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Infrared Spectroelectrochemical Studies of Divided Carbon Electrodes in Acetonitrile-Sodium Tetrafluoroborate Solutions

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Fourier transform infrared spectroelectrochemistry has been used to study the vibrational spectrum of a thin layer of the organic electrolyte in contact with a divided carbon supercapacitor electrode. Variations in the absorption of peaks characteristic of the solvent and of the support electrolyte during an anodic potential scan have been observed. The presence of adsorbed water was detected. The formation of a stable adduct of CH₃CN and BF₃ under anodic potential was identified.

Electrical energy produced by renewable sources such as wind power or photovoltaic devices is fluctuant by nature. In order to use it reliably, it is necessary to have a means of storing electricity. These storage devices are also of prime importance in systems where surges of power are frequent; *e.g.* applications such as transportation and regenerative braking.

Storage of electrical energy can be accomplished in an elegant way through the use of lightweight capacitors. Recently, devices based on the use of the electrochemical double-layer capacitor (EDLC) have been developed: the supercapacitors.¹ Supercapacitors are intermediate systems between electrochemical batteries, which can store high energy associated with medium power values, and dielectric capacitors, which can deliver very high power during times of the order of a few milliseconds. Supercapacitors are used for energy storage over time periods ranging from seconds to minutes; their peak power is up to 10-20 times higher than that of batteries, but their energy density is 20-50 times lower.

Their principle relies on the use of high specific area electrodes placed in an electrolyte and separated by a thin inert microporous membrane. This work focuses on organic electrolyte capacitors with electrodes manufactured using carbon dispersed in an aqueous solvent. To be useful, these devices must be able to remain charged in open-circuit conditions for great lengths of time. This implies that no irreversible reactions induced by the variation of the potential of each electrode should occur; thus, it is important to understand the mechanisms occurring during charge and spontaneous discharges.

During the charge of the EDLC, several phenomena can occur.² An increase in the number of ions forming the double layer can be caused by the application of a voltage. A local increase in ionic concentration near the carbon surface, but not directly connected with the double layer, can also be produced if a current flows through the capacitor at or above the electrolyte potential range.

Self-discharge processes are complex and involve mechanisms occurring on a short or a long time scale. When the supercapacitor is fully charged, its removal from the power supply induces a fast relaxation phenomenon. This process is reversible at short times. An irreversible process corresponding to faradaic reactions can also be observed on the same time scale. Another reason for self-discharge are the faradaic reactions of various groups at the surface of the carbon during *ca.* the first 500 h of use of the device. This phenomenon is irreversible. Another cause for voltage drop is the presence of an "electrochemical shuttle" due to electroactive redox couples involving impurities in the carbon layer.

To gain some insight into self discharge phenomena, a knowledge of the variations of composition of the electrolyte in the immediate vicinity of the electrode or even modifications of the electrode itself as the potential is swept is of prime importance. *In situ*

spectroelectrochemical measurements are well suited to fulfill this goal. Vibrational spectroscopy yields structural information on all the species present in the solution or on the electrode. Therefore, it appears to be a good method to couple with electrochemistry. Raman spectroscopy associated with confocal microscopy seems ideal because of the spatial resolution that enables one to select which part of the system is studied: electrode or solvent.³ However, Raman spectroscopy is not very sensitive to the presence of minor components, and the previous studies were not able to detect new species, although variations of the intensities of the major peaks during potential scans were recorded. Rapid scan Fourier transform infrared (FTIR) spectroscopy associated with electrochemistry *in situ* was used in this work. Preparation of new electrodes allowed us to keep enough IR light to obtain high-quality spectra.

Experimental

The spectroelectrochemical cell and its installation in an IR spectrometer have been previously described.⁴ The cell was designed to accommodate various electrodes. The distance between the electrode and the optical window could be adjusted by a micrometric screw so that the cell path length was small enough (*ca.* 100 μm) to avoid complete absorption of radiation. The window was made of CaF₂, and the working range was from 1100 to 4000 cm^{-1} . The electrolyte was a 1 M solution of tetraethylammonium tetrafluoroborate (Et₄NBF₄) in dry acetonitrile (Merck Supercapacitor Electrolyte LES 100; H₂O: 25 ppm; HF: 68 ppm as given by the supplier) used as provided and kept inside the glove box. The other salts, NaBF₄, Et₄NClO₄ were dried at 120°C under vacuum (10⁻⁵ Torr) for 24 h. A solution of the adduct CH₃CN·BF₃ in CH₃CN was prepared by letting BF₃ stay in contact with CH₃CN in a greaseless, mercury-free, vacuum line. BF₃ was prepared according to published methods.⁵

Electrodes such as those used in industrial supercapacitors absorb all incident radiation from UV to IR. The major technological innovation in this work was the capability to manufacture "finely divided carbon electrodes" that would reflect enough light to record high-quality IR spectra. The electrodes were aluminum cylinders 12 mm o.d. (grade 1050) whose bases were finely polished. Heat-shrinkable poly(tetrafluoroethylene) (Adtech Polymer Eng. Ltd, Stroud, U.K.) was used to insulate the sides of the cylinder. A thin layer of "ink" made of divided carbon together with a binder^c was spread on the electrode using a spin-coating technique. The layer's thickness was not measured but adjusted by trial and error so that enough IR energy was reflected from the surface. These electrodes were cured at 130°C under vacuum (10⁻⁵ Torr) for 24 h. Afterward, all handlings were performed in a glove box (Jacomex) filled with

^c Activated carbon, synthetic origin, Brunauer, Emmett, and Teller method area 1600 m²/g; carboxymethyl cellulose and styrene butadiene rubber as binder in aqueous dispersion.

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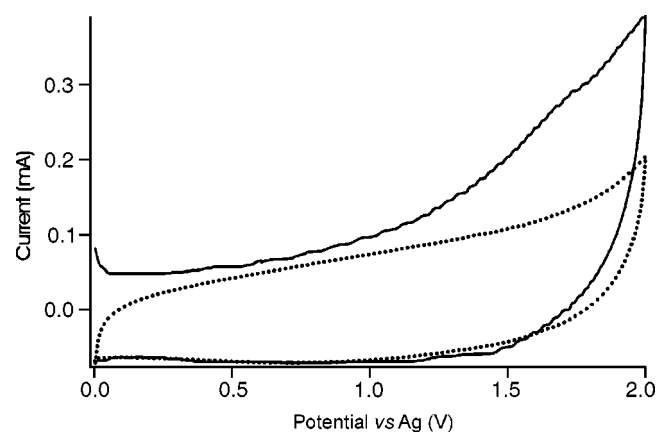


Figure 1. Cyclic voltammogram of finely divided carbon electrode prepared by spin-coating. Scan rate: 5 mV s^{-1} ; Et_4NBF_4 (1 M) in acetonitrile. Solid line: first sweep; dotted line: following cycles.

dry, oxygen-free, purified argon. The potential of the working electrode was controlled with a three-electrode setup; the counter electrode was a platinum loop and a silver wire acted as a pseudoreference. The potential sweep was provided by a potentiostat (PG30 Autolab). The FTIR spectrophotometer used was either a MagnaRAM 860 or an Avatar (Nicolet-Thermo-Optek)

Results

The electrochemical behavior of a carbon spin-coated aluminum electrode during a potential cycle 0, +2 V, 0 V (vs. Ag) is shown in Fig. 1. (A similar curve is obtained during cycles toward negative potentials.) It is always observed that the first curve is markedly different from the following ones. This current vs. voltage curve is characteristic of a capacitive system associated with a series resistance as is observed in capacitors for potentials below 1.5 V. For potentials higher than this value, faradaic processes are probably involved, coming from either carbon surface groups or impurities linked to the carbon manufacturing process. The slight curvature observed on the negative going potential sweep observed between 0.6 and 0 V is possibly due to a reduction of a small quantity of species that were produced in the forward scan. Because there are no redox species in the solution, no peaks are observed or expected. Uncoated aluminum or platinum electrodes have only a resistive behavior and much weaker currents under these conditions.

To detect spectral modifications during a potential scan, the first spectrum was subtracted from the following ones. In this configuration, production of new species show as positive signals. As shown in Fig. 2, during an oxidative scan, the intensities of the major peaks decrease (solvent and support electrolyte: $1050\text{-}1150$, $1360\text{-}1500$, $2250\text{-}2350$, $2850\text{-}3150 \text{ cm}^{-1}$). These variations follow linearly the potential increase and are reversible. The disappearance of species in regions where the original spectrum shows very small absorbance is observed at 1600 and 1640 cm^{-1} . The intensities of these peaks follow linearly the potential from 0 to 1.1 V and then remain constant. This process is reversed on the return scan. New sharp peaks are formed in the region around 2360 and 1200 cm^{-1} where no absorbing species were present in the starting spectrum, and a broader band grows between 3200 and 3500 cm^{-1} . Evolution of the new peaks around 1220 and 2360 cm^{-1} while the potential was scanned from 0 to 2 V, are shown in Fig. 3a and b, respectively. These modifications begin at potentials higher than 1.25 V and they are not reversible.

To determine the origin of these new peaks, Et_4NBF_4 was replaced with either Et_4NClO_4 or NaBF_4 . No spectral modifications were detected with Et_4NClO_4 , but the same behavior was observed with NaBF_4 , thus implying the role of the anion BF_4^- . Another origin of these peaks could be the formation of CO_2 in the acetonitrile

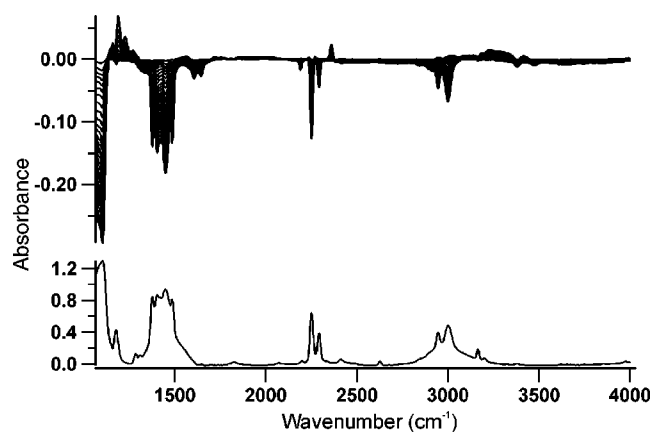


Figure 2. Difference absorption spectrum during scan from 0 to +2 V (vs. Ag). Scan rate 2 mV s^{-1} , 64 spectra recorded, Et_4NBF_4 (1 M) in acetonitrile. Bottom part: original spectrum.

trile solution because a peak in this spectral region was previously reported.⁶ To answer these questions, two key experiments were performed. In one of them, CO_2 gas was bubbled through the solution, and in the other one $\text{CH}_3\text{CN}\cdot\text{BF}_3$ dissolved in acetonitrile was added into the cell. IR spectra were recorded with the same electrodes as used previously. The addition of CO_2 to the solution produces a new peak at 2340 cm^{-1} and almost no variation in the range of 1200 cm^{-1} . However, the addition of BF_3 produces a peak at 2360 cm^{-1} and a broad peak at 1190 and at 1220 cm^{-1} . Similar peaks were observed for the adduct $\text{CH}_3\text{CN}\cdot\text{BF}_3$ in the solid state.^{7,8}

Potential scans toward the negative potentials did not produce any new absorbing species. Control experiments using bright platinum or aluminum working electrodes were also performed; the current flowing through the cell was much lower, and no new peaks were detected in the region of 1200 or 2360 cm^{-1} , even in long duration experiments.

Discussion

FTIR spectroelectrochemistry is a well-established technique for the study of processes occurring next to an electrode.⁹ However, it is the first time that it was used to investigate electrochemical processes occurring in the vicinity of a dispersed carbon electrode.

During positive potential scans, the difference absorption spectra are complex. Although the thickness of the solution layer used in our experiments is huge compared to that of the double layer, it is in this

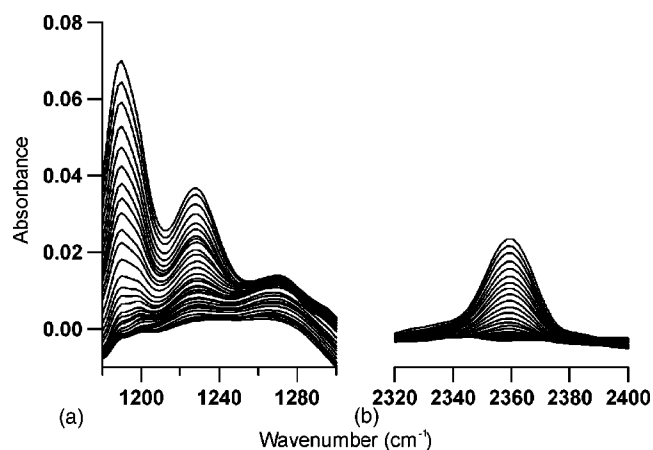


Figure 3. Spectral modifications observed at (a) 1220 cm^{-1} and (b) 2360 cm^{-1} as function of the applied potential. Bottom spectrum is at +1 V; topmost at +2 V. Each spectrum is separated by 32 mV.

last layer that all the variations of concentration occur. Near the positive electrode, BF_4^- becomes trapped in the diffuse layer or in pores of the carbon coating, thus decreasing the concentration in the bulk. According to the electroneutrality of the solution, the concentration of the cation also decreases. As expected, the variation of concentration follows linearly the potential and is reversible. The same behavior and the possible mechanisms were described in a previous spectroelectrochemical study of a supercapacitor using Raman spectroscopy.³

The intensity of the acetonitrile peak at 2250 cm^{-1} decreases in a linear and reversible way when the potential increases. This means that in the path of the light, solvent molecules are replaced by anions that are attracted to the positively charged electrode. This variation was not observed in a previous study using the same electrolytic solution but with bright platinum electrodes.¹⁰ The explanation for this difference could be that our divided electrodes have a much larger area than the polished platinum and thus they amplify the phenomenon. Sharp negative peaks observed at 1608 and 1643 cm^{-1} are attributed to water and suggest that this molecule is desorbed from the double layer or from the electrode as the potential becomes positive. The water bending mode is observed at 1600 cm^{-1} in the vapor phase. The bands observed in this work are shifted to higher energies, indicating several kinds of interactions with the components of the solution. This is correlated with the appearance of broad peaks in the $3200\text{-}3500\text{ cm}^{-1}$ region corresponding to extensively hydrogen-bonded water associated with anions.

New absorption peaks produced in the regions of 1200 and 2360 cm^{-1} indicate the formation of stable species, rather than a simple adsorption on the electrode, because they do not vanish when the potential returns to its initial value. They appear only when the anion BF_4^- is present in the solution. It is then logical to look for new compounds originating from the major components of the system CH_3CN and Et_4NBF_4 , the most obvious being the formation of the well-known addition complex $\text{CH}_3\text{CN}\cdot\text{BF}_3$.

The spectroscopic evidence strongly supports the hypothesis of adduct formation. The new peak appearing at 2360 cm^{-1} is located in the range of the vibration frequency ν_2 of the triple bond $\text{C}\equiv\text{N}$ (occurring at 2266 cm^{-1} in pure acetonitrile). Modifications of the force constants of this vibrator when adducts were formed has first been published by Purcell and Drago.¹¹ Theoretical calculations on model molecules indicated that this frequency increase was due to an electronic transfer of the lone pair of the nitrogen toward the receptor molecule. Subsequent Raman and IR studies⁷ have enabled a complete indexing of all the lines. The IR spectrum of the adduct in solid argon matrix has also been reported.⁸ The geometry of $\text{CH}_3\text{CN}\cdot\text{BF}_3$ is known in the gas phase¹² and in the solid state.^{7,13} Other peaks were also detected in the 1250 cm^{-1} range; they were assigned to the ν_{13} mode corresponding mainly to BF_3 stretching.¹⁴ Similar conclusions were reached by various investigators who used similar electrolytes but on different electrode materials.^{10,15,16}

It is important to investigate the possible pathways leading to the formation of this adduct under an oxidizing potential. From this work, it is known that a divided carbon electrode and the presence of BF_4^- are required and that, as far as the IR spectrum indicates the composition of the solutions in the vicinity of such an electrode does not evolve with time in the absence of an applied potential. This observation rules out the possibility of a catalytic decomposition of the constituents of the solution.

Tetrafluoroborate anion has been extensively used as an electrolyte for the anodic oxidation of organic compounds in aprotic solvents, and it is generally assumed that these anions are stable. However, fluorination of some organic molecules that are electrochemically oxidized in the presence of this anion was reported some time ago in the literature.¹⁷ Although there are no substances undergoing oxidation in our solution, the possibility of decomposition of BF_4^- cannot be overlooked.

We have postulated, based on spectroscopic results, that the formation of a stable neutral compound such as the adduct $\text{CH}_3\text{CN}\cdot\text{BF}_3$ could explain the new peaks observed. However, in BF_3 or BF_4^- , the boron atoms are in the same oxidation state: a simple electrochemical process cannot lead to the formation of BF_3 . Considering the minute amount of material present on our electrode, it is unlikely that oxidation of trace impurities contained in the carbon alone would lead to the observed spectral modification through a reaction with BF_4^- . However, the possibility that active sites are generated that could catalyze this reaction cannot be completely overruled.

One must then look for electrochemical reactions of other molecules present in the solution or adsorbed on the electrode material, keeping in mind that its area is very large. The carbon-coated electrode was dried under high vacuum but only at a temperature of 130°C ; the presence of water trapped in the pores is thus possible. The spectroscopic evidence shows that water is desorbed under oxidizing potentials.¹⁰ Furthermore, in the electrolyte solution, H_2O and HF are present at a concentration in the order of 10^{-3} M . Oxidation of fluoride anion leading to fluorine is very unlikely while that of water is possible in the potential range being studied. It can lead to the formation of H^+ and oxygen.

It can then be tentatively proposed that the following reaction, independent of the potential, possibly catalyzed by the carbon material, could be triggered: $\text{BF}_4^- + \text{H}^+ \rightarrow \text{HF} + \text{BF}_3$. As soon as produced, BF_3 would form the adduct $\text{CH}_3\text{CN}\cdot\text{BF}_3$ that we have spectroscopically identified.

One can argue that, to strengthen our hypothesis, a deliberate addition of water to the system could be made to see if the growth of new peaks would be modified. This was not done for several reasons. First, as we have seen, there is already water adsorbed on the electrode, and a further addition would completely modify the nature of the interface. Second, this would be very different from the conditions of the real supercapacitor, and the results would be of little utility.

Conclusion

We have shown that FTIR can be used to probe the variation of concentration of species in the vicinity of a high specific area electrode covered with divided carbon. The magnitude of the area of the electrode thus obtained allows a relatively large current to flow, hence producing large chemical effects that can be detected. The variation of the concentration of ions in the double layer under a potential sweep was put into evidence. The desorption of water from the electrode occurred at positive potentials. However, all these phenomena were reversible and did not lead to permanent modifications.

It has been established that a new species identified as $\text{CH}_3\text{CN}\cdot\text{BF}_3$ was formed when the electrode was subjected to an oxidizing potential. This new species is not reduced during the discharge cycle and is stable. However the influence of the presence of this complex on the performances of supercapacitors has not yet been investigated.

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