

## Raman microspectroscopy in Electrochemistry: Study of a Lithium Battery

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Raman microspectroscopy covers a wide range of activities and Electrochemistry can profit from this technique to set up *in situ* analyses to track kinetic phenomena. A lithium polymer battery cycling mechanism is driven by the ionic transport in a polymer electrolyte (polyethylene Oxide (PEO) –Lithium salt) and the intercalation of Lithium in the cathode ( $V_2O_5$ ). Information to monitor these properties in the battery can be obtained by Raman microspectroscopy.

### Measure of the Salt concentration in the polymer electrolyte

An electrolyte is a medium able to transport electric current using the ions it contains. The diffusion of the ions, which occurs most often under the influence of a concentration gradient and their migration, triggered by an electric field, are the two main characteristics that need to be checked when designing a new polymer electrolyte. The higher their value, the more powerful the battery is. The diffusion of an electrolyte is measured by the diffusion coefficient  $D$  ( $cm^2.s^{-1}$ ) and the migration is measured by the transport numbers  $t^-$  and  $t^+$ . Well-known techniques are available to measure those parameters in liquid electrolytes but those techniques become uncertain in the case of polymer electrolyte. So Raman microspectroscopy appears as an alternative tool.

In this example the electrolyte is composed of PEO heated up to 80°C as the solvent in which the Lithium  $Li^+$  salt of tetra fluorosulfonamide, TFSI $^-$  is solvated. At 80°C, PEO is completely amorphous and participates in the motion of  $Li^+$ .

PEO has a characteristic peak located at 1420  $cm^{-1}$ , which is assigned to the deformation,  $\delta(CH_2)$ . The anion TFSI $^-$  has a unique Raman signature with one characteristic peak which does not overlap with the Raman spectrum of PEO. This peak is the symmetric deformation

vibration of the  $CF_3$  group ( $\delta_s(CF_3)$  at 742 $cm^{-1}$ ). - See Figure 1a. The relation between the ratio of the area corresponding to these peaks  $A[\delta_s(CF_3)]/ A[\delta(CH_2)]$  is demonstrated to be linear in a wide range of concentrations (Fig. 1b).

Using this prime relation, ionic diffusion and ionic migration can be observed using Raman microspectroscopy as  $P(EO)_nLiTFSI$  films.

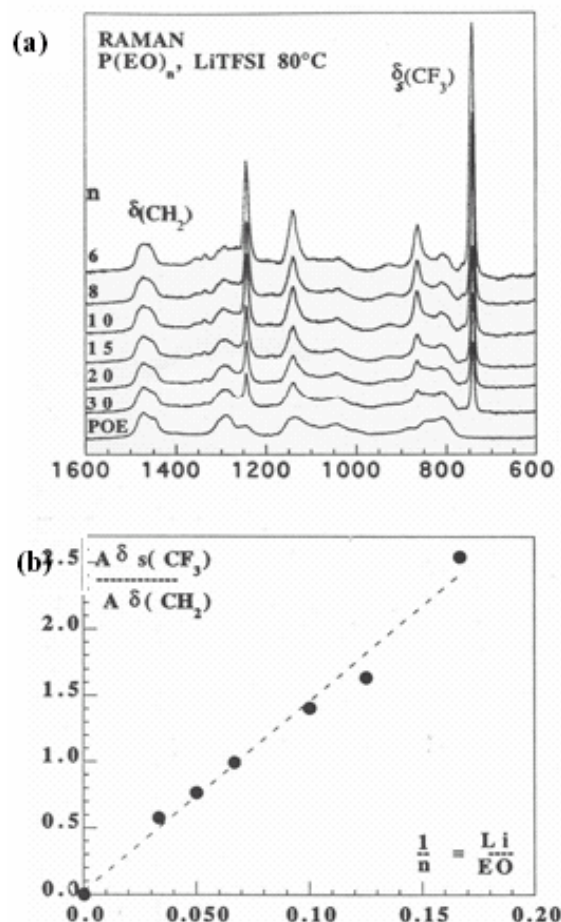


Fig. 1 : (a) Raman spectra of several  $P(EO)_n LiTFSI$  concentrations. (b) Linear relation between relative area of TFSI peak -  $A[\delta_s(CF_3)]/ A[\delta(CH_2)]$ - and concentration of TFSI in PEO.

The assembly of two polymers films (~100µm thick) with different LiTFSI salt concentrations at 80°C induces a concentration gradient. Thus a diffusion of the salt from the higher to the lower concentration film can be observed by Raman microspectroscopy. A line of Raman analysis points is defined on the edge of the 2 films assembly to measure the concentration at several points of the cross-section (see Fig. 2).

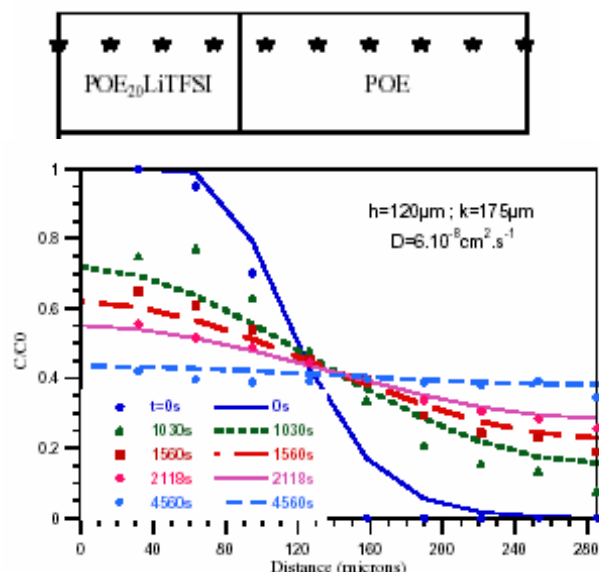


Fig. 2 : Evolution of the concentration profile of TFSI by self diffusion in the assembly consisting of a P(EO)<sub>20</sub> LiTFSI and a PEO film at 80°C. Plain lines: theoretical function (with  $D=6.10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ ); Dots: experimental results.

### Study of a Lithium/polymer/Lithium symmetric cell

The Raman observation of the concentration profile while current densities are passing through a Lithium /polymer/lithium symmetric cell allows the determination of the salt diffusion coefficient and ionic transport numbers.

Fig. 3 displays the experiment performed on a Li/PEOLiTFSI/Li cell. Before applying any current some lines are recorded to check the homogeneity of the concentration throughout the electrolyte. Then successive opposite constant currents are applied and the concentration gradient established in the electrolyte at the steady state can be

measured. Fig. 3 shows that, as expected, the amplitude of the concentration gradient increases with the current applied. One can extract information about concentration variation during the establishment of the steady state and its relaxation [1] and this allows the determination of the diffusion coefficient and the anionic transport number.

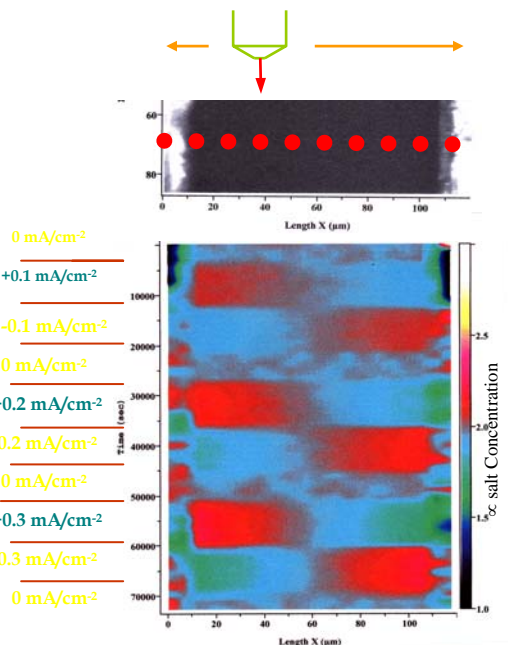


Figure 3: (a) photograph of the PEO LiTFSI electrolyte between the lithium electrodes displaying the investigated line of points. (b) image of the salt concentration -depending on position (x) and time (y)- The applied current densities are reported on the left of the image, the color scale displayed on the right allows the visualisation of the value of concentration. The edges of the line correspond to points over the electrodes.

### Study of the intercalation and release of lithium in the cathode material $\text{Li}_x\text{V}_2\text{O}_5$

A large panel of cathode materials have been considered; in this study we analyse a cathode that is mainly composed of  $\text{V}_2\text{O}_5$  powder and a small quantity of carbon. The homogeneity of the blend is monitored by Raman microspectrometry.

The first intercalation of lithium in the initial cathode material  $\alpha\text{-V}_2\text{O}_5$  induces phase transitions to the  $\epsilon$ ,  $\delta$ ,  $\gamma$  and  $\omega$  phases. The

Raman spectrum of  $\alpha$ - $V_2O_5$  has been thoroughly studied [4]. During the first discharge of a Li/electrolyte/ $V_2O_5$  battery, the Raman spectrum of each phase has been recorded.

The characteristic spectra of phases  $\alpha$ ,  $\epsilon$ ,  $\epsilon'$ ,  $\delta$ ,  $\gamma$  are plotted figure 4. Each phase is characterized by a shift of the V-O<sub>A</sub> stretching mode located respectively at  $995\text{cm}^{-1}$ ,  $982\text{cm}^{-1}$ ,  $973\text{cm}^{-1}$  and  $1006\text{cm}^{-1}$ . The  $\gamma$  phase is unique by exhibiting two peaks at  $865$  and  $915\text{cm}^{-1}$ . No characteristic spectrum of the  $\omega$  phase has been obtained as it seems that this phase does not provide any significant Raman spectrum.

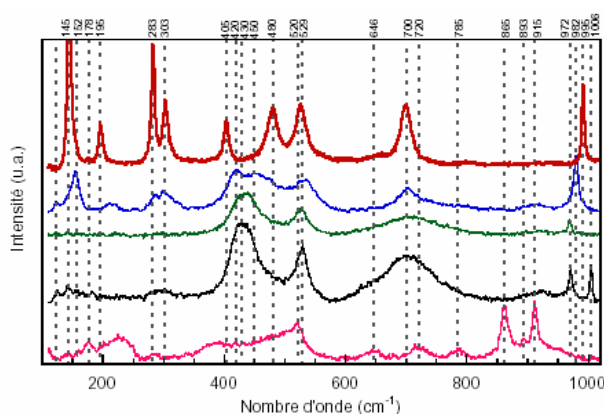


Fig. 4: Raman spectra of  $\alpha$ ,  $\epsilon$ ,  $\epsilon'$ ,  $\delta$ ,  $\gamma$  phases. (from top to bottom)

When the discharge is performed too rapidly (high current) there are risks for an inhomogeneous intercalation of Li in  $V_2O_5$  that could lead to short term aging or failure of the battery. Thus these reference spectra are used to monitor the homogeneity of the lithium intercalation process in  $Li_xV_2O_5$  grains throughout the cathode during rapid discharge. As the battery is discharged, spectra are recorded on 25 different  $V_2O_5$  grains of the cathode. Preliminary results evidenced marked differences among 25 spectra for a given average intercalation rate  $x$ , revealing the inhomogeneous intercalation process of  $Li^+$  into  $V_2O_5$ . It is reckoned that this was essentially due to poor electrical contacts between the active material and the current collector and/or to discharge rates that were too high. Improvements of these two aspects in the cell led to similar spectra for the 25 investigated points. Fig. 5 plots simultaneously

the potential curve and the characteristic Raman intensities of the consecutive  $Li_xV_2O_5$  phases. Each plateau of the potential curve indicates a phase transition and each drop corresponds to a monophasic domain. It appears that the Raman results are very well correlated with the potential curve since each plateau see the increase of a new phase at the expense of the previous one. Confocal Raman microspectrometry is thus a complementary probe beside the electrical tests to have a better understanding of the intercalation occurring in the composite electrode.

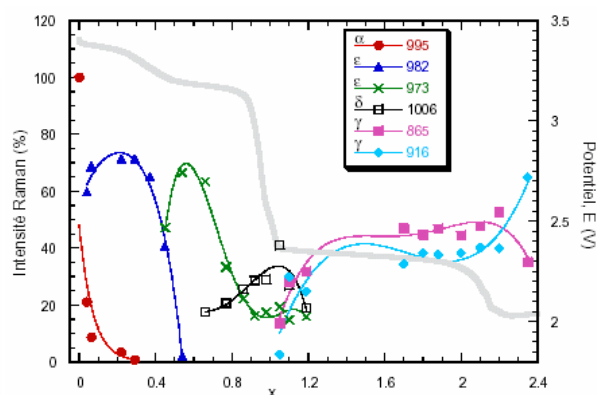


Fig. 5: Intensity of the different phases  $\alpha$ ,  $\epsilon$ ,  $\delta$ ,  $\gamma$  as a function of the Lithium intercalation rate ( $x$ ). For each  $x$  value, the Raman intensity is averaged over 25 spectra recorded on the electrode.

### Summary

In general, Raman allows the *in situ* characterization of microbatteries through an observation window. This will enable correlations between battery performance and molecular/crystallinity changes. In addition, the capabilities of current Raman microscopes, which include

- fast mapping and high throughput to follow the rapid ion diffusion and migration.
- high spatial resolution to discriminate down to  $\sim 1\mu\text{m}^3$  volumes in the transparent electrolyte.

will make characterization of microbatteries quite feasible with a Raman microscope.



## Acknowledgements

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## References:

- 1- Raman spectroelectrochemistry of a Lithium/polymer electrolyte symmetric cell, Isabelle rey, jean-Luc Bruneel, Joseph Grondin, Laurent servant and jean-Claude Lassègues, *J. Electrochem. Soc.*, 145(9), pp3034-3042.
- 2- IR and Raman studies of the components of a Lithium polymer battery. Thesis of the University of Bordeaux. Coralie Naudin (2002).
- 3- M. Doyle, T. F. Fuller and J. Newman, *J. Electrochem. Soc.*, **146**, 1526 (1993).
- 4- L. Abello, E. Husson, Y. Repelin and G. Lucazeau, *Spectrochim. Acta*, **39A**, 641 (1983).
- 5- Microscopic measurement of diffusion, Electrochemistry 01, a HORIBA JobinYvon Application Note available at [www.jobinyvon.com](http://www.jobinyvon.com)