

PERFORMANCE OF LITHIUM ALLOY/LITHIUM AND CALCIUM/ LITHIUM ANODES IN THIONYL CHLORIDE CELLS*

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Summary

A laminar composite anode construction comprising an inner metal completely surrounded by Li foil was studied as a means of obtaining an end-of-life indicator in a thionyl chloride cell. Inner metals of Ca, 14 - 2.9 at.% Ca in Li alloys, and 6.7 - 2.1 at.% Mg in Li alloys were evaluated. Discharge characteristics of cells using these sandwich anodes as well as cells containing the inner anode material alone were determined. It was concluded that cells made with inner anode materials of Ca and Ca/Li alloys containing more than 7 at.% Ca showed promise as a means of obtaining a reliable end-of-life indication.

Introduction

The critical nature of implantable medical devices requires that power sources for such devices provide adequate warning of the approach to battery end-of-life. This can be accomplished by monitoring either a gradual predictable approach to the elective replacement voltage or a drop to a detectably lower but still operational voltage. Soluble cathode cells normally show a rather abrupt drop from operating voltage to end-of-life voltage, and therefore their suitability as power sources for medical or other critical applications would be enhanced by a reliable end-of-life indicator.

Several approaches to this problem have been discussed in the literature. The use of two solid cathodes in combination [1], cosolvents in soluble cathode cells [2], mechanical end-of-life indicators [3], cathode limitation [4], and composite anode construction [5, 6] have all been described as potential end-of-life indicators in lithium cells. Our method was very similar to that described recently by Goebel and co-workers [5, 6] where approaching end-of-life was signalled by a drop in cell potential to that of the inner metal upon depletion of the outer Li layer.

Inner anode materials of Ca, 14 - 2.9 at.% Ca in Li alloys, and 6.7 - 2.1 at.% Mg in Li alloys surrounded by Li were studied. The behavior of Ca

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[7], Mg [8], and Li alloys [9] in thionyl chloride has been reported. The objectives of this work were to evaluate the concept of sandwich anodes to signal end-of-life in cell designs compatible with implantable devices, to determine the discharge characteristics of the inner-material anodes and sandwich-construction anodes in SOCl_2 cells, to model sandwich anode design with respect to the ratio of inner metal to Li required to give a voltage indication at a particular point in cell capacity, and to assess the reliability of the indication point.

Experimental

A rounded prismatic hermetically-sealed cell design of nominal dimensions 7 mm \times 45 mm \times 28 mm was chosen for this study. The basic cell design comprised a central flat sandwich anode placed between two flat carbon plate cathode current collectors welded to the inner case wall. The inner anode part was fabricated as a separate operation from the sandwich construction.

In cells containing Ca metal, 0.020 inch thick foil was cut and welded to one side of a nickel current collector. The Ca and Mg alloys were either manufactured in-house by melting appropriate stoichiometric amounts of the elements in a stainless steel crucible in a dry box equipped with a nitrogen removal catalyst under a helium atmosphere or obtained from Foote Mineral. They were pressed or rolled into foils 0.015 - 0.020 inches thick and cut and pressed onto an anode current collector to form the inner anode part.

Lithium foils from 0.010 to 0.022 inches thick were cut and pressed on either side of the inner part to completely seal the inner metallic element. All foils were scraped with polypropylene or a wire brush to expose a bright surface just prior to the pressing operations. Cells were also constructed using only the inner anode component.

All test cells were designed to be anode limited. The stoichiometric ratios of inner metal to lithium were varied by using foils of different thicknesses in order to characterize the reproducibility of the voltage drop from lithium potential to inner metal potential. Typical theoretical anode capacities were 0.4 A h Ca or 0.6 - 1.0 A h alloy and 1.2 or 1.6 A h Li.

Test cells were discharged under constant load at rates ranging from 815 to 3 $\mu\text{A}/\text{cm}^2$. Hundreds of cells were evaluated in this study. All discharge tests were conducted at 37 °C.

Diffusion in the Ca/Li and Ca alloy/Li systems was studied by forming anodes and sealing them under an argon atmosphere in hermetic cases. After six months of storage the anodes were removed, cross-sectioned, and studied by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The ability of the SEM/EDX technique to map the presence of calcium in the cross-sections allowed a qualitative determination of the extent of diffusion of calcium into the lithium anode during the storage period.

Results and discussion

Calcium has the advantage of showing a sharp indication point and a flat voltage plateau. Its disadvantages are that it must be welded rather than pressed onto an anode collector, and its rather high self-discharge leads to inefficient utilization.

Cells with an inner anode material of pure calcium showed a consistent drop in potential from 3.65 V to a voltage in the range 2.8 - 3.2 V. Figure 1 presents a typical result for a cell discharged at $50 \mu\text{A}/\text{cm}^2$. Cells discharged at current densities ranging from 50 to $850 \mu\text{A}/\text{cm}^2$ showed an indication point at 88% - 92% of total cell capacity delivered, indicating that the appearance of the voltage drop is reasonably independent of current drain in this range. The indication point was defined arbitrarily as the point at which the voltage fell below 3.5 V.

Calcium utilization in sandwich anodes as well as alone was approximately 50% at these discharge rates based on the theoretical capacity of the calcium in the anode construction. Destructive analysis of end-of-life cells revealed the anode current collector to be covered with a thick layer of white to yellow salts. Microcalorimetric measurements of Ca anode cells during discharge supported a prediction of nearly 50% corrosion of Ca. Utilization of Li was 85% - 90% both when alone and in Ca/Li laminate anodes.

Alloys of Ca and Li in the range studied offer the advantage of being extrudable and relatively easy to fabricate, and they offer voltage profiles similar to elemental Ca. The major disadvantage is the lowered melting point of the alloys, which may cause some concern over safety.

Results of the use of Li/Ca alloys varied depending on the alloy. At compositions below the eutectic point (7.5 at.% Ca) a rather indefinite and unreliable indication point was seen. For example, use of an inner alloy of composition 4.2 at.% Ca resulted in indication points which were dependent on the rate of discharge and varied from 95% to 79% of the total cell

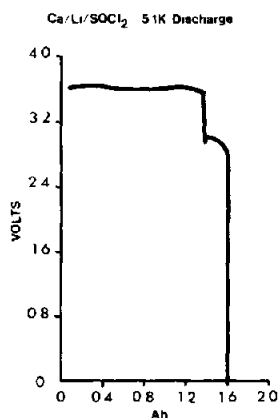


Fig 1 Typical discharge curve for sandwich-anode cell with calcium inner anode.

capacity delivered in the current density range 25 - 300 $\mu\text{A}/\text{cm}^2$. At alloy compositions of 7.5 and 14 at.% Ca more encouraging results were obtained. Figure 2 shows a typical discharge curve for a cell with an inner anode consisting of a 7.5 at.% Ca alloy. Both the 7.5 and the 14 at.% Ca alloys consistently showed indication points at $80\% \pm 3\%$ cell capacity over the current density range 25 - 300 $\mu\text{A}/\text{cm}^2$. Destructive analysis of cells indicated that the integrity of the sandwich anode was maintained during cell discharge as there were no unused pieces of metal foil found detached from the screen, only salts and a greyish powder surrounding the current collector.

The 14 - 2.9 at.% Ca alloys delivered 60% - 70% theoretical capacity, respectively, in cells containing alloy-only anodes. The theoretical capacity of the alloys was calculated by summing the theoretical capacities of Ca and Li in the alloy. It appears from the preliminary work on these systems that the higher the Ca content in the alloy the higher the corrosion. Self-discharge rates for the alloys were found to be between those of pure Li and pure Ca. Microcalorimetric measurements of the alloy cells also support predicted corrosion rates of 30% to 40% at low discharge rates.

Utilization of Ca alloys in sandwich-anode constructions was calculated to be of the order of 30% - 40% of the theoretical capacity of the material in the anode. It has been difficult to determine whether this is a function of the choice of indication point at 3.5 V or whether the alloy does corrode more severely or otherwise degrade in a sandwich construction. Other cut-off voltages were considered with no better success. A problem with the analysis is determining the end of Li discharge and the beginning of alloy discharge, as the initial portion of the alloy discharge occurs at the Li voltage.

It is recorded in the Li-Ca phase diagram that these alloys are composites of Li and Li_2Ca . The 33 at.% alloy corresponding to Li_2Ca discharges at the Ca voltage. One might expect discharge of the alloys in the range studied to show a plateau at the Li voltage followed by one at the Ca voltage corresponding to the relative amounts of Li and Li_2Ca in the alloy. However,

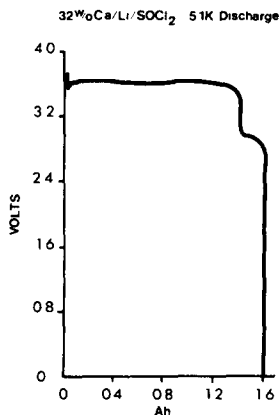


Fig 2 Typical discharge curve for sandwich-anode cell with inner anode of calcium/lithium alloy

this could be seen only at the lowest discharge rates. At the rates studied in this work, a greater percentage of the alloy discharged at the lower potential than would be expected from this model.

Alloys of Mg and L_1 offer relatively easier handling and manufacturing and a high melting point. The voltage plateau obtained from Mg and its alloys may, however, be too low for many practical applications.

Results of the use of L_1 and Mg alloys for reliable end-of-life indication were less encouraging than the results of the Ca systems. Appearance of the indication point was highly dependent on discharge rate for all alloy compositions studied. For example, cells with an inner anode material of composition 4.4 at.% Mg showed a rather sloping discharge profile ranging from 3.5 to 1.8 V at a discharge rate of $218 \mu\text{A}/\text{cm}^2$. At a rate of $24 \mu\text{A}/\text{cm}^2$ the discharge profile of such a cell showed a more abrupt drop to 1.8 V followed by a brief plateau at this point before a final drop to 0 V. Appearance of the indication point varied from 83% of cell capacity to 70% of cell capacity over the current density range $24 \mu\text{A}/\text{cm}^2$ - $200 \mu\text{A}/\text{cm}^2$ for the 4.4 at.% alloy, and similar wide variability was seen for other compositions studied.

Utilization of the Mg alloys was 80% - 85% in alloy-only cells and was calculated to be between 40% and 90% in sandwich cells. Analysis of Mg utilization in the sandwich construction was hampered by the same difficulties as in the Ca alloy systems.

Using SEM/EDX, studies of sandwich anodes with inner material of Ca and L_1 alloys showed that considerable diffusion had occurred at the interface after six months of storage at room temperature for the 4.2 at.% Ca alloy. Alloys with 7.5 and 14 at.% Ca showed much less diffusion even after subsequent heat treatment for 3 days at 130°C . Sandwich alloys using pure Ca showed negligible diffusion using the EDX mapping technique. This result for Ca may have been due to the presence of passivating oxides on the Ca surface prior to bonding.

Conclusions

This preliminary study shows that the use of the sandwich-anode concept to provide an end-of-life indicator for low-rate soluble cathode cells holds considerable promise. The integrity of the sandwich-anode construction was maintained throughout the cell life in all systems studied. No unused metal foils were found in end-of-life cells.

Cells with an inner anode material of pure Ca produced reliable indication points of $90\% \pm 2\%$ of cell capacity over a wide range of discharge rates. Likewise, cells with an inner anode material of 7.5 and 14 at.% Ca produced reliable indication points of $80\% \pm 3\%$ of cell capacity over an equally wide range of discharge rates.

Cells with an inner anode of 4.2 at.% Ca showed a variability in the appearance of the indication point with current drain. Cells using Mg alloys

as the inner anode material also showed such variability as well as a generally unsatisfactory lower plateau.

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