

IN SITU MICRO-RAMAN STUDY OF DISCHARGE PRODUCTS OF Li/SOCl₂ CELLS

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Summary

Raman spectroscopy, and especially micro-Raman spectroscopy, is a technique particularly well suited to the study of chemical species formed in lithium cells during discharge in the electrolyte, as well as at the electrode surface. This non-destructive method allows an *in situ* study of the reaction.

A microcell, directly adaptable to the stage of the spectrometer, has been constructed in order to observe the phenomena appearing in the solution near the electrodes and also at the surfaces of the electrodes. The low-rate discharge of Li/SOCl₂ cells at about 20 mA at room temperature has been studied. The formation of an Li(SOCl₂) (SO₂)⁺ complex characterized by a band appearing at 1160 cm⁻¹ has been identified. When the laser beam was focused on the surface of the lithium electrode, a broad band was observed with a frequency which suggested that a complex species, probably Li(SO₂)₃⁺, had been produced.

Introduction

Although the overall reaction of the lithium/thionyl chloride cell is well established, there continues to be controversy regarding the mechanism and the chemical nature of intermediates involved in the reaction. In particular, the pressure generated in Li/SOCl₂ cells has been found to be significantly less than that predicted on the basis of the accepted discharge reaction. This is believed to be due to the SO₂ generated being complexed by LiAlCl₄ and/or absorbed by the carbon cathode [1, 3]. Several studies have been devoted to this problem, but no Raman study has been hitherto described in the literature. Nevertheless, Raman spectroscopy (and especially micro-Raman spectroscopy) is a technique particularly well suited to investigating complex chemical species and allows an *in situ* study during the discharge.

Experimental

The electrolyte was 1.8 M LiAlCl_4 in thionyl chloride. The amounts of solid LiCl and AlCl_3 and liquid SOCl_2 were adjusted in a glove box by gravimetric or volumetric measurements before their introduction into the cell.

The cell and the electrodes are shown in Fig. 1. The working electrode (b) was made of lithium ribbon mechanically attached to the upper end of a stainless steel rod protected by Teflon coating. The reference (c) and the counter electrode (c) were identical carbon rods placed parallel to each other. The cell was airtight, all seals being made with Viton O rings. The construction and the filling of the cell were carried out in a glove box filled with oxygen-free argon. The top of the cell, especially made for micro-Raman observations, was an optical plane window (a).

Raman spectra were obtained with a spectral resolution of 8 cm^{-1} using a micro-Raman spectrometer, Microdil 28, Dilor (France). The instrument was equipped with a multi-channel detector (intensified Reticon linear

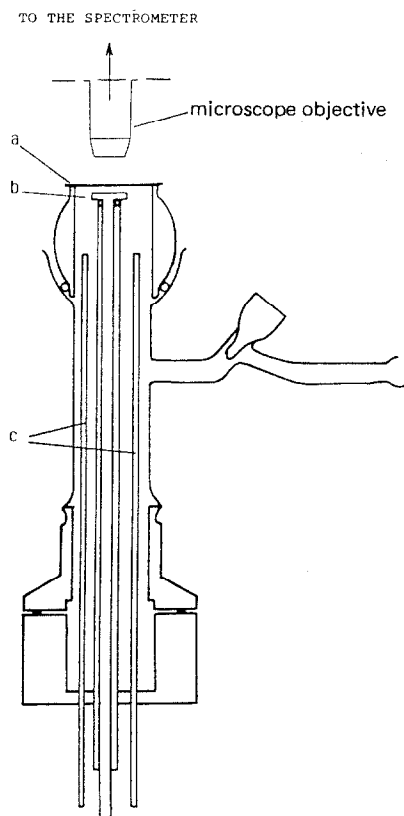


Fig. 1. Schematic diagram of experimental cell: (a) optical plane window; (b) lithium electrode; (c) graphite electrodes.

photodiode array) which allowed a spectral range of about 500 cm^{-1} to be recorded in times varying from several seconds to several minutes (for weak signals). The Raman microspectrometer was linked to an Apple II computer which undertook data acquisition, signal averaging, and data treatments. The source was the 514.5 nm line of an ionized argon laser (Spectra Physics), giving a power of about 50 mW at the sample.

The Raman spectra were recorded with an integration time of 10 s and 10 spectra were systematically added in order to obtain good signal-to-noise ratios. A long working distance objective (5 mm) was used in order to obtain spectra at the surfaces of the electrodes or within the electrolyte. The spatial resolution and the probed volume were, respectively $1\text{ }\mu\text{m}$ and $10\text{ }\mu\text{m}^3$.

Results and discussion

Since the configuration of the cell is such that the ohmic resistance is high, only low-rate discharge at about 40 mA cm^{-2} at room temperature can be observed.

Figure 2(a) and (b) show the spectra of the electrolyte in the spectral range of the S—O vibrational stretching mode. In spectrum (a), recorded before the discharge, the band at 1230 cm^{-1} and the shoulder at 1202 cm^{-1} were assigned, respectively, to free SOCl_2 and SOCl_2 molecules bonded to Li^+ [2]. Spectrum (b) was taken after several hours at low-rate discharge. The formation of an $\text{Li}(\text{SOCl}_2)(\text{SO}_2)^+\text{AlCl}_4^-$ complex was characterized by the band appearing at 1160 cm^{-1} . Figure 3(a) shows a more pronounced complex band shoulder at about 350 cm^{-1} , corresponding to the vibrational modes of the following species: AlCl_4^- , free SOCl_2 , $\text{Li}(\text{SOCl}_2)_2^+$ and $\text{Li}(\text{SOCl}_2)(\text{SO}_2)^+$ studied in a previous work [3]. These bands have weak intensities because the concentration of the species appearing during the low discharge remains small, even after an extended time.

Spectrum (c) in Fig. 2 was obtained when the laser beam was focused at the surface of the lithium electrode, after a discharge at 90 mA cm^{-2} . A broad band is observed at about 1100 cm^{-1} . This frequency suggests that a complex, probably $\text{Li}(\text{SO}_2)_3^+$ or a charge-transfer complex between lithium and SO_2 , was generated at the surface of the lithium electrode. The formation of lithium chloride cannot be observed because this compound has no first-order Raman spectrum.

Under the above experimental conditions, free SO_2 is not detected in the electrolyte, nor in the gas phase present at the top of the cell. Indeed, free SO_2 , in the solution or in the gas phase, should have exhibited Raman lines at 1148 cm^{-1} and 1152 cm^{-1} , respectively. The configuration of the cell did not permit a study to be made of the surface of the carbon cathode. This surface was located at about 1 cm from the cell window which is well below the working distance of the objective.

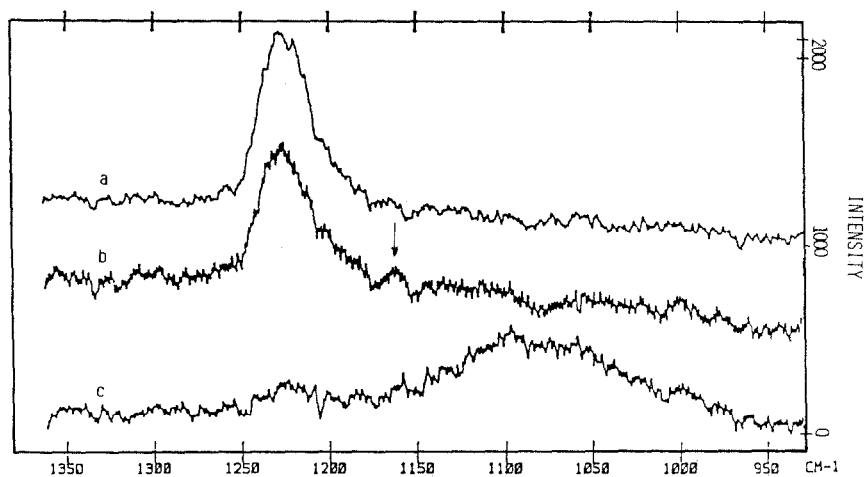


Fig. 2. Raman spectra (spectral range of S—O mode): (a) before discharge in the electrolyte; (b) after several hours at low-rate discharge in the electrolyte; (c) after forced discharge at the lithium electrode surface. The arrow, shown in the Figure, indicates the band corresponding to the $\text{Li}(\text{SOCl}_2)(\text{SO}_2)^+$ species formed during the discharge.

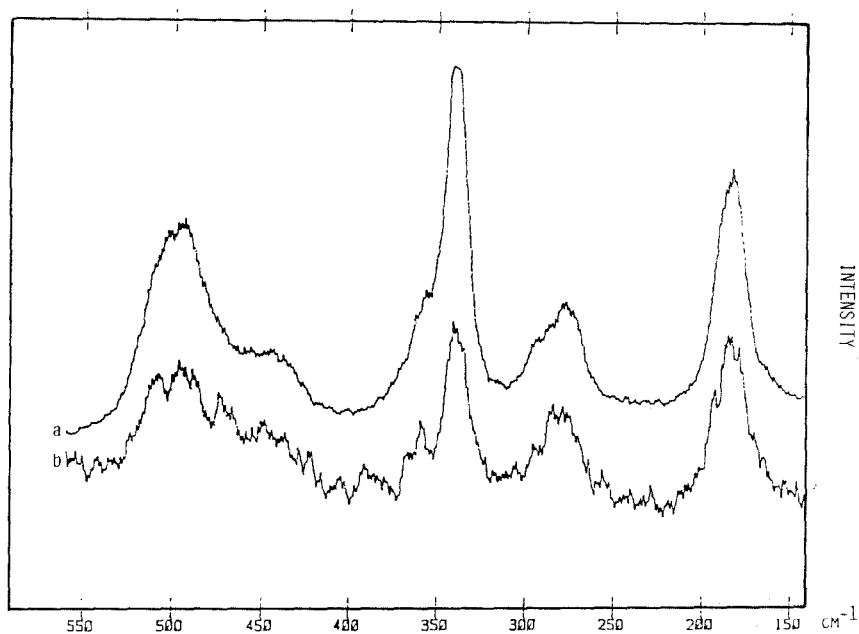


Fig. 3. Raman spectra (spectral range of S—Cl mode): (a) before discharge in the electrolyte; (b) after several hours at low-rate discharge in the electrolyte.

This work will be continued by constructing a cell which will allow higher rate discharge in order to increase the concentration of the different species forming during the discharge and will enable studies to be made of

the species formed at the surface of the carbon cathode. It is argued that micro-Raman spectroscopy, which allows investigation of species without any extraction or manipulation of the electrolyte, could prove to be a valuable tool in the study of electrochemical reactions during the discharge of lithium cells.

References

- 1 K. M. Abraham, L. Pitts and W. P. Kirby, *J. Electrochem. Soc.*, *132* (1985) 2301.
- 2 Y. Bedfer, J. Corset, M. C. Dhamelincourt, F. Wallart and P. Barbier, *J. Power Sources*, *9* (1983) 267.
- 3 M. C. Dhamelincourt, F. Wallart, P. Barbier, G. Mairesse and P. Descroix, *J. Power Sources*, *14* (1985) 77.