

Optimized lithium oxyhalide cells

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Abstract

Lithium thionyl chloride cells were optimized with respect to electrolyte and carbon cathode composition. Wound 'C-size' cells with various mixtures of Chevron acetylene black with Ketjenblack EC-300J and containing various concentrations of LiAlCl_4 and derivatives, LiGaCl_4 , and mixtures of SOCl_2 and SO_2Cl_2 were evaluated as a function of discharge rate, temperature, and storage condition.

Introduction

There is an abiding interest in improving the performance of lithium oxyhalide batteries for military applications because of their high energy density and potential for providing high power. Recent investigations to improve cell performance have included the use of mixed depolarizers to increase energy [1], catalyst studies to improve rate capability [2], and ion-conducting polymers to coat Li anodes to improve their corrosion resistance during storage [3].

In this study, wound 'C-size' cells were used as test vehicles to address areas where significant improvements are still needed. These include improvements in rapid activation, low temperature performance, high temperature storage, and increased energy.

An iterative process was employed that began with evaluating the effects of carbon thickness [1] and developing a new carbon-blend cathode. This was followed by evaluating electrolyte salts and was completed by an investigation of mixed depolarizers using various electrolyte salt concentrations. At each stage in this systematic development process, the start-up and capacity data were compared with control SOCl_2 cells. The test matrix consisted of discharging both fresh and stored cells in triplicate at 1, and 10 mA cm^{-2} at 0 and 25 °C. Combinations of the best components were also evaluated at 20 mA cm^{-2} .

Experimental

Electrolyte

Each electrolyte solution was prepared by refluxing an excess of 5 mol% of LiCl in a solution of SOCl_2 (MOBAY) or SO_2Cl_2 containing AlCl_3 (Fluka) or 99.999%

GaCl_3 (Eagle-Picher). The LiCl was heated in vacuum to 200°C for at least 16 h. Hydrolysis products were removed from the electrolytes by refluxing until infrared spectra indicated concentrations of both $-\text{OH}$ and HCl were below 50 ppm. The concentration was confirmed by conductometric titration using SOCl_2 solutions of dried standardized trimethylamine hydrochloride [4].

(i) *Type A*. This was the control electrolyte, and consisted of 1.8 M LiAlCl_4 with 1% $\text{LiAl}(\text{SO}_3\text{Cl})_4$ [5] refluxed in SOCl_2 with excess LiCl .

(ii) *Type B*. A BEI proprietary electrolyte was prepared by additional processing of the control electrolyte to remove traces of AlCl_3 .

(iii) *Type C*. This electrolyte was prepared by first refluxing 1.0 M AlCl_3 in SOCl_2 with an equivalent amount of trifluoromethane-sulfonate (triflate). Some residual precipitate remained. This was followed by additional refluxing in the presence of excess LiCl . The theoretical maximum concentration of LiAlCl_4 was 1.0 M. The capacity data discussed in the section 'electrolyte evaluation' (p. 719) indicate the actual concentration was more likely 0.5 M.

(iv) *Type D*. This electrolyte consisted of a 1.4 M LiGaCl_4 solution in SOCl_2 prepared by adding excess LiCl to GaCl_3 prior to refluxing.

The sulfuryl chloride was purified by refluxing over 0.2 M AlCl_3 , followed by fractionation on a Berl saddle column from 0.2 M LiAlCl_4 until absorption between 3000 and 4000 cm^{-1} was negligible. Electrolytes were prepared by refluxing solutions of AlCl_3 with 5 mol% of excess LiCl .

The mixed $\text{SOCl}_2/\text{SO}_2\text{Cl}_2$ depolarizer solution was prepared by mixing the separate components in the appropriate ratio.

Cathode fabrication

The cathodes contained mixtures of Chevron 50% compressed acetylene black and Ketjenblack EC-300J (AKZO). In order to control the thickness, porosity, and loading of the carbon cathodes, the carbon mixture which contained 10% Teflon binder, was dry-pressed onto the nickel screen, rather than rolled wet. Prior to winding the cell, the cathodes were dried at 150°C for 20 min in a dry-room with less than 2% relative humidity at 75°F (16°C). Lithium thionyl chloride cells containing dry-pressed cathodes with 10% Teflon showed improvement in capacity to a 2.0 V cutoff when compared with similar cells containing dry-pressed cathodes having only 5% Teflon. At $1.5\ \Omega$ loads and 25°C , the average capacities of cells with the 10% Teflon were 3.76 A h compared with 2.82 A h for cells with 5% Teflon.

Control cells

The control cells were a wound 'C-size' design, in a 304 SS case negative container with a Fusite 225 psi rated vent. The cell contained 20.5 to 21.0 g (~ 7.9 A h) of the type A electrolyte. The separator was 'Hovosorb' (Hollingsworth Vose) binderless Pyrex fabric 0.13 mm to 0.2 mm thick. The anode contained 2.3 g Li (8.89 A h) on a $279\text{ mm}\times 38\text{ mm}\times 0.58\text{ mm}$ nickel screen. The cathode consisted of a mixture of 25% Ketjenblack-75% Chevron acetylene black with Teflon binder 10% of the 2.0 ± 0.1 g carbon weight that was dry-pressed onto a nickel screen. The dimensions before winding were $254\text{ mm}\times 38\text{ mm}\times 0.69\text{ mm}$.

Test cells

Test cells were identical to the control cells except for variations noted in the carbon composition, electrolyte salt, or thionyl chloride to sulfuryl chloride ratio.

No attempt was made to improve cell performance by altering the quantity or dimensions of carbon in these generally carbon-limited cells.

Cells were stored and discharged under constant loads of 0.75, 1.5 and 17 Ω , a minimum of three replicate tests in Blue M ovens at constant temperature.

Results and discussion

Effect of the percentage Ketjenblack in the carbon blend cathode

The ratio of Ketjenblack to Chevron acetylene black carbon was initially investigated using the type A electrolyte, with the intention of optimizing voltage regulation on start-up and to improve high rate and low temperature performance.

As previously reported [1], the capacity of cells with dry-pressed cathodes was generally not as high as cells with wet-rolled cathodes, but the dry-pressed method was more reproducible and better suited to an optimization study.

Fresh LiAlCl₄ cells

Figure 1 shows the average capacity of fresh cells with type A electrolyte discharged at 17 Ω (1 mA cm⁻²) at 25 °C to a 2.0 V cut-off. The data compare the control cells containing cathodes with 25% Ketjenblack with similar test cells containing 30, 35 and 40% Ketjenblack. The balance of the carbon was Chevron acetylene black. The data show that the capacity of the control cells was improved at low rates by increasing the percentage of Ketjenblack. At the 17 Ω rate, the cell capacities apparently became thionyl chloride limited. Figure 2 shows that increasing the cathode composition to 30% Ketjenblack also provides better average capacity at the 1.5 Ω (10 mA cm⁻²) rate.

At 0 °C, the cell capacity was not improved by increasing the percentage of Ketjenblack. The average capacities at 0 °C for the 17 Ω load were 4.84, 4.91, 5.05, and 5.04 A h. At 1.5 Ω , the capacities were 2.80, 3.02, 2.92, and 2.83 A h, as partially shown in Fig. 2, for the 25%, 30%, 35%, 40% blends, respectively.

Stored LiAlCl₄ cells

Figure 3 shows the capacity of Li/SOCl₂ cells with 25 and 30% Ketjenblack cathodes after storage for two weeks at 70 °C. The LiAlCl₄ cells with 30% Ketjen-

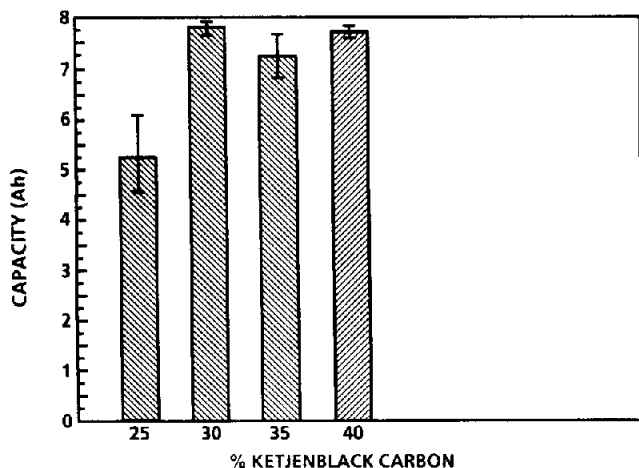


Fig. 1. Average capacity of 'C-size' 1.8 M LiAlCl₄/SOCl₂ cells discharged at 1 mA cm⁻² at 25 °C vs. % Ketjenblack carbon.

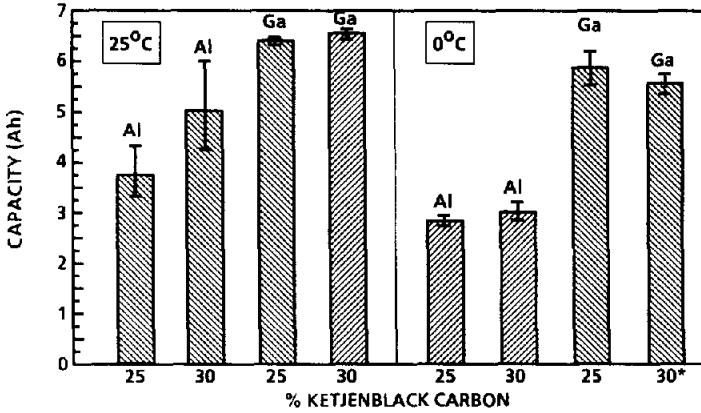


Fig. 2. Effect of cathode composition and electrolyte salt on the average capacity of fresh 'C-size' Li/SOCl₂ cells discharged at 10 mA cm⁻² at 25 and 0 °C; *cells discharged at 20 mA cm⁻²; Al: 1.8 M LiAlCl₄, 1% LiAl(SO₃Cl)₄; Ga: 1.4 M LiGaCl₄.

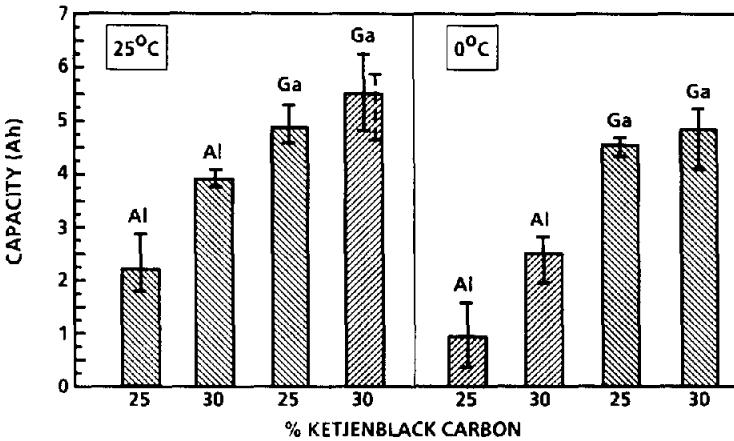


Fig. 3. Effect of cathode composition and electrolyte salt on the average capacity of 'C-size' Li/SOCl₂ cells stored two weeks at 70 °C and discharged at 10 mA cm⁻² at 25 and 0 °C; dashed bar is the range for cells discharged at 20 mA cm⁻²; Al: 1.8 M LiAlCl₄, 1% LiAl(SO₃Cl)₄; Ga: 1.4 M LiGaCl₄.

black were clearly better than those with 25% Ketjenblack at the 1.5 Ω rate. However, in contrast to the fresh cells, the capacity of stored cells discharged at 25 °C was not noticeably affected at the 17 Ω rate by increasing the percentage Ketjenblack. At 0 °C, the overall capacities were improved only minimally, by an average 10%.

Start-up time for LiAlCl₄ cells

The LiAlCl₄ cells containing increased amounts of Ketjenblack proved to have higher running potentials under high rate discharge. The cathodes containing 30% Ketjenblack carbon were judged to be superior to the other carbon blends, primarily because these cells consistently recovered to 3.0 V more rapidly under all test conditions.

Both fresh and stored cells with 30% Ketjenblack recovered to 3.0 V in less than half the time of the 35% and 40% blends when discharged at 1.5 Ω and 25 $^{\circ}\text{C}$. The control cells never reached 3.0 V when discharged at high rates either at low temperature or after storage.

Electrolyte evaluation

Capacity

In order to improve cell activation and provide better high temperature storageability, four electrolytes were evaluated in 'C-size' Li/SOCl₂ cells containing 25% Ketjenblack cathodes.

The average capacities of fresh and stored cells discharged at 17 and 1.5 Ω to a 2.0 V cut-off at 25 $^{\circ}\text{C}$ are displayed as a function of various electrolyte salts in Figs. 4 and 5, respectively. The corresponding data for these cells discharged at 0 $^{\circ}\text{C}$ are shown in Fig. 6 (17 Ω) and Fig. 7 (1.5 Ω).

As the ambient temperature discharge data in Fig. 4 show, the refluxed 1.0 M LiAlCl₄-saturated triflate electrolyte demonstrated the best average capacity at low discharge. The fresh cells appear to have become thionyl chloride limited. Figures 5 and 7 show that under higher rate discharge, especially after high temperature storage, this electrolyte had comparatively poor capacity.

The overall performance, both capacity and activation time, of the control (type A) electrolyte was consistently improved by use of the type B electrolyte which employed a proprietary processing technique to reduce the AlCl₃ concentration. As the discharge data in Figs. 5 and 7 show, this was most notable in stored cells discharged at high rates. This improvement in stored cells was attributable to reduced rates of corrosion of the anode.

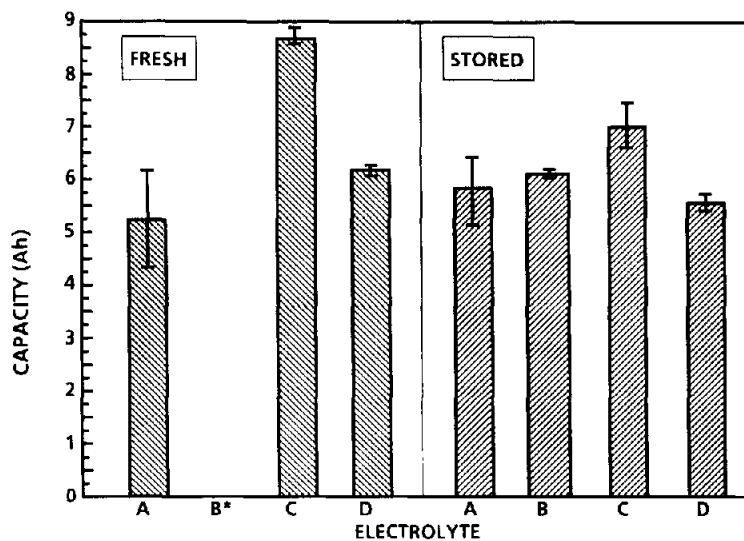


Fig. 4. Effect of electrolyte salt on the average capacity of fresh and stored 'C-size' Li/SOCl₂ cells with 25% Ketjenblack cathodes discharged at 17 Ω at 25 $^{\circ}\text{C}$; (A) 1.8 M LiAlCl₄, 1% LiAl(SO₃Cl)₄; (B) electrolyte A with low AlCl₃; (C) 1.0 M LiAlCl₄ saturated with LiCF₃SO₃, and (D) 1.4 M LiGaCl₄.

*No cells tested.

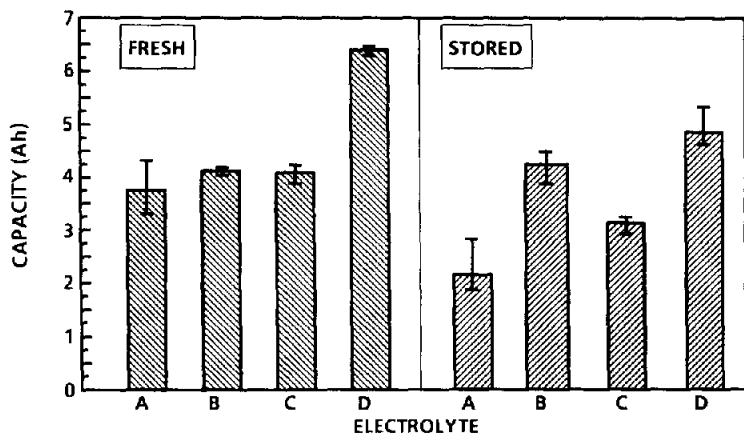


Fig. 5. Effect of electrolyte salt on the average capacity of fresh and stored 'C-size' Li/SOCl₂ cells with 25% Ketjenblack cathodes discharged at 1.5 Ω at 25 °C: (A) 1.8 M LiAlCl₄, 1% LiAl(SO₃Cl)₄; (B) electrolyte A with low AlCl₃; (C) 1.0 M LiAlCl₄ with saturated LiCF₃SO₃, and (D) 1.4 M LiGaCl₄.

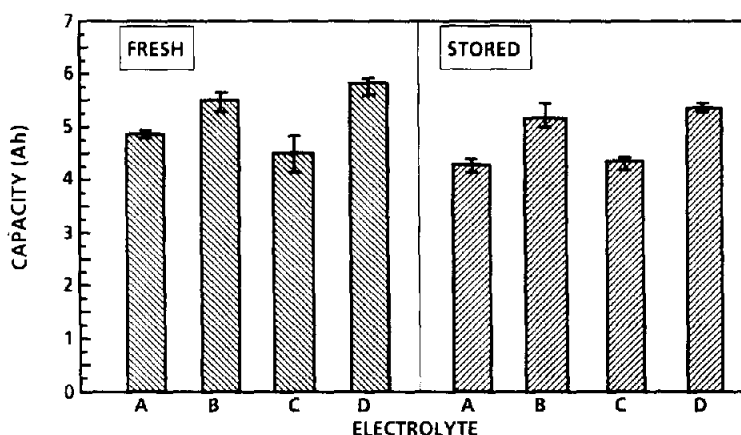


Fig. 6. Effect of electrolyte salt on the average capacity of fresh and stored 'C-size' Li/SOCl₂ cells discharged at 17 Ω at 0 °C: (A) 1.8 M LiAlCl₄, 1% LiAl(SO₃)₄; (B) electrolyte A with low AlCl₃; (C) 1.0 M LiAlCl₄ with saturated LiCF₃SO₃, and (D) 1.4 M LiGaCl₄.

The enhanced performance observed at 25 °C in cells with type C electrolyte is attributed to a reduction in the concentration of LiAlCl₄. Assuming the LiAlCl₄ concentration of the type C electrolyte is 1.0 M, the Li ion concentration would be reduced by more than 40% with respect to the type A control electrolyte. In stored cells, the observed improvement in capacity was the result of a decrease in the rate of corrosion because of the lower salt concentration [6, 7]. In fresh cells, it is tempting to believe that the improvement was caused by the triflate. However, a lower LiAlCl₄ concentration would be expected to account for a greater capacity because of the proportionate increase in the SOCl₂ available. In actuality, if one assumes the concentration of LiAlCl₄ was 1.0 M, then the measured average capacity of 8.79 A h to

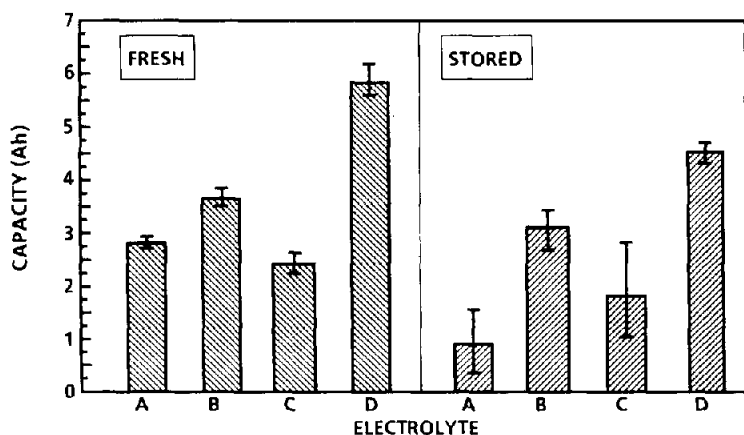


Fig. 7. Effect of electrolyte salt on the average capacity of fresh and stored 'C-size' Li/SOCl₂ cells with 25% Ketjenblack cathodes discharged at 1.5 Ω at 0 °C: (A) 1.8 M LiAlCl₄, 1% LiAl(SO₃Cl)₄; (B) electrolyte A with low AlCl₃; (C) 1.0 M LiAlCl₄ with saturated LiCF₃SO₃, and (D) 1.4 M LiGaCl₄.

a 1.0 V cut-off exceeded the average theoretical cell capacity of 8.34 A h for cells containing 20.66 ± 0.12 g of a 1.0 M LiAlCl₄ electrolyte solution. The triflate electrolyte is presumed to have reduced the initial concentration of AlCl₃ so that the final concentration of LiAlCl₄ was below that of the 1.0 M anticipated. The 8.79+ A h capacity can be explained by a LiAlCl₄ concentration of approximately 0.5 M.

Infrared studies indicate that some of the AlCl₃ is coordinated to the triflate. In LiAlCl₄-triflate/SOCl₂, a strong shoulder occurs at 1050 cm⁻¹, in addition to a strong triflate band at 1034 cm⁻¹. In the absence of AlCl₃, the 1050 cm⁻¹ band is absent and the 1034 cm⁻¹ band is weak because of the relative insolubility of the triflate in neat SOCl₂.

Cells with the LiGaCl₄ electrolyte provided an average 6.1 A h capacity in fresh cells and demonstrated the highest capacity under high rate discharge, and with the exception of the triflate cells discharged at low rates at ambient temperature, these cells provided consistently superior performance under all conditions.

Start-up performance

Often a critical military requirement is the time to activate a cell or battery to a minimum voltage on start-up. The most stringent start-up conditions occur at low temperature or under high rate discharge or both, after high temperature storage. Consequently, the activation time to 2.0 V was measured at 1.5 Ω after two weeks storage at 70 °C for each of the electrolytes. The LiGaCl₄ electrolyte demonstrated the fastest activation times at both 25 and 0 °C. At 0 °C, the average start-up time for the LiGaCl₄ was 4.8 s, an average eight times faster than the type B electrolyte, which in turn was about 25 and 50 times faster than the control and triflate electrolytes, respectively. Only the LiGaCl₄ electrolyte ever reached the 3.0 V plateau at 1.5 Ω at 0 °C after storage.

Optimized cell evaluation

The next iterative improvement to optimize the performance of Li/SOCl₂ cells, was to combine the best electrolyte, namely the LiGaCl₄, with the best cathode composition, i.e., cathodes with 30% Ketjenblack.

The average capacities of fresh and stored SOCl_2 cells containing LiGaCl_4 and LiAlCl_4 electrolytes discharged at $\sim 10 \text{ mA cm}^{-2}$ are compared as a function of Ketjenblack content in the cathodes in Figs. 2 and 3. The data reveal that the use of LiGaCl_4 electrolyte was the most effective in improving the high rate performance of SOCl_2 cells. The use of the 30% Ketjenblack cathodes may provide a small additional benefit for cells that are stored and discharged at high rate. However, the capacity was not improved by either the LiGaCl_4 or higher Ketjenblack content when stored cells were discharged at the low 17Ω rate. It is conceivable to consider that under storage conditions, the cells became Li limited, especially since the average capacities of all twelve (Al-Ga/25-30% Ketjenblack) cells that were stored and discharged at 17Ω at 25°C , were closely grouped at $5.79 \pm 0.16 \text{ A h}$. This is somewhat confirmed by the data in Fig. 4 that show lower concentrations of LiAlCl_4 provide a beneficial effect by reducing the loss of Li via corrosion. This is supported by the data in Fig. 8 that also show improved cell capacity at 25°C after high temperature storage, regardless of the depolarizer employed. The relatively good capacity of the SOCl_2 system may be attributable to a less than 1.0 M concentration of LiAlCl_4 as previously discussed.

Mixed depolarizer study

The optimized cells, i.e., cells containing LiGaCl_4 and 30% Ketjenblack carbon were evaluated in a mixed depolarizer consisting of 75% SO_2Cl_2 and 25% SOCl_2 . In order to avoid potential Li limited behaviour, the tests were carried out under the most stringent conditions, namely, storage at 70°C and high rate discharge at 0°C . Figure 9 illustrates that the capacity of these cells was not influenced by the nature of the depolarizer, each of the LiGaCl_4 cells discharged at 1.5Ω had nearly equivalent capacity. However, at the 0.75Ω load (20 mA cm^{-2}), the LiGaCl_4 in the SOCl_2 depolarizer demonstrated better capacity than the mixed depolarizer. If one compares the behaviour of the LiGaCl_4 and LiAlCl_4 electrolyte salts in the mixed depolarizer,

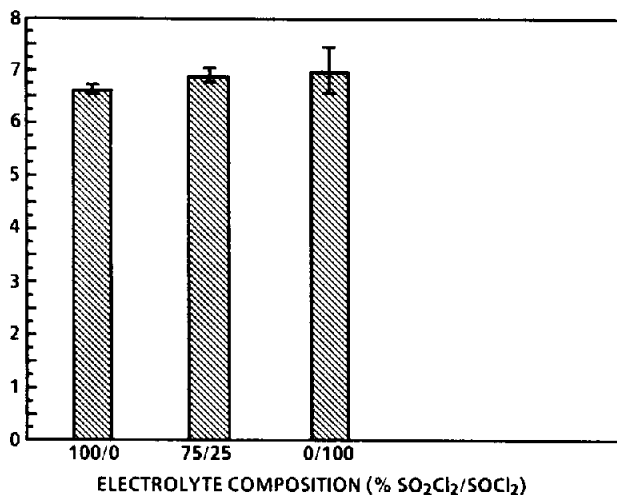


Fig. 8. Average capacity of 'C-size' cells with 1.0 M LiAlCl_4 discharged at 17Ω (1 mA cm^{-2}) at 25°C after two week storage at 70°C . The cells with the 100/0 and the 75/25 composition employed 30% Ketjenblack cathodes. The cells with the 0/100 composition contained 25% Ketjenblack cathodes and type C electrolyte.

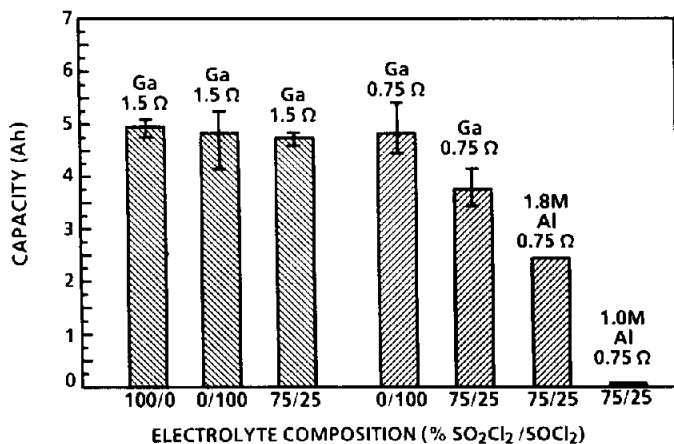


Fig. 9. Average capacity of cells with 30% Ketjenblack cathodes as a function of electrolyte composition, cells were stored two weeks at 70 °C and discharged at 0 °C at 1.5 or 0.75 Ω loads; Ga: 1.4 M LiGaCl₄; Al: LiAlCl₄.

the cells with LiGaCl₄ performed much better than cells with the LiAlCl₄ at high rate discharge after storage. Cells with the LiAlCl₄ often failed to discharge under these extreme conditions.

Conclusions

The ability to improve the capacity and start-up performance of Li/SOCl₂ cells was found to be dependent on the specific discharge requirements and the condition of the cell. The best overall start-up, rate capability, and capacity was realized when both fresh cells and cells stored at 70 °C for two weeks, contained 30 wt.% Ketjenblack/70 wt.% Chevron acetylene black carbon cathodes in 1.4 M LiGaCl₄-Li/SOCl₂.

References

- 1 W. P. Kilroy, C. R. Schlaikjer, R. Yetman, M. Alamgir and K. M. Abraham, *J. Power Sources*, 36 (1991) 1.
- 2 W. P. Kilroy, K. M. Abraham, M. Alamgir and E. Willstaedt, *Electroch. Acta*, 37 (1992) 531.
- 3 K. M. Abraham, D. M. Pasquariello, M. Alamgir and W. P. Kilroy, *J. Power Sources*, 43-44 (1993) 385.
- 4 H. Spandau and E. Brunneck, *Z. Anorg. Allg. Chem.*, 270 (1952) 201; 278 (1955) 197.
- 5 (a) D. Vallin, J. Grassien, P. Chenebault and A. Kerovanton, *US Patent 4 547 441* (Oct. 15, 1985); D. Vallin and P. Chenebault, *Proc. 32nd Power Sources Symp., Cherry Hill, NJ, June 9-12, 1986*, p. 41.
- 6 A. N. Dey, *Thin Solid Films*, 43 (1977) 131.
- 7 A. N. Dey, *DELET-TR-74-0109-F*, Fort Monmouth, July 1978.