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REDUCTION OF CALCIUM CORROSION IN THIONYL CHLORIDE-BASED ELECTROLYTES

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Summary

Concern in respect of the safety of lithium oxyhalide cells has led to a search for alternative anode materials. A well-documented alternative is calcium; but this corrodes more rapidly than does lithium. This corrosion is a fundamental shortcoming of the calcium–thionyl chloride system and must be improved before exploitation is feasible.

We have demonstrated that modification of the electrolyte can result in a considerable decrease in the calcium corrosion rate.

Introduction

Over the past 25 years there has been a growing demand for compact, high performance, primary cells. Lithium-based battery systems have been shown to be versatile and have a very good performance on load. They have an excellent shelf life that can be in excess of 15 years. Unfortunately the low melting point of lithium (180 °C) and the tendency to deposit finely-divided, "mossy" lithium at the cathode on accidental reversal or overdischarge raise serious doubts about their safety. The adoption of calcium as an anode material eliminates both of these problems. First, calcium has a much higher melting point (839 °C) than lithium and so any problems traceable to a molten anode are eliminated. Second, Peled [1] has shown that it is very difficult to plate out calcium using electrolytes such as calcium tetrachloroaluminate, since the solid–electrolyte interface layer (SEI) presents a diode-type barrier to the flow of current in the reverse (charging) direction.

The principle drawback to the calcium system in oxyhalide electrolytes is that of corrosion of the calcium anode, which reduces the shelf life to

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about 1.5 - 2 years [2]. For the calcium-anode system to become competitive with lithium technology the open circuit corrosion problem will have to be overcome.

Peled *et al.* [3] have shown that a calcium–thionyl chloride cell exhibits a volumetric energy density at low rates close to that of a lithium–sulphur dioxide cell. In addition, it can deliver a similar continuous current to that permitted for the lithium cell, which has to work under severe restrictions and within safety limits. They conclude that the calcium–thionyl chloride system is a very promising candidate for high power, multicell batteries.

Higgins and Cloyd [4] demonstrated, by spike penetration tests, that the calcium–thionyl chloride system was safe up to cell sizes of 1800 W h. They stated that an accidental penetration of the cell would cause no damage, other than that expected from exposure to electrolyte fumes, to an object only a few inches away.

In addition to evaluating the calcium–thionyl chloride couple for use as a dry reserve system, we have investigated electrolyte modifications with a view to increasing the shelf life of a wet battery to a level such that commercial exploitation becomes viable.

We have carried out corrosion experiments on discs cut from calcium foil. These were stored in an excess of electrolyte to provide a more aggressive environment than that found in the more normal "electrolyte-starved" configuration of a commercial cell. The electrolyte used throughout was 1.0 M calcium tetrachloroaluminate in thionyl chloride. It was found that the addition of sulphur dioxide to the electrolyte dramatically reduced the corrosion of the calcium anode. Sulphur dioxide had been added to the electrolyte previously to improve cell performance. Peled [5] reported that the addition of 10% (v/v) of sulphur dioxide to the electrolyte increased conductivity by 40 - 50%. We found in our experiments that a saturated electrolyte solution was achieved at around 12% (v/v) sulphur dioxide. We have shown previously [6] that the addition of 12% (v/v) of sulphur dioxide produced about a 400% increase in discharge time and that the cell failure mode switched from the calcium anode to the carbon current collector. The addition of sulphur dioxide also decreases both the viscosity and the density of the electrolyte [6].

Experimental

Calcium metal foil (New Met) was punched into discs which were then polished mechanically in a dry air (10 - 20 ppm water) glove box. The discs were then degreased by stirring in acetone (3 - 4 min) before being individually weighed and placed in either the electrolyte containing sulphur dioxide or a control of normal 1.0 M electrolyte.

We chose 1.0 M Ca $(AlCl_4)_2$ for our calcium corrosion studies at room temperature. This was a compromise, since Meitav and Peled [7] have shown that a 0.7 M electrolyte gave a good performance at lower temperatures,

whereas for higher temperatures they recommended a 1.3 M electrolyte. At electrolyte concentrations above 1.3 M the conductivity has been shown to decrease [8] due to ion pairing and the increased viscosity of the solution.

The electrolyte was prepared by dissolving aluminium chloride in thionyl chloride, followed by calcium chloride in 10% excess to ensure electrolyte neutrality. Without the excess calcium chloride there was a danger of forming free Lewis acid. The mixture was then refluxed for 6 h before being returned to the dry box for filtration to remove the excess calcium chloride. Staniewicz [9] suggested that any excess aluminium chloride might react directly with the calcium metal anode.

$$3Ca + 2AlCl_3 \longrightarrow 2Al + 3CaCl_2$$
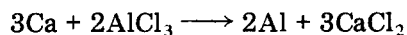
This would be in addition to the aluminium chloride attacking the calcium chloride of the protective SEI to form the tetrachloroaluminate, thereby removing it and leaving the bare metal open to attack by the solvent. When anode samples were removed from the electrolyte they were washed three times in pure thionyl chloride, then dried, and stored in a separate electrolyte-free dry box in sealed containers before being photographed. This ensured that corrosion did not continue after the time of measurement.

It was decided to follow the degree of corrosion by using acetone to preferentially dissolve the calcium chloride SEI from the calcium metal. The acetone was purified and dried using a proceedure outlined by Vogel [10] which involved refluxing with potassium permanganate then drying over potassium carbonate before being fractionated using a Vega column. The acetone was then stored over 4 Å molecular sieves in the dry box. Acetone was the solvent of choice since earlier tests had shown that calcium metal had no measureable solubility, whereas calcium chloride and the higher oxides of sulphur exhibit finite solubility. (The higher oxides of sulphur would be expected to be present as air oxidation products of any dithionite produced in the corrosion process.) The discs were periodically removed from the solvent, dried, and weighed. This process was repeated until no weight change could be detected.

Discs of calcium prepared as outlined above were placed in either the modified or the unmodified electrolyte and their weight losses were recorded. The results are shown in Fig. 1.

Results and discussion

As can be seen, there is a marked difference in the amount of corrosion taking place in each of the electrolytes. The sample in the unmodified electrolyte corroded to a greater extent after 96 h than did that in the modified electrolyte after 1944 h. In addition, the difference in the gradient of each line suggests that the relative reduction of corrosion in the sulphur dioxide-containing sample will be even greater at longer times.
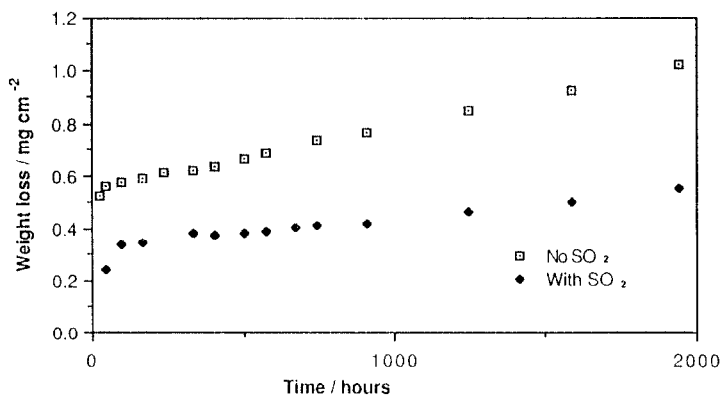
Fig. 1. Graph contrasting weight losses of calcium discs. ⊡, unmodified; ◆, modified electrolytes. The weight losses were obtained by preferentially dissolving the calcium chloride SEI in acetone.

We also studied the corrosion with, and without, sulphur dioxide by means of electron microscopy. Results from this investigation support those obtained from the weight loss experiments and indicate that in the normal electrolyte the SEI appears to have an open, porous, corrosion layer. This allows continuous attack of the underlying metal by the electrolyte, as may be seen in Fig. 2.

By contrast, the modified electrolyte appears to induce a more compact, tenacious, film (Fig. 3) which seems to protect the bare metal from the worst corrosive effects of the electrolyte. Both samples were corroded over 101 days. The micrographs are at ×1000 magnification with the black bar signifying 10 μm. These, and other micrographs, show that the surface of the calcium is changed from the onset of corrosion; the porous layer of the SEI can be seen to be developing in a manner different from that of the SEI establishing itself and then being modified by the sulphur dioxide in the
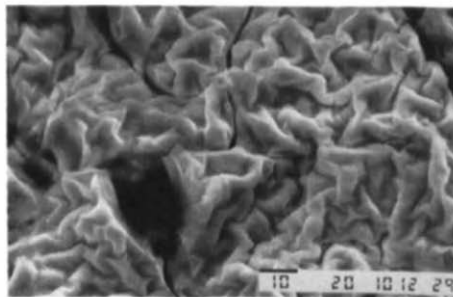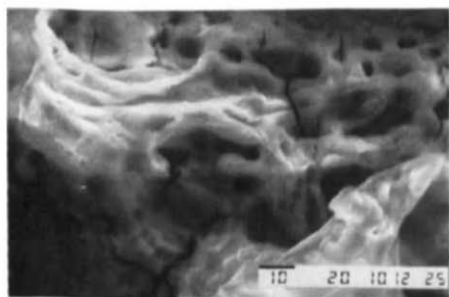

Fig. 2. SEM of calcium surface (×1000) after 101 days of corrosion in an unmodified 1.0 M calcium tetrachloroaluminate, thionyl chloride electrolyte.

Fig. 3. SEM of calcium surface (×1000) after 101 days of corrosion in a modified 1.0 M calcium tetrachloroaluminate, thionyl chloride electrolyte.

electrolyte. This observation is in agreement with the weight loss data, since a difference in weight loss is apparent from the start of the experiment.

Conclusions

As can be seen from our results, after a period of 3 months we have almost halved the calcium corrosion by reducing it from 1.02 mg cm^{-2} in an unmodified electrolyte to 0.55 mg cm^{-2} in an electrolyte modified by the addition of sulphur dioxide to saturation at atmospheric pressure (approximately 12% (v/v)). Both weight loss experiments and scanning electron micrographs confirmed that the addition of sulphur dioxiode modifies the corrosion process of the calcium. This can be seen in the changed physical appearance of the surface film. ESCA analysis showed no appreciable difference in the sulphur content of either of the electrolyte systems, suggesting that the corrosion product in both electrolytes is primarily calcium chloride.

A later paper will show electrochemical data contrasting this information with on load corrosion and discharge performance studies undertaken with, and without, the addition of sulphur dioxide to the electrolyte.

Acknowledgements

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