

AN ELECTROCHEMICAL INVESTIGATION OF THE TEMPERATURE DEPENDENCE OF INORGANIC ELECTROLYTES IN RECHARGEABLE LITHIUM BATTERIES

T. J. LEE and G. T. K. FEY*

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

P. C. YAO and S. Y. CHEN

*Materials R & D Center, Chung-Shan Institute of Science and Technology,
Lung-Tan, Taiwan (Republic of China)*

Summary

The temperature dependence on the electrolyte stability of LiAlCl_4 and LiGaCl_4 in sulfur dioxide on a platinum electrode was studied by cyclic voltammetry and conductivity methods, whereas the temperature dependence on the electrolyte stability and electrode film conductivity on a lithium electrode was studied by the a.c. impedance technique. LiGaCl_4 with a better conductivity behavior is more stable than LiAlCl_4 . For both electrolytes below 25°C , the conductivity increases with increasing temperature, but above 25°C it decreases with increasing temperature. The implication of an ionic transport mechanism change is discussed.

Introduction

The Li/SO_2 system is the first highly developed, high-energy-density, primary lithium battery system and has been widely used for military applications for over a decade. Recently, increasing attention has been paid to the development of ambient temperature, secondary lithium battery systems [1 - 6] used as electrochemical power sources for such applications as portable VCR cameras, portable computers, portable communication equipments, portable power tools, and industrial and medical instrumentation. The Li/SO_2 system in which the electrolyte contains LiAlCl_4 or LiGaCl_4 has demonstrated excellent rechargeability and high conductivity at ambient temperature [3 - 5].

The stability of an electrolyte and the internal impedance of a battery determine the ability of a battery to function as a power source. There has been no systematic investigation of the temperature dependence on the

*Author to whom correspondence should be addressed.

stability and internal impedance for LiAlCl_4 and LiGaCl_4 electrolytes in the Li/SO_2 secondary system. In recent work [7, 8], we have partially completed an investigation using cyclic voltammetry, conductivity, and the a.c. impedance technique.

The aim of this paper is to report on the continued study of the temperature dependence on electrolyte conductivity, high temperature storage, and electrolyte stability toward lithium for LiAlCl_4 and LiGaCl_4 in the Li/SO_2 secondary battery system. Further research in these areas is essential to an understanding of the chemistry associated with the battery safety, and the charge/discharge behavior of these two salts in liquid sulfur dioxide, in rechargeable lithium cells.

Experimental

The material, electrolyte preparation, conductivity, and cyclic voltammetric measurements, in addition to cell performance tests have been described in detail previously [8].

The impedance spectra were recorded on an HP-4194A impedance/gain-phase analyser connected to an HP-7550A graphics plotter. The frequency range was from 100 Hz to 15 MHz. The a.c. impedance test cell consisted of three electrodes: a lithium foil (1 cm \times 1 cm), a carbon electrode (1 cm \times 1 cm), and a platinum wire (o.d. 0.03 mm) which is placed between the other two electrodes. The distance between any two electrodes is 0.2 cm.

The electrolyte resistance data were derived from the a.c. impedance measurements whose spectra agree quite well with the model [9] in Fig. 1(a). The equivalent circuit of the model incorporates an electrolyte resistance (R_e) in series with an electrode impedance which consists of a geometric film capacitance (C_g) in parallel with an electrode film resistance (R_f).

The temperature effect on the electrolyte stability in the presence of a lithium electrode was studied by an a.c. impedance technique, while the temperature effect on the electrolyte stability in the presence of a platinum electrode was studied by a conductivity method. The conductivity values of both LiAlCl_4 and LiGaCl_4 electrolytes at 25 °C obtained from these methods were similar; for example, 17.4 mS cm^{-1} by the impedance method *versus* 18.8 mS cm^{-1} by the conductivity method for LiAlCl_4 , and 17.6 mS cm^{-1} *versus* 19.1 mS cm^{-1} for LiGaCl_4 .

Results and discussion

Temperature dependence on electrolyte stability and film conductivity in the presence of a lithium electrode

Figure 1 illustrates the conductivity variation of 0.2 M LiAlCl_4 and LiGaCl_4 in liquid sulfur dioxide in contact with lithium electrodes at various

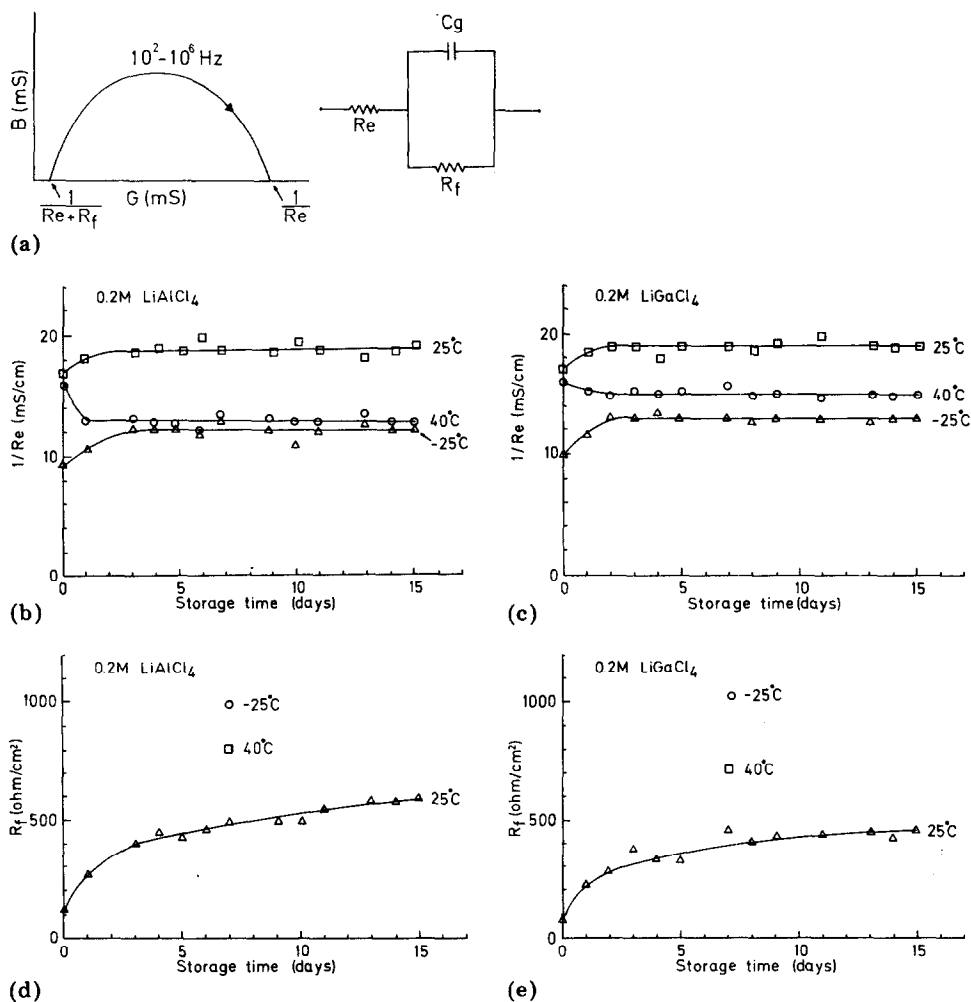


Fig. 1. (a) Model equivalent circuit; (b) - (e) temperature dependence on the stability of LiAlCl₄ and LiGaCl₄ electrolytes and the conductivity of a passivated lithium electrode.

temperatures. Both electrolytes at 25 °C and at -25 °C showed an increase in conductivity, whereas the electrolytes at 40 °C displayed a distinct decrease in conductivity. The cause of the decrease in conductivity at 40 °C is uncertain, probably due to the formation of ion-pairings or intimate ionic aggregates at high temperatures [10]. After the initial passivation period of the first two days, the conductivity values of these electrolytes were steady for the entire storage time of 15 days, as shown in Fig. 1(b) and (c).

The film conductivity (R_f) profiles of the lithium electrodes stored in 0.2 M LiAlCl₄ or 0.2 M LiGaCl₄ at 25 °C for 15 days are given in Fig. 1(d) and (e), respectively. As the storage time is increased, R_f gradually increases from 116 to 577 ohm cm⁻² for LiAlCl₄ and from 88 to 433 ohm cm⁻² for

LiGaCl_4 . This reflects a gradual growth of the film during the storage time. The impedance measurements at low (-25°C) and elevated (40°C) temperatures were uncertain due to the low frequency limit of the instrument. However, approximate R_f values are shown in Fig. 1(d) and (e), and they are much higher than those at 25°C . This suggests that a much thicker film is formed at low and elevated temperatures.

Temperature dependence on electrolyte stability in the presence of a platinum electrode

Figure 2 shows that the conductivity values of both LiAlCl_4 and LiGaCl_4 electrolytes are virtually unchanged at various temperatures over a storage time of 50 days. For either electrolyte in the presence of a platinum electrode, below 25°C the conductivity increases with increasing temperature while above 25°C the conductivity decreases with increasing temperature. A similar situation was also observed in the presence of a lithium electrode (*cf.* Fig. 1). This is an indication that there are two different ionic transport mechanisms: one is normal in terms of conductivity and the other is abnormal and detrimental to the cell performance.

The Arrhenius plots of the electrolyte conductivity (Fig. 3) yield two slopes for each electrolyte, implying the above two ionic transport mechanisms. The activation energies (E_a) are 0.063 and 0.053 eV in the range $0 - 25^\circ\text{C}$ for LiAlCl_4 and LiGaCl_4 respectively. A positive slope in the range $25^\circ\text{C} - 40^\circ\text{C}$ is unacceptable, because in this case activation energy becomes negative. The apparent negative energy of activation for conduction at high temperatures has been suggested to result from the breaking of ionic aggregates and shifting from solvent-separated ionic aggregates to intimate ionic aggregates [10]. This implies that an abnormal conductivity behavior occurs due to an ionic structure change as a result of a temperature increase.

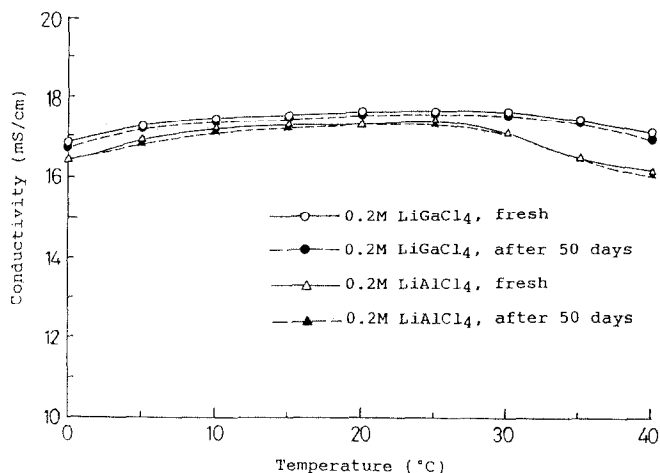


Fig. 2. Conductivity variations of 0.2 M LiAlCl_4 and LiGaCl_4 electrolytes at various temperatures over 50 days storage.

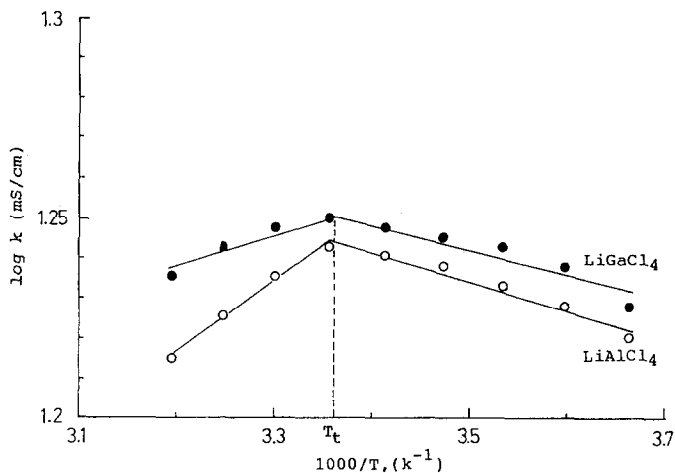


Fig. 3. Arrhenius plots of the electrolyte conductivity of 0.2 M LiAlCl_4 and LiGaCl_4 in sulfur dioxide.

It is interesting to note that the transition temperature (T_t) at which the slope changes is found to be very close between these two electrolytes, namely, 24.6 °C for LiAlCl_4 and 24.3 °C for LiGaCl_4 . A similar temperature dependence of the conductivity, irrespective of the anion of the lithium salt and the nature of the organic solvent, was observed with lithium electrodes in 1 M LiClO_4 -propylene carbonate solution [11]. These similarities in E_a and T_t are in line with the similar atomic sizes and chemical properties between aluminum and gallium.

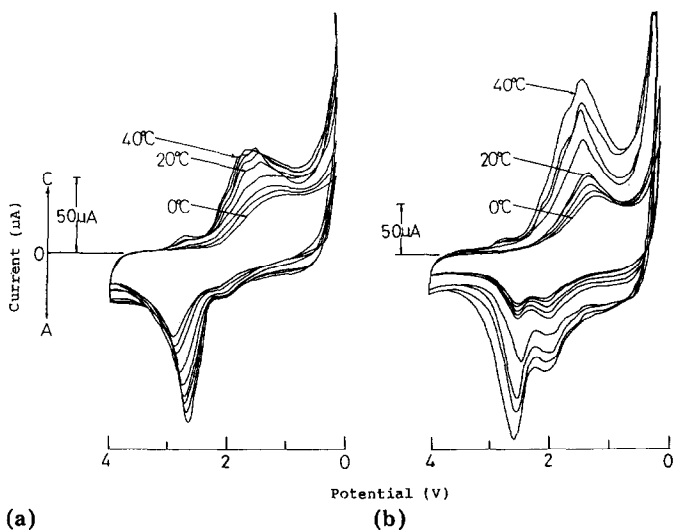


Fig. 4. Cyclic voltammograms of (a) 0.2 M LiAlCl_4 ; (b) 0.2 M LiGaCl_4 in sulfur dioxide from 0 °C to 40 °C. (Scan rate = 100 mV s^{-1} ; temperature interval: 5 °C.)

The cyclic voltammograms of 0.2 M LiAlCl_4 and LiGaCl_4 in sulfur dioxide at various temperatures are presented in Fig. 4(a) and (b), respectively. Scans were arranged at intervals of 5 °C from 0 °C to 40 °C. The redox behaviors of these two electrolytes have been discussed previously [8].

As temperature increased, the reduction potentials of the tetrachloroaluminate electrolyte were obviously shifted in a more positive direction, and the oxidation potentials were shifted in a less positive direction. In the LiGaCl_4 case, the potential shifts were not so obvious. As temperature increased from 0 °C to 20 °C, the reduction potentials of the tetrachlorogallate electrolyte appeared to be shifted slightly in a more positive direction and the oxidation potentials were virtually unchanged. Above 20 °C, both the reduction and oxidation potentials appeared to be shifted slightly in a more positive direction. This indicates that ions of different electrochemical behavior were formed above 20 °C for these two electrolytes. In fact, the discharge products on carbon electrodes at room temperature are LiCl and $\text{Li}_2\text{S}_2\text{O}_4$ for LiAlCl_4 and LiGaCl_4 electrolytes, respectively [8].

Figure 4 clearly illustrates the temperature dependence on the electrolyte stability and high temperature storage. Based on the reduction behavior of both complexes, LiGaCl_4 is apparently more stable, with better conductivity behavior, than LiAlCl_4 in the above temperature range (*cf.* Fig. 2).

Interestingly, a distinct, sharp increase in the cathodic current at 1.3 V and the anodic current at 2.5 V at, or above 25 °C was observed in the case of LiGaCl_4 but not in the case of LiAlCl_4 . The temperature of the current change at 25 °C is very close to T_t . This reveals that the ionic structure change of the electrolyte not only affects its conductivity behavior but also its redox behavior. In addition, it also explains why the LiGaCl_4 electrolyte is more stable and conductive than the LiAlCl_4 electrolyte at various temperatures.

The concentration effects on the electrolyte properties, the cell performance tests at various temperatures, the effects of charge cycles and depth of discharge on impedance parameters, will be reported elsewhere. Our preliminary results indicate that the Li/SO_2 cell with LiGaCl_4 electrolyte has reached 75 cycles and shown a capacity seven times greater than that with LiAlCl_4 electrolyte.

Conclusions

Both LiAlCl_4 and LiGaCl_4 complexes in liquid SO_2 are temperature dependent, which has an adverse effect on the electrolyte conductivity above 25 °C. LiGaCl_4 is more stable with better conductivity behavior than LiAlCl_4 in the temperature range considered. The electrochemistry and cell performance tests of these electrolytes at high temperatures require further investigations for safety considerations.

Acknowledgement

The authors thank Mr. T. H. Kao and Mr. C. S. Shiue for their technical assistance during the course of this work which was supported by grants from CCIST and the National Science Council of the Republic of China.

References

- 1 F. W. Dampier and R. T. Kalivas, *Proc. 30th Power Sources Symp., Atlantic City, NJ, 1982*, The Electrochemical Society, Inc., Pennington, NJ, 1982, p. 73.
- 2 K. M. Abraham and S. B. Brummer, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983, Ch. 14, p. 395.
- 3 H. C. Kuo, D. L. Foster, C. R. Schlaikjer, M. L. Gopikanth and A. N. Dey, *U.S. Pat. 4,513,067* (1983).
- 4 W. L. Bowden and A. N. Dey, *U.S. Pat. 4,515,875* (1985).
- 5 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.
- 6 C. De La Franier, A. Harkness and G. Donaldson, *Proc. 32nd Power Sources Symp., 1986*, The Electrochemical Society, Inc., Pennington, NJ, 1986, p. 185.
- 7 G. T. K. Fey, W. T. Liu, F. C. Leu, T. J. Lee, C. S. Hao, C. C. Chang, S. Y. Chen and P. C. Yao, *Ext. Abstr. No. 45, Electrochem. Soc. Fall Meeting, Honolulu, HI, Oct. 18 - 23, 1987*, Vol. 87-2, The Electrochemical Society, Inc., Pennington, NJ, 1987, pp. 70 - 71.
- 8 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.
- 9 M. Kleitz and J. Dupuy, *Electrode Processes in Solid State Ionics*, 1976, pp. 261 - 275.
- 10 R. Cohen, J. Kimel, E. Elster and E. Peled, *Ext. Abstr., 4th Int. Meet. on Lithium Batteries, May 24 - 27, 1988, Vancouver, B.C., Canada*.
- 11 Y. Geronov, B. Puresheva and B. Pavlova-Stoynov, *J. Power Sources*, 20 (1987) 37.