-methyl-2-pyrrolidone) solution, followed by casting the resultant slurry onto an Al foil current collector. For AC/CNT/IL composite (AC/CNT/IL/PVdF (wt %): 64.0/20.3/7.7/8.0), IL [EMIM][Tf₂N] (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) (from Covalent Associates) was introduced during the above slurry preparation. The obtained composite/Al foil panels were pre-heated at 80 °C for 1 h and then annealed at 260 °C for another hour, resulting in the formation of sheet electrodes with a uniform composite film (thickness: 100–200 μm; loading density: 5–10 mg/cm²) on the Al foil. Throughout this work, a conventional AC electrode (thickness: 150 μm, carbon loading: 9 mg/cm², from WL Gore & Associates) currently employed for commercial supercapacitors was used as the baseline electrode for evaluating the performance of the newly developed composite electrodes.

All electrochemical measurements were performed with a PGSTAT30 potentiostat (Eco Chemie B.V.). For the testing of electrode materials in [EMIM][Tf₂N], a three-electrode electrochemical cell was employed, consisting of the test electrode (1 cm²) as the working electrode, a platinum wire (1.5 mm diameter) as the auxiliary electrode, and a silver wire (1.5 mm diameter) as the quasi-reference electrode. In a KEMEX GB1000 dry glovebox, the test capacitors (CR2032 coin cells) were fabricated by sandwiching an [EMIM][Tf₂N]-soaked PTFE membrane separator (thickness: 23 μm, from WL Gore & Associates)

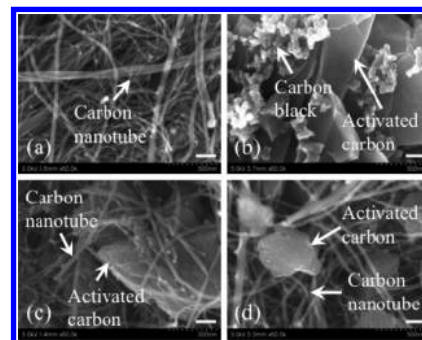


Figure 2. SEM images of (a) a CNT paper electrode, (b) a conventional AC electrode, (c) an AC/CNT binary composite electrode, and (d) an AC/CNT/IL ternary composite electrode. Scale bar: 500 nm.

between two identical electrodes (1.23 cm²/each). For the testing of capacitors, a two-electrode system was used.

Owing to its superior properties of a large electrochemical window, high ionic conductivity, low viscosity, high decomposition temperature, and good water immiscibility,²¹ [EMIM][Tf₂N] was used as the IL electrolyte in the present work. In [EMIM][Tf₂N], the bare CNT electrode showed a rapid charge storage and delivery kinetics (i.e., high rate capability), which can be evidenced by its rectangle shape and sharp transient responses at both ends of the cyclic voltammogram (CV) (Figure 1A(a)), along with a small IR drop of the galvanostatic charge/discharge profile (Figure 1B(a)). The excellent electrical conductivity, mesoporosity, and electrolyte accessibility of CNTs could be responsible for the observed high rate capability.^{6,22} The CNT electrode showed a very small CV current (Figure 1A(a)) and hence a low capacitance (20 F/g). Such a low capacitance has been previously reported^{18,19} and was attributed to the low specific surface area of the CNT electrode (82 m²/g, Micromeritics Gemini 2375 surface area analyzer). Because of its higher specific surface area (1486 m²/g), however, a conventional AC electrode showed a higher CV current (Figure 1A(b)) with an improved capacitance (90 F/g). Nevertheless, the increase in capacitance (90 vs 20 F/g) is not proportional to the increase in surface area (1486 vs 82 m²/g) because of the poor electrolyte accessibility of ACs.² Furthermore, the non-rectangle-shaped CV (Figure 1A(b)) and the large IR drop during the charge/discharge process (Figure 1B(b)) associated with the AC electrode indicate its low rate capability in the IL electrolyte.

Unlike the morphology of the CNT electrode shown by the scanning electron microscopic (SEM) image (Hitachi S-4800 high-resolution SEM) (Figure 2a), carbon black particles in the

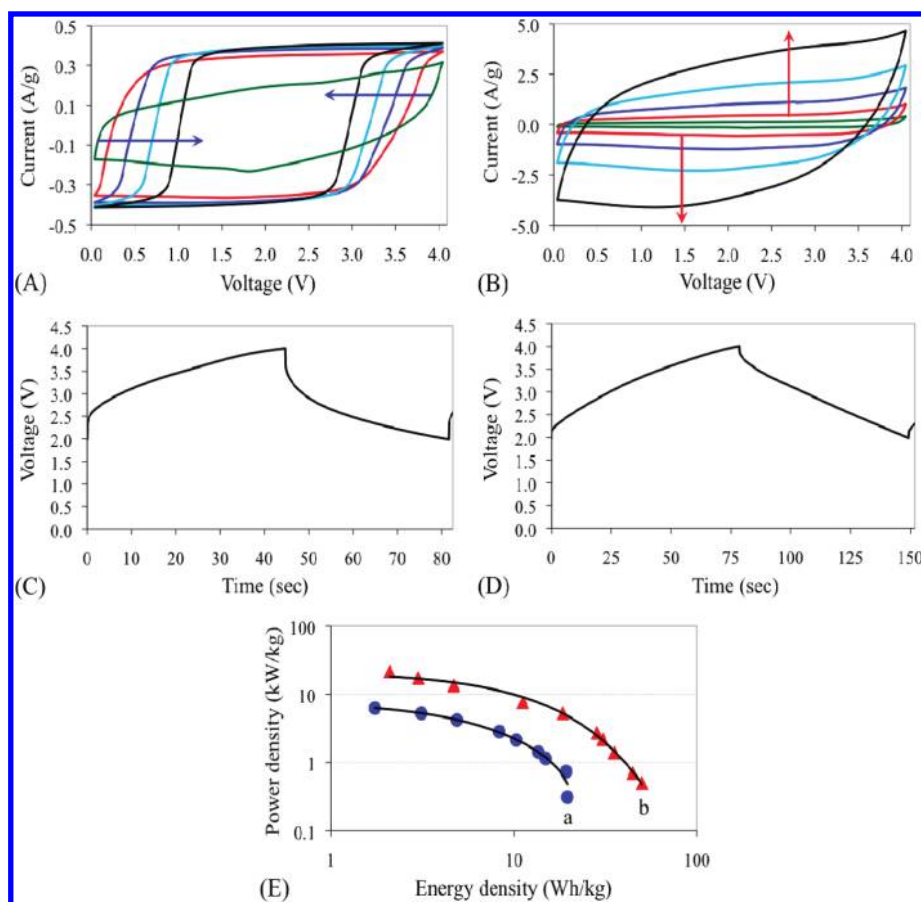


Figure 3. (A,B) CV and (C,D) galvanostatic charge/discharge curves obtained for an (A,C) AC-IL capacitor and a (B,D) AC/CNT/IL-IL capacitor. Scan rates for CV: increasing from 5, 20, 50, 100, to 200 mV/s, as indicated by arrows. Current density for galvanostatic charging/discharging: 10 mA/cm². Cut-off voltage: 2.0/4.0 V. (E) Ragone plots of (a) the AC-IL capacitor and (b) the AC/CNT/IL-IL capacitor. Current density: 2–50 mA cm⁻². Cut-off voltage: 2.0/4.0 V. Performances of the capacitors are based on the mass of the active electrode materials.

AC electrode typically aggregate together (Figure 2b) to form a poor conducting network. This, coupled to the low mesoporosity of ACs and the relatively high viscosity of ILs with respect to conventional aqueous and organic electrolytes, led to a poor electrolyte accessibility and low rate capability for the AC electrode in the IL electrolyte. Therefore, both a high surface area and high electrolyte accessibility are needed for the carbon electrode to be used to develop high-performance supercapacitors with the large-electrochemical-window IL electrolytes. In this regard, we modified a slurry procedure commonly used for preparing conventional AC electrodes for combining commercially available ACs and CNTs with a polymer binder (e.g., PVdF) to fabricate the AC/CNT nanocomposite electrodes. Here AC, CNT, and PVdF provide the surface area, conductivity and mesoporosity, and film formidability, respectively, leading to a balanced surface area and electrolyte accessibility for the composite. The optimal composition of the composite was determined to be 61.5/20.5/18.0 (AC/CNT/PVdF, wt %). Upon potential cycling in [EMIM][Tf₂N], it was found that the transient response at the ends of CV for the AC/CNT composite electrode is similar to that of a pure CNT electrode, both sharper than that of the conventional AC electrode (cf. curves a–c of Figure 1A). These results indicate the improved electrolyte accessibility and rate capability for the composite electrode over the AC electrode, which is further confirmed by its

galvanostatic charge/discharge scanning that shows a similar IR drop to that of a pure CNT electrode, but much smaller than that of a conventional AC electrode, for the AC/CNT composite electrode (Figure 1B). Morphologically, unlike the aggregation of carbon black particles in a conventional AC electrode (Figure 2b), CNTs in the AC/CNT composite electrode were fairly well-distributed (Figure 2c) to provide a uniform conductive network for the electrode. This, together with the high mesoporosity of CNTs,^{6,7} produced a high electrolyte accessibility and hence an enhanced rate capability for the AC/CNT composite electrode in the IL electrolyte. CNTs have been previously investigated as conductive additives to provide a highly conductive and electrolyte-accessible network in high-rate composite electrodes for lithium-ion batteries, including graphite anode²³ and a range of cathode materials (e.g., LiCoO₂,²⁴ LiFePO₄,²⁵ MnO₂,²⁶ and V₂O₅).²⁷ Our results demonstrated that CNTs can also function as an effective conductive additive to improve electrolyte accessibility and rate capability for ACs even in a (high-viscosity) IL electrolyte. Furthermore, the presence of high-surface-area ACs in the AC/CNT composite significantly increased the specific surface area for the composite electrode over its pure CNT counterpart (1326 vs 82 m²/g). Along with the enhanced electrolyte accessibility, the improved surface area led to an increased CV current for the AC/CNT composite electrode (Figure 1A(c)) and hence a significantly enhanced

capacitance (142 F/g) with respect to both the pure CNT electrode (20 F/g) and the conventional AC electrode (90 F/g). These results clearly show that the combination of ACs with CNTs has provided a balanced surface area and mesoporosity for the resultant AC/CNT electrode material to achieve a high capacitance.^{3–5}

To improve further the performance of the AC/CNT composite electrode, we introduced IL [EMIM][Tf₂N] to prepare a novel class of nanocomposite electrodes (denoted as: AC/CNT/IL). Previous work has demonstrated that gel polymer electrolytes (GPEs) could be used to effectively increase the number of ion diffusion paths inside the electrode by binding with ACs to lower the interfacial resistance between the electrolyte and the electrode, and hence improving the performance for the resultant gelled composites.²⁸ However, the performance of these ternary composites was rather limited because of the thermal instability of the organic solvents/plasticizers used in a GPE. We have previously developed a direct gelling approach to successfully incorporate ILs into a polymer network, producing the IL-incorporated gel polymer electrolytes (ILGPEs).²⁰ In an ILGPE, the IL serves as a unique plasticizer, leading to excellent thermal and electrochemical stability for the ILGPEs.²⁰ In the present work, we developed AC/CNT/IL composite electrodes by adopting this direct gelling approach to introduce [EMIM]-[Tf₂N] to the AC/CNT composites. As a general rule for composite electrodes (for both supercapacitors and batteries), a polymer binder is usually needed to form a composite with the active material and the conductive additive. The content of the polymer binder has an impact on the performance of the resultant composite electrodes. While a minimum amount of binder is needed to form a robust composite, too much binder will inevitably introduce a high resistance (and thus poor performance) to the electrodes. For a specific composite system, therefore, the content of the binder should be maintained at a possibly lowest level. In our AC/CNT/IL composite, the thermally stable [EMIM][Tf₂N] is free from evaporation under heating during the compositing process and serves as a unique conductive plasticizer to gel the entire system into a stable composite. This could reduce the amount of the polymer binder and increase the amount of ACs to lower the resistance and increase the surface area for the resultant ternary composite electrodes. The optimized electrode consists of AC/CNT/IL/PVdF (64.0/20.3/7.7/8.0, wt %) with a specific surface area of 1380 m²/g. ILs have recently been combined with CNTs to form a stable and uniform nanocomposite gel with a well-distributed CNT/IL network.^{29,30} In our AC/CNT/IL composite electrode, the presence of IL weakened the van der Waals forces between tubes and facilitated the distribution of CNTs in a more uniform and less entangled manner (Figure 2d), providing a more conductive and more electrolyte-accessible network. All of these features led to a further improved CV current and charge storage capability (i.e., capacitance) for the AC/CNT/IL composite electrode (188 F/g) (Figure 1A(d)) with respect to the AC/CNT composite (142 F/g). Compared with conventional aqueous and organic electrolytes, the relatively high viscosity of IL electrolytes is a major disadvantage for their electrochemical applications with conventional electrode materials. Our results have demonstrated that the AC/CNT/IL ternary nanocomposites could serve as appropriate electrode materials to overcome this problem. In conjunction with the large electrochemical window of IL electrolytes, they can be used to develop high-performance supercapacitors.

The performance of the AC/CNT/IL composite electrode in a prototype supercapacitor with [EMIM][Tf₂N] electrolyte (i.e., AC/CNT/IL-IL) was investigated against a control capacitor (i.e., AC-IL) fabricated from conventional AC electrodes as reference. Because of the large electrochemical window of [EMIM][Tf₂N], a large cell voltage of 4 V was observed for both capacitors. As can be seen in Figure 3A, the current of the AC-IL capacitor increased with the scan rate from 5 to 20 mV/s. Further increase in the scan rate caused no change in current but a shrunken CV (shown by arrows) with a low capacitance retention of 4.3% (capacitance retained at 200 mV/s vs that at 5 mV/s). It is known that when the voltage of a supercapacitor drops to one-half of the rated voltage, there is only 25% of the energy stored remaining. Thus, in the supercapacitor industry, it is widely accepted that the common operational voltage range for a supercapacitor is from rated voltage to one-half rated voltage. On the basis of this protocol, a voltage range of 2–4 V was selected for the charge/discharge tests of our capacitors. In a range of current densities (2–50 mA cm⁻²), the capacitors were tested at each current density for 10 cycles. However, only one cycle is shown in Figure 3C,D for clarity. Upon galvanostatic charging/discharging, the AC-IL capacitor showed a large IR drop and bent charge/discharge curves (Figure 3C). The above observation indicates a poor charge storage and delivery capability for the AC-IL capacitor, which could be attributed to the poor electrolyte accessibility and low rate capability of ACs in the IL electrolyte. In contrast, the AC/CNT/IL-IL capacitor showed an excellent charge storage and delivery performance (Figure 3B, D) due to the enhanced capacitive behavior of the AC/CNT/IL composite in the IL electrolyte. This is clearly demonstrated by the continuous increase in current while retaining the rectangular CV (capacitance retention: 64.5%) during CV (Figure 3B) and a small IR drop with well-defined charge/discharge straight lines upon galvanostatic charging/discharging (Figure 3D).

The AC/CNT/IL-IL capacitor showed a much higher maximum energy density (50 Wh/kg) and power density (22 kW/kg) than those of the AC-IL capacitor (19.6 Wh/kg, 6.3 kW/kg) (Figure 3E). On the basis of a simplified estimation method,³¹ these data can be converted to those for packaged capacitors (AC/CNT/IL-IL capacitor: 17.5 Wh/kg, 7.7 kW/kg; AC-IL capacitor: 6.9 Wh/kg, 2.2 kW/kg). The performance of the AC-IL capacitor is still slightly higher than that of the currently available supercapacitors,¹ albeit poorer than that of the AC/CNT-IL or AC/CNT/IL-IL capacitors. This improvement could be attributed to the high cell voltage of the AC-IL capacitor (4 V) versus that (2.5–2.7 V) of commercially available supercapacitors. Compared with the AC-IL capacitor, the AC/CNT/IL-IL capacitor can store much more energy and rapidly deliver this energy to achieve a much higher power (Figure 3E), significantly outperforming the current supercapacitor technology.¹ It is the combination of the superior capacitive properties of the AC/CNT/IL composite electrodes with the large electrochemical window of IL electrolytes that is responsible for this achievement. Furthermore, the excellent safety-related properties of IL electrolytes and the environmental stability of CNTs and ACs will ensure an inherently safe operation and long lifetime for the AC/CNT/IL-IL supercapacitors.

In summary, we have developed a simple method to produce a novel class of ternary nanocomposite electrodes for fabricating high-performance supercapacitors with environmentally friendly IL electrolytes. We found that the combination of ACs and CNTs provided a good balance between the surface area and the

electrolyte accessibility for the resultant AC/CNT binary composite with an improved capacitance (142 F/g) with respect to a pure CNT electrode (20 F/g) and a conventional AC electrode (90 F/g) in an IL electrolyte. The introduction of ILs to an AC/CNT composite led to a more conductive and more electrolyte-accessible network for the resultant AC/CNT/IL ternary composite with further improved capacitance (188 F/g) in the IL electrolyte. By combining the excellent capacitive behavior of AC/CNT/IL composite electrodes with the large electrochemical window of IL electrolytes, we have successfully developed prototype supercapacitors with a high cell voltage (4 V) as well as superior energy and power densities (50 Wh/kg and 22 kW/kg, respectively, based on the mass of the active electrode materials). These results significantly exceeded those of the commercially available supercapacitors. Moreover, superior safety-related properties of IL electrolytes would ensure excellent operation safety and lifetime for these newly developed supercapacitors.

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REFERENCES

- Burke, A.; Arulepp, M. *Recent Developments in Carbon-Based Electrochemical Capacitors: Status of the Technology and Future Prospects*; Research Report UCD-ITS-RR-01-20; Institute of Transportation Studies, University of California, Davis: Davis, CA, 2001.
- Frackowiak, E.; Béguin, F. Carbon Materials for the Electrochemical Storage of Energy in Capacitors. *Carbon* **2001**, *39*, 937–950.
- Mayer, S. T.; Pekala, R. W.; Kaschmitter, J. L. The Aerocapacitor: An Electrochemical Double-Layer Energy-Storage Device. *J. Electrochem. Soc.* **1993**, *140*, 446–451.
- Tanahashi, I.; Yoshida, A.; Nishino, A. Electrochemical Characterization of Activated Carbon-Fiber Cloth Polarizable Electrodes for Electric Double-Layer Capacitors. *J. Electrochem. Soc.* **1990**, *137*, 3052–3057.
- Kastening, B.; Sprinzig, S. Electrochemical Polarization of Activated Carbon and Graphite Powder Suspensions: Part II. Exchange of Ions between Electrolyte and Pores. *J. Electroanal. Chem.* **1986**, *214*, 295–302.
- Yu, D.; Dai, L. Self-Assembled Graphene/Carbon Nanotube Hybrid Films for Supercapacitors. *J. Phys. Chem. Lett.* **2010**, *1*, 467–470.
- Niu, C.; Sichel, E. K.; Hoch, R.; Moy, D.; Tennent, H. High Power Electrochemical Capacitors Based on Carbon Nanotube Electrodes. *Appl. Phys. Lett.* **1997**, *70*, 1480–1482.
- 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. *Adv. Funct. Mater.* **2001**, *11*, 387–392.
- Portet, C.; Taberna, P. L.; Simon, P.; Flahaut, E. Influence of Carbon Nanotubes Addition on Carbon–Carbon Supercapacitor Performances in Organic Electrolyte. *J. Power Sources* **2005**, *139*, 371–378.
- Liu, T.; Sreekumar, T. V.; Kumar, S.; Hauge, R. H.; Smalley, R. E. SWNT/PAN Composite Film-Based Supercapacitors. *Carbon* **2003**, *41*, 2440–2442.
- Hughes, M.; Shaffer, M. S. P.; Renouf, A. C.; Singh, C.; Chen, G. Z.; Fray, D. J.; Windle, A. H. Electrochemical Capacitance of Nanocomposite Films Formed by Coating Aligned Arrays of Carbon Nanotubes with Polypyrrole. *Adv. Mater.* **2002**, *14*, 382–385.
- Jurewicz, K.; Delpoux, S.; Bertagna, V.; Béguin, F.; Frackowiak, E. Supercapacitors from Nanotubes/Polypyrrole Composites. *Chem. Phys. Lett.* **2001**, *347*, 36–40.
- Hughes, M.; Chen, G. Z.; Shaffer, M. S.; Fray, D. J.; Windle, A. H. Electrochemical Capacitance of a Nanoporous Composite of Carbon Nanotubes and Polypyrrole. *Chem. Mater.* **2002**, *14*, 1610–1613.
- Kim, I.-H.; Kim, J.-H.; Cho, B.-W.; Kim, K.-B. Synthesis and Electrochemical Characterization of Vanadium Oxide on Carbon Nanotube Film Substrate for Pseudocapacitor Applications. *J. Electrochem. Soc.* **2006**, *153*, A989–996.
- Lee, C. Y.; Tsai, H. M.; Chuang, H. J.; Li, S. Y.; Lin, P.; Tseng, T. Y. Characteristics and Electrochemical Performance of Supercapacitors with Manganese Oxide-Carbon Nanotube Nanocomposite Electrodes. *J. Electrochem. Soc.* **2005**, *152*, A716–A720.
- Ma, S.-B.; Nam, K.-W.; Yoon, W.-S.; Yang, X.-Q.; Ahn, K.-Y.; Oh, K.-H.; Kim, K.-B. Electrochemical Properties of Manganese Oxide Coated onto Carbon Nanotubes for Energy-Storage Applications. *J. Power Sources* **2008**, *178*, 483–489.
- Buzzeo, M. C.; Evans, R. G.; Compton, R. G. Non-Haloaluminate Room-Temperature Ionic Liquids in Electrochemistry - A Review. *ChemPhysChem* **2004**, *5*, 1106–1120.
- Barisci, J. N.; Wallace, G. G.; MacFarlane, D. R.; Baughman, R. H. Investigation of Ionic Liquids as Electrolytes for Carbon Nanotube Electrodes. *Electrochem. Commun.* **2004**, *6*, 22–27.
- Xu, B.; Wu, F.; Chen, R.; Cao, G.; Chen, S.; Wang, G.; Yang, Y. Room Temperature Molten Salt as Electrolyte for Carbon Nanotube-Based Electric Double Layer Capacitors. *J. Power Sources* **2006**, *158*, 773–778.
- Lu, W.; Henry, K.; Turchi, C.; Pellegrino, J. Incorporating Ionic Liquid Electrolytes into Polymer Gels for Solid-State Ultracapacitors. *J. Electrochem. Chem.* **2008**, *155*, A361–A367.
- Galiński, M.; Lewandowski, A.; Stępiak, I. Ionic Liquids as Electrolytes. *Electrochim. Acta* **2006**, *51*, 5567–5580.
- Frackowiak, E.; Béguin, F. Electrochemical Storage of Energy in Carbon Nanotubes and Nanostructured Carbons. *Carbon* **2002**, *40*, 1775–1787.
- Endo, M.; Hayashi, T.; Kim, Y.-A. Large-Scale Production of Carbon Nanotubes and Their Applications. *Pure Appl. Chem.* **2006**, *78*, 1703–1713.
- Sheem, K.; Lee, Y. H.; Lim, H. S. A New Electrode Material for Nickel–Metal Hydride Batteries: MgNiPt Alloy Prepared by Ball-Milling. *J. Power Sources* **2006**, *158*, 1425–1430.
- Wang, L.; Huang, Y.; Jiang, R.; Jiaz, D. Nano-LiFePO₄/MWCNT Cathode Materials Prepared by Room-Temperature Solid-State Reaction and Microwave Heating. *J. Electrochem. Soc.* **2007**, *154*, A1015–A1019.
- Wang, G. X.; Zhang, B. L.; Yu, Z. L.; Qu, M. Z. Manganese Oxide/MWNTs Composite Electrodes for Supercapacitors. *Solid State Ionics* **2005**, *176*, 1169–1174.
- Sakamoto, J. S.; Dunn, B. Vanadium Oxide-Carbon Nanotube Composite Electrodes for Use in Secondary Lithium Batteries. *J. Electrochem. Soc.* **2002**, *149*, A26–A30.
- Osaka, T.; Liu, X.; Nojima, M.; Momma, T. An Electrochemical Double Layer Capacitor Using an Activated Carbon Electrode with Gel Electrolyte Binder. *J. Electrochem. Soc.* **1999**, *146*, 1724–1729.
- Fukushima, T.; Kosaka, A.; Ishimura, Y.; Yamamoto, T.; Takigawa, T.; Ishii, N.; Aida, T. Molecular Ordering of Organic Molten Salts Triggered by Single-Walled Carbon Nanotubes. *Science* **2003**, *300*, 2072–2074.

(30) Du, P.; Liu, S.; Wu, P.; Cai, C. Preparation and Characterization of Room Temperature Ionic Liquid/Single-Walled Carbon Nanotube nanocomposites and Their Application to the Direct Electrochemistry of Heme-Containing Proteins/Enzymes. *Electrochim. Acta* **2007**, *52*, 6534–6547.

(31) Mastragostino, M.; Arbizzani, C.; Paraventi, R.; Zanelli, A. Polymer Selection and Cell Design for Electric-Vehicle Supercapacitors. *J. Electrochem. Soc.* **2000**, *147*, 407–412.

(32) Lu, W.; Fadeev, A. G.; Qi, B.; Smela, E.; Mattes, B. R.; Ding, J.; Spinks, G. M.; Mazurkiewicz, J.; Zhou, D.; Wallace, G. G.; et al. Use of Ionic Liquids for π -Conjugated Polymer Electrochemical Devices. *Science* **2002**, *297*, 983–987.