RAMAN SPECTROSCOPIC STUDIES OF THE STRUCTURE OF ELECTROLYTES USED IN THE Li/SOCl$_2$ BATTERY

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Summary

The importance of the Li/SOCl$_2$ cell using thionyl chloride as a liquid cathode has given rise to studies of the structure of the electrolytes used in this lithium cell. The electrolytes are made from LiAlCl$_4$ dissolved in SOCl$_2$ in which SO$_2$ is formed during the discharge process. This paper deals with a structural study, using Raman spectroscopy, of solutions of LiAlCl$_4$ in pure SOCl$_2$ and SO$_2$, and in mixtures of both solvents. The complexes |Li(SOCl$_2$)$_2$|$^+$|AlCl$_4$|$^-$ and |Li(SO$_2$)$_3$|$^+$|AlCl$_4$|$^-$ were characterized at room temperature in the pure solvents SOCl$_2$ and SO$_2$, respectively. In the ternary system LiAlCl$_4$–SOCl$_2$–SO$_2$ the existence of |Li(SO$_2$, SOCl$_2$)|$^+$|AlCl$_4$|$^-$ was established.

1. Introduction

The composition of electrolytes plays an important role in the performance of Li/SOCl$_2$ batteries. Structural analysis of solutions by Raman vibrational spectroscopy enables all species to be characterized. In this paper, the structures of solutions of LiAlCl$_4$ in pure SOCl$_2$, pure SO$_2$, and mixtures of both solvents are presented. A method of *in situ* quantitative analysis of SO$_2$ has been developed.

Raman scattering [1] relates to the change of frequency observed when a monochromatic light beam (ν_0 frequency) is scattered by polyatomic molecules. Like infrared spectra, Raman spectra can be used to characterize and identify species by their vibrational modes ν_i in all phases of matter and to

derive information on the local molecular environment. The great advantage of the Raman technique over infrared spectroscopy, however, is that the analysis may be conducted directly with samples contained in transparent glass cells, since exciting line, ν_0, and scattered light are usually in the visible part of the electromagnetic spectrum.

All samples were prepared in sealed Pyrex tubes and their compositions were precisely adjusted by gravimetric or volumetric measurements. Raman spectra were recorded by the use of double and triple monochromator Raman spectrometers, both equipped with an Ionized Argon Laser light source.

2. *In situ* quantitative analysis of SO_2

Raman spectra of binary mixtures of SO_2–$SOCl_2$ have been recorded in the range of molar ratios $\rho = |SO_2|/|SOCl_2|$ 0.004 to 0.4 at 298 K.

In this range, the bands assigned to $SOCl_2$ and SO_2 were compared with those recorded for pure solvents. No significant modification either in band shape or frequency position was detected proving that only very weak interactions may exist between these molecules. The intense bands at 1148 cm^{-1} and 1230 cm^{-1} assigned to the stretching mode of the S–O bond in SO_2 and $SOCl_2$, respectively, were then used for drawing the calibration curve (Fig. 1). From the excellent signal to noise ratio obtained on the spectra, an accuracy of about 3% may be expected in the determination of the amount of SO_2.

Raman spectra were also recorded at 218 K and 183 K (temperatures where the vapour pressure of pure $SOCl_2$ and pure SO_2 may be neglected) in order to check that the quantities of SO_2 and $SOCl_2$ in the gas phase did not significantly affect the liquid composition.

3. Solutions of $LiAlCl_4$ in pure $SOCl_2$ and pure SO_2

From solutions of $LiAlCl_4$ in pure solvents, increasing salt concentrations were obtained by successive evaporation of the solvent under vacuum until a pure solvate was obtained at 298 K. After each step of evaporation, Raman spectra were recorded.

3.1. *$LiAlCl_4$ in pure $SOCl_2$*

Raman spectra (*cf.* Figs. 2 and 4(a)) show, in addition to pure solvent bands, a set of new bands whose relative intensities and frequencies remain unchanged, indicating that the same scattering species are present throughout. The assignment of these bands has been done by comparison with spectra of alkaline earth chloroaluminates [2]. Six bands at 1202, 502, 463, 359, 295 and 200 cm^{-1} are assigned to the vibrational modes of $SOCl_2$ molecules bonded to Li$^+$ and the remaining three at 347, 174 and 117 cm^{-1} correspond to the vibrational modes of the $AlCl_4^-$ ion. For a molar ratio $\rho_{Li} = |LiAlCl_4|/|SOCl_2| = 0.42$, pure solvent bands almost vanish. This proves that the stoi-
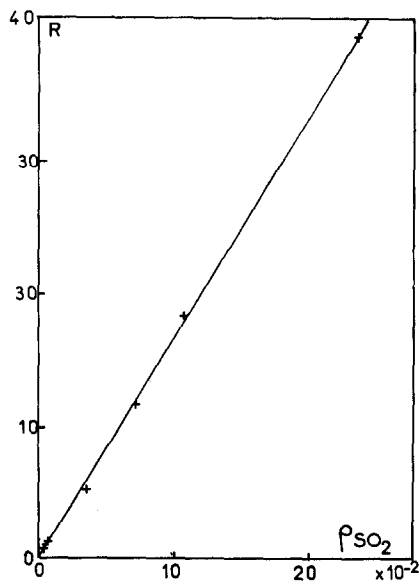
Fig. 1. Calibration curve for quantitative analysis of SO_2. R = area of SO_2 peak/area of $SOCl_2$ peak; $\rho = nSO_2/nSOCl_2$.
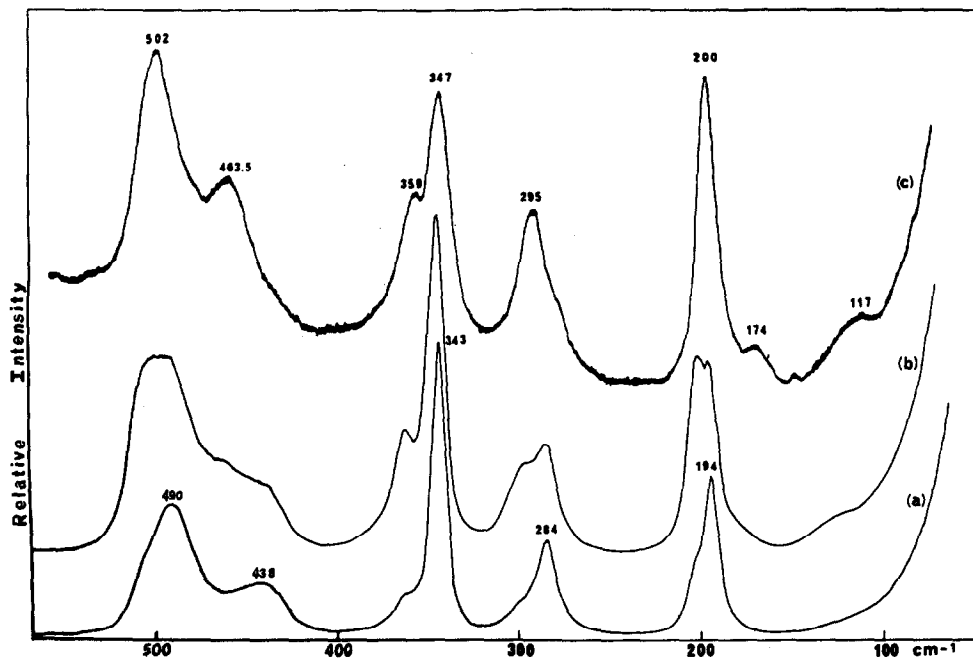

Fig. 2. Raman spectra of $LiAlCl_4$ solutions in $SOCl_2$. (a) $\rho_{Li^+} = 0.073$; (b) $\rho_{Li^+} = 0.21$; (c) $\rho_{Li^+} = 0.42$.

chiometry of the solvate is two $SOCl_2$ molecules per Li^+ cation. Such solvates with two, or one, solvent molecules per cation have already been shown to exist for Ca, Ba and Sr [2].

3.2. LiAlCl₄ in pure SO₂

The compound $Li(3SO_2)^+AlCl_4^-$ was isolated in the solid state at 298 K in 1978 [3]. It was first characterized by its Raman spectrum. The existence of this compound was also confirmed by the establishment of the $LiAlCl_4-SO_2$ binary diagram, then by X-ray structure determination and vibrational spectroscopy [4]. We have shown by Raman spectroscopy that in solution the same solvate, $Li(3SO_2)^+$, exists over all the studied range of $\rho_{Li} = |LiAlCl_4|/|SO_2|$. Three bands at 1330, 1161 and 530 cm^{-1} have been assigned to the vibrational modes of SO_2 molecules bonded to the Li^+ cation. As an example, the evolution of the bands corresponding to the vibration stretching modes (ν_s SO_2) for both the solvate and solvent are presented in Fig. 3. The X-ray structure of the solvate shows an octahedral oxygen surrounding the Li^+ cations in a chain-like arrangement which seems unlikely to persist in the solution. The frequency shift observed between the bands assigned to the solvate in the solid state and in the liquid state probably reflects this structure difference.

4. LiAlCl₄ in SO₂–SOCl₂ mixtures

Ternary mixtures have been studied in the $SOCl_2$-rich composition range $\rho_{SO_2} = |SO_2|/|SOCl_2| = 0.05$ to 0.3 for initial $LiAlCl_4$ concentrations between 1 and 2M. The recorded spectra show a band at 1157 cm^{-1} in addition to the bands previously assigned to $Li(2SOCl_2)^+$, free SO_2 and $AlCl_4^-$ (Fig. 4). This band is assigned to the S–O stretching vibrational mode of SO_2 molecules bonded to a Li^+ cation. When increasing amounts of SO_2 are added to a given initial solution of $LiAlCl_4$ in pure $SOCl_2$, the intensity ratio between bands corresponding to $Li(2SOCl_2)^+$ and free $SOCl_2$ is found to decrease, indicating partial superseding of $SOCl_2$ molecules by SO_2 molecules in the Li^+ solvation shell. Band intensities corresponding to solvating and free $SOCl_2$ were determined by means of a computer decomposition program (Fig. 4) and concentrations of free SO_2 were drawn from the calibration curve (cf. Fig. 1). We have attempted to fit these intensities to a mass action law corresponding to a first step of the SO_2–$SOCl_2$ exchange

$$Li(2SOCl_2)^+ + nSO_2 \rightleftarrows Li|(2-m)SOCl_2, nSO_2|^+ + mSOCl_2.$$
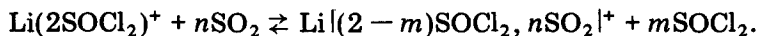
Various assumptions for n and m were tested against experimental results (dependence of the intensity ratio for free SO_2 and free $SOCl_2$ on the amount of added SO_2 on the one hand, and m/n ratios obtained from comparison of the intensity decrease for $Li(2SOCl_2)^+$ bands with the measured amount of SO_2 bonded to Li^+ on the other hand). We arrived at a fairly good match when $n = m = 1$ with an equilibrium constant = 6.2.
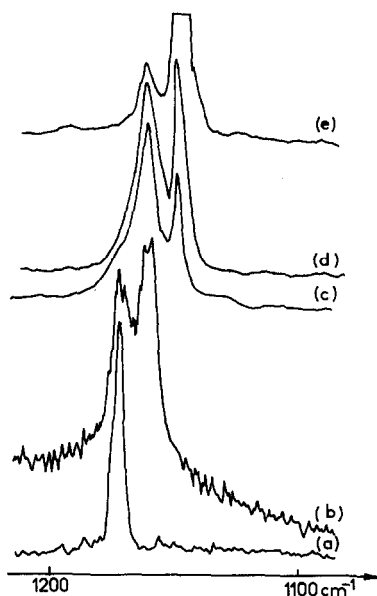
Fig. 3. Raman spectra of $LiAlCl_4$ solutions in SO_2. (a) Pure crystallized solvate; (b) $\rho_{Li^+} = 0.33$; (c) $\rho_{Li^+} = 0.25$; (d) $\rho_{Li^+} = 0.16$; (e) $\rho_{Li^+} = 0.05$.
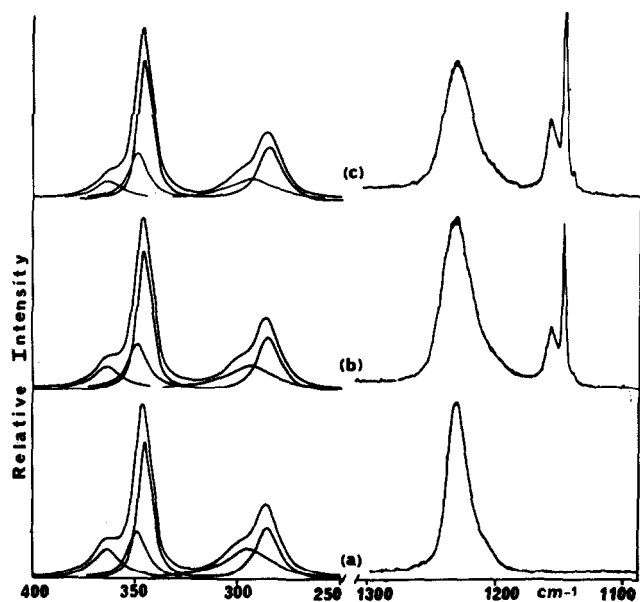

Fig. 4. Raman spectra of $LiAlCl_4$ in $SOCl_2$ (1.45M) with added amounts of SO_2. (a) $\rho_{SO_2} = 0.0$; (b) $\rho_{SO_2} = 0.11$; (c) $\rho_{SO_2} = 0.21$.

Thus a preferential solvation of the Li$^+$ cation by SO$_2$ molecules takes place. This leads, for a 1M LiAlCl$_4$–2M SO$_2$ solution in SOCl$_2$, to a 0.4M concentration for the new Li(SO$_2$, SOCl$_2$) AlCl$_4$ species which might play an important role in the discharge process of lithium batteries.

Acknowledgment

References

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