A Novel Carbon Electrode Material for Highly Improved EDLC Performance

Baizeng Fang* and Leo Binder

Institute for Chemical Technology of Inorganic Materials, Graz University of Technology, Stremayrgasse 16/III, A-8010 Graz, Austria

Porous materials, developed by grafting functional groups through chemical surface modification with a surfactant, represent an innovative concept in energy storage. This work reports, in detail, the first practical realization of a novel carbon electrode based on grafting of vinyltrimethoxysilane (vtmos) functional group for energy storage in electric double layer capacitor (EDLC). Surface modification with surfactant vtmos enhances the hydrophobisation of activated carbon and the affinity toward propylene carbonate (PC) solvent, which improves the wettability of activated carbon in the electrolyte solution based on PC solvent, resulting in not only a lower resistance to the transport of electrolyte ions within micropores of activated carbon but also more usable surface area for the formation of electric double layer, and accordingly, higher specific capacitance, energy density, and power capability available from the capacitor based on modified carbon. Especially, the effects from surface modification become superior at higher discharge rate, at which much better EDLC performance (i.e., much higher energy density and power capability) has been achieved by the modified carbon, suggesting that the modified carbon is a novel and very promising electrode material of EDLC for large current applications where both high energy density and power capability are required.

1. Introduction

The electric double-layer capacitor (EDLC) is an unique electrical storage device, which can store much more energy than conventional capacitors and offers much higher power density than batteries, and the EDLC is considered to have a position somewhere between the batteries and the capacitors.[1,2] Porous carbonaceous materials, especially activated carbons, are promising electrode materials for EDLCs because of their relatively low cost and very high specific surface area.[3−10] Generally, the more developed the specific surface area of carbon, the higher the ability for charge accumulation and the higher the specific capacitance. However, specific capacitances obtained from carbon materials are usually much lower than expected, resulting in a lower energy density of EDLC, which greatly hinders its practical application in some areas where a high energy density is required, i.e., in electric vehicles. The micropores wetted by the electrolyte solution contribute extensively to the adsorption of ions on the electrochemically active surface of the carbon electrode. The lower capacitance than expected from carbonaceous material is primarily attributed to poor wettability of the electrode material in electrolyte solution, which results in a less accessible surface area for the formation of EDL. In addition, poor wettability of electrode material brings about high resistance to the transport of electrolyte ions within micropores of porous carbon during charge/discharge processes, resulting in a low usable operating voltage for charging or discharging, and a large energy consumption by EDLC itself. Therefore, it is mandatory for the electrode material to have good wettability to the electrolyte solution if good EDLC performance is expected. To improve wettability and capacitance performance of carbon materials, chemical surface modification in nitric acid solutions have been reported by some authors.[11−14]

It has been reported that capacitance performance of carbon materials in aqueous solutions could be improved greatly due to the introduction of hydrophilic functional groups onto the carbon material by surface treatment. However, no positive effect has been reported from surface modification of carbons with nitric acid in a nonaqueous electrolyte solution (i.e., electrolyte based on propylene carbonate solvent), from which a high operating voltage and energy density of EDLC can be expected. In comparison with polar water molecules, propylene carbonate (PC) molecules are somewhat nonpolar and are expected to have good affinity toward and wet easily the hydrophobic electrode material. To improve the hydrophobisation of material, physical or chemical methods can be employed. Physical methods are conventional because they are usually based on a thermal treatment in a flow of hydrogen or inert gas,[15,16] but the removal of hydrophilic surface functional groups (i.e., hydroxyl) is seldom complete. In addition, high temperature may cause a serious problem to the pore texture of porous materials. Chemical methods, such as coating with organosilicon or fluorination by fluorocarbon (C_2F_4 or C_2F_6), either by plasma surface treatments,[17] or through chemical reaction in liquid or gas phase in the case of organosilicon compounds,[18,19] lead to the hydrophobisation of the surface, but cause a dramatic decrease in the pore volumes. Budarin[20] and Cosnier[21] improved hydrophobisation of activated carbon by reaction of vinyltrimethoxysilane (vtmos) in liquid phase, but large amounts of vtmos were employed, and pore volumes of modified carbons decreased considerably. Although the selectivity of the vtmos-modified carbon toward volatile organic compounds has been improved by this mothod, it seems unsuitable for modification of carbon for EDLC application due to drastically reduced pore volume for the modified material.

Attachment of hydrophobic functional groups on the surface of carbon by surface modification with a surfactant represents an opportunity for the design of novel materials with improved

* Corresponding author phone: (+43)316-873-8767; fax: (+43)316-873-8272; e-mail: fang@TUGraz.at.

properties and enhanced energy-storage capability. Our previous preliminary study has shown that the hydropobisation of carbonaceous materials can be improved by the attachment of hydrophobic moiety of surfactant sodium oleate (OAS),[22] and as a result, the affinity of carbon materials toward and the wettability in nonaqueous electrolyte solution based on PC solvent has been improved, resulting in enhanced performance of EDLCs.[23,24] However, the improvement in the performance of EDLCs by surface modification with OAS is relatively limited, primarily attributable to the limited enhancement in the hydrophobisation of carbon due to the existence of remaining hydrophilic functional groups (i.e., hydroxyl) after the modification. Therefore, further enhancement in hydrophobisation of carbon is necessary to improve the wettability of carbon in PC solvent. Recently, we have paid more attention to surfactant vtmos, which can enhance greatly hydrophobisation of carbon materials by grafting of vtmos functional groups.[21] We have conducted extensive investigation onto effects of this surfactant, and found that a better EDLC performance (high specific capacitance, energy density, and power capability) can be expected from the vtmos-modified activated carbon than from the OAS-modified one. Here, we report the details of surface modification of activated carbon with surfactant vtmos and the excellent EDLC performance obtained from vtmos-modified activated carbon.

2. Experimental Section

Surface modification of activated carbon (Norit, "SX plus") with surfactant vtmos was performed as follows: 2 g of activated carbon was soaked by 20 mL of surfactant (vtmos) aqueous solution (0.25 wt %) and shaken for 12 h at 25 °C. After filtration the carbon slurry was dried at 120 °C under vacuum for 24 h.

Surface area and pore-volumes of carbon materials were calculated from nitrogen adsorption isotherms at 77 K (Micrometrics ASAP2010) using the Brunauer, Emmett, and Teller (BET), and Barrett, Joyner, and Halenda (BJH) methods, respectively. Activated carbon and vtmos-modified activated carbon were characterized by Fourier transform infrared (FT−IR) spectrum to ascertain the attachment (or grafting) of surfactant species, which was recorded on a FT−IR spectrometer (FT-IR-6200, PS-4000, JASCO). Each of the IR spectra was the average of 32 scans at a speed of 2 s per scan. The resolution of the spectrometer was set to 4 cm^{-1}.

The fabrication of carbon electrodes was as follows: activated carbon (active material), graphite powder (conductivity enhancing material), polytetrafluoroethylene (PTFE, binder), and carboxymethylcellulose (CMC, auxiliary binder) were mixed in a mass ratio of 90:4:4:2 and dispersed in deionized water (the mass ratio of carbon to water was set as 1:3). After stirring for several hours (typically 3 h), the slurry was cast onto aluminum foil (as a current collector, 30 mm in thickness) with an applicator. The carbon coated aluminum foil was then dried under vacuum at 120 °C for ca. 12 h, and punched in required size (16 mm in diameter) as electrodes. Apparent surface area of the electrode was ca. 2 cm^2 and thickness was about 150 mm. Mass of active material in the activated carbon electrode was 4.96 mg.

All electrochemical measurements were carried out in a two-electrode coin-type cell (capacitor), in which a separator soaked with 200 mL nonaqueous electrolyte solution (1 M Et$_4$NBF$_4$−PC) was sandwiched between two carbon electrodes. One electrode of the cell was used as the positive electrode and another one as the negative electrode. Electrochemical imped-

TABLE 1: Specific Surface Area and Pores Volume for the Original Activated Carbon and Vtmos-Modified Carbon

material	BET surface area (m^2/g)	total pore volume (cm^3/g)	micropore volume (cm^3/g)
activated carbon (AC)	853	0.85	0.30
modified AC	796	0.75	0.21

ance spectroscopy measurements were carried out in the range of 100 kHz to 10 mHz with ac amplitude of 10 mV and dc potential of 100 mV.

For constant−current charge−discharge tests, a battery test system (Maccor Inc., U.S.) was employed, and a voltage range of 0.05 to 3.0 V was set. Current density for charging was set as 3 mA/cm^2 in all cases. Discharge capacitance (*C*) of a capacitor was obtained by integration of the constant−current discharge curve. Specific capacitance of electrode material was defined as electrode capacitance per unit mass active material in the electrode. Energy delivered to a load (E_{load}) by a capacitor was calculated according to the formula $E_{load} = 1/2\ C\ [(V_{initial} - IR)^2 - V_{final}^2]$, where $V_{initial}$, V_{final}, I, and R stands for the initial voltage limit, final voltage limit, discharge current, and direct current internal resistance of a discharge process, respectively. Specific energy of a capacitor was defined as the energy delivered to a load (i.e., E_{load}) divided by total mass of the active material in two electrodes. IR drop was collected at the beginning of a discharge process.

3. Results and Discussion

3.1. Surface Characterization of Activated Carbon and Vtmos-Modified Activated Carbon. Table 1 summarizes data obtained from BET measurements for the original activated carbon and vtmos-modified one. It is clear that both samples contained micropores (less than 2 nm in diameter) and mesopores (greater than 2 nm in diameter). After surface modification with vtmos, the specific surface area, total pore volume, and micropore volume decreased slightly, indicating a partial filling of porosity by the surfactant species. A larger decrease was observed in microporosity, indicating that more micropores than mesopores were filled by the surfactant species.

3.2. Electrochemical Characteristics of Vtmos-Modified Activated Carbon. Figure 1 show cyclic voltammograms at various scan rates for the capacitors using activated carbon or vtmos-modified activated carbon as electrodes, respectively, where the current has been transferred into the specific capacitance based on the mass (4.96 mg) of active material in one electrode. For an ideal supercapacitor, its capacitance is independent of frequency, so the charge stored by a capacitor is proportional to the voltage imposed. Therefore, in the case of the CV measurements, for a constant sweep rate (mV/s), the current response will stay constant. Because of the same configuration of the electrochemical cell for every CV measurement, the effect of solution resistance on the deviation of the CV profile from the ideal capacitive behavior can be excluded. At the same scan rate, more ideal capacitive behavior was observed for the modified carbon with a steeper current change at the switching potentials (−1.0 and 1.0 V), resulting in a more rectangular-shaped *i*−V curve. An important characteristic of electrical energy storage in a capacitor is that energy is retrievable on discharging over the same potential range as that required to store the energy on charging, otherwise the energy storage is limited. The slower changes at the switching potentials in the cyclic voltammogram of the activated carbon electrode stem from the slower re-organization of the double layer owing to slower ionic motions in micropores.[25]
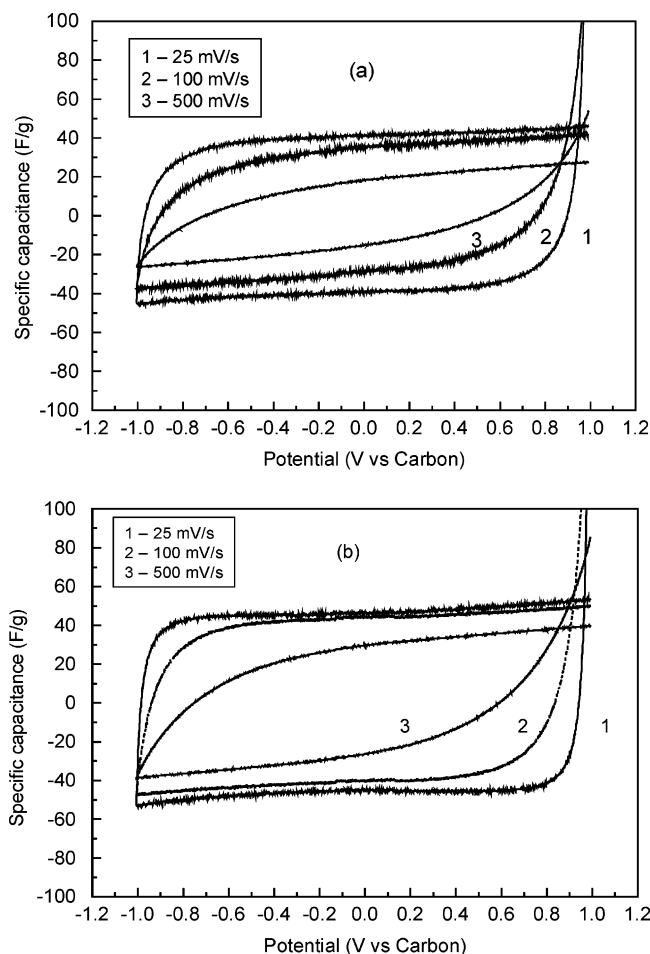
Carbon Electrode for Highly Improved EDLC Performance

J. Phys. Chem. B, Vol. 110, No. 15, 2006 **7879**

Figure 1. Cyclic voltammograms at various scan rates for the capacitors using activated carbon (a) or vtmos-modified activated carbon (b) as electrodes, where the current has been transferred into specific capacitance based on the mass (4.96 mg) of active material.

In addition, higher capacitances were obtained from the modified carbon at all the applied scan rates, suggesting that, after the modification, more surface area of the carbon was accessible to electrolyte ions due to the improved wettability of carbon and more quick charge propagation.[26,27]

Figure 2a shows Nyquist plots for the capacitors using activated carbon (AC) or vtmos-modified activated carbon (MAC) as electrode material, respectively. A depressed semicircle was observed in the high frequency region (between 100 k and 400 Hz), which represents a parallel combination of resistive and capacitive components. Electrolyte resistance was estimated around 2 Ohms from the crossover point of the highest frequency with the real part of the impedance. Charge-transfer resistance was estimated ca. 3.4 and 4.3 Ohms from the diameter of the semicircle for MAC and AC electrode, respectively. The lower resistance for MAC is probably attributable to more rapid mass transport within micropores of porous carbon due to the improved wettability of active material. At low frequency (lower than 400 Hz), the imaginary part of the impedance increases, showing the capacitive behavior of the supercapacitor. In low-frequency region, the cell behavior can be represented by a series $R(\omega)-C(\omega)$ circuit, traducing the supercapacitive behavior. $R(\omega)$ and $C(\omega)$ represent the series resistance and capacitance of the cell, respectively, and both depend on the frequency. A simple way can be employed to modelize the supercapacitor frequency behavior in this region, shown as the following:[28,29]

$$Z(\omega) = 1/j\omega C(\omega) \tag{1}$$

The impedance $Z(\omega)$ can be written under its complex form:

$$Z(\omega) = Z'(\omega) + j\,Z''(\omega) \tag{2}$$

Equations 1and 2 lead to eq 3:

$$C(\omega) = 1/[\omega(j\,Z'(\omega) - Z''(\omega))] =$$
$$-(Z''(\omega) + j\,Z'(\omega))/(\omega|Z(\omega)|^2) \tag{3}$$

It is then possible to define the following:

$$C(\omega) = C'(\omega) - j\,C''(\omega) \tag{4}$$

leading to

$$C'(\omega) = -\,Z''(\omega)/(\omega|Z(\omega)|^2) \tag{5}$$

$$C''(\omega) = Z'(\omega)/(\omega|Z(\omega)|^2) \tag{6}$$

Where $C'(\omega)$ is the real part of the capacitance $C(\omega)$, corresponding to the capacitance of the cell measured during constant current discharge (direct current) or under low frequency alternating current condition, and $C''(\omega)$ is the imaginary part of the capacitance $C(\omega)$, corresponding to losses in the form of energy dissipation.[29]

Figure 2b presents the variation of the real part of the capacitance (C') with the frequency for AC and MAC. At low frequency (10 mHz), the capacitance of the electrode has reached 48 mF/cm^2 for AC and 65 mF/cm^2 for MAC. This low-frequency capacitance C_{LF} corresponds to the cell capacitance measured during galvanostatic cycling at ± 3 mA/cm^2, which will be presented later. When the frequency is increased, the capacitance decreases, and at high frequency, the supercapacitor behaves like a pure resistance. The change of C' with the frequency depends on many parameters, such as the nature of the electrolyte, the electrode thickness, and the porous structure of the electrode.

Figure 2c presents the variation of the imaginary part of the capacitance (C'') with the frequency for the capacitors based on AC or MAC. It is possible to deduce the relaxation time constant, which is a quantitative measure of how fast the device can be discharged. The relaxation time constant is deduced from the frequency f_0 with $\tau_0 = 1/2\pi f_0$, while f_0 can be obtained from the real capacitance plot at $C' = C_{LF}/2$ (Figure 2b) and from the imaginary capacitance plot (Figure 2c) where it corresponds to the peak frequency. C'' passes through a maximum at 0.63 Hz for AC and 1.58 Hz for MAC, and thus the capacitors based on AC or MAC has a relaxation time constant of 253 and 101 ms, respectively. It indicates that, after the surface modification, the power capability of the activated carbon has been improved greatly.

Ideal capacitive behavior and superior power capability for the capacitor based on MAC is primarily attributable to the improved wettability of MAC in the organic electrolyte based on PC solvent, which facilitates rapid transport of the electrolyte ions within micropores of porous carbon, resulting in a higher useable surface area for EDL formation and lower resistance, and accordingly, a lower energy dissipation by capacitor itself and a superior power capability.

Figure 3 shows typical galvanostatic charge−discharge curves at 3 mA/cm^2 for the capacitors using activated carbon or vtmos-modified activated carbon as electrode material. It is clear that the IR drop, which can be observed from the initial discharge, decreases after the surface modification. A decrease in the IR drop, namely, decrease in the polarization resistance R, is primarily attributable to the improved wettability of electrode
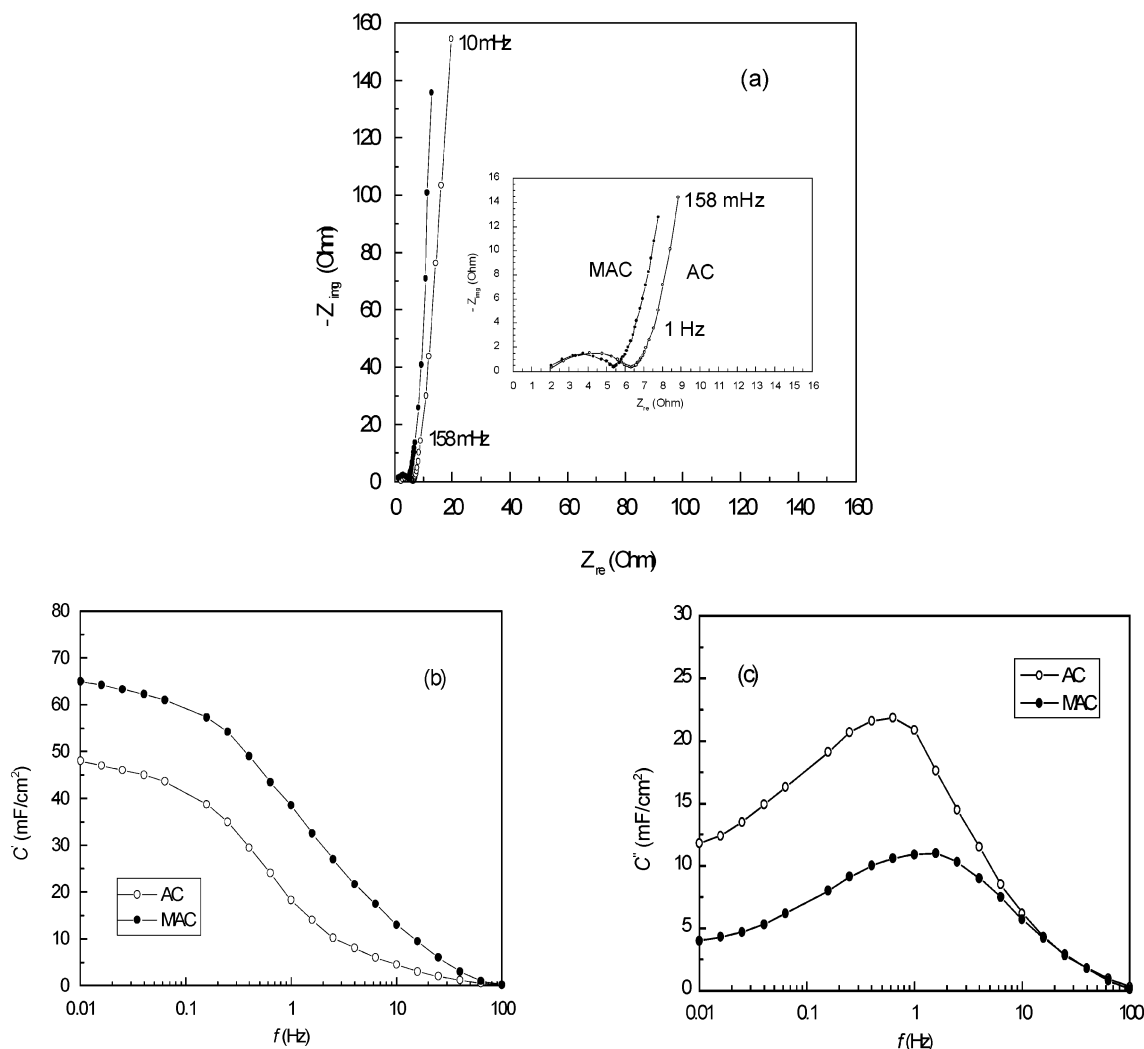
Figure 2. Nyquist plots (a) for capacitors based on AC (empty circle) and MAC (solid circle) in the frequency range of 100 k to 10 mHz (the inset shows the expanded high-frequency region of the plot) and variation of the real part (b) and imaginary part (c) of the capacitance with the frequency for AC and MAC.
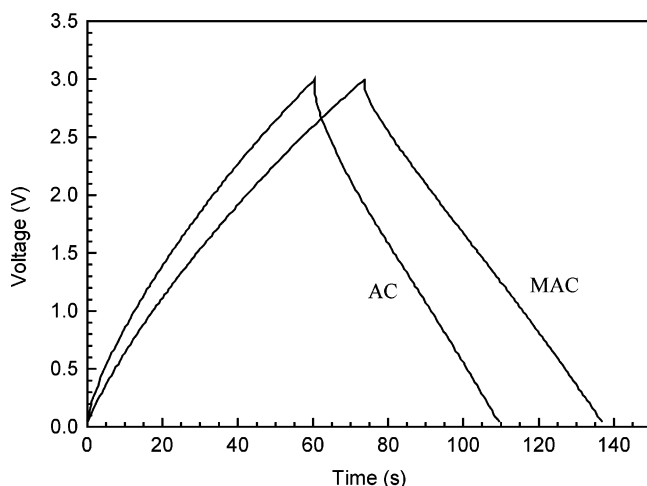

Figure 3. Typical charge−discharge curves at 3 mA/cm² for the capacitors using activated carbon (AC) or vtmos-modified AC (MAC) as electrodes.

material, facilitating rapid ions transport. A decrease in the IR drop contributes to higher usable voltage for discharge if the discharge voltage limit is fixed, and accordingly, longer discharge time and higher discharge capacity (energy) can be expected.

Figure 4 shows specific capacitance and energy density obtained at various discharge rates for the activated carbon and vtmos-modified activated carbon. It is clear from Figure 4a that with increasing discharge rate the specific capacitances decrease for both carbon materials, which is attributable to the decreased sites for EDL formation. Higher capacitance and slower decrease in the capacitance with increasing discharge rate was observed for the vtmos-modified carbon, suggesting more rapid ions transport for the modified material under the same condition. A similar tendency was observed for the energy density at various discharge rates as shown in Figure 4b, i.e., higher energy density and slower decrease in the energy density were achieved by the modified carbon material. In comparison with specific capacitance shown in Figure 4a, the energy density has a more noticeable decrease with increasing discharge rates due to additional effects from the polarization resistance, which becomes a primary source for the energy loss at a high discharge rate. The enhancement in capacitance and energy density after surface modification is primarily attributed to the improvement in wettability of the electrode material, resulting in more usable sites for EDL formation, and a lower internal resistance, resulting from the improved wettability for rapid ions transport within micropores of activated carbon. In addition, the surfactant species attached on the carbon surface probably affect the structure of electric double layer (EDL) through the presence
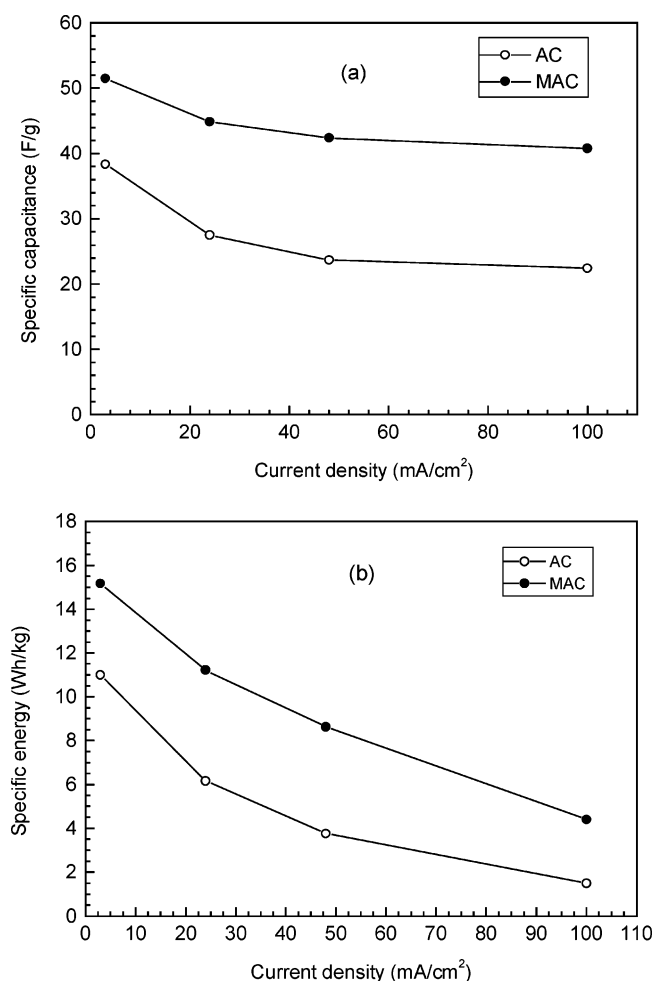
Carbon Electrode for Highly Improved EDLC Performance

J. Phys. Chem. B, Vol. 110, No. 15, 2006 **7881**

Figure 4. Specific capacitance (a) and energy density (b) at various discharging rates for the capacitors using AC or vtmos-modified AC (MAC) as electrode material.

Figure 5. FTIR spectra for the activated carbon (AC) and vtmos-modified AC (MAC).

as electrical component or by the change of EDL thickness, which also contributes a lot to the capacitance.

For a further insight into the mechanism for surface modification more detailed information obtained from the constant−current discharge profiles is shown in Table 2 for the original activated carbon (AC) and modified activated carbon (MAC), where $\Delta IR/(IR)$, $\Delta C/C$, $\Delta E/E$ stand for variation percentage of IR drop, C (specific capacitance), and E (specific energy) after surface modification, respectively.

It is clear that at all the discharge rates IR drop decreased after the surface modification while specific capacitance and energy increased. The decrease in the IR drop is mainly attributed to improvement of wettability of the electrode material, which results from the enhanced hydrophobisation of carbon due to the attached organic functional groups ($-(CH_3O)_2$-$SiCH=CH_2$). Figure 5 shows FT−IR spectra to confirm the attachment (or grafting) of surfactant species.

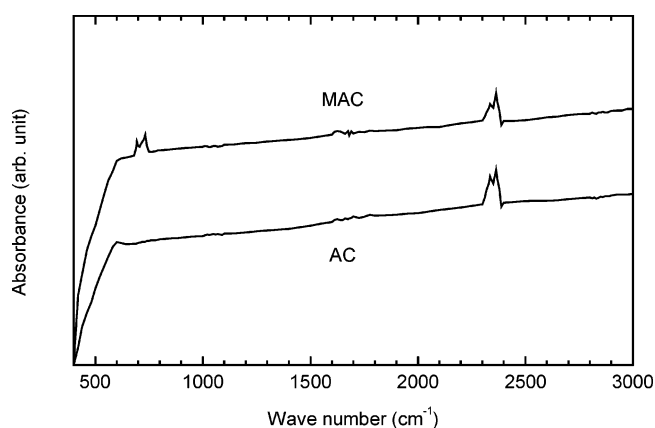The spectrum of vtmos-modified activated carbon comprises two small bands at 731 and 694 cm^{-1}, not observed for the activated carbon. In addition, the characteristic bands of vtmos are not observed in the spectrum of modified activated carbon, suggesting that the organosilicon compound was not adsorbed. However, the two small peaks at 731 and 694 cm^{-1}, could correspond to those, shifted, of vtmos, usually occurring at 773 cm^{-1} and 817 cm^{-1}, which were attributed to the vibrations of Si−O bonds and Si−C ones within the group Si−CH=CH2, respectively. Such a shift of the peaks toward lower wavenumbers may account for a possible increase of the rigidity of the molecule, induced by the grafting.[21]

Various grafting possibilities of the vtmos may be conjectured. A simple schematic illustration for grafting of functional groups onto carbon surface is shown in Figure 6a. In a silylation reaction, water induces the hydrolysis of the alkoxysilane molecules which can next condense with the hydroxyl groups already present. Depending on the surface density of the latter, the binding of the vtmos to the activated carbon surface may be achieved through one, two, or three bridging hydroxyls.[21,30,31] The mechanism for grafting needs further investigation in the future.

Grafting of vtmos functional groups improves the hydrophobisation of carbon and the affinity of the carbon material toward nonpolar organic solvent, propylene carbonate (PC) (as shown in Figure 6b), and accordingly improves the wettability of carbon in PC-based electrolyte, facilitating the electrolyte ions to access micropores of porous carbon.

For the modified carbon, the enhancement in capacitance is primarily attributed to the two improvements, namely in the wettability and in the EDL structure, as mentioned previously. The improvement in the wettability provides more accessible surface area for EDL formation, and a change in EDL structure probably contributes additional capacitance. The improvement in energy density is attributed to the increase in capacitance and attributed to the decrease in IR drop. From the expression for energy to a load (E_{load}), $E_{load} = 1/2\ C\ [(V_{initial} - IR)^2 - V_{final}^2]$, it is clear that E_{load} is approximately proportional to $(V_{initial} - IR)^2$, which means that IR drop plays a very important role in energy delivery, especially, at a high discharge rate, at which a large energy loss is inevitable if IR drop is high. From

TABLE 2: IR Drop (IR), Specific Capacitance (C), and Specific Energy (E) at Various Discharge Rates for the Capacitors Using the Original Activated Carbon (AC) or Modified Activated Carbon (MAC) as Electrodes Material

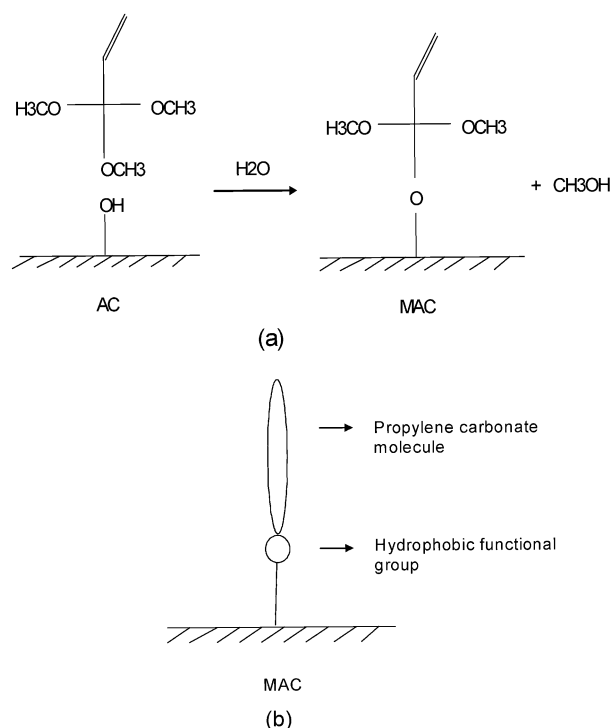| current density (mA/cm²)	IR (V)		$\Delta(IR)/(IR)$ (%)	C (F/g)		$\Delta C/C$ (%)	E (Wh/kg)		$\Delta E/E$ (%)
	AC	MAC		AC	MAC		AC	MAC	
3	0.126	0.885	-29.93	38.35	51.50	34.29	10.99	15.16	37.85
24	0.458	0.316	-31.01	27.46	44.86	63.36	6.16	11.22	82.11
48	0.832	0.578	-30.59	23.67	42.35	83.57	3.76	8.63	129.35
100	1.619	1.167	-27.91	22.43	40.74	68.26	1.49	4.40	195.76

Figure 6. Schematic illustrations for grafting of vtmos functional group onto AC to form modified AC (MAC) (a), and for propylene carbonate molecule adsorbed on the surface of the vtmos-modified activated carbon (MAC) (b).

Table 2 it was found that at a high discharge rate, i.e., 100 mA/cm^2, the variation in specific capacitance and energy density is ca. 68% and 196%, respectively, which indicates that about 128% of improvement in energy density is due to the decrease in IR drop.

Therefore, the improvement in wettability enhances not only the capacitance by increasing the accessible surface area, but also lowers energy loss (i.e., the energy dissipated by a capacitor itself) by lowering the internal resistance. Both improvements in capacitance and energy loss contribute to the enhancement in the energy delivery.

Interestingly, in comparison with the results obtained from OAS-modified carbon at the same discharge rate (i.e., 100 mA/cm^2), namely, 18% of enhancement in capacitance and 124% of enhancement in energy density,[22] better EDLC performance has been realized by vtmos-modified carbon, which is probably attributable to better hydrophobisation of vtmos-modified carbon material, resulting from the replacement of larger amount of hydrophilic hydroxyl by hydrophobic vtmos functional groups.

4. Conclusions

In this study, a novel carbon electrode material was developed by surface modification with surfactant vinyltrimethoxysilane (vtmos) to improve EDLC performance. Grafting of vtmos functional groups on the surface of activated carbon enhances the hydrophobisation of carbon electrode and the affinity toward propylene carbonate (PC) solvent, which improves the wettability of carbon electrode in the electrolyte solution based on PC solvent. The enhanced wettability results in not only a lower resistance to the transport of electrolyte ions within micropores of activated carbon electrode, but also more usable surface area for the formation of EDL, and accordingly, higher specific capacitance, energy density, and power capability available from the capacitor based on the modified carbon. Especially, the effects from the surface modification become more marvelous

at a higher discharge rate, i.e., 100 mA/cm^2, at which about three times the energy density and power capability (estimated from the *RC* time constants) of the original carbon can be achieved from the modified carbon, suggesting that the vtmos-modified carbon is a novel and very promising electrode material of EDLC for large current applications for both high-energy density and power capability.

References and Notes

(1) Conway, B.-E. *Electrochim. Acta* **1991**, *138*, 1539.

(2) Kötz, M.; Carlen, M. *Electrochim. Acta* **2000**, *45*, 2483.

(3) Yoneda, H. *The Electrochemical Society Extended Abstracts*, Abstract 37, May 16−21; The Electrochemical Society: Honolulu, HI, 1993; Vol. 93−1, p 66.

(4) Zheng, J.-P.; Huang, J.; Jow, T.-R. *J. Electrochem. Soc.* **1997**, *144*, 2026.

(5) Miller, J.-M.; Dunn, B.; Tran, T.-D.; Pekala, R.-W. *J. Electrochem. Soc.* **1997**, *144*, L309.

(6) Liu, X.; Osaka, T. *J. Electrochem. Soc.* **1997**, *144*, 3066.

(7) Liu, X.; Osaka, T. *J. Electrochem. Soc.* **1996**, *143*, 3982.

(8) Saliger, R.; Fischer, U.; Herta, C.; Fricke, J. *J. Non-Cryst. Solids* **1998**, *225*, 81.

(9) Fang, B.; Heuveln, F.-V.; Dias, F.-B.; Plomp, L. *Rare Met.* **2000**, *19*, 1.

(10) Probstle, H.; Schmitt, C.; Fricke, J. *J. Power Sources* **2002**, *105*, 189.

(11) Boehm, H.-P. *Carbon* **1994**, *32*, 469.

(12) Nakajima, T.; Matsuo, Y. *Carbon* **1994**, *32*, 759.

(13) Momma, T.; Liu, X.; Osaka, T.; Ushio, Y.; Sawada, Y. *J. Power Sources* **1996**, *60*, 249.

(14) Ma, R.; Liang, J.; Wei, B.; Zhang, B.; Xu, C.; Wu, D. *J. Power Sources* **1999**, *84*, 126.

(15) Menendez J.-A.; Xia B.; Phillips J.; Radovic L.-R.; *Langmuir* **1997**, *13*, 3414.

(16) Polakov N.-S.; Petukhova G.-A.; Vnukov S.-P.; Shevchenko A.-O. *Adsorpt. Sci. Technol.* **1993**, *10*, 165.

(17) Wertheimer M.-R.; Klemberg-Sapieha J.-E.; Cerny J., Liang S. *Plasma Polym.* **1998**, *3*, 151.

(18) Nakanishi Y.; Honjo K.; Honjo T. EP Patent. 0765840, **1997**.

(19) Ryan T.-A.; Sharrock H. UK Patent. 2391224, **2004**.

(20) Budarin V.-L.; Clark J.-H.; Mikhalovsky S.-V.; Gorlova A.-A.; Boldyreva N.-A.; Yatsimirsky V.-K. *Adsorpt. Sci. Technol.* **2000**, *18*, 55.

(21) Cosnier, F.; Celzard, A.; Furdin, G.; Begin, D.; Mareche, J.-F.; Barres, O. *Carbon* **2005**, *43*, 2554.

(22) Fang, B.; Wei, Y.-Z.; Suzuki, K.; Kumagai, M. *Electrochim. Acta* **2005**, *50*, 3616.

(23) Fang, B.; Wei, Y.-Z.; Maruyama, K.; Kumagai, M. *J. Appl. Electrochem.* **2005**, *35*, 229.

(24) Wei, Y.-Z.; Fang, B.; Iwasa, S.; Kumagai, M. *J. Power Sources* **2005**, *141*, 386.

(25) Lee, J.; Yoon, S.; Hyeon, T.; Oh*a*, S.-M.; Kim, K.-B. *Chem. Commun.* **1999**, 2177.

(26) Jurewicz, K.; Vix-Guterl, C.; Frackowiak, E.; Saadallah, S.; Reda, M.; Parmentier, J. *J. Phys. Chem. Solids* **2004**, *65*, 287.

(27) Shi, H. *Electrochim. Acta* **1996**, *41*, 1633.

(28) Portet, C.; Taberna, P. L.; Simon, P.; Flahaut, E. *J. Power Sources* **2005**, *139*, 371.

(29) Taberna, P. L.; Simon, P.; Fauvarque, J. F. *J. Electrochem. Soc.* **2003**, *150*, A292.

(30) Derouet, D.; Forgeard, S.; Brosse, J.-C.; Emery, J.; Buzare, J.-Y. *J. Polym. Sci. Polym. Chem.* **1998**, *36*, 437.

(31) Yoshida, W.; Castro, R.-P.; Jou, J.-D.; Cohen, Y. *Langmuir* **2001**, *17*, 5882.