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Energy-Density Enhancement of Carbon-Nanotube-Based Supercapacitors with Redox Couple in Organic Electrolyte

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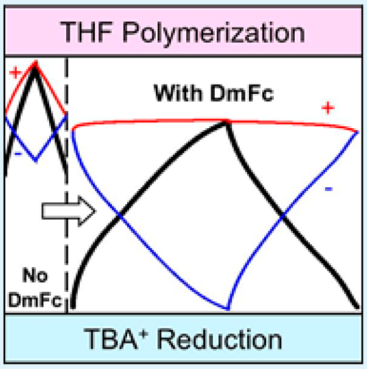
Supporting Information

ABSTRACT: We demonstrate for the first time that the incorporation of a redox-active molecule in an organic electrolyte can increase the cell voltage of a supercapacitor. The redox molecule also contributes to increasing the cell capacitance by a faradaic redox reaction, and therefore the energy density of the supercapacitor can be significantly increased. More specifically, the addition of redox-active decamethylferrocene in an organic electrolyte results in an approximately 27-fold increase in the energy density of carbon-nanotube-based supercapacitors. The resulting high energy density (36.8 Wh/kg) stems from the increased cell voltage (1.1 V → 2.1 V) and cell capacitance (8.3 F/g → 61.3 F/g) resulting from decamethylferrocene addition. We found that the voltage increase is associated with the potential of the redox species relative to the electrochemical stability window of the supporting electrolyte. These results will be useful in identifying new electrolytes for high-energy-density supercapacitors.



KEYWORDS: *supercapacitor, energy storage, redox molecule, organic electrolyte, carbon nanotube*

Supercapacitors are energy-storage devices, and they are attracting increasing attention because of their high power densities and long cycling lives.[1,2] These characteristics result from an energy-storage mechanism based on fast physical adsorption/desorption of ions in an electrical double-layer developed at the interface of a carbon-based electrode and an electrolyte.[3,4] However, the energy densities of electrical double-layer capacitors (EDLCs) are lower than those of batteries by an order of magnitude, and this greatly limits the range of their applications.[1,4−6]

Conventional approaches to increasing the energy densities of supercapacitors include using pseudocapacitive materials and adopting asymmetric configurations.[5,7,8] The energy density of a supercapacitor is proportional to the capacitance and the square of the operating voltage window, and these can be increased using pseudocapacitive materials and an asymmetric configuration, respectively. Pseudocapacitive materials such as transition-metal oxides and electrically conducting polymers have theoretical capacitances as high as a few thousand farads per gram (F/g), but in practice, the values are much lower because only the materials near the surface are involved in charge-storage reactions. The power performance of a pseudocapacitor is also significantly lower than that of an EDLC.[7,9] Moreover, pseudocapacitive materials are mainly used with aqueous electrolytes, and water decomposition thermodynamically constricts the operating voltage windows to within 1.23 V. Stable operation beyond this thermodynamic restriction on the aqueous electrolytes can be achieved by using an asymmetric configuration with two different electrode materials, e.g., a carbon-based material and a pseudocapacitive material,[8,10] but surface-limited energy storage and the slow kinetics of the pseudocapacitive materials still restrict the performance. Various approaches have been used to overcome these problems, such as developing composite materials with elaborate nanoarchitectures.[1]

Recently, a promising alternative strategy, using redox-active materials in electrolytes, has been shown to enhance the energy densities of supercapacitors. The incorporation of redox-active materials such as potassium iodide, hydroquinone, and cupric chloride into aqueous electrolytes can increase the capacitance of carbon-electrode-based supercapacitors,[11−16] but aqueous electrolytes limit the cell voltage to ~1 V. To extend the cell voltage beyond 1 V, a few studies have been conducted on the supercapacitors with nonaqueous redox electrolytes; however, the addition of redox molecules to the electrolytes increased the energy density by only a factor of 2 or 3.[17−19] The development of such electrolytes is only at a very early stage, and there is much room for improvement, especially in the operating voltage window. The development and extensive investigation of redox-active organic electrolytes are therefore desirable, to achieve a better understanding of the fundamentals and significant improvements in performance.

In this paper, we describe how the incorporation of redox-active decamethylferrocene (DmFc) in an organic electrolyte can significantly enhance the energy density of carbon-nanotube (CNT)-based supercapacitors. More specifically, we

Received: September 12, 2014
Accepted: November 3, 2014
Published: November 16, 2014

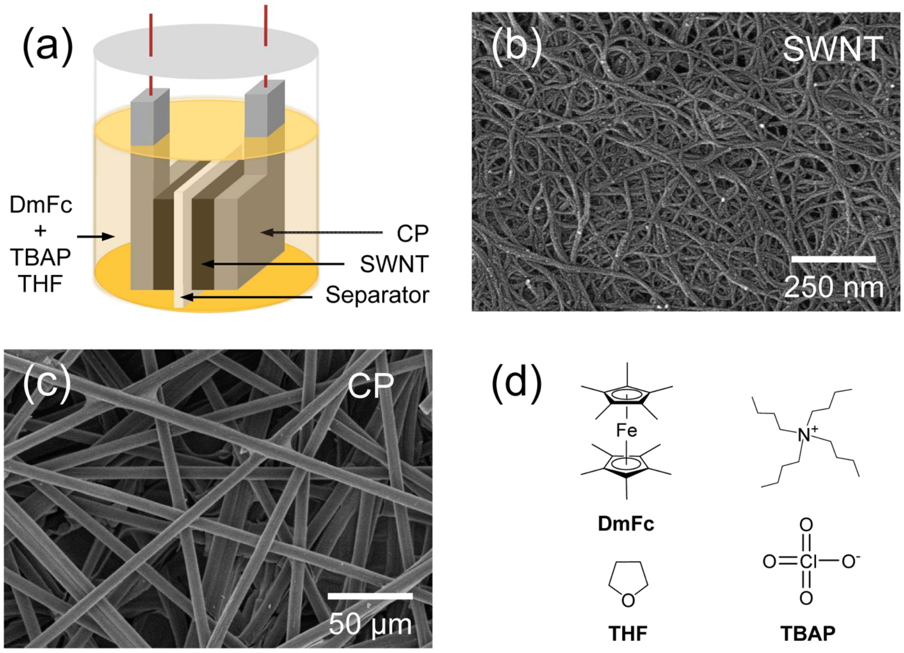


Figure 1. (a) Schematic diagram of supercapacitor cell. SEM images of (b) single-walled carbon nanotubes (SWNTs) and (c) a carbon paper (CP). (d) Molecular structures of decamethylferrocene (DmFc), tetrabutylammonium perchlorate (TBAP), and tetrahydrofuran (THF).

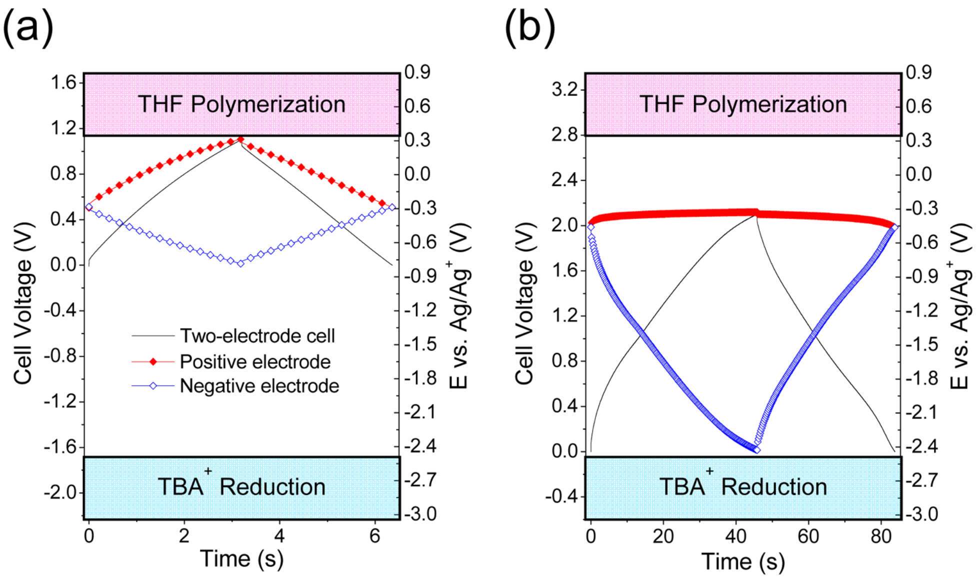


Figure 2. Galvanostatic charge−discharge (GCD) curves and working potentials of positive and negative electrodes in (a) TBAP/THF and (b) DmFc/TBAP/THF measured at current density of 2.5 A/g.

discuss the influence of the DmFc faradaic reaction on the capacitance and the operating voltage span of each electrode. CNTs and tetrabutylammonium perchlorate (TBAP) in tetrahydrofuran (THF) were used as the electrode material and electrolyte, respectively. CNTs have excellent properties as electrode materials; they may complement or replace conventional activated carbons in certain areas of supercapacitor applications in the future.[20−22] DmFc forms a stable redox couple with decamethylferrocenium ($DmFc^+$), and is reasonably soluble in the supporting electrolyte, TBAP/THF, which is a good model electrolyte for studying the effect of DmFc on the voltage window, as described in later sections of this paper. Moreover, we identify the factors that limit the cell voltages and suggest a general strategy, based on our findings, for developing new electrolytes to further improve the energy density.

The supercapacitor was fabricated using single-walled CNTs (SWNTs), DmFc/TBAP/THF, and carbon paper (CP) as the electrode material, electrolyte, and current collector, respectively (Figure 1a). A scanning electron microscopy (SEM) image clearly shows intertwined bundles of SWNTs of diameter 0.7−1.4 nm deposited on a piece of CP (Figure 1b). The CP is a mat of carbon fibers (diameter ∼7 μm) (Figure 1c) of thickness ∼280 μm and with an in-plane resistivity of ∼5.6 mΩ cm; CP is often used as a current collector in fuel-cell and supercapacitor research.[23−25] DmFc was used as the redox species and was added to a supporting electrolyte composed of TBAP and THF (Figure 1d). DmFc forms a redox couple with

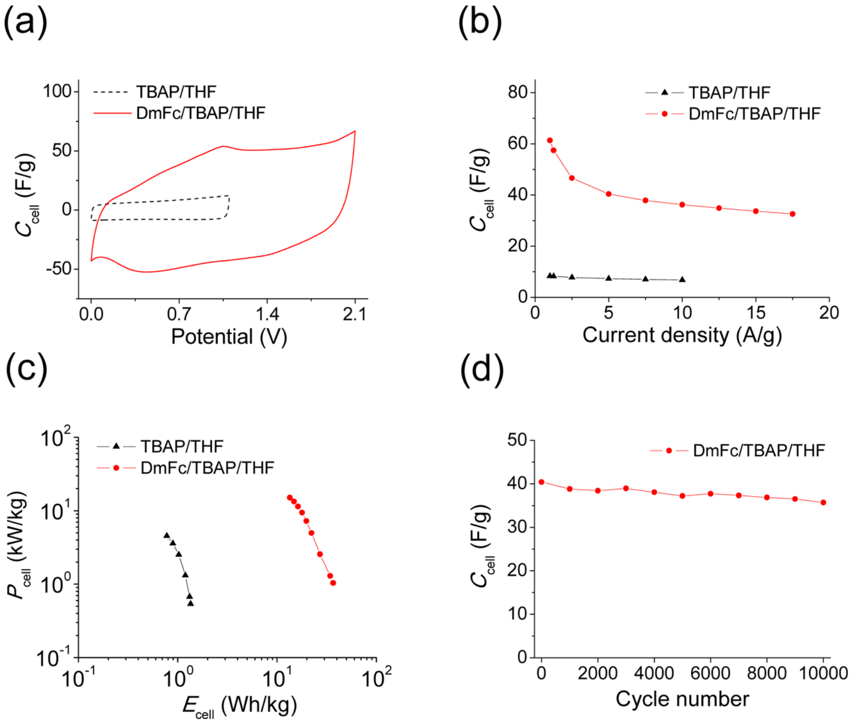


Figure 3. (a) Cyclic voltammetry (CV) curves measured at 100 mV/s, with and without DmFc in TBAP/THF. (b) Plots of specific cell capacitance (C_{cell}) vs current density. (c) Corresponding Ragone plots. (d) Cycling stability of supercapacitor with DmFc/TBAP/THF, measured at 5 A/g.

Table 1. Mass, Operating Voltage Range, and Capacitance of Each Electrode, and (specific) Cell Capacitances, And Energy and Power Densities of Supercapacitors (at I = 2.5 A/g), with and without DmFc in TBAP/THF

	positive electrode			negative electrode			cell capacitance			
	m_+ (mg)	ΔV_+ (V)	C_{elec+} (mF)	m_- (mg)	ΔV_- (V)	C_{elec-} (mF)	C (mF)	C_{cell} (F/g)	power density P_{cell}(kW/kg)	energy density E_{cell}(Wh/kg)
TBAP/THF	0.4	0.576	11.0	0.4	0.479	13.2	6.0	7.5	1.32	1.16
DmFc/TBAP/THF	0.4	0.117	651.0	0.4	1.931	39.3	37.1	46.3	2.56	27.00

$DmFc^+$ because Fe(II) in DmFc can easily be oxidized to Fe(III) in $DmFc^+$ and reduced back to Fe(II).

The cell voltage of the supercapacitor without DmFc is limited to 1.1 V (Figure 2a). Without the DmFc redox couple, the cell voltage is almost evenly divided between each electrode during galvanostatic charge−discharge (GCD). The potential of the positive electrode varies between approximately −0.29 and 0.32 V (vs Ag/Ag^+), and that of the negative electrode changes in the range of −0.29 to −0.79 V (vs Ag/Ag^+). The cell voltage is mainly limited by the positive electrode. The potential of the positive electrode should not exceed 0.33 V (vs Ag/Ag^+), at which electropolymerization of the THF solvent occurs;[26,27] this limit is shown by the colored area in Figure 2.

The cell with DmFc has an extended operating voltage window of 2.1 V (Figure 2b). We clearly show the effect of DmFc incorporation by comparing the electrochemical properties of supercapacitors with and without DmFc (Figure 2). With DmFc, the cell voltage is asymmetrically distributed between each electrode, and the operating window of each electrode also alters correspondingly. The asymmetry arises from the different charge-storage mechanism in each electrode; faradaic and nonfaradaic processes occur in the positive and negative electrode, respectively. As a result, the positive and negative electrodes show battery-type and EDLC-type behaviors, respectively. The potential of the positive electrode varies only slightly, from −0.46 to −0.33 V (vs Ag/Ag^+), which is close to the redox potential of DmFc (−0.32 V). This value was obtained from a cyclic voltammogram (CV) measured using a three-electrode configuration (see the Supporting Information, Figure S1). This result indicates that the $DmFc/DmFc^+$ redox reaction occurs at the positive electrode. Because pseudocapacitance is based on the redox reaction, the positive electrode shows a high capacitance, namely 1626 F/g, at 2.5 A/g. In contrast to the relatively constant potential of the positive electrode, that of the negative electrode varies widely, from −0.46 to −2.43 V vs Ag/Ag^+, and shows an electrode capacitance of 98 F/g.

The operating voltage window of the supercapacitor with DmFc is defined by the redox potential of DmFc and the TBA^+ reduction potential. The redox potential of DmFc (−0.32 V) is lower than the potential of THF electropolymerization (0.33 V), and therefore it sets the upper limit of the cell voltage. On the other hand, the potential of the negative electrode should not be lower than approximately −2.4 V vs Ag/Ag^+, at which TBA^+ cations in the electrolyte are reduced (see the Supporting Information, Figure S2).[28] Consequently, the operating voltage window of the supercapacitor with DmFc is 2.1 V; this is approximately twice that of the supercapacitor without DmFc.

In addition to the increase in cell voltage, the cell capacitance is also significantly increased by the presence of DmFc (7.5 F/g → 46.3 F/g at 2.5 A/g). The enhanced capacitance with DmFc

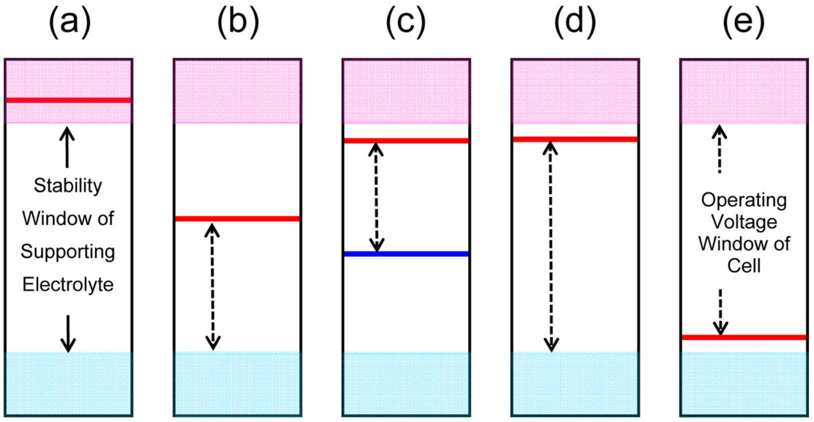


Figure 4. Positions of redox potential relative to stability window of supporting electrolyte. Nonideal cases: (a) redox potential is located beyond electrochemical stability window of supporting electrolyte (solid arrow), (b) redox potential is near middle of window, and (c) side reaction of redox molecule occurs within window. Ideal cases: redox potential is close to (d) upper or (e) lower end of window. Red line indicates potential of redox molecule. Blue line is potential at which side reaction of redox molecule occurs. Dotted arrow indicates size of operating voltage window.

is clearly seen from the less steep slope ($\Delta V/\Delta t$) of the discharge curve (Figure 2), and can be attributed to pseudocapacitance caused by the faradaic reaction of DmFc. As a result of the increased voltage window and capacitance, the energy density increases significantly (1.2 Wh/kg → 27.0 Wh/kg at 2.5 A/g). In addition, an increase in the capacitance (7.7 F/g → 38.3 F/g) is consistently observed in the CVs (Figure 3a). Detailed information on the cell and each electrode, such as capacitances, energy and power densities, and operating voltage windows are presented in Table 1. The equations used to calculate important properties such as the electrode and cell capacitances and energy and power densities are provided in the Supporting Information.

The supercapacitor with DmFc has a good rate capability. The rate capability is an important factor to be considered when evaluating the performances of pseudocapacitors, because although pseudocapacitors have high energy densities, they are usually slower than EDLCs because of the different energy-storage mechanisms (chemical vs physical).[29] Figure 3b shows how C_{cell} decreases with increasing current density. In general, the cell capacitance with DmFc decreases more quickly than that without DmFc, which is reasonable considering the redox chemical reaction of DmFc. Although the decrease is significant when the current density is relatively low, it becomes less pronounced as the current density increases. At a current density of 1 A/g, the C_{cell} value is approximately seven times larger for a supercapacitor with DmFc (61.3 vs 8.3 F/g). At a current density of 10 A/g, the C_{cell} value is still five times larger (36.2 vs 6.8 F/g). These results indicate that the redox reaction of DmFc on the CNT electrode is fast and reversible; this accounts for the good power characteristics of the supercapacitors with DmFc.

Ragone plots consistently show that the incorporation of DmFc significantly improves the energy performance without causing a critical deterioration in the power performance (Figure 3c). The energy and power densities were estimated from GCD curves measured at different current densities. The incorporation of the redox couple greatly increases the capacitance (8.3 F/g → 61.3 F/g at 1 A/g) and operating voltage window (1.1 V → 2.1 V), and hence the energy and power densities. The energy and power densities increase approximately 27-fold (1.35 Wh/kg → 36.76 Wh/kg at 1 A/g) and 2-fold (0.54 kW/kg → 1.04 kW/kg at 1 A/g), respectively, on incorporation of DmFc. Moreover, the supercapacitor with DmFc shows excellent cycling stability. The retention of C_{cell} was 88.4% over 10 000 charge−discharge cycles at 5 A/g (Figure 3d); this indicates that the DmFc/DmFc$^+$ redox couple is highly stable against repeated charge−discharge processes over a wide operating voltage window. Electrochemical impedance spectroscopy data are also presented in Figure S3 in the Supporting Information.

We found that the cell voltage is limited by the electrochemical stability of the supporting ions (TBA$^+$ reduction) and solvent (THF polymerization), and the redox potential of the redox couple (DmFc). We suggest guidelines, based on these results, for the rational selection of a set of electrolyte elements, which may be useful in developing novel electrolytes for further improving supercapacitor energy densities. First, the redox potential should be located within the electrochemical stability window of the supporting electrolyte. If the redox potential is beyond this scope, the cell voltage is limited by degradation of either the ions or solvent, but not by the redox reaction. This means that additional capacitance arising from the redox reaction is not accessible (Figure 4a). In our case, the stability window of the supporting electrolyte (2.7 V) is set by the THF electropolymerization and TBA$^+$ reduction potentials (0.3 to −2.4 V vs Ag/Ag$^+$). It should be noted that the actual operating voltage windows are within the stability window and are approximately 2.1 and 1.1 V with and without DmFc, respectively. Second, the redox potential should be close to either end of the stability window of the supporting electrolyte. If the redox potential is located near the middle of the window, the stability window is not fully used, and the operating voltage window of the cell is narrowed by the redox potential, as shown in Figure 4b. In our case, the operating voltage window (2.1 V) is determined by the redox potential of DmFc and the TBA$^+$ reduction potential (−0.3 to −2.4 V vs Ag/Ag$^+$). This means that the operating voltage window can be increased by up to ~0.6 V if a redox molecule with a potential in the range of 0.3 to −0.3 V (vs Ag/Ag$^+$) is used. Third, the redox molecules should not participate in unwanted side reactions within the stability window of the supporting electrolyte. If there is a side reaction, the potential for this side reaction will determine the cell voltage, as indicated in Figure 4c. Additionally, the redox reaction should be fast and reversible, and the redox molecule and supporting electrolyte should have sufficiently high solubility and a large electrochemical stability window, respectively. We show ideal situations, based on the above discussion, in Figure 4d, e. In these cases, the operating voltage window is maximized and the pseudocapacitance is accessible.

In summary, our work demonstrates that the addition of a DmFc redox couple in a TBAP/THF electrolyte greatly enhances the energy density (1.3 Wh/kg → 36.8 Wh/kg at 1 A/g) compared with that of a supercapacitor without DmFc in TBAP/THF. The DmFc redox couple increases the cell capacitance (8.3 F/g → 61.3 F/g at 1 A/g) and widens the voltage window (1.1 V → 2.1 V), based on the pseudocapacitive reaction and modulation of the operating voltage of each electrode. Moreover, the supercapacitor with DmFc shows a good rate capability and cyclability (C_{cell} retention = 88.4% over 10 000 cycles at 5 A/g). In addition, we show that the cell voltage is defined by the electrochemical stability window of TBAP/THF, and the redox potential of DmFc. We suggest a general strategy, based on these results, for developing novel electrolytes that may lead to great improvements in supercapacitor energy densities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. CV curves, measured in a three-electrode configuration, with and without DmFc in TBAP/THF. Nyquist plots measured in a two-electrode configuration. Equations used to calculate electrode capacitance, (specific) cell capacitance, energy density, and power density. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MISP) (NRF-2012R1A2A2A01046950).

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