

RAMAN SPECTROSCOPIC STUDY OF $\text{LiAlCl}_4/\text{SOCl}_2/\text{SO}_2$ SYSTEMS

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Summary

In the Li/SOCl_2 cell, the discharge process implies an evolution of the electrolyte composition from a binary mixture, $\text{LiAlCl}_4/\text{SOCl}_2$, to a ternary mixture, $\text{LiAlCl}_4/\text{SOCl}_2/\text{SO}_2$, and then to a final $\text{LiAlCl}_4/\text{SO}_2$ binary mixture.

Raman spectroscopic studies coupled with pressure measurements have been carried out at various temperatures (from 10 to 100 °C) on $\text{LiAlCl}_4^-/\text{SOCl}_2-\text{SO}_2$ systems in order to identify the species being formed in the electrolyte during the discharge and to understand the pressure evolution.

The Raman spectroscopic results show that the low pressures observed during the discharge process are due to the formation of the $\text{Li}(\text{SOCl}_2)(\text{SO}_2)^+$ and $\text{Li}(\text{SO}_2)_3^+$ species which are stable throughout the temperature range studied.

Introduction

When discharging an Li/SOCl_2 cell, the electrolyte composition changes from a binary mixture, $\text{LiAlCl}_4-\text{SOCl}_2$, to a binary mixture, $\text{LiAlCl}_4-\text{SO}_2$, at the end of the discharge. During discharge, the electrolyte is a ternary mixture, $\text{LiAlCl}_4-\text{SOCl}_2-\text{SO}_2$, the consumption of 2 moles of SOCl_2 producing 1 mole of SO_2 .

Raman spectroscopic studies coupled with pressure measurements were undertaken at various temperatures (from 10 to 100 °C) on binary and ternary mixtures in order to study the formation of Li^+ complexes previously detected at room temperature and to predict and to understand the pressure evolution during the discharge of an $\text{LiAlCl}_4-3\text{MSOCl}_2$ cell (Fig. 1).

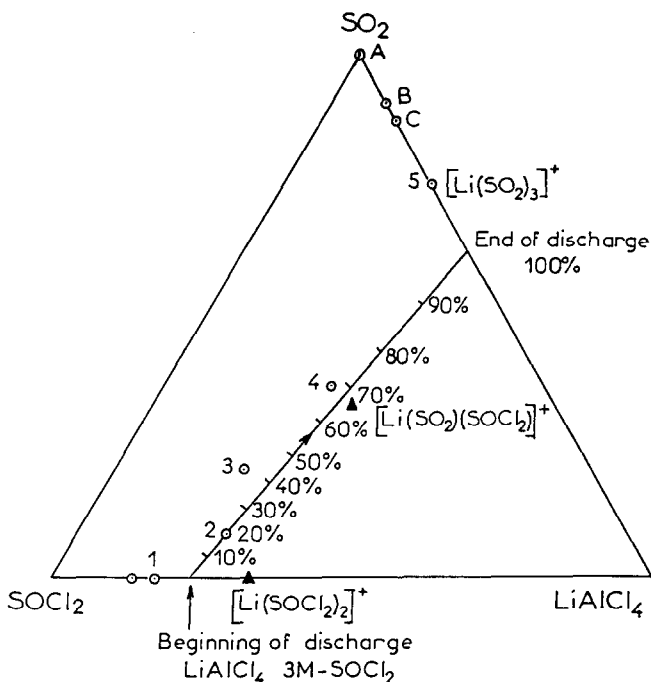


Fig. 1. Diagram giving the evolution of electrolyte composition during the discharge of LiAlCl_4 3M SOCl_2 . Point 1, LiAlCl_4 -4.9 SOCl_2 ; Point 2, 3LiAlCl_4 -8 SOCl_2 -1 SO_2 ; Point 3, 3LiAlCl_4 -8 SOCl_2 -2.82 SO_2 ; Point 4, 3LiAlCl_4 -4 SOCl_2 -4 SO_2 ; Point 5, LiAlCl_4 , 3 SO_2 .

Experimental

Raman spectra were recorded using a special Pyrex cell supporting pressures up to 50 bar and equipped with a pressure gauge.

All the samples were prepared directly in the Raman cell. The amounts of solid LiAlCl_4 and liquid SOCl_2 were adjusted in a glove box by gravimetric or volumetric measurements before their introduction into the cell. Precise amounts of SO_2 , previously determined by weighing, were then directly transferred to the cell as a gas phase.

In order to make measurements at precise and uniform temperatures, the cell was completely immersed in a water or ethylene-glycol thermostated glass vessel. This vessel was directly mounted in the sample compartment of the Raman spectrometer.

Raman spectra were recorded with a spectral resolution of 5 cm^{-1} using a triple monochromator spectrometer, RT 30 Dilor, equipped with an Apple II computer for data acquisition. The source was the 514.5 nm line of an ionized argon laser, Spectra-Physics, giving a power of 150 mW at the sample.

Binary mixtures $\text{LiAlCl}_4\text{-SO}_2$

Mixtures were studied for an $\text{SO}_2/\text{LiAlCl}_4$ ratio varying from 10 to 3. When the molar ratio equals 3, a pure solvate is isolated.

For each molar composition, pressure *vs.* temperature was recorded. The results are reported on Fig. 2 and compared with pure SO_2 . As predicted by Raoult's law, vapour pressure decreases with increasing salt concentration. The pressure corresponding to the pure solvate is nearly four times lower than the one measured for pure SO_2 .

Raman spectra for the pure complex $\text{Li}(\text{SO}_2)_3^+\text{AlCl}_4^-$ have been previously reported [1]. Figure 3 shows the band corresponding to the vibrational stretching mode of SO_2 molecules in the fused compound. This band is complex and can be resolved into 3 components located at 1148, 1151 and 1170 cm^{-1} . The first two bands correspond to the vibrational modes of free SO_2 molecules and SO_2 molecules bonded to Li^+ cations, respectively. The third — at 1170 cm^{-1} — corresponds to the band observed in the solid salt. The existence of this last band has been related to the presence in the fused solvate of SO_2 molecules bonded to Li^+ cations in a way similar to the chain-like arrangement observed in the solid phase.

When increasing amounts of SO_2 are added to pure solvate, only the first two bands are observed throughout the studied temperature range. No new species are detected. The evolution of the intensity ratio of these two

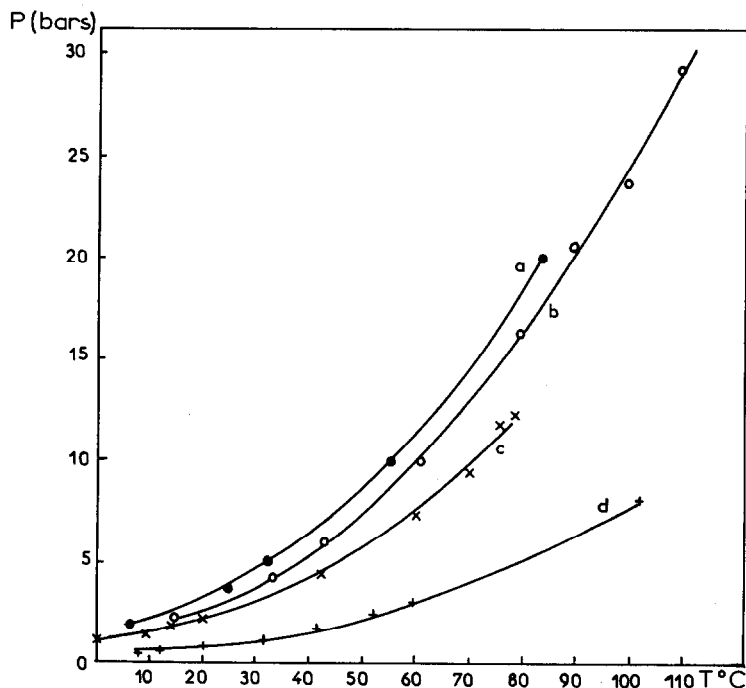


Fig. 2. Vapour pressure *vs.* temperature of $\text{LiAlCl}_4/\text{SO}_2$ binary mixtures. (a) Pure SO_2 ; (b) $\text{LiAlCl}_4\text{-}2.25\text{M SO}_2$; (c) $\text{LiAlCl}_4\text{-}3.2\text{M SO}_2$; (d) $\text{LiAlCl}_4, 3\text{SO}_2$ (fused solvate).

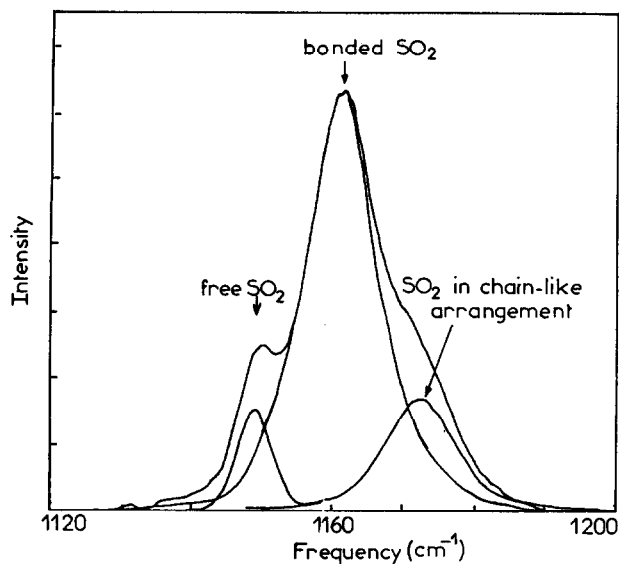


Fig. 3. Computer resolution of the complex band corresponding to the vibrational stretching mode of SO_2 molecules in the fused $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ solvate.

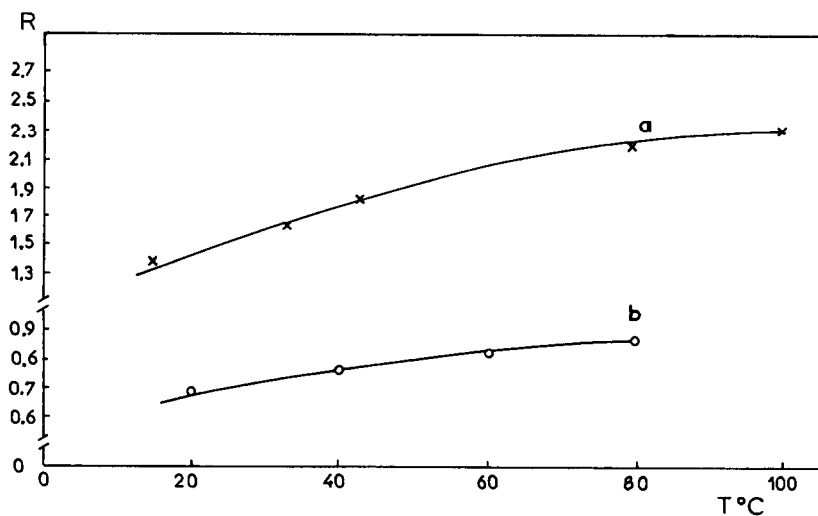


Fig. 4. Evolution vs. temperature of intensity ratio of SO_2 bands in binary mixtures $\text{LiAlCl}_4/\text{SO}_2$.

$R = \text{Area of free } \text{SO}_2 \text{ band} / \text{Area of bonded } \text{SO}_2 \text{ band}.$

(a), $\text{LiAlCl}_4\text{-}2.25\text{M } \text{SO}_2$; (b), $\text{LiAlCl}_4\text{-}3.2\text{M } \text{SO}_2$.

bands vs. the temperature is reported on Fig. 4. (The intensity of the AlCl_4^- band has been used as a standard.) With increasing temperature, the amount of free SO_2 increases, showing a decomposition of the solvate at high temperature.

Ternary mixtures $\text{LiAlCl}_4\text{-SOCl}_2\text{-SO}_2$

Spectra and pressure were recorded for three solutions corresponding to three different steps of the discharge: composition 2 (20% of discharge), 3 (40% of discharge) and 4 (70% of discharge) of Fig. 1.

As previously reported [1], at room temperature, two types of solvates are present in SOCl_2 rich $\text{LiAlCl}_4\text{-SOCl}_2\text{-SO}_2$ mixtures: $\text{Li}(\text{SOCl}_2)_2^+\text{AlCl}_4^-$ and $\text{Li}(\text{SOCl}_2)(\text{SO}_2)^+\text{AlCl}_4^-$. When the system evolves towards an SO_2 rich composition, these solvates are in equilibrium with $\text{Li}(\text{SO}_2)_3^+\text{AlCl}_4^-$ whatever the temperature may be.

Figure 5 shows the evolution of pressure *vs.* temperature for ternary mixtures. These pressures range from that of $\text{LiAlCl}_4\text{-SOCl}_2$ binary mixtures to that of the $\text{Li}(\text{SO}_2)_3^+\text{AlCl}_4^-$ complex. They never reach the value corresponding to pure SO_2 .

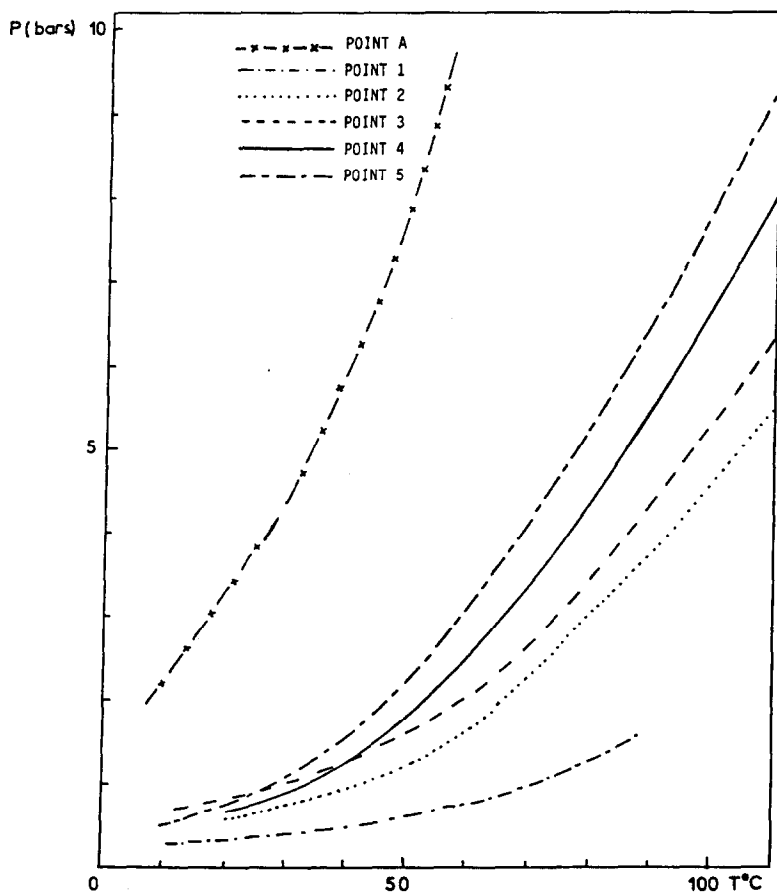


Fig. 5. Vapour pressure *vs.* temperature of $\text{LiAlCl}_4/\text{SOCl}_2/\text{SO}_2$ ternary mixtures.

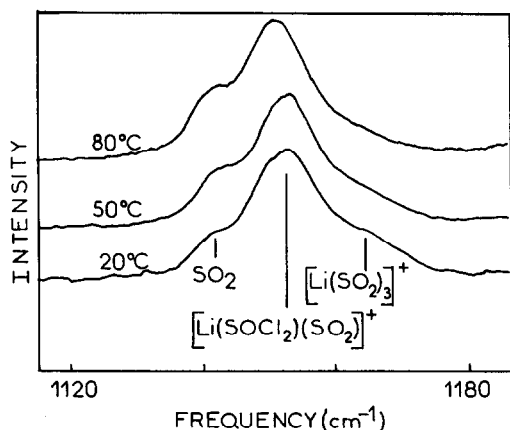


Fig. 6. Evolution of Raman spectra of the $3\text{LiAlCl}_4\text{-}4\text{SOCl}_2\text{-}4\text{SO}_2$ ternary mixture as a function of temperature.

As an example, Raman spectra of the $3\text{LiAlCl}_4\text{-}4\text{SOCl}_2\text{-}4\text{SO}_2$ mixture, in the $\nu(\text{S-O})$ vibrational stretching range, are reported on Fig. 6. When the temperature increases, concentrations of SO_2 and $\text{Li}(\text{SOCl}_2)(\text{SO}_2)^+\text{AlCl}_4^-$ increase, while the amount of $\text{Li}(\text{SO}_2)_3^+$ decreases. Simultaneously, the $\text{SOCl}_2/\text{SO}_2$ intensity ratio increases in the gas phase. These observations show the preferential formation of the $\text{Li}(\text{SOCl}_2)(\text{SO}_2)^+$ species in the liquid phase at high temperature in SO_2 rich mixtures.

Conclusion

The studies, as a function of the temperature, of $\text{LiAlCl}_4\text{-SOCl}_2\text{-SO}_2$ mixtures have led to a better understanding of the behaviour of Li/SOCl_2 batteries.

The solvates of Li cations previously identified at room temperature are stable in a constrained system throughout the studied temperature range and no new species are formed.

The formation of these solvates, particularly the appearance of $\text{Li}(\text{SOCl}_2)(\text{SO}_2)^+$ and $\text{Li}(\text{SO}_2)_3^+$ species, plays a predominant role in limiting the pressure above electrolytes during discharge.

For electrolytes initially 3M in LiAlCl_4 (≈ 10 moles of SOCl_2), the upper limit for the pressure after discharge will always be lower than the pressure of SO_2 above the $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ solvate.

Reference

- 1 Y. Bedfer, J. Corset, M. C. Dhamelincourt, F. Wallart and P. Barbier, Raman spectroscopic studies of the structures of electrolytes used in the Li/SOCl_2 battery, *J. Power Sources*, 9 (1983) 267.