

## Lithium-cycling efficiency in inorganic electrolyte solution

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### Abstract

Lithium-cycling efficiencies and corrosion rates were measured in half cells. The elaborated inorganic electrolyte solution, consisting mainly of  $\text{LiAlCl}_4$  and  $\text{SO}_2$ , has a conductivity of 2.2 mS/cm at  $-25^\circ\text{C}$  and 98 mS/cm at  $60^\circ\text{C}$ . Lithium-cycling efficiencies of about 98% at  $40\text{ mA/cm}^2$  for at least 50 cycles were achieved. Depending on improved electrolyte preparation, the current density for the lithium corrosion could be reduced from 12.1 to  $6.5\ \mu\text{A/cm}^2$ . The results indicate stability, compatibility and high rate capability of the system lithium/inorganic electrolyte solution.

### Introduction

Rechargeable lithium cells offer much promise for a wide variety of applications. One of the limitations in Li secondary cells is the cycling efficiency of Li itself. Because of poor cycling efficiency, three to five times excess of Li must be included in practical cells. But the formation of chemically-reactive ‘dead lithium’ remains a severe problem concerning the safety of the cells.

In the majority of the rechargeable Li cells described in the past, organic solvents like propylene carbonate or ethers were used [1]. Cycling efficiencies of Li in organic electrolyte solutions have been shown to vary with several parameters, especially with plating and stripping current densities. Cycling efficiency dropped down to 90% and lower applying current densities higher than  $1\text{ mA/cm}^2$ . Adding  $\text{CO}_2$  to ester-based electrolyte solutions led to high Li-cycle efficiencies [2]. But the incompatibility of organic electrolytes to overall cell reaction results in irreversible products. So for high cycle life an excess of Li and of electrolyte solution is needed.

Inorganic electrolyte is known for high cycling efficiencies at higher current densities, e.g., 95% at  $10\text{ mA/cm}^2$  [3], and its overcharge ability by the chlorine shuttle mechanism [4].

### Experimental

The inorganic electrolyte solution contains mainly lithium chloride, aluminium chloride and sulfur dioxide. Electrolyte preparations were done in an argon-filled glove

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box to minimize pollution with atmospheric gases, especially  $\text{H}_2\text{O}$  and  $\text{N}_2$ . Chemicals were dried before using. The produced electrolyte solution was a water-clear liquid.

Ion conductivity was measured between  $-25$  and  $60$  °C using a conductivity flow cell, LDM/S from WTW.

Measurements of cycling efficiencies and corrosion rates were done in an argon-filled glove box (BRAUN) with  $\text{H}_2\text{O}$ ,  $\text{O}_2$  and  $\text{N}_2$  concentrations lower than 2 ppm. Lithium was plated and stripped galvanostatically in a three-electrode glass cell with a smooth nickel or stainless-steel disc as working electrode. The discharge potential was limited to 1.0 V versus Li. The total plating charge was usually between 3 and  $18 \text{ C/cm}^2$ .

## Results and discussion

### Conductivity

As shown in Fig. 1 the conductivity of the inorganic electrolyte solution increases from  $2.2 \text{ mS/cm}$  at  $-25$  °C up to  $98 \text{ mS/cm}$  at  $60$  °C. So, in practical cells, this electrolyte can be used for high rate applications in the whole range up to the boiling point at about  $60$  °C.

### Cycling efficiencies

Plating and stripping Li galvanostatically results in flat voltage versus time curves. At the end of stripping the potential of the working electrode increases to the limit within seconds. As shown in Fig. 2, cycling efficiency at current density of  $40 \text{ mA/cm}^2$  reached 98% for about 50 cycles.

It seems that cycling efficiency strongly depends on traces of different impurities. So a greater quantity of sodium ( $>0.2\%$ ) leads to a slow increase of the electrode potential at the end of stripping. Decreasing the water content through intensive drying of the chemicals and preparation of the electrolyte in very dry argon and nitrogen-free atmosphere led to higher cycling efficiencies (Fig. 3).

### Corrosion

Like cycling efficiency, the corrosion of Li seems to depend on very small amounts of different impurities. The corrosion rate of Li was measured as shown in Fig. 4. The equivalent of three coulomb of Li was plated on  $1.3 \text{ cm}^2$  nickel disc. The electrolyte

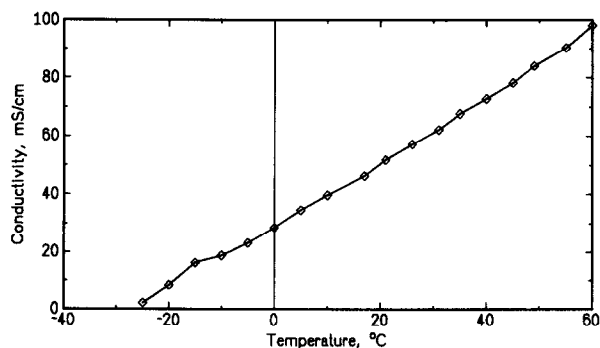


Fig. 1. Conductivity of inorganic electrolyte consisting of  $\text{LiAlCl}_4$  and  $\text{SO}_2$  vs. temperature.

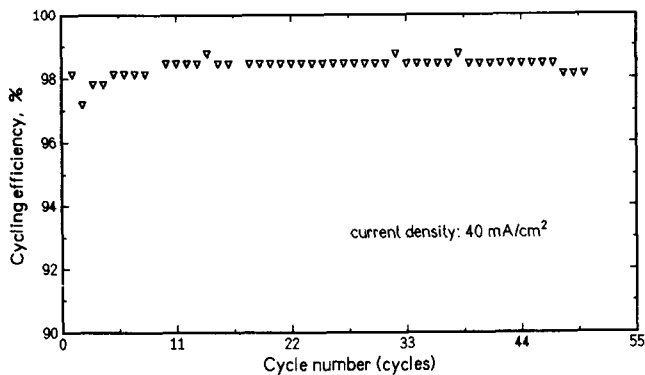


Fig. 2. Lithium-cycling efficiency vs. cycle number.

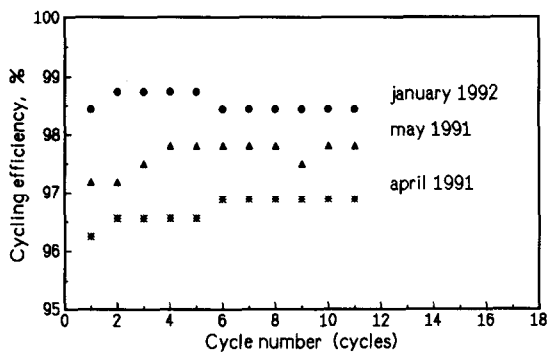


Fig. 3. Improvement of lithium-cycling efficiency vs. cycle number.

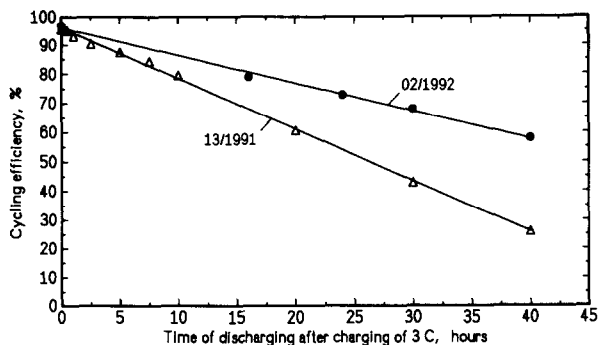


Fig. 4. Decrease of lithium-cycling efficiency by corrosion vs. time.

13/1991 showed a corrosion-current density of  $12.1 \mu\text{A}/\text{cm}^2$ . Depending on improved preparation (02/1992), corrosion-current density was reduced to  $6.5 \mu\text{A}/\text{cm}^2$ . The effect of different, especially gaseous impurities are still on investigation by means of DEMS [5].

## Conclusions

Inorganic electrolyte solutions are attractive for use in rechargeable Li cells because of their high conductivity and good electrochemical stability. Their main limitations were poor cycling efficiencies and high corrosion rates of Li.

Using electrolyte solutions, consisting mainly of  $\text{LiAlCl}_4$  and  $\text{SO}_2$ , Li-cycling efficiency of 98% at  $40 \text{ mA/cm}^2$  and corrosion rate of  $6.5 \mu\text{A/cm}^2$  were achieved. The present targets are a cycling efficiency above 99.5% and a corrosion rate lower than  $2 \mu\text{A/cm}^2$ .

These presuppositions are required to use the electrolyte for safe rechargeable Li batteries without excess of Li. Lithium combined with a positive  $\text{CoO}_2$  intercalation electrode [6] promises high energy and high rate cells.

## References

- 1 J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983.
- 2 W. B. Ebner, J. A. Simmons and D. L. Chua, *Proc. 33rd Int. Power Sources Symp., Cherry Hill, NJ, USA, 1988*, p. 11.
- 3 C. W. Walker, Jr. and M. Binder, *J. Electrochem. Soc.*, *135* (1988) 1061.
- 4 A. N. Dey, W. L. Bowden, H. C. Kuo, M. L. Gopikanth, C. R. Schlaikjer and D. Foster, *J. Electrochem. Soc.*, *136* (1989) 1618.
- 5 G. Hambitzer, M. Joos and U. Schriever, *J. Power Sources*, submitted for publication.
- 6 J. Dreher, B. Haas and G. Hambitzer, *J. Power Sources*, submitted for publication.