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Organogel Electrolytes Based on a Low Molecular Weight Gelator: 2,3-Bis(*n*-decyloxy)anthracene

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Since 2,3-bis(*n*-decyloxy)anthracene (DDOA) is a good gelling agent for a large number of solvents including propylene carbonate (PC), the electrochemical properties of organogel electrolytes based on DDOA have been investigated. The presence of tetraalkylammonium salts in DDOA/PC gels is shown to preserve the three-dimensional network of DDOA fibers. In addition, at a given temperature, the conductivity is practically the same in the gel as in the corresponding solution with or without DDOA. The gelation temperature, T_{gel}, is slightly affected by the presence and nature of the salt. Thus, at 1M salt concentration, T_{gel} is increased by 9 °C with Et_4NBF_4 and decreased by 7 °C with Bu_4NBF_4, presumably because of a surfactant effect of the Bu_4N^+ cation. The electrochemical stability window of the liquid electrolyte is limited by the stability of DDOA, which displays the typical redox behavior of anthracene. However, in the gel state, DDOA is apparently protected within the fibers and the electrochemical stability extends up to 3 V. The performances of a DDOA gel electrolyte have been tested in a carbon double-layer capacitor.

Introduction

During the past 10 years, several low molecular weight organic molecules able to produce thermoreversible gels with organic solvents have been discovered.[1−6] 2,3-Bis(*n*-decyloxy)anthracene (DDOA, see Figure 1) belongs to this series;[2,3] its gelation efficiency is remarkable since 1 DDOA molecule can gel up to 20 000 solvent molecules at 25 °C. In the gel, the DDOA molecules are assembled by van der Waals interactions to form a three-dimensional network of fibers. The molecular organization within a fiber has been described in a separate study by polarized infrared microscopy.[7] The DDOA gels have also been studied by a number of techniques such as UV and fluorescence spectroscopies, X-ray and neutron diffraction, or rheological methods,[2,3] but as far as we know, their potential application as gel electrolytes has never been considered.

In modern electrochemical energy storage devices, it is of increasing importance to substitute the classical liquid electrolytes by solid or highly viscous electrolytes in order to eliminate separators, decrease the electrolyte thickness, and prevent leakage problems. Polymer electrolytes are obvious candidates, and there have been strong developments,[8] but their conductivity remains several orders of magnitude lower than that of liquid electrolytes. A few recent literature studies on organogel electrolytes based on other types of low molecular weight gelators indicate that the conductivity is practically identical in the gel and in the corresponding solution at the same temperature, and their application in electrochemical devices has been foreseen.[4−6] Thus, it was of interest to explore the ability of DDOA to gel a liquid electrolyte made of a tetraalkylammonium salt dissolved in a polar solvent and test the conductivity of the material. In the present work, we have selected propylene carbonate (PC) as the solvent, and the gelation of neat PC and of PC/salt solutions has first been investigated. Then, some electrochemical properties of DDOA/PC/salt electrolytes have been studied, and finally, these gel electrolytes have been tested in a carbon double-layer supercapacitor.

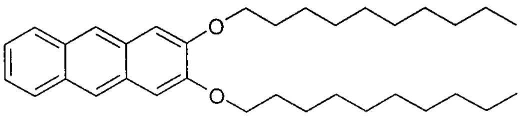

Figure 1. 2,3-Bis(*n*-decyloxy)anthracene (DDOA).

Experimental Section

Samples. DDOA is synthesized as previously described.[2] PC (Aldrich, 99,9%) is distilled under low pressure (160 °C, 0.1 mmHg) and acetonitrile (Aldrich, 99,5%) over CaH_2. The

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(1) Terech, P.; Weiss, R. *Chem. Rev.* **1997**, *97*, 3133.

(2) Brotin, T.; Utermöhlen, R.; Fages, F.; Bouas-Laurent, H.; Desvergne, J. P. *Chem. Commun.* **1991**, 416.

(3) Terech, P.; Bouas-Laurent, H.; Desvergne, J. P. *J. Colloid Sci.* **1995**, *174*, 258.

(4) Yasuda, Y.; Ishi, E.; Inada, H.; Shirota, Y. *Chem. Lett.* **1996**, 575.

(5) Hanabusa, K.; Hiratsuka, K.; Kimura, M.; Shirai, H. *Chem. Mater.* **1999**, *11*, 649.

(6) Hanabusa, K.; Inoue, D.; Suzuki, M.; Kimura, M.; Shirai, H. *Polym. J.* **1999**, *31*, 1159.

(7) Placin, F. Thesis, University Bordeaux I, No. 2125, 1999.

(8) Gray, F. In *Polymer Electrolytes*; Connor, J., Ed.; RSC Materials Monographs, A; The Royal Society of Chemistry: Cambridge, U.K., 1997.

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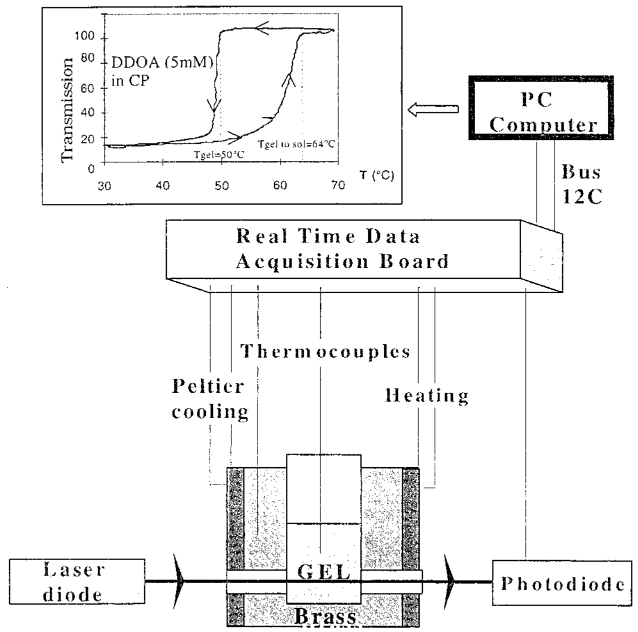

Figure 2. Experimental setup for the T_{gel} measurement (see text). An example of the transmission curve is given in the insert for the DDOA (5 mM)/PC system.

Et_4NBF_4 and Bu_4NBF_4 salts (Aldrich, 99%) are recrystallized in acetone and dried under vacuum at 200 °C. For the gel preparation, DDOA is dissolved in PC at 80 °C to obtain 10^{-2} to 10^{-3} M concentration ranges with a precision of less than 3%.

Sol–Gel Transition Temperature Measurement. To determine T_{gel}, we have built an optical setup where the variation of visible light transmission is monitored as a function of the temperature.[7] As shown in Figure 2, the sample is placed in a 12 mm diameter glass tube which is held inside a cylindrical brass furnace which can be thermostated between −10 and +100 °C by the combined effects of a thermocoax wire and a Peltier effect device. The furnace is bored by two opposite holes to allow a laser diode beam ($\lambda_0 = 670$ nm) to cross the sample and a photodiode to measure the transmitted light. A program has been written in order to control and record all the experimental parameters via a personal computer. Typically, a DDOA solution is heated to 70 °C, and the system is then cooled at 1 °C/mn while the transmission curve is recorded. A sharp decrease of the transmission occurs at the sol–gel transition because of diffusion losses by the gel phase. Repeated measurements indicate that T_{gel} can be determined with an accuracy of ±0.5 °C. The cooling/heating cycles exhibit systematic hysteresis, the gel-to-sol transition temperature being about 15 °C higher than T_{gel} which is defined by the sharp variation observed during the sol-to-gel transition (see insert of Figure 2). This hysteresis is related to the existence of an enthalpy for the sol–gel transition, and its magnitude depends certainly on the cooling/heating speed. However, we could not study this effect because our experimental setup works at a fixed speed of 1.5 °C/mn.

Conductivity and Electrochemical Stability. The conductivity of DDOA/PC/salt solutions and gels is measured by impedance spectroscopy using a Solartron 1260 frequency response analyzer with an alternating current (ac) voltage amplitude of 20 mV. The samples are contained in a standard conductivity cell for liquids (Tacussel XL150) equipped with fixed platinum electrodes. The cell constant is periodically controlled by comparison with a 0.1 M KCl aqueous solution. Cyclic voltammograms are recorded with a DEA332 potentiostat (33V/1A, Voltalab32 system) with a platinum working electrode of 1 mm^2 surface area polished with 1 μm abrasive paper and washed in an ultrasonic bath. The reference and counter electrodes are standard platinum electrodes (Tacussel XM100). All potentials are referenced to the ECS scale.

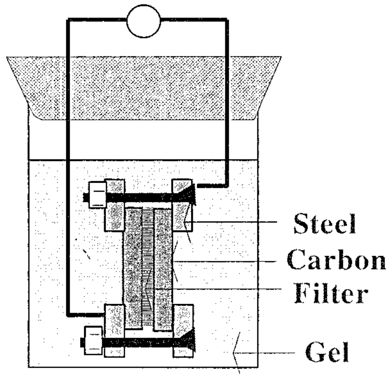

Figure 3. Schematic view of the carbon supercapacitor cell.

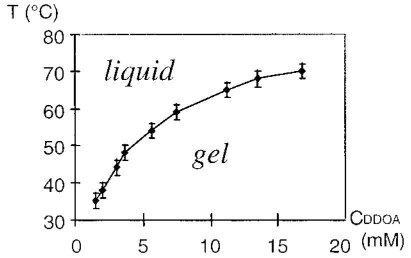

Figure 4. Phase diagram of T_{gel} as a function of DDOA concentration for the DDOA/PC system.

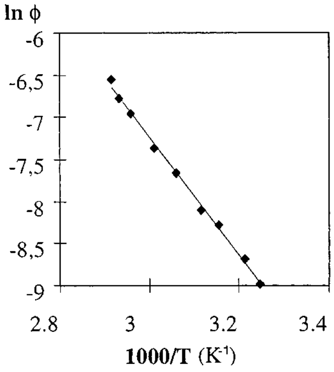

Figure 5. Plot of ln(ϕ) versus 1/T for the DDOA/PC system.

Double-Layer Carbon Supercapacitor. The experimental setup is schematized in Figure 3. A paper filter separator of 250 μm thickness and 1.2 cm diameter is placed between two activated carbon fabric electrodes (Kynol Europa GmbH, Hamburg) of 300 μm thickness, 1 cm diameter, 2000 $m^2 \cdot g^{-1}$ specific surface area and 86 $g \cdot m^{-2}$ weight. These three elements are pressed between two stainless steel rings and immersed in the electrolyte. The latter is contained in an hermetically closed glass vessel and can be heated or cooled to produce the sol or gel phases. The two electrodes are connected to a Tacussel PGP 201 potentiostat in order to record either voltammograms or charge/discharge curves by applying a constant current or voltage.

Results and Discussion

DDOA/PC Gels. DDOA is known to be a good gelator for a large number of solvents ranging from alkanes to alcohols, ethers, ketones, or halogenated molecules,[2,3] but we have found that DDOA can also easily gelify polar solvents such as propylene carbonate.[7] PC is a very commonly used solvent in electrochemistry due to its good solvating and stability properties. In particular, its electrochemical stability window extends over about 6.6 V. Before studying electrolytes, we have characterized the binary DDOA/PC gels as a function of concen-

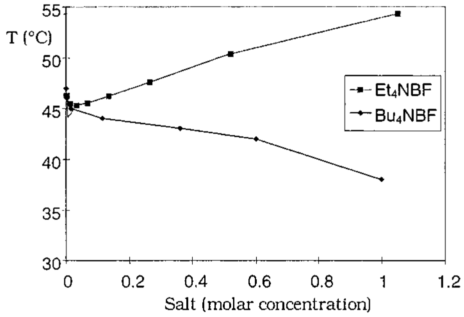

Figure 6. Variation of $T_{\rm gel}$ as a function of salt concentration in DDOA (5 mM)/PC.

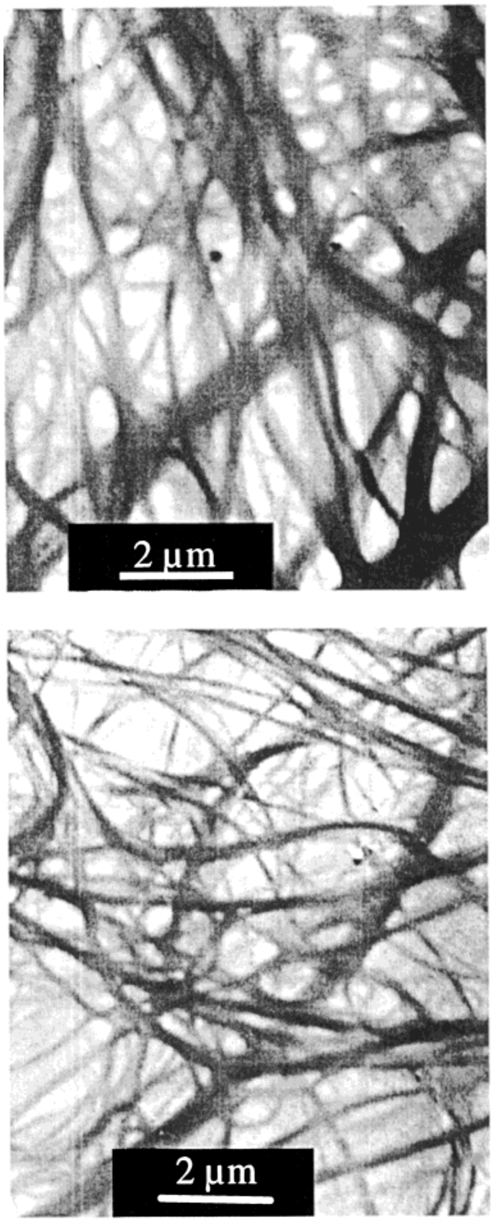

Figure 7. TEM images of a DDOA (5 mM)/PC gel (a, top) and of a DDOA (5 mM)/Et_4NBF_4 (10 mM)/PC gel (b, bottom).

tration and temperature. The phase diagram of the sol–gel transition is reported in Figure 4. Above 85 °C, it is limited by the melting of the DDOA fibers. At low concentration, the limitation comes from the decreasing percolation ability of the fiber network. If this latter value is difficult to evaluate, relevant thermodynamic information can be extracted from the available data.

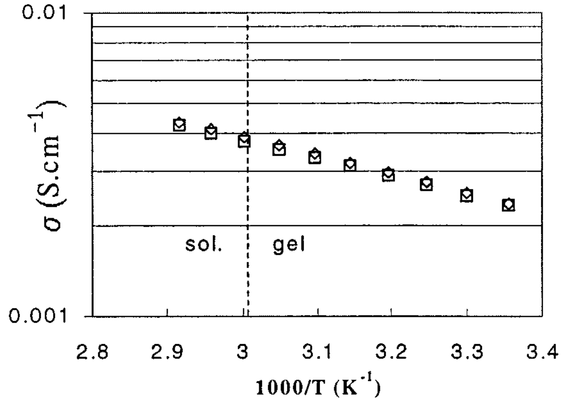

Figure 8. Conductivity of the solution Et_4NBF_4 (9.6 mM)/PC (squares without DDOA, diamonds with 8 mM DDOA). $T_{\rm gel}$ temperature is indicated by a dashed line. The activation energy is 11.6 ± 0.4 kJ/mol.

Indeed, the chemical potential of DDOA in solution is given by

$$\mu = RT \ln(\phi) \tag{1}$$

where ϕ is the DDOA molar fraction, assimilated to the activity in the investigated low-concentration domain. Since DDOA can be considered to be in a pseudo-solid state when it forms fibers in the gel state, its activity tends toward 1 and its chemical potential toward 0. The following expression for the sol–gel transformation is then derived:

$$\Delta G_{\rm sol\rightarrow gel} = RT \ln(\phi) = \Delta H_{\rm sol\rightarrow gel} - T\Delta S_{\rm sol\rightarrow gel} \tag{2}$$

$\Delta H_{\rm sol\rightarrow gel}$ and $\Delta S_{\rm sol\rightarrow gel}$ can be determined from a plot of $\ln(\phi)$ versus $1/T$. As shown in Figure 5, the DDOA/PC data give the expected linear plot and values of -56 kJ·mol^{-1} and -115 J·mol^{-1}·K^{-1} for $\Delta H_{\rm sol\rightarrow gel}$ and $\Delta S_{\rm sol\rightarrow gel}$, respectively.

DDOA/PC/Salt Gels. Alkylammonium salts have been selected due to their good electrochemical stability and conductivity in PC[9] and also for their utility in supercapacitors.[10] Figure 6 shows the variation of $T_{\rm gel}$ for a 5 mM DDOA/PC solution as a function of salt concentration. Surprisingly, addition of Et_4NBF_4 increases $T_{\rm gel}$ (for example by +9 °C at 1 M), whereas addition of Bu_4NBF_4 decreases $T_{\rm gel}$ (−7 °C at 1 M). It is not yet clear why the gel is stabilized by Et_4NBF_4 and destabilized by Bu_4NBF_4. The solvent structuration in the gel electrolyte is certainly different from that of the binary DDOA/PC system because the cations and anions have to be solvated. This probably introduces a competition between DDOA and ions solvation. In addition, hydrophobic-like effects are certainly more pronounced with Bu_4N^+ than with Et_4N^+ because of its longest aliphatic chains. One can infer that the Bu_4N^+ cation could act as a surfactant, its alkyl chains may facilitate partial insertion within the DDOA fibers and contribute to a destabilization of the gel.

At a microscopic scale, the salts do not seem to affect the morphology of the gel nanofibers. TEM images of DDOA/PC gels in the presence and absence of salt

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(9) Ue, M.; Ida, K.; Mori, S. *J. Electrochem. Soc.* **1994**, *141*, 2989.

(10) Ue, M.; Kateda, M.; Katehara, M.; A, S. Mori, A. S. *J. Electrochem. Soc.* **1997**, *144*, 2684.

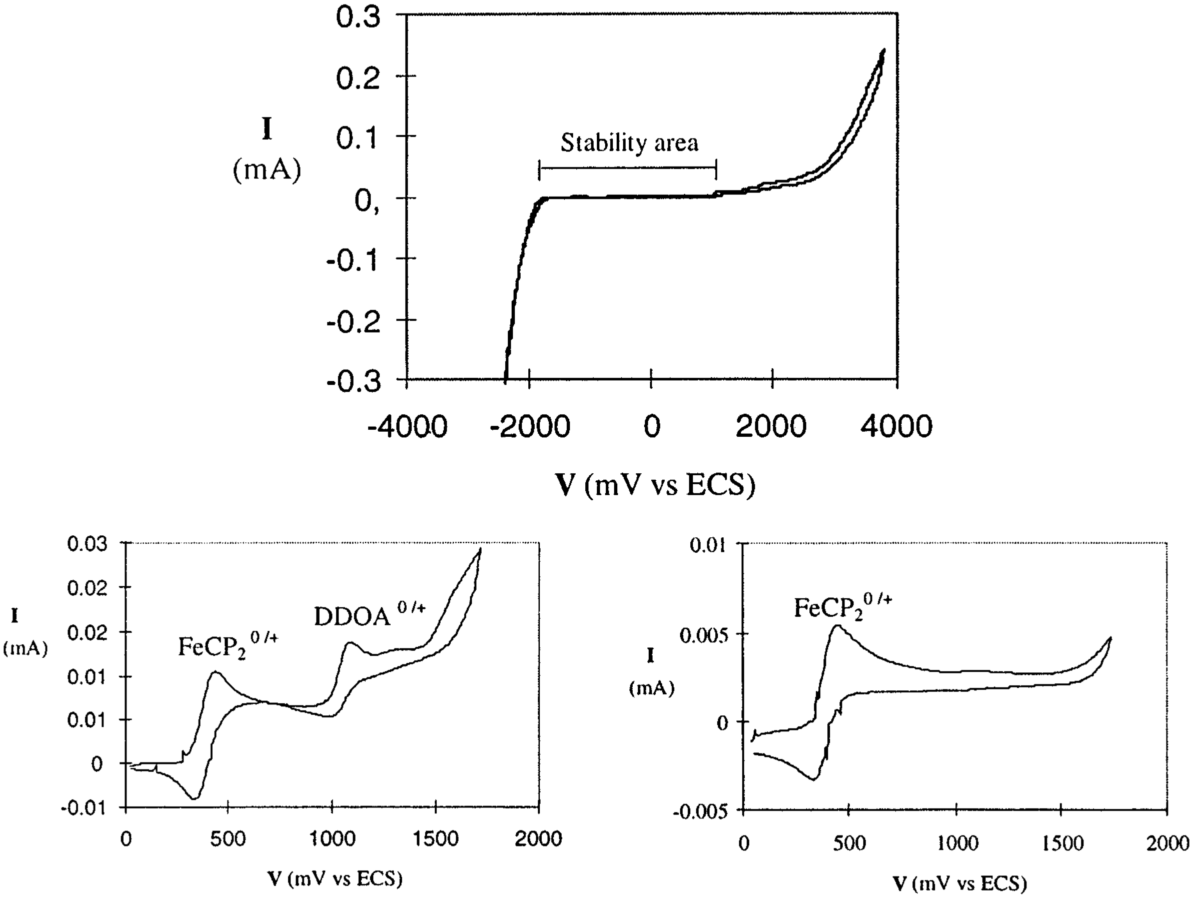

Figure 9. Voltammograms of DDOA (5 mM)/Bu_4NBF_4 (0.1 M)/$FeCP_2$ (4 mM)/CH_3CN in the liquid state at 50 °C (a, top) and in the gel state at 0 °C (b (left), c (right), bottom).

display very similar 3D fiber networks with bundles of fibers of 100 to 200 nm diameter (Figure 7).

Electrochemical Properties of DDOA/PC/Salt Gel Electrolytes. As shown in Figure 8, the presence of DDOA does not affect the conductivity of electrolyte solutions: no significant difference is found between the conductivity of a DDOA (8 mM)/PC/Et_4NBF_4 (9.6 mM) gel and that of a PC/Et_4NBF_4 (9.6 mM) solution without gelling agent. This result is in agreement with previous observations[4,6] and confirms that the 3D network of fibers does not modify the ionic diffusion in the large interconnected liquid domains even at high concentrations of gelator. The activation energy for the conductivity in these systems is 11.6 ± 0.4 kJ/mol. For DDOA concentrations lower than 10 mM, the conductivity values do not differ significantly from those shown in Figure 8 for 8 mM. We have not studied the conductivity of solutions with DDOA concentrations higher than 10 mM in order to avoid any problem of precipitation at low temperature.

As far as applications of these gel electrolytes in various devices are concerned, a very important aspect, not considered up to now, is the limitation of electrochemical stability brought about by the presence of the gelator. To determine the limitations, voltammetric measurements have been performed on DDOA solutions and gel electrolytes. Due to the presence of some impurities of unknown origin, in both Et_4NBF_4 salts and PC, a Bu_4NBF_4/acetonitrile solution was selected. With 5 mM DDOA, its T_{gel} occurs at 30 °C. The potential was calibrated with Ferrocene (4 mM) as internal reference ($E_{ox} = +0.38$ V in acetonitrile).[11] Figure 9 shows voltammograms of the CH_3CN/DDOA (5 mM)/Bu_4NBF_4 (0.1 M)/$FeCP_2$ (4 mM) system. A stability window of 3 V (−1.9 V to 1.1 V/ECS) was observed in the liquid state at 50 °C (Figure 9a). Similar reduction and oxidation values are found for anthracene.[12] Actually, expanded views (Figure 9b,c) demonstrate that the oxidation limit is extended in the gel phase. The condensation of DDOA into fibers reduces the concentration of DDOA molecules in the surrounding solutions by about 2 orders of magnitude. As a result, the oxidation wave of DDOA in the gel phase at 0 °C becomes very weak (Figure 9c). One can infer that the pseudo-solid DDOA molecules in the fibers are protected from oxidation and reduction. This useful property can be exploited for several electrochemical applications of these gels as electrolytes.

Carbon Supercapacitors with Gel Electrolyte. A PC/Et_4NBF_4 (1 M)/DDOA (5 mM) mixture was used as the electrolyte in a double-layer carbon supercapacitor using two carbon sheets of 1 cm diameter. Voltammograms at 25 °C (gel) and 70 °C (liquid) are compared in Figure 10. They indicate that the device can be cycled between +1.5 and −1.5 V without any detectable redox feature even at 70 °C. The capacitance per total carbon weight increases from 14 $F \cdot g^{-1}$ at 25 °C to 39 $F \cdot g^{-1}$ at 70 °C. Such a strong increase of capacitance with temperature has already been reported for other carbon

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(11) Ruiz, J.; Astruc, D. *C. R. Acad. Sci., Ser. IIc: Chim.* **1998**, *1*, 21.

(12) Ebersen, L.; Utley, J. H. P.; Hamerich, O. *Org. Electrochem.* **1991**, *13*, 509.

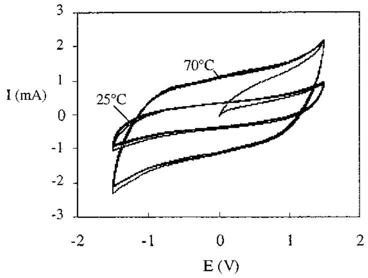

Figure 10. Voltammograms between ±1.5 V of a supercapacitor using a DDOA (5 mM)/Et_4NBF_4 (1 M)/PC electrolyte either at 25 °C (gel) or at 70 °C (liquid).

double-layer capacitors and assigned to several factors, including conductivity increase, better impregnation of the carbon surface, etc.[13] It is however likely that the oxidation and reduction of DDOA at 70 °C would limit the lifetime of the device at this temperature. Charge and discharge cycles under 1 and 0 V for the gel electrolyte at 25 °C are presented in Figure 11. The capacitance is 20 F·g^{-1} without DDOA and decreases to 14 F·g^{-1} with 5 mM DDOA. Since these results are obtained at the same temperature and for nearly the same conductivity, the loss of capacitance in the gel is tentatively explained by adsorption of DDOA molecules on the carbon surface.

Conclusion

DDOA has proved to be an efficient gelator for PC and PC/salt solutions. The presence of salts produces unexpected effects: T_{gel} is increased with Et_4N^+ and decreased with Bu_4N^+, presumably because of a surfactant effect of the longer alkyl chains of Bu_4N^+. At a microscopic scale, the presence of ions does not affect the 3D network of DDOA fibers and does not modify the conductivity of the solution. The electrochemical stability of DDOA/PC/salt electrolytes is limited by the stability window of DDOA, which has the typical redox properties of anthracene, but, in the gel state, DDOA seems to be protected from oxidation and reduction within the fibers. The performances of such gel electrolyte has been tested in a double-layer carbon supercapacitor. Reversible cycling can be performed between ±1.5 V, but the presence of DDOA decreases the capacitance by about 30%, presumably because of adsorption of DDOA molecules on the carbon surface.

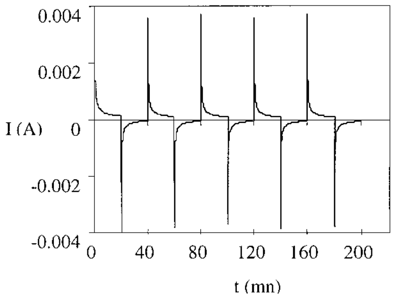

Figure 11. Charge under 1 V and discharge under 0 V of the supercapacitor of Figure 10 at 25 °C.

DDOA is apparently not the best candidate for a gel electrolyte to be used in electricity storage devices such as supercapacitors because of its limited temperature and electrochemical stabilities and also because of its possible adsorption on the carbon surface. However, several other gelators of the same family are being developed,[8] and it is not excluded that the above limitations can be circumvented. These low molecular weight gelators keep the unique advantage of gelling classical electrolytic solutions at millimolar concentrations while keeping the ionic conductivity of the solution unchanged.

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(13) Lassègues, J. C.; Grondin, J.; Becker, T.; Servant, L.; Hernandez, M. *Solid State Ionics* **1995**, *77*, 311.