

Raman and ^7Li NMR spectroscopic studies of Li/SO_2 rechargeable cells*

T. J. Lee, P. C. Yao and G. T.-K. Fey**

Department of Chemical Engineering, National Central University, Chung-Li 32054 (Taiwan)

(Received December 3, 1990)

Abstract

Both Raman and ^7Li NMR spectroscopic data of 0.2 M LiAlCl_4 and LiGaCl_4 in liquid sulfur dioxide indicate that ionic structural changes occur near 25 °C, thus supporting observations from conductivity and cyclic voltammetric studies. The solvation number of the lithium cation is 4 for both salts of interest. The activation energies of spin-lattice relaxation, the formation constants of lithium ion pairs, and the chemical shifts due to the free lithium ions and lithium ion pairs of LiAlCl_4 and LiGaCl_4 in sulfur dioxide are presented.

1. Introduction

The Li/SO_2 rechargeable battery system containing an LiAlCl_4 solvate electrolyte has shown high conductivity and excellent rechargeability at ambient temperature [1–3]. Recently, we have completed an investigation of temperature effects on the electrolyte properties of LiAlCl_4 and LiGaCl_4 in liquid sulfur dioxide using cyclic voltammetry, conductivity measurement, and a.c. impedance spectroscopy [4, 5].

Ionic structure in solution is one of the most important factors in determining the electrochemical properties of the electrolyte solution. The lack of adequate models for describing electrolytes is augmented when dealing with Li/SO_2 rechargeable cells.

Sulphur dioxide is an effective solvating agent for the lithium cation. The degree of solvation depends on the properties of the electrolyte salt. Unfortunately, our knowledge of the ion–ion and ion–solvent interactions are still very limited. Nevertheless, Raman spectroscopy [6] and NMR spectroscopy [7] are techniques particularly well-suited to the determination of solvation numbers for certain ions. Only a few fragmentary Raman spectroscopic studies on $\text{LiAlCl}_4/\text{SO}_2$ electrolytes have been reported in the literature

*Paper presented at the 5th International Meeting on Lithium Batteries, Beijing, China, May 28–June 2, 1990.

**Author to whom correspondence should be addressed. Present address: 3167, Toba Drive, Coguitlam, BC, V3B 6A3, Canada.

[8–10]. No ^7Li NMR studies of the above two salts have been described hitherto.

In this paper, the Raman and ^7Li NMR spectroscopy of LiAlCl_4 and LiGaCl_4 salts in liquid sulfur dioxide are presented. The lithium cation and SO_2 solvent interactions are discussed in terms of Raman and NMR spectroscopic data in order to explain the transport phenomenon and cell performance associated with the electrolyte behavior of LiAlCl_4 and LiGaCl_4 salts in liquid sulfur dioxide in rechargeable lithium cells.

2. Experimental

Materials

The electrolytes used in this study were $\text{LiAlCl}_4/\text{SO}_2$ and $\text{LiGaCl}_4/\text{SO}_2$. High purity grade SO_2 was obtained from Matheson, and reagent grade LiAlCl_4 and LiGaCl_4 were obtained from Anderson Physics Laboratory. All materials were handled in an argon-filled glovebox.

NMR measurements

The ^7Li NMR spectra were obtained on a Bruker MSL-300 spectrometer. All the measured samples were sealed in 10 mm NMR tubes. A 5 mm coaxial insert containing lock solvent solution was used as the internal reference. The reference solution was 0.5 M LiCl in D_2O (99.8%, E. Merck) for ^7Li measurements.

The chemical shifts reported were corrected for differences in bulk diamagnetic susceptibility between samples and references, in accordance with the relationship established by Live and Chan [11] for high field spectrometers.

$$S_{\text{corr}} = S_{\text{obs}} - 4/3(X_{\text{ref}} - X_{\text{sample}})$$

where X_{ref} and X_{sample} are the unitless volume susceptibilities of the reference and sample, respectively; S_{corr} and S_{obs} are the corrected and observed chemical shifts, respectively.

The measurements of spin-lattice relaxation rates ($1/T_1$) were obtained by using the standard technique of repeated 180° – 90° pulse sequences at a resonance frequency of 46.073 MHz for the deuterons and 116.638 MHz for ^7Li nuclei. The probe temperature was varied at 10 K intervals between 270 and 310 K. In the measurement of T_1 , 14 different pulse intervals were used and the delay time was maintained at greater than five times T_1 .

Raman measurements

Raman spectra were recorded on a Jobin-Yvon U-1000-type Raman spectrometer with a 476.5 nm argon ion laser line, a double-monochromator with holographic gratings, and a computer-controlled photon-counting system. The laser outlet power was kept at 200 mW by using an intensity stabilizing system for the power supply. The samples were placed in a sealed, cylindrical

quartz cell (10 mm dia.) that was kept in a constant temperature bath, an accessory of the Raman spectrometer. The temperature was varied at 10 K intervals between 253 and 313 K.

3. Results and discussion

Figures 1 and 2 illustrate temperature effects on Raman spectra of 0.2 M $\text{LiAlCl}_4/\text{SO}_2$ and $\text{LiGaCl}_4/\text{SO}_2$ electrolytes, respectively, in the $1100\text{--}1200\text{ cm}^{-1}$ region. The intense S–O stretching band of LiAlCl_4 or LiGaCl_4 in SO_2 solution appears near 1146 cm^{-1} [8–10] with a weak shoulder near 1139 cm^{-1} . The S–O stretching frequency increases with temperature, corresponding to a change in ionic structure. From 233 to 313 K, the change in S–O stretching frequency was small between temperature intervals, except for near 298 K (25 °C) where the change was significant for both LiAlCl_4 and LiGaCl_4 , as shown in Table 1. In our previous studies using conductivity

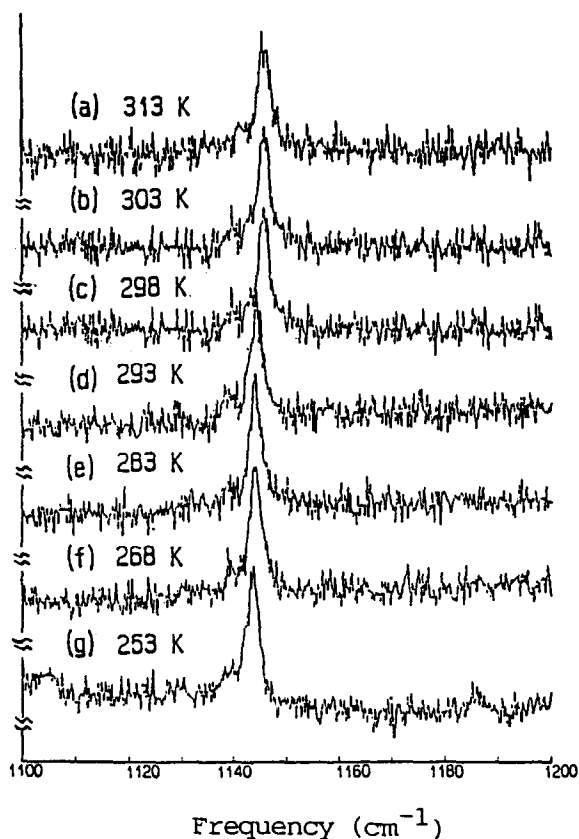


Fig. 1. Raman spectra of 0.2 M $\text{LiAlCl}_4/\text{SO}_2$ electrolyte as a function of temperature.

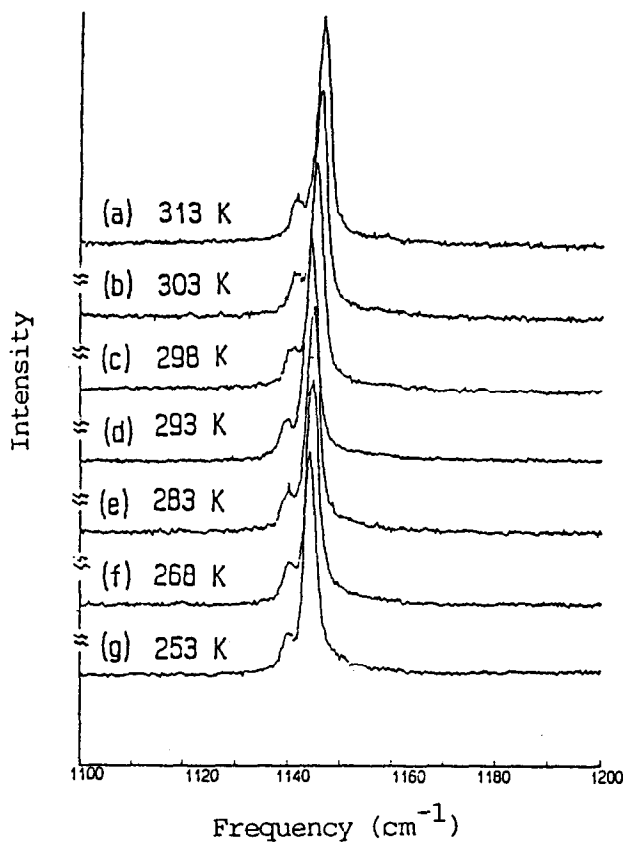


Fig. 2. Raman spectra of 0.2 M $\text{LiGaCl}_4/\text{SO}_2$ electrolyte as a function of temperature.

TABLE 1

Temperature effects on Raman S-O bands

Temperature (K)	$\text{LiAlCl}_4/\text{SO}_2$ (cm^{-1})	Δ ($\text{cm}^{-1} \text{K}^{-1}$)	$\text{LiGaCl}_4/\text{SO}_2$ (cm^{-1})	Δ ($\text{cm}^{-1} \text{K}^{-1}$)
233	1143.9		1144.2	
263	1144.1	0.0067	1144.3	0.0033
273	1144.2	0.01	1144.4	0.01
293	1144.4	0.01	1144.2	0.01
298	1145.4	0.20	1145.3	0.22
303	1145.8	0.08	1146.1	0.16
313	1146.0	0.02	1146.5	0.04

and cyclic voltammetric methods [5] we also discovered similar ionic structural changes near 25 °C.

The effects on Raman spectra of different concentrations of LiAlCl_4 and LiGaCl_4 in SO_2 solutions in the $1100\text{--}1180\text{ cm}^{-1}$ region at 24 °C are shown in Figs. 3 and 4, respectively. Solutions ranging from 0.2 M to 9.5 M were used for LiAlCl_4 . At higher concentrations, the appearance and growth of a second peak near 1152 cm^{-1} indicate that a new ionic species was formed. In the 9.5 M solution, the second peak's intensity surpassed that of the first peak near 1146 cm^{-1} . Similar results were obtained for LiGaCl_4 , where solutions ranging from 0.2 M to 5.0 M were used.

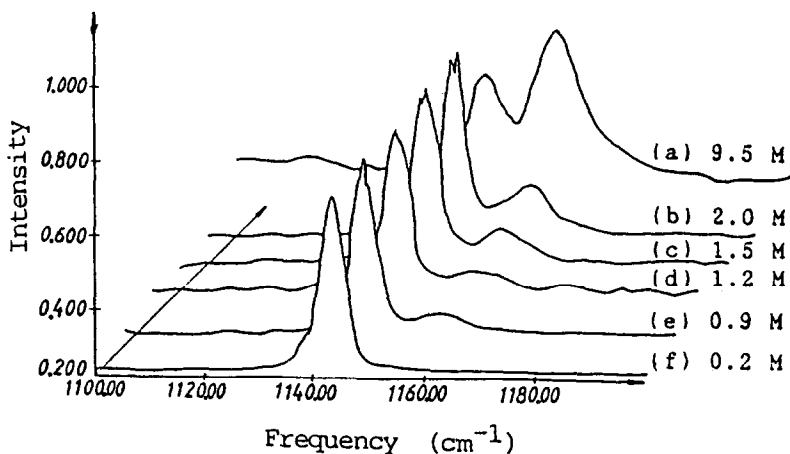


Fig. 3. Raman spectra of the $\text{LiAlCl}_4/\text{SO}_2$ electrolyte as a function of concentration at 24 °C.

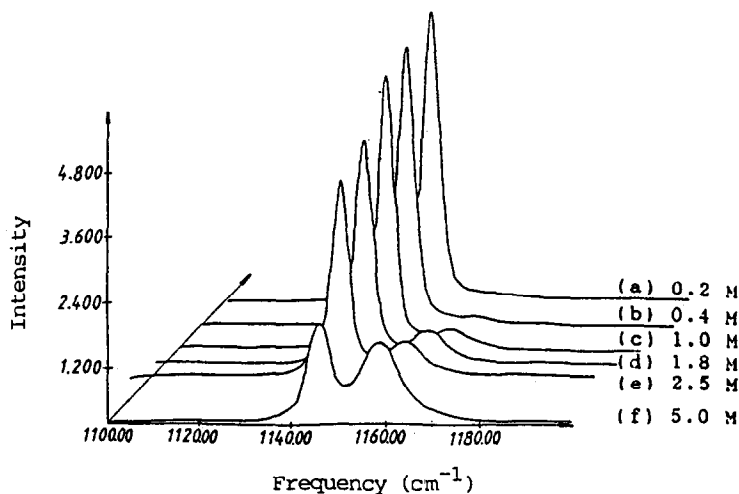


Fig. 4. Raman spectra of the $\text{LiGaCl}_4/\text{SO}_2$ electrolyte as a function of concentration at 24 °C.

We can use the concentration and spectral intensity data shown in Figs. 3 and 4 to calculate the solvation number of the lithium cation by Hyodo's method [6], briefly described as follows: C_b and C_f are defined as the concentrations of SO_2 molecules which interact with, and without, lithium cations, respectively. The corrected intensity, I , is related to the intensity per unit concentration, T^* , as:

$$I_f = (C_f/C)T_f^* \quad (1)$$

$$I_b = (C_b/C)T_b^* \quad (2)$$

with $C_f + C_b = C$

where

C is the concentration of lithium salt;

f denotes a free solvent;

b denotes a bound solvent.

From eqns. (1) and (2), we obtain the following relations:

$$(I_f/T_f^*) + (I_b/T_b^*) = 1 \text{ or } I_b = -(T_b^*/T_f^*)I_f + T_b^* \quad (3)$$

and

$$(I_f/I_b)(T_b^*/T_f^*) = C_f/C_b \quad (4)$$

By plotting I_b versus I_f for various concentrations, a line with a slope of $(-T_b^*/T_f^*)$ is generated according to eqn. (3). The values of the slope were 0.57 for LiAlCl_4 and 0.17 for LiGaCl_4 . Since the ratio of I_f/I_b can be directly measured from the spectrum, the ratio of C_f/C_b can be obtained using eqn. (4). A general description of solution structure can be derived by transforming the above ratio into the solvation number for the lithium cation, n . If we define M as:

$$M = [\text{SO}_2]/[\text{Li}^+] \quad (5)$$

where $[\text{SO}_2]$ is the number of SO_2 molecules and $[\text{Li}^+]$ is the number of lithium cations, n can be expressed by the following equation:

$$(M - n)/n = C_f/C_b \text{ or } n = M/[1 + (C_f/C_b)] \quad (6)$$

The solvation numbers can be obtained by substituting the values of C_f/C_b and M from eqns. (4) and (5) into eqn. (6). The derived n are slightly greater than 4; the lithium cation is tetrahedrally coordinated by four solvent molecules in the concentration range of interest. This result agrees well with most of the coordination numbers for lithium cations in ionic structures [12].

Various NMR techniques have been used to study the environments of ions or ionic structures in solutions by means of resonance peaks associated with the bulk solvent and bound solvent. Since the exchange of solvent molecules between the different environments is very rapid, the separate resonance peaks expected for each environment are time averaged to a single peak. Thus, the average time that a lithium cation resides in any environment is proportional to its instantaneous mole fraction.

We have analyzed the ${}^7\text{Li}$ spin-lattice relaxation rates ($1/T_1$) of 0.2 M LiAlCl_4 and LiGaCl_4 in sulfur dioxide, and have plotted them against temperature, as shown in Fig. 5. For each salt, two straight lines with a transition point near 25 °C were obtained, implying an Arrhenius dependence of the relaxation rate on temperature and a significant change in the ionic structure of the electrolyte near 25 °C. These results are again consistent with those obtained using conductivity, cyclic voltammetric methods [5], and Raman spectroscopy. We found the activation energies of the spin-lattice relaxation to be 5.98 and 3.72 kJ mole $^{-1}$ for LiAlCl_4 and LiGaCl_4 , respectively.

As shown in Fig. 6, the lithium-7 chemical shifts of LiAlCl_4 and LiGaCl_4 salts in liquid sulfur dioxide were anion-dependent and changed nonlinearly with salt concentration. These results are indicative of contact-ion-pair formation. The non-linear plot associated with the lithium ion is symptomatic of an ion-ion interaction equilibrium [13, 14].

The formation constants of ion pairs were calculated according to Popov's method [15, 16], by fitting the experimental parameters (total concentration of the electrolyte, chemical shift of free lithium ions, chemical shift of lithium ion pairs, and observed chemical shifts) with the nonlinear least-squares program PC-MTLAB. The values of the ion-pair-formation constants were

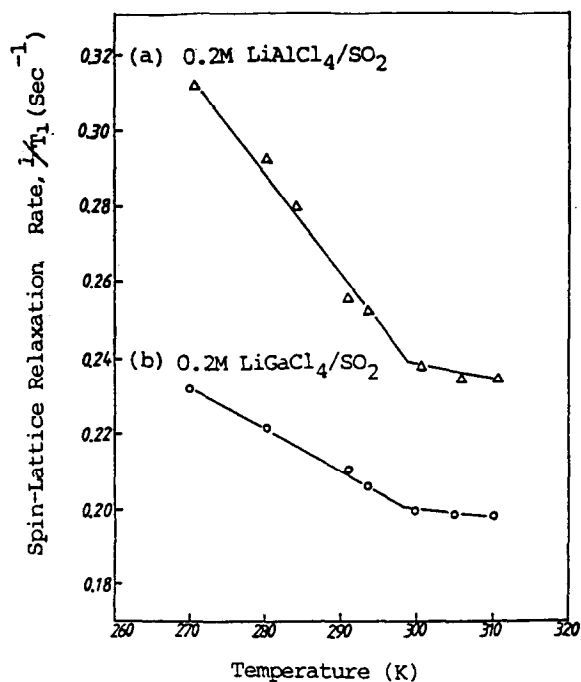


Fig. 5. Temperature effects on spin-lattice relaxation rates.

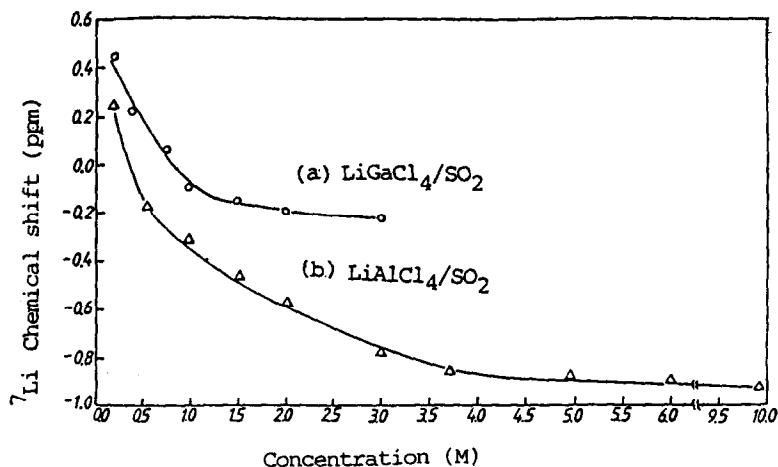


Fig. 6. Concentration effects on ${}^7\text{Li}$ NMR chemical shifts.

TABLE 2

Ion-pair formation constants and ${}^7\text{Li}$ chemical shifts of $\text{LiGaCl}_4/\text{SO}_2$ and $\text{LiAlCl}_4/\text{SO}_2$ electrolytes

	K_f	δ_f	δ_{ip}
$\text{LiGaCl}_4/\text{SO}_2$	2.72	0.95	-0.78
$\text{LiAlCl}_4/\text{SO}_2$	2.36	0.95	-1.05

δ_f : Chemical shift of free Li ion.

δ_{ip} : Chemical shift of Li ion pair.

2.36 M^{-1} for LiAlCl_4 and 2.75 M^{-1} for LiGaCl_4 . The small values of the formation constants imply a low presence of interionic association. In addition, the chemical shifts due to free lithium ions are shown in Table 2. A decrease in electron density around the lithium cation results in an upfield shift of the metal resonance.

4. Conclusions

The results of the NMR study of LiAlCl_4 and LiGaCl_4 salts in sulfur dioxide show that lithium-7 chemical shifts depend on salt concentration and the nature of the counterion, indicating the presence of ion-ion interactions. The ion-pair formation constants of LiAlCl_4 and LiGaCl_4 are 2.36 M^{-1} and 2.75 M^{-1} , respectively. The solvation number of the lithium cation in this system is 4, indicating that the lithium cation is tetrahedrally coordinated by four SO_2 molecules in the concentration range of interest. Both Raman and NMR results confirm that there is an ionic structural change in both salts near 25°C , consistent with those from conductivity and cyclic voltammetric methods.

Acknowledgements

This work was supported by grants from CSIST and the National Science Council of the Republic of China. The authors thank Mr M. L. Hu and Mrs N. L. Ho for their technical assistance during the course of this work.

References

- 1 H. C. Kuo, D. L. Foster, C. R. Schlaikjer, M. L. Gopikanth and A. N. Dey, *U.S. Patent*, 4 513 067 (1983).
- 2 W. L. Bowden and A. N. Dey, *U.S. Patent*, 4 515 875 (1985).
- 3 A. N. Dey, H. C. Kuo, D. L. Foster, C. R. Schlaikjer and M. Kallianidis, *Proc. 32nd Power Sources Symp.*, 1986, The Electrochemical Society, Inc., Pennington, NJ, 1986, p. 173.
- 4 G. T. K. Fey, T. J. Lee, F. C. Leu, P. C. Yao, S. Y. Chen and C. S. Hao, in J. P. Gabano, Z. Takehara and P. Bro (eds.), *Proc. Symp. Primary and Secondary Ambient Temperature Lithium Batteries*, Vol. 88-6, The Electrochemical Society, Inc., Pennington, NJ, 1988, pp. 363-381.
- 5 T. J. Lee, G. T. K. Fey, P. C. Yao and S. Y. Chen, *J. Power Sources*, 26 (1989) 511.
- 6 S. Hyodo and K. Okabayashi, *Electrochim. Acta*, 34 (1989) 1557.
- 7 J. F. Hinton and E. S. Amis, *Chem. Rev.*, 67 (1967) 367.
- 8 Y. Bedfer and J. Corset, *J. Power Sources*, 9 (1983) 287.
- 9 M. C. Dhamelincourt, F. Wallart and J. P. Lelieur, *J. Power Sources*, 20 (1987) 69.
- 10 M. C. Dhamelincourt and F. Wallart, *J. Power Sources*, 14 (1985) 77.
- 11 D. H. Live and S. I. Chan, *Anal. Chem.*, 42 (1970) 1791.
- 12 J. F. Hinton and E. S. Amis, *Chem. Rev.*, 71 (1971) 627.
- 13 L. I. Soong, G. E. Leroi and A. I. Popov, *Inorg. Chem.*, 29 (1990) 1366.
- 14 L. I. Soong, G. E. Leroi and A. I. Popov, *J. Solution Chem.*, 18 (1989) 561.
- 15 E. T. Roach, P. R. Handy and A. I. Popov, *Inorg. Nucl. Chem. Lett.*, 9 (1973) 359.
- 16 W. J. DeWitte, L. Liu, E. Mei, J. L. Dye and A. I. Popov, *J. Solution Chem.*, 6 (1977) 337.