Li/SO$_2$ RECHARGEABLE CELLS CONTAINING ADDED BROMINE

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Summary

Hermetically sealed "C" sized Li/LiAlCl$_4$·6SO$_2$/carbon cells containing bromine or bromide as additives have been prepared and galvanostatically cycled at room temperature. The discharge and charging curves for these cells were compared with baseline cells. Cells containing 10% added bromine showed approximate 20% increase in initial cell discharge capacity, and their charging potentials were approximately 0.2 V lower than baseline cells. These performance improvements were observed even after extensive cell storage. Cells containing added bromide had poorer performance than did baseline cells.

Introduction

Rechargeable cells utilizing the Li/SO$_2$ couple have been actively investigated and reported in the patent [1 - 3] and scientific literature [4 - 9]. Cells constructed with a lithium anode, a porous carbon black cathode, and a highly conductive liquid electrolyte of the form LiAlCl$_4$–xSO$_2$ (where x = 3) have open circuit potentials of 3.2 V. Although this liquid LiAlCl$_4$–3SO$_2$ electrolyte is initially formed when SO$_2$ gas is passed over LiAlCl$_4$ powder, electrolytes with higher SO$_2$ concentrations can be readily prepared by diluting the initial solution with additional SO$_2$ [10, 11]. As SO$_2$ concentrations (and SO$_2$ vapor pressures) increase, electrolyte conductivity, lithium metal corrosion and electrolyte freezing point all decrease [6]. The Li/LiAlCl$_4$–6SO$_2$/C system is attractive due to its high energy density, discharge rate capability, cycle life, shelf life, and ability to sustain limited overcharge [6]. The theoretical energy density of the system is 540 W h kg^{-1}. Practical gravimetric and volumetric energy densities of a typical "C" size cell are 135 h kg^{-1} and 3.6 W h in^{-3}, respectively, at a discharge rate of 3 mA cm^{-2} [6].

Two limitations currently prevent active commercial development of this system. The first is cell safety. Cell charging potentials (typically in the

3.9 - 4.1 V range) oxidize $AlCl_4^-$ anions in the electrolyte to form molecular chlorine and aluminium chloride. Chlorine generated during overcharge has been shown to degrade polypropylene and, to a lesser extent, polyethylene separator materials. This degradation process promotes cell pressure build-up and loss of separator integrity, resulting in internal shorting and/or mild venting. The second problem is that cathode capacities in these rechargeable Li/SO_2 cells are typically one-half that of well known primary SO_2 cells using LiBr and acetonitrile. In contrast to an average discharge capacity of almost 4.0 A h for "C" sized Li/SO_2 primary cells, to highest capacities of sealed "C" sized Li/SO_2 cells using $LiAlCl_4-6SO_2$ electrolyte average only 1.7 ± 0.1 A h and decrease with repetitive cycling.

In previous papers [7 - 9], the effects of adding various halogens to $LiAlCl_4-3SO_2$ electrolyte were studied. Laboratory cells containing added molecular bromine were shown to have higher initial load voltages and cell charge potentials were 0.1 - 0.2 V lower than those for baseline cells not containing bromine. The explanation offered was that during cell discharge, bromine in the electrolyte is preferentially reduced first to bromide ions in the form of relatively insoluble lithium bromide. The potential for this reduction process lies higher than that for SO_2 reduction. Unreduced molecular bromine can slowly diffuse to the cathode and oxidize the normally formed insoluble discharge product. During cell charging, bromide ions now localized in the cathode (in the form of lithium bromide) can become oxidized back to molecular bromine which can then chemically oxidize the cathode discharge product. The choice of the Br_2/Br^- couple is deliberate. Redox potentials of Cl_2/Cl^- are in the same potential region as $AlCl_4^-$ oxidation and the corrosion problems mentioned above are still present, while potentials of I_2/I^- are too low and therefore unable to oxidize cell discharge products. Interhalogen compounds such as BrCl although not studied here, are also expected to perform the same function as Br_2.

The present paper explores hermetically sealed "C" sized cells containing added bromine and bromide. We show that previously observed improvements in overall cell capacity and lowered cell charging potentials are likewise observed in these scaled-up cells even after prolonged storage. Cells in the present study were constructed with higher vapor pressure $LiAlCl_4-6SO_2$ electrolyte containing either 0.1 M added molecular bromine or a mixture of 90% $LiAlCl_4-6SO_2$ and 10% $LiAlCl_3Br-6SO_2$. These cells are referred to as bromine and bromide cells, respectively. Although bromide-containing cells were not expected to have increased cell capacity, they were expected to have lower charging potentials due to Br^- oxidation.

Experimental

Duracell "C" sized cells were constructed with a 19 in. × 1.3 in. × 0.015 in. porous Ketjenblack carbon cathode, two layers of #K857 (Celanese Corp.) polyethylene separator and a 20 in. × 1.2 in. × 0.006 in.

lithium foil anode. Two modified electrolytes were used to fill the cells. The first was $LiAlCl_4$–$6SO_2$ electrolyte containing 0.1 M molecular Br_2. The second was a mixture of 90 mol% $LiAlCl_4$–$6SO_2$ and 10 mol% $LiAlCl_3Br$–$6SO_2$. This was prepared by mixing appropriate amounts of LiBr, LiCl and $AlCl_3$. Cells were filled with 16 - 19 g of the respective electrolytes, hermetically sealed, and then stored for 1 month at room temperature prior to initiating the actual discharge/charge cycling. During this time, the cell OCVs were monitored. Cells were then discharged at a 1.0 A rate to 2.0 V and charged at 0.1 A to a 3.9 V cutoff. Additional cells were stored for an additional month at room temperature and at 55 °C before being placed on room temperature discharge/charge cycles.

Results and discussion

Open circuit potentials of bromine- and bromide-containing cells were monitored as a function of time. Cells containing 0.1 M added Br_2 had initial OCVs of 3.52 V (reflecting the high potential of the Li/Br_2 couple) which gradually decreased over a 1 month room temperature storage period to 3.42 V. This may be due to some lithium anode corrosion. Cells containing 10% $LiAlCl_3Br$–$6SO_2$ electrolyte had initial OCVs of 3.19 V which increased to 3.29 V overnight at room temperature. The open circuit potential remained at 3.29 V during the one month stay. The 3.29 V open circuit potential is typical of baseline cells.

Figure 1 shows room temperature discharge curves, for various cycles, of $Li/LiAlCl_4$–$6SO_2/C$ cells, one containing 0.1 M Br_2 and one containing 10% $LiAlCl_3Br$–$6SO_2$. The average ampere hour capacity for the first four discharge cycles of the two cells containing added bromine were 1.98 ± 0.03 A h as compared with 1.7 ± 0.1 A h for baseline cells. This represents a 20% increase in initial cell capacity for bromine-containing cells. The two cells containing added bromide vented between the fifth and tenth cycles. However, since the venting was mild, it was not possible to determine exactly when the cells vented just by looking at the discharge/charge plots. The fact that venting had occurred was only detected visually by increased can corrosion in the vicinity of the vent. The vent became clogged with electrolyte salt and the cell continued to be cycled.

Although the presumed charge mechanism in both bromine- and bromide-containing cells involves bromide ions being oxidized to molecular bromine which then chemically oxidizes the discharge product, there is a major difference between the two cell types. During discharge of cells containing molecular bromine, the more electroactive bromine is first electrochemically reduced to bromide. The relatively insoluble LiBr formed is deposited in the cathode pores. As cell reduction proceeds and the small quantity of bromine diffusing towards the electrode is reduced, the normally formed cathode discharge products deposit in the cathode. The bromide (formed during discharge) and the normal cell discharge product are then
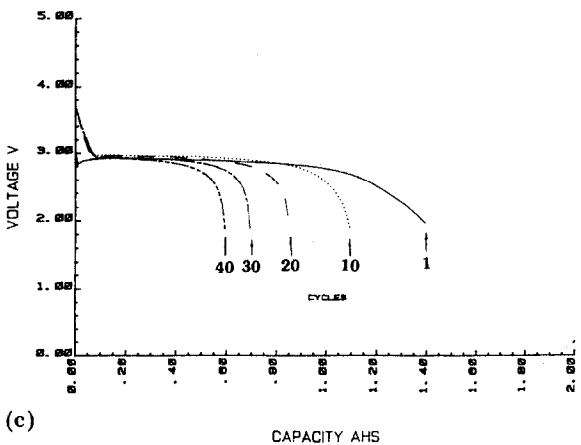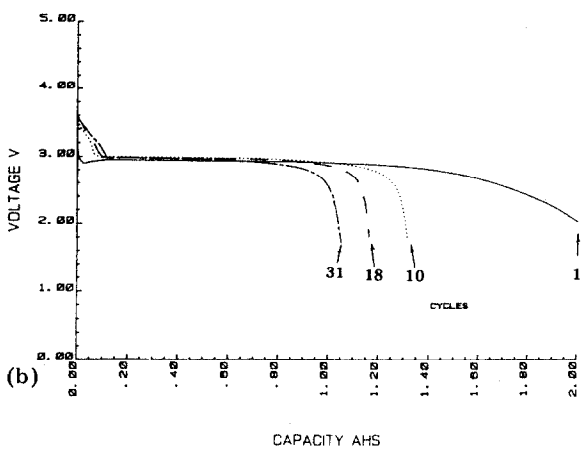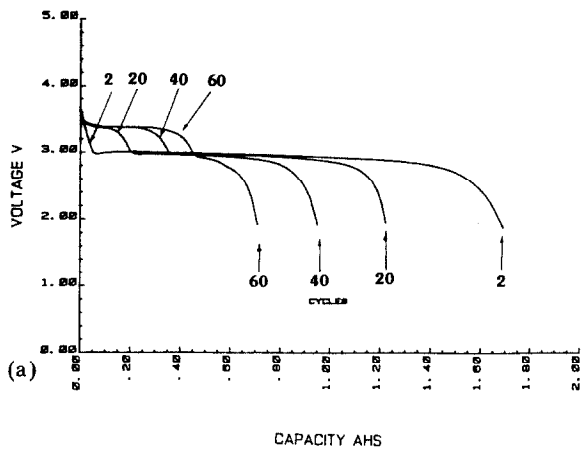
Fig. 1. Room temperature 1 A galvanostatic discharge (3 mA cm^{-2}) profiles for various cycles of hermetically sealed "C" sized cells. (a) Li/LiAlCl$_4$–6SO$_2$/C; (b) Li/LiAlCl$_4$–6SO$_2$ + 0.1 M Br$_2$/C; (c) Li/90 mol% LiAlCl$_4$–6SO$_2$ + 10 mol% LiAlCl$_3$Br–6SO$_2$/C.

necessarily in close proximity. During cell charging, Br^- is first oxidized to bromine. Since the formed bromine is located in/near the porous carbon cathode, it can chemically oxidize the cathode discharge product efficiently. In the process, bromine is chemically reduced back to bromide and the cycle continues. When all of the cathode discharge product and bromide have thus been chemically oxidized, the cell charging potential now rises due to $AlCl_4^-$ oxidation to $AlCl_3$ and Cl_2. An added advantage of bromine-containing cells is that while lithium is being redeposited on the anode during charge, the molecular bromine at the cathode formed may rapidly react with filamentary dendrites or mossy lithium and thus, in a way, prevent extensive lithium dendrites from forming. This may lead to cells with greater safety characteristics.

During discharge of bromide-containing cells, the normal cell discharge product is formed. However, during the charge cycle, Br^- (which we had hoped would be preferentially oxidized) is not localized near the cathode. It is distributed throughout the electrolyte in the form $LiAlCl_3Br-6SO_2$ and can only reach the cathode by relatively slow diffusion. Thus, incomplete discharge product oxidation would occur which would account for greater loss in cathode capacity as a function of discharge cycle in the bromide containing cells.

During charging of baseline cells, the potential immediately rises to 3.7 V and then slowly but gradually rises to 3.9 V. On the other hand, as shown in Fig. 2, during charging of bromine-containing cells, the potential rises to, and remains at, 3.6 V for a long period of time before rising
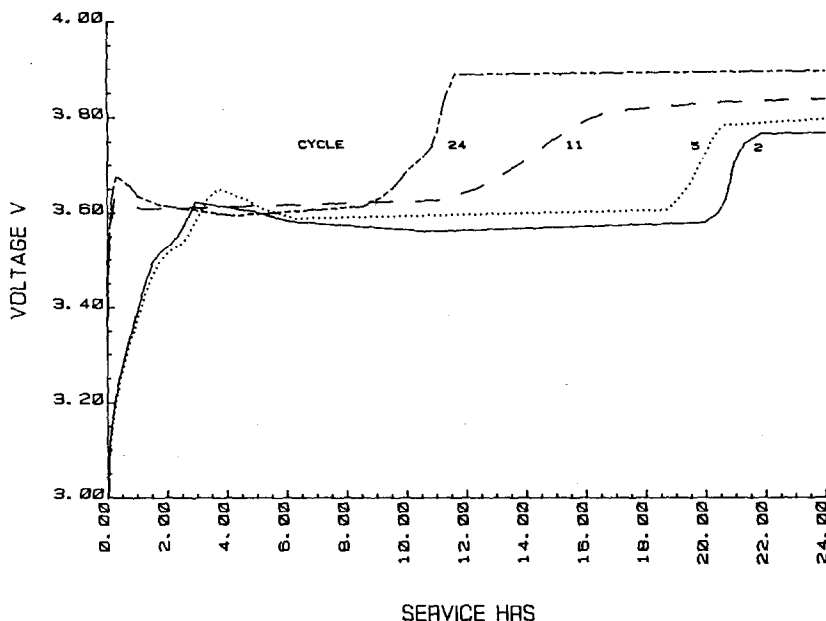

Fig. 2. Charging potentials (0.3 mA cm^{-2}) for "C" sized $Li/LiAlCl_4-6SO_2$ cells containing 0.1 M Br_2.

abruptly to 3.9 V. Lowering of charge potentials is due to oxidation of bromide to bromine. The potentials of the bromide-containing cells are similar to those of the bromine cells during charge.

Figure 3 shows discharge curves for bromine-containing cells that had been stored for 1 month at 55 °C. These cells showed no significant capacity loss and cycled with approximately the same efficiency as baseline cells. This implies that molecular bromine in the cell does not significantly disappear through reaction with the lithium anode. The lack of a significant higher voltage plateau may be attributable to the low bromine concentrations used. Capacity loss on extended continued cell cycling may be due to formation of $LiAlCl_3Br$ from LiBr discharge product and $AlCl_3$. As shown above, cells containing $LiAlCl_3Br$ in the electrolyte do not perform as well as baseline cells. Although, in laboratory cells, electrolytes with bromine concentrations up to 2 M have been prepared, sealed cells with such high bromine concentrations have not been prepared. Cell capacities and load potentials are expected to increase with higher bromine concentrations, but so may the corrosion rates.
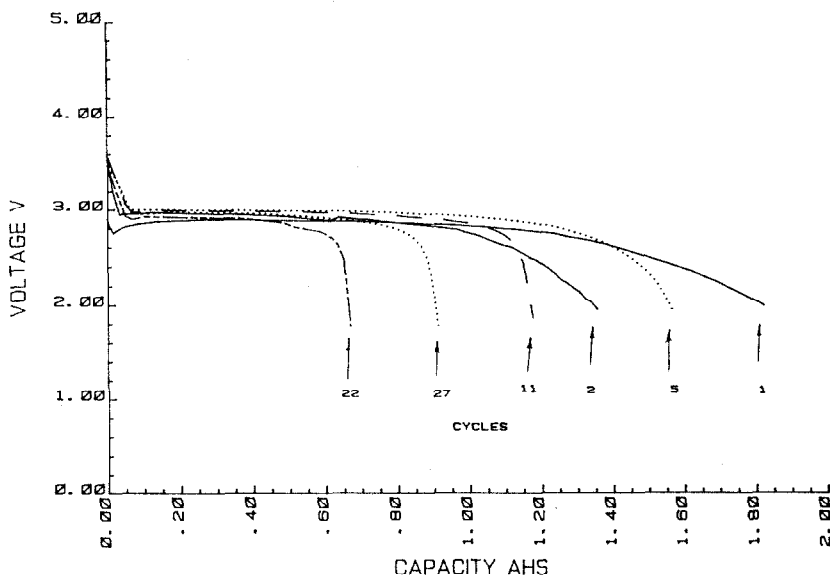

Fig. 3. Room temperature 1 A galvanostatic discharge (3 mA cm^{-2}) profiles for various cycles of hermetically sealed "C" sized Li/$LiAlCl_4$–6SO$_2$ cells that had been stored for 1 month at R.T. and 1 month at 55 °C prior to cycling.

Conclusion

Cycling behavior and storability of wound "C" size cells containing 0.1 M Br$_2$ and 10% LiAlCl$_3$Br additions to LiAlCl$_4$–6SO$_2$ electrolyte in

rechargeable Li/SO_2 cells was investigated. The Br_2-containing cells show a 20% increase in capacity on primary discharge over baseline cells. However, the capacity fades on repetitive cycles as it does with baseline cells. The bromide-containing cells offer no capacity advantage. On charging, the potential is initially 3.6 V then rises to the 3.9 V cutoff for both bromine- and bromide-containing cells as compared with 3.8 V charging potentials for baseline cells. Capacity loss on cycling is, however, greater for bromide containing-cells. Bromine-containing cells showed good storage capability with no significant capacity loss after one month storage at 55 °C. The safety impact of bromine addition has not yet been resolved.

Acknowledgements

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