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Free Lewis acid effects in electrolytes for Li/SOCl$_2$ cells

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Electrolyte solutions containing lithium tetrachloroaluminate with free aluminum chloride added, have been evaluated for use in Li/SOCl$_2$ cells. The optimum electrolyte composition contained 1.0 M LiAlCl$_4$ plus 2.0 M AlCl$_3$ in SOCl$_2$. Such a solution, when used in cells in place of the more usual 1.8 M LiAlCl$_4$ electrolyte, results in 45% longer reaction times. This increase can only be explained in part by a two stage discharge process. The beneficial effect of free Lewis acid in the electrolyte was found to be greater for cells containing lower surface area carbon black cathodes.

1. Introduction

High rate lithium-thionyl chloride cells have been developed recently, mainly for military applications (e.g. propulsion). In these cells a salt, usually lithium tetrachloroaluminate is added to the thionyl chloride in order to increase the conductivity and to facilitate Li$^+$ ion transport. The optimum concentration of this salt is reported to be between 1.5 M and 1.8 M [1–3]. The overall cell discharge reaction is usually summarized as follows:

$$4\mathrm{Li} + 2\mathrm{SOCl_2} \longrightarrow 4\mathrm{LiCl} + \mathrm{SO_2} + \mathrm{S} \qquad (1)$$

High rate Li-SOCl$_2$ cells often have a reserve construction by which the electrolyte is contained in a separate compartment from the electrode stack and is admitted only as power is required. This arrangement prevents the build up of a thick, porous LiCl film on the lithium anode. Such a film often leads to severe voltage delay problems during the first few moments of discharge [4]. Reserve cells also favour the use of aluminium chloride, a Lewis acid (i.e. electron pair acceptor), in the electrolyte solution. Aluminium chloride behaves as a Lewis acid in thionyl chloride by increasing the relative concentration of SOCl$^+$.

$$\mathrm{AlCl_3} + \mathrm{SOCl_2} \longrightarrow [\mathrm{SOCl}][\mathrm{AlCl_4}] \longrightarrow \mathrm{SOCl^+} + \mathrm{AlCl_4^-} \qquad (2)$$

In this media chloride ions behave as Lewis bases, partaking in the following neutralization reaction:

$$\mathrm{Cl^-} + \mathrm{AlCl_3} \longrightarrow \mathrm{AlCl_4^-} \qquad (3)$$

Free AlCl$_3$ in the electrolyte has been found to substantially increase the cell capacity and the average discharge voltage [1, 5–7]. It is thought to achieve this by complexing with LiCl produced during the cell reaction, thereby delaying passivation of the cathode. The reserve design prevents AlCl$_3$ dissolving the protective LiCl layer on the anode, which would otherwise allow premature reaction between lithium and SOCl$_2$. Any capacity loss due to lithium corrosion and leakage currents during discharge is likely to be minimized for short cell lifetimes.

The concentrations of Lewis acids used are not often mentioned in the literature although Klinedinst [1, 5] found 3.0 M AlCl$_3$ most suitable for cells using thick carbon cathodes and 4.5 M AlCl$_3$ more effective for thinner ones (37 μm). The aim of this work was to comprehensively examine a range of electrolyte compositions with respect to performance in lithium-thionyl chloride cells. In this way the optimum electrolyte composition could be identified.

2. Experimental details

Details of cell design, electrolyte and anode preparation are as outlined in a previous communication [8]. The porous carbon cathodes were fabricated by slurrying a mixture of carbon and PTFE (10% w/w, ICI Plastics) in propanol and drying the mixture in an oven at 100° C. After powdering, the mixture was pressed to form cathodes. The carbon/PTFE loading was 20 mg cm^{-2}. This was twice as great for the thickest cathodes employed previously, thus being well in excess of the 'penetration depth' [8].

For most of these experiments the carbon used was Shawinigan acetylene black, although some of the work used Ketchenblack EC, a high surface area carbon black found to give a superior performance with 1.8 M LiAlCl$_4$ [9]. A glassy carbon disc (area 1.77 cm^2, le Carbone), was also used as a cathode for some of the cells discharged at low rates, in order to study electrolyte effects at a planar surface.

Experiments using cells containing a small lithium reference electrode showed that the potential between the anode and cathode was almost identical to that between the cathode and reference electrode. The lithium anode overpotential remained both low and approximately constant during the cathode reaction. Therefore for most of this work, a reference electrode was not employed.

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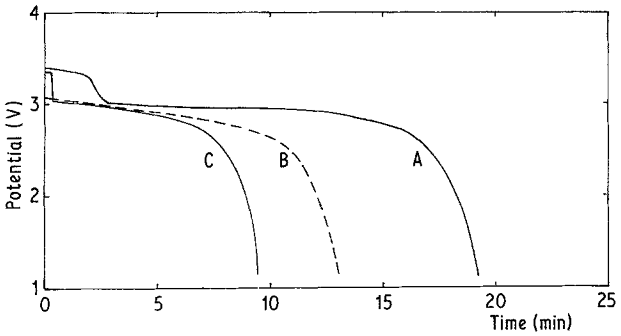

Fig. 1. Discharge profiles for Li/$SOCl_2$ cells at $50\,mA\,cm^{-2}$. A – 1.0 M $LiAlCl_4$ + 2.0 M $AlCl_3$, B – 1.8 M $LiAlCl_4$, C – 0.5 M $LiAlCl_3$ + 0.5 M $AlCl_3$.

3. Results and discussion

3.1. *Cell discharge in acid electrolyte*

Fig. 1 shows the improvement in Li-$SOCl_2$ cell performance which is possible using free Lewis acid electrolyte. A cell containing 1.0 M $LiAlCl_4$ + 2.0 M $AlCl_3$ gives a higher load voltage and greater reaction time than one containing neutral 1.8 M $LiAlCl_4$. Fig. 1 also shows that a low concentration of $AlCl_3$ (0.5 M) with LiCl initially present is not a viable strength of electrolyte salt. Our work has shown that overall concentrations of electrolytes (acid or neutral) which are much less than 1.8 M yield less favourable performance in high rate Li-$SOCl_2$ cells. The general shape of the transient obtained for acid electrolyte is similar to the one corresponding to the neutral electrolyte, except for the early stages where there is a clearly visible step, reportedly [1] due to the participation of $AlCl_3$ in the electrode process for lithium dissolution:

$$4\,Li + 2\,SOCl_2 \xrightarrow{AlCl_3} LiAlCl_4 + S + SO_2 \quad (4)$$

Although the duration of this step was usually between 90 and 120 seconds, the improvement in cell lifetime possible by using the electrolyte was greater than 5 min, at $50\,mA\,cm^{-2}$. It would therefore appear that this additional acid reaction is by itself insufficient to totally account for the increased capacity. Halving the volume of acid electrolyte used in the cells did not significantly affect the cell performance. Therefore the electrolyte is adequate for the reaction and not all of the free $AlCl_3$ is neutralized by LiCl produced during the discharge. This confirms theoretical calculations based on the results which show the cell lifetime could be extended further, should all of the free $AlCl_3$ present react as in equation 4. It must be borne in mind however that anode corrosion during discharge and the difficulty of exactly balancing (neutralizing) the electrolyte solution will make the optimization difficult.

3.2. *Optimization of the electrolyte*

Free Lewis acid electrolytes for Li-$SOCl_2$ cells are usually made from $AlCl_3$ which is partly neutralized by added LiCl. We considered it of interest to study the cell performance for a range of free $AlCl_3$ additions to a 1.0 M $LiAlCl_4$–$SOCl_2$ solution (Fig. 2); and then to examine the effect of various amounts of LiCl initially present in an electrolyte containing 3.0 M $AlCl_3$ (Figs 3a and 3b).

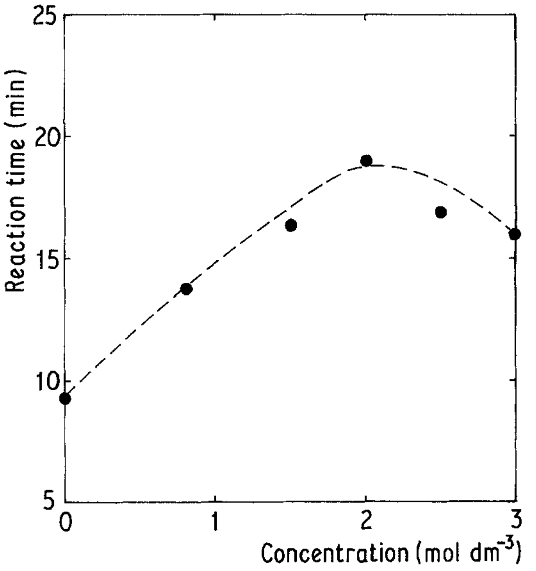

Fig. 2. Discharge time vs free $AlCl_3$ concentrations of a $SOCl_2$ solution containing 1.0 M $LiAlCl_4$. Current density = $50\,mA\,cm^{-2}$.

Fig. 2 shows that there is an improvement in cell reaction time as the amount of free $AlCl_3$ present increases, up to a maximum at about 2.0 M $AlCl_3$ (+ 1.0 M $AlCl_4$). Clearly this increase is due to more free acid being available to delay cathode pasivation by LiCl insulation and also the effects of lithium corrosion neutralizing $AlCl_3$ become less significant at higher acid strengths.

Increasing the free Lewis acid concentration beyond this maximum must somehow hinder the discharge process. Cells containing more than 4.0 M of Al^{3+} ions were often unable to sustain discharge. Thus for example it was impossible to discharge such cells at $100\,mA\,cm^{-2}$, attempts to do so resulted in rapid cell failure.

Such poor performance is a likely result of increased viscosity and reduced conductivity of $LiAlCl_4$–$SOCl_2$ solutions as $AlCl_3$ is added [1, 11]. This is probably due to the formation of ion pairs and triple ions such as $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ as well as more complex aggregates [11]. Such effects hinder the diffusion of lithium ions through the solution.

The optimum electrolyte composition identified by this present work is similar to that suggested for commercial use [12, 13].

Figs 3a and b show the effect of increasing amounts of LiCl initially present in the electrolyte solutions, based on 3.0 M $AlCl_3$. The influence of these solutions on cell performance at $50\,mA\,cm^{-2}$ and $100\,mA\,cm^{-2}$ are displayed. Pure acid electrolyte (3.0 M $AlCl_3$) was able to function well as an electrolyte as has been noted elsewhere [1, 5]. That it can sustain any discharge current at all, is by virtue of anode corrosion, which takes place prior to discharge to produce suf-

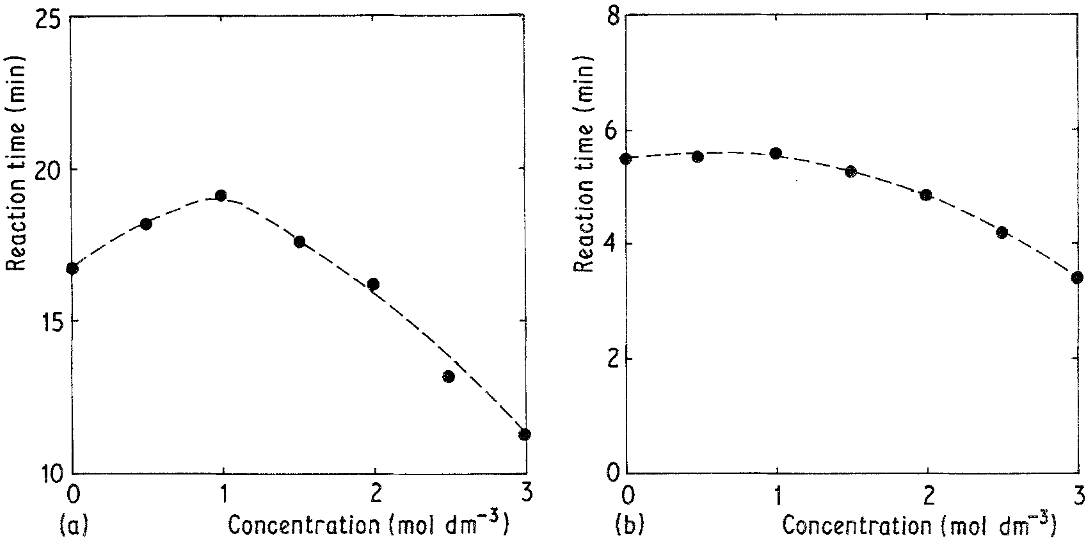

Fig. 3. (a) Discharge time as a function of LiCl concentration, for a solution based on 3.0 M AlCl$_3$–SOCl$_2$. Current density = 50 mA cm^{-2}. (b) as (a) but at 100 mA cm^{-2}.

ficient Li$^+$ and AlCl$_4^-$ ions to suitably raise the solution conductivity. The initial presence of up to 1.0 M LiCl in a 3.0 M AlCl$_3$–SOCl$_2$ based electrolyte does, however, extend the cell life, particularly at the lower of the two current densities investigated. Initial additions of LiCl to AlCl$_3$–SOCl$_2$ solutions rapidly increase the solution conductivity to give an optimum level for cell performance [14]. However, further additions of LiCl reduce the effectiveness of the acid electrolyte. The likely reasons for these observations include the reduction of free AlCl$_3$ in the electrolyte and an increase in the viscosity, resulting in a hindrance of the electrode reduction process. Experimental data have shown the viscosity of a 3.0 M AlCl$_3$–SOCl$_2$ solution increasing 2.5 times as 3.0 M LiCl is added [15].

3.3. *The effect of free Lewis acid on glassy carbon electrodes*

Although glassy carbon is not a practical electrode material for high rate Li–SOCl$_2$ cells, it was considered of interest to examine the effects of free Lewis acid electrolytes for cells containing such cathodes. Fig. 4 compares the discharge characteristics for cells containing glassy carbon cathodes with neutral and acid electrolyte. The improvement in cell discharge time and average load voltage using acid electrolyte is spectacular, particularly when compared to Fig. 1, where porous carbon was used. This improvement is due to LiCl from the cell discharge being accommodated in the acid electrolyte.

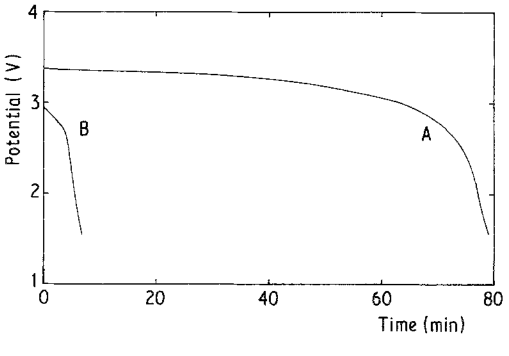

Fig. 4. Discharge profiles of cells containing glassy carbon cathodes comparing 1.8 M LiAlCl$_4$ (A) and 1.0 M LiAlCl$_4$ + 2.0 M AlCl$_3$ (B). Current density = 3 mA cm^{-2}.

At such low current densities (3 mA cm^{-2}), the rate of LiCl formation is relatively low, thus the solution capacity to accommodate this produce becomes significant. LiCl accommodation occurs either by precipitation on the surface followed by dissolution in the electrolyte, or by LiCl immediately reacting with the electrolyte solution to produce LiAlCl$_4$ as in equation 4. Redissolution of LiCl was shown to occur when a passivated glassy carbon cathode, left on open circuit 'rest' for half an hour, recovered some of its capacity for SOCl$_2$ reduction in 1.8 M LiAlCl$_4$ [8]. However such redissolution is less likely to take place in a polarized cell, making the process given by equation 4 more likely [16].

Faradaic charge calculations show that 5.85 mg of LiCl cm^{-2} of glassy carbon cathode are produced during the discharge process in acid electrolyte with 0.31 mg in neutral electrolyte. Thus in acid electrolyte about 5.54 mg of LiCl cm^{-2} of cathode is accommodated into the solution before the onset of passivation. This amount is much less than the maximum quantity of LiCl which is required to neutralize the AlCl$_3$ present. Considering the situation for a porous carbon cathode discharged at 50 mA cm^{-2}, 25 mg of LiCl cm^{-2} of cathode is produced, in acid electrolyte, with 17.5 mg in neutral electrolyte. Clearly in this case most of the LiCl produced in the cell reaction is accommodated in the pores of the cathode, making the enhancement due to free AlCl$_3$ proportionately less.

3.4. *Free Lewis effects with high surface area carbon cathodes*

So far, the cells with porous carbon cathodes, the widely used type of amorphous carbon, Shawinigan

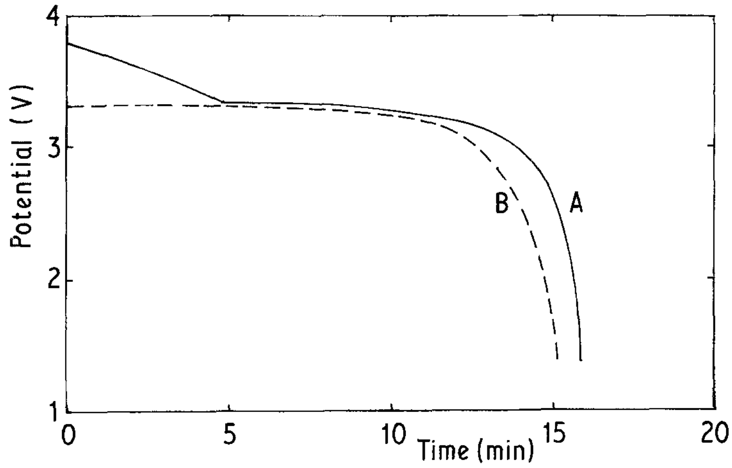

Fig. 5. Discharge profiles for cells containing cathodes made from Ketchenblack carbon; 1.8 M $LiAlCl_4$ (A) and 1.0 M $LiAlCl_4$ + 2.0 M $AlCl_3$ (B).

Acetylene Black (SAB) has been employed. However, other carbon blacks are also used in battery manufacture, one such being Ketchenblack EC (KEC). This particular carbon has a greater specific surface area and porosity than SAB and improves cell performance [9]. Fig. 5 shows discharge curves for cells containing KEC cathodes in acid and neutral electrolyte. Clearly in neutral electrolyte, cells with KEC cathodes are superior in performance to those with SAB cathodes, exhibiting an increase in both cell voltage and active reaction time. This improvement is particularly significant at elevated temperature [17]. However there is little further enhancement of capacity by using acid electrolyte in conjunction with KEC cathodes. Thus the free Lewis acid is not able to improve the performance in an identical manner to that for cells containing SAB cathodes.

The nature of the 'acid step' differs also. Discharge curves for cells containing SAB cathodes show distinct plateaux at about 3.3 V for about 90 s, before the potential falls rapidly over a period of about 30 s to about 3.0 V. For KEC cathodes the step is more like a voltage ramp between 3.55 and 3.2 V, which lasts for about 4 min. This suggests that equations 1 and 4 occur simultaneously during this period, the usual cell reaction becoming increasingly dominant.

Previous workers have found poor performances using acid electrolyte in cells containing catalysed carbon cathodes [12]. A 20% addition of iron to a SAB cathode was found to greatly increase cell capacity for cells containing neutral electrolyte. In acid electrolyte however the cell capacity was in fact less for the same cell containing neutral solution.

4. Conclusions

1. The well established improvement in $Li-SOCl_2$ cell performance obtained by the use of free Lewis acid electrolytes has been confirmed. The optimum concentration of Al^{3+} ion present in an electrolyte was found to be 3.0 M. For low concentrations of Al^{3+}, cathode passivation due to LiCl precipitation is favoured and lithium corrosion is enhanced. If concentrations of Al^{3+} much higher than 3.0 M are present, the reaction is hindered by excessive concentrations of large complex $AlCl_4^-$ based species.

2. For an electrolyte solution based on 3.0 M $AlCl_3$, the initial presence of LiCl enhances cell performance, due to an increase in solution conductance. The optimum initial concentration of LiCl under these conditions was found to be 1.0 M, increasing quantities of LiCl were found to decrease the cell performance.

3. The duration of the 'acid step' at the start of the cell discharge does not wholly account for the additional capacity obtained by using acid electrolye.

4. With low specific area carbons (glassy carbon in the limit) the beneficial effect of the free acid in the electrolyte is greatest. High specific surface carbons derive less benefit from free Lewis acid additions.

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