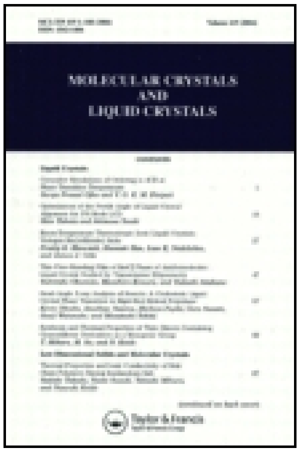

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# Spectroelectrochemistry by Confocal Raman Microspectrometry

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# Spectroelectrochemistry by Confocal Raman Microspectrometry

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Confocal Raman Microspectrometry is shown to be a powerful technique to study electrochemical devices under working conditions with a spatial resolution of about 1 $\mu m^3$. This is first illustrated on a Li/P(EO)$_{20}$,LiTFSI/Li symmetrical cell where salt concentration gradients in the polymer electrolyte are measured as a function of current density and time. These data give access to transport properties of the polymer electrolyte, namely transport numbers and diffusion coefficients. A second example is provided by electrostatic supercapacitors using activated carbon fabrics of high specific surface area and proton conducting liquid electrolytes. A mapping of a carbon fiber and of the surrounding electrolyte is recorded for ± 1V polarizations. The relative intensity and the frequencies of the D and G Raman lines of carbon are found to be very sensitive to the carbon charge.

keywords: Confocal Raman Microspectrometry; Spectroelectrochemistry; Lithium Battery; Polymer Electrolyte; Supercapacitor; Activated Carbon.

## INTRODUCTION

With Confocal Raman Microspectrometry (CRM), it is possible to obtain the Raman spectra of very small volumes ( $\leq 1\ \mu m^3$) at a selected position x,y,z in the sample. Depending on sample transparency, in-depth "optical sectioning" can be performed down to tens of microns. In addition, Raman imaging of a given species is made very efficient by taking advantage of the high sensitivity of two-dimensional CCD detectors, combined for example with confocal line illumination[1,2]. As the Raman spectrum at a given point is obtained in a few seconds, dynamical processes occuring in electrochemical devices can be followed provided the charge or discharge times are of a few minutes (supercapacitors) or of a few hours (batteries).

We have already shown that CRM can usefully be applied to the study of a lithium battery under working conditions[3]. Some new results are given here and a preliminary CRM study of a carbon supercapacitor is presented.

## EXPERIMENTAL PART

We have previously described the principle of the lithium battery cell[3] (Fig.1a) and the nature and spectroscopic properties of the polymer electrolyte $P(EO)_{20}$,LiTFSI [4]. CRM is applied to the edge of the cell, along a line of about 20 points separated by 6 μm, going repeatedly from one electrode to the other, at a depth of about 20 μm in the polymer electrolyte (PE).

The supercapacitor is made of activated carbon fabrics (ACF Kynol, 2000 $m^2.g^{-1}$) and of a proton conducting liquid or polymer electrolyte[5]. For the CRM experiment, two strands of approximately 5 cm lenght and 15 μm diameter have been extracted from this fabrics and disposed as shown in Fig.1b. The CRM observation is made every 1 μm on a line of 30 points covering part of one carbon electrode and of the surrounding electrolyte.

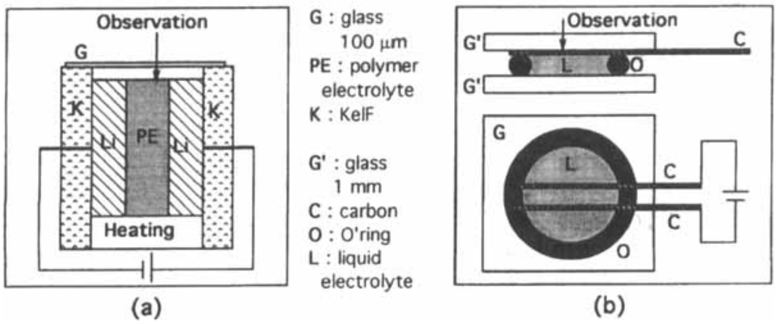

FIGURE 1 Schematic representation of the lithium (a) and supercapacitor (b) cells. In (b), the O' ring has 1 cm internal diameter and the two carbon fibers are separated by about 2 mm.

For these experiments, we have used a Labram IB spectrometer (Dilor)[2]. The cell is adjusted below the objective on a motorized and computer controlled 2D actuator system. For a reasonable signal-to-noise ratio, 30 s are spent to record a single spectrum with a resolution of 4 $cm^{-1}$.

## RESULTS AND DISCUSSION

### Li/PE/Li Symmetrical cell

In a preliminary Raman study of the $P(EO)_{20}$,LiTFSI electrolyte, we have shown that the intense $\delta sCF_3$ line of the TFSI anion, $(CF_3SO_2)_2N^-$, normalized by the $\delta CH_2$ polymer line, is proportional to the salt concentration in the 30 < n < 6 domain[4]. For n > 6, the salt is fully dissociated and ion-pairing effects are negligible. In addition, the n = 20 composition is melted at 80°C and a good contact is achieved with the Li electrodes. The comparison of the Raman spectra of pure PEO and of the complex reported in Fig.2 indicates the relative contribution of the polymer and anion lines.

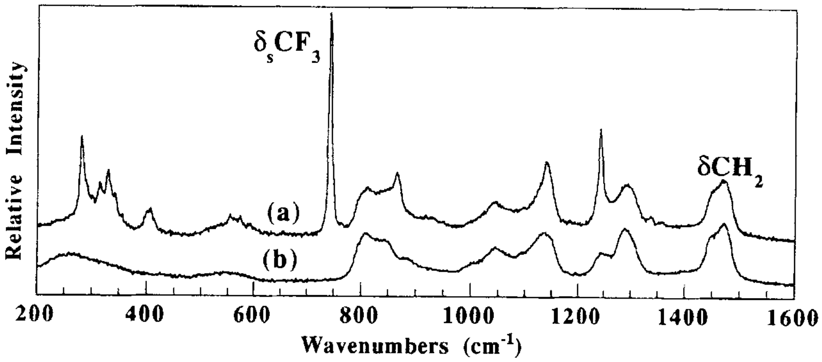

FIGURE 2 Raman spectra of $P(EO)_{20}$,LiTFSI (a) and of pure PEO (b) at 80°C obtained in 30s with a laser power of 17 mW. The lines used for the concentration measurement are indicated (see text).

For the cell in open circuit, an identical spectrum of the complex is obtained for all the points on a line going from one electrode to the other. When a constant current is passed through the cell, the salt concentration is no more constant: as shown in the map of Fig.3, it increases near the anode and decreases near the cathode. This gradient is reversed when the current is reversed and the concentration goes back to a constant value when the current is interrupted.

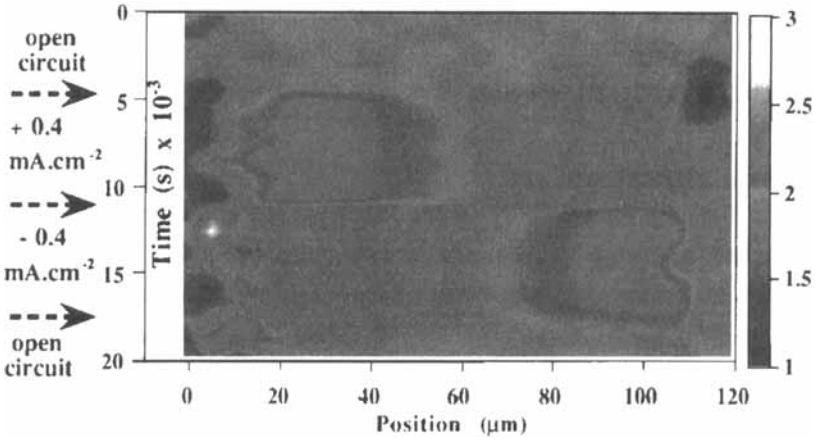

FIGURE 3 Map of the salt concentration at 80 °C as a function of time and position in the electrolyte (L = 80 µm). Polarizations are indicated on the left and the right scale associates colors to intensities. (See Color Plate I).

These results are more quantitatively represented in Fig.4.

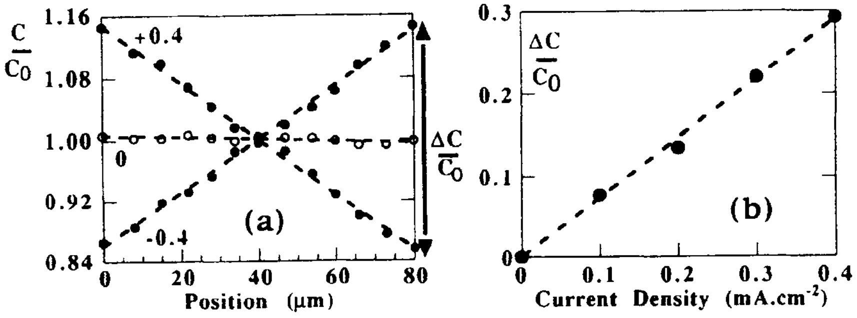

FIGURE 4 (a) : steady state salt concentration gradients taken from Fig.3 at +0.4 , -0.4 and 0 mA.cm$^{-2}$; (b): gradient variation with current density. $C_0$ is the initial salt concentration measured on a separated PE film also at 80°C.

As expected from theoretical predictions in the hypothesis of ideal solutions[6,7], the steady state concentration gradient is linear and symmetric within the cell (Fig.4a). We have also checked that $\Delta C/C_0$, defined in Fig.4a, is proportional to the current density I (Fig.4b) according to[7]:

$$\frac{\Delta C}{C_0} = \frac{I t_-^0 L}{F D C_0} \qquad (1)$$

where F is the Faraday constant, $D = (2D_-D_+)/(D_-+D_+)$ the salt diffusion coefficient, $t_-^0 = 1 - t_+^0 = (D_-)/(D_++D_-)$ the anion transport number and L the electrolyte thickness. $D_+$ and $D_-$ are the cation and anion diffusion coefficients.

Then, by focussing the analysis at the Li/electrolyte interface, we have measured the establishment of this steady state. For sufficiently short times, i.e. for $t \ll D/L^2$, the concentration is unchanged in the middle of the cell (semi-infinite diffusion regime), but varies at the interface according to[7] :

$$\frac{\Delta C(t)}{C_0} = \frac{4 t_-^0}{F C_0 \sqrt{\pi D}} I \sqrt{t} \qquad (2)$$

From these two experiments, it is possible to deduce the values $t_-^0 = 0.52$ and $D = 5.1\ 10^{-8}\ \mathrm{cm^2.s^{-1}}$ for $P(EO)_{20}$,LiTFSI at 80°C. It follows that $t_+^0 = 0.48$, $D_- = 5.3\ 10^{-8}\ \mathrm{cm^2.s^{-1}}$ and $D_+ = 4.9\ 10^{-8}\ \mathrm{cm^2.s^{-1}}$.

## Carbon supercapacitor

We have developed supercapacitors using activated carbon fabrics and liquid or polymer proton conducting electrolytes which reach capacities of 100 F/ g carbon[5]. From the simplified system schematized in Fig.1b, good quality Raman spectra are obtained on the carbon, in the bulk of the electrolyte $H_3PO_4$ 7.3M and at the interface (Fig.5a). The carbon spectrum is characterized by the so-called G (Graphite) and D (Defect) lines which have been often used to evaluate the degree of disorder of the material, for example in terms of crystallite size or of $sp^2/sp^3$ character[8-10]. The space and time resolutions are unsufficient to follow concentration changes occuring at the interface in the electric double layer but we have found that the carbon spectrum was modified in an unexpected way. When the charge of the observed fiber is made alternatively positive ($C^+$) and negative ($C^-$), one can see that a huge intensity enhancement occurs for both G and D lines by comparison with the initial state spectrum ($C^0$) (Fig.5b). In addition, these lines are blue-shifted by more than 10 $cm^{-1}$ and their intensity ratio $I_G/I_D$ is modified. As the laser power is kept at very low values ($\leq$ 6 mW), degradation effects by heating seem to be excluded. One could rather invoke a better penetration of the electrolyte into the carbon pores. Indeed, small gas bubbles are observed at the beginning of the polarization process. This gas evolution comes from desorption of the material and not from any electrolyte dissociation as checked from the voltammograms recorded independently with a reference electrode.

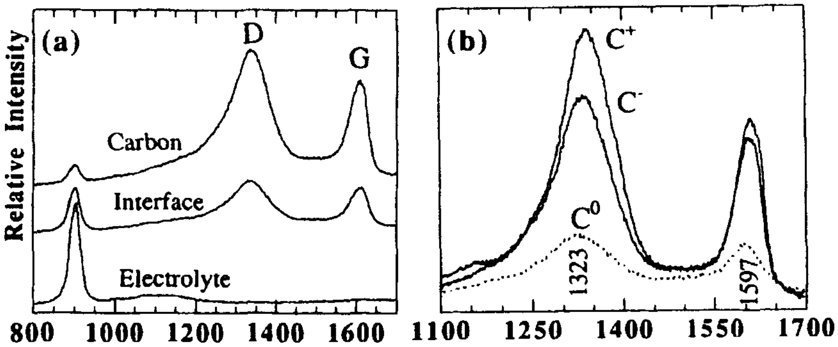

FIGURE 5 (a): Typical Raman spectra taken on the open circuit system; (b): Changes of the carbon spectrum between the $C^0$, $C^-$ and $C^+$ states.

After several charge/discharge cycles at ± 1V, the spectral characteristics of the $C^+$ and $C^-$ states tend smoothly towards asymptotic values. This is illustrated in Fig.6 for $I_G/I_D$ and in Fig.7 for the frequencies. The latter are systematically higher for the $C^+$ state than for the $C^-$ state and the difference is more pronounced for the D band than for the G one.

As far as we know, such spectral changes for carbon *via* the electric double layer have never been reported previously. Proton intercalation and/or specific

Raman effects (resonance, SERS,..) could be invoked, but we have at present no argument to support any of these hypotheses. It is still possible that the electric double layer simply induces a polarisability change of the carbon surface. Further experiments are in progress with other electrolytes including $Li^+$ conducting ones and as a function of the incident laser wavelength.

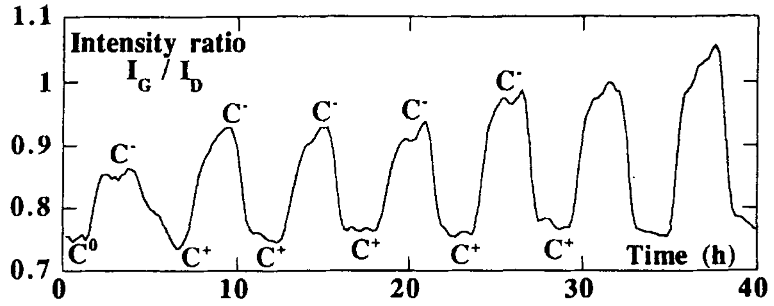

FIGURE 6 Relative intensity $I_G/I_D$ of the G and D carbon lines in the $C^0$ initial state and in the $C^+$ and $C^-$ states during the charge/discharge cycles.

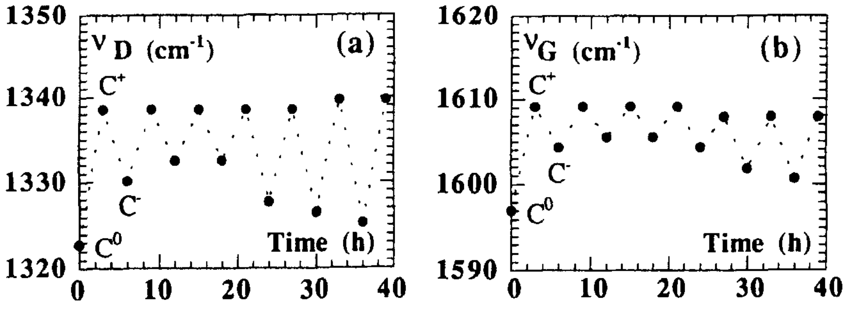

FIGURE 7 Frequencies of the D (a) and G (b) bands in the $C^0$ initial state and in the $C^+$ and $C^-$ states during charge/discharge cycles at ± 1V.

## CONCLUSION

Two applications of CRM to spectroelectrochemical studies have been described. On a symmetrical lithium/polymer electrolyte cell, it is shown that the steady state salt concentration gradients and their establishment can be measured with a very good precision. These results confirm previous theoretical predictions of a linear steady state gradient and open the way to the *in situ* determination of transport numbers and diffusion coefficients.

A prototype of carbon supercapacitor using two parallel carbon fibers soaked in a liquid electrolyte has also been investigated. Unexpected changes of the carbon spectrum are observed between its positively and negatively charged states. They might come from a modulation of the surface electronic distribution and hence of the polarisability, by the nature of the electric double layer.

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## References

[1.] P. Dhamelincourt, J. Barbillat and M. Delhaye, *Spectroscopy Europe*, **5/2**, 16 (1993).

[2.] K. P. J. Williams and D. N. Batchelder, *Spectroscopy Europe*, **6/1**, 19 (1994).

[3.] I. Rey, J-C. Lassègues, P. Baudry and H. Majastre, *Electrochim. Acta*, in press.

[4.] I. Rey, J-C. Lassègues, J. Grondin and L. Servant, *Electrochim. Acta*, in press.

[5.] J-C. Lassègues, J. Grondin; T. Becker, L. Servant and M. Hernandez, *Solid State Ionics*, **77**, 33 (1995).

[6.] P. G. Bruce, M. T. Hardgrave and C. A. Vincent, *Solid State Ionics*, 53-56, 1087 (1992).

[7.] Y. Ma, M. Doyle, T. F. Fuller, M. M. De Jonghe and J. Newman, *J. Electrochem. Soc.*, **142**, 1858 (1995).

[8.] A. M. Rao, A. W. P. Fung, M. S. Dresselhaus and M. Endo, *J. Mater. Res.*, **7**, 1788 (1992).

[9.] A. Cuesta, P. Dhamelincourt, J. Laureyns, A. Martinez-Alonso and J. M. D. Tascón, *Carbon*, **32**, 1523 (1994).

[10.] T. Jawhari, A. Roid and J. Casado, *Carbon*, **11**, 1561 (1995).