

PERFORMANCE OF CALCIUM/THIONYL CHLORIDE CELLS CONTAINING $\text{Sr}(\text{AlCl}_4)_2$ ELECTROLYTE

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Summary

Room temperature (RT) and -30°C discharges of hermetically sealed, D-sized calcium thionyl chloride cells, prepared with $\text{Sr}(\text{AlCl}_4)_2$ electrolyte containing 20% added SO_2 , were carried out on cells after storage for various lengths of time at R.T. and at 55°C . The performance of these cells was considerably poorer than that typically observed for Li/SO_2 cells.

Introduction

Calcium/thionyl chloride cells have long been investigated by various research groups as a safer substitute for Li/SO_2 primary cells for high rate and high energy density applications [1 - 9]. Calcium-based cells are expected to be more abuse resistant during forced charging or overdischarge because of the difficulty in plating metallic calcium from nonaqueous electrolytes [7]. The high melting point of calcium implies that incineration should have a diminished impact on safety. Problems facing full development of this technology include shorter cathode life (when compared with analogous Li/SOCl_2 cells) and excessive calcium anode corrosion in $\text{Ca}(\text{AlCl}_4)_2$ /thionyl chloride electrolyte. Recent efforts by Wade [10] employing various additives and pretreatments *in situ* to provide a protective coating for the calcium anode were unsuccessful.

In a series of papers, Walker *et al.* [3, 4] showed that the underload voltage and discharge capacity of carbon cathodes in Ca/SOCl_2 cells could be dramatically improved by fabricating porous cathodes from a blend of high- and low-surface area carbon blacks. Also, use of SO_2 as a cosolvent was shown to improve cell capacity dramatically and to raise cell load voltages. Performance improvements observed in calcium oxyhalide cells with added SO_2 were subsequently explained via NMR [5] and Raman [6] spectra as being due to preferential solvation of Ca^{2+} by SO_2 . Using this model, Walker

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[8] explained the poor low temperature performance in Ca/SOCl₂ cells and suggested methods to alleviate it.

Recently, Peled [7, 11 - 13] showed that strontium or barium tetrachloroaluminate electrolyte (*i.e.*, Sr(AlCl₄)₂ or Ba(AlCl₄)₂) in thionyl chloride provides calcium with better resistance to corrosion than does Ca(AlCl₄)₂ electrolyte. These concepts were investigated by Staniewicz *et al.* [9]. It appeared that use of strontium-based electrolytes would be sufficient to make practical Ca/SOCl₂ cells a reality.

In this paper we present performance data of hermetically sealed, D-sized calcium-thionyl chloride cells employing cathodes made from a blend of high- and low-surface-area carbon blacks, and an electrolyte containing Sr(AlCl₄)₂ salt together with 20% SO₂. We thus evaluated whether these collective improvements increased the feasibility of commercialization of full sized Ca/SOCl₂ cells.

Experimental

D-size Ca/SOCl₂ cells containing *strontium*-based electrolyte were constructed and delivered by SAFT America, Cockeysville, MD, as part of a final deliverable item under a U.S. Army Research Contract. Time and financial restraints did not permit SAFT to prepare control cells containing *calcium*-based electrolyte. These cells were tested after being stored for either one month at room temperature, four months at room temperature, or two months at room temperature and one month at 55 °C. Cells were fabricated using 0.90 M Sr(AlCl₄)₂-SOCl₂ electrolyte which was diluted to 0.75 M by the addition of 20% SO₂. The 237 cm², 80% porous carbon cathodes (62.2 cm × 3.8 cm × 0.076 cm) with a nickel center tab were made from a blend of 75% high surface area (Black Pearls 2000), and 25% low surface area (YS Carbon) carbon black containing 12% Teflon emulsion as binder. A calcium foil anode (58.4 cm × 3.8 cm × 0.025 cm) was attached to a nickel foil current collector and scraped prior to use. Scimat 200/80 Tefzel separator (80% porous) was used since ordinary glass separators tend to tear and short from roughened edges of calcium foil. These hermetically sealed D size cells weighed approximately 107 g.

Results and discussion

Discharge currents on these cells correspond to approximately 1, 2 and 4 mA cm⁻² for the 0.5, 1.0, and 2.0 A discharges, respectively, considering utilization of both sides of the anode and cathode. Due to the small number of cells available, only a few were tested for given storage conditions, discharge temperature, and current density.

*(i) Discharge of cells stored for one month at RT**(a) RT discharge*

Table 1 lists data for cells that were stored for one month at RT. The observed 5.6 A h average capacity is considerably lower than the 8 A h capacity found with fresh Ca/SOCl₂ cells [9] or even stored D-size Li/SO₂ cells. The diminished capacity in these stored Ca/SOCl₂ cells implies that the calcium anode was becoming increasingly corroded.

TABLE 1

Summary of performance tests of D-size cells stored for one month at RT

Discharge load (A)	Temp. (°C)	Average voltage (V)	Capacity (A h)	Voltage delay (s)
1.0	25	2.5	5.6	<3
2.0	25	2.5	5.6	<3
1.0	-30	2.1	3.5	<60
2.0	-30	2.0	2.0	<180

(b) -30 °C discharge

Walker [8] has shown that Ca/SOCl₂ cell polarization at -30 °C is almost solely determined by polarization of the calcium anode. Under constant current discharge these cells showed severe voltage polarization, and cell potentials fell below 0.0 V.

Upon applying a 1 A drain at -30 °C, cell potentials fell to approximately -0.75 V. Within 3 s cell potentials had risen to close to 2.0 V, fell back to approximately 1.9 V, and then slowly rose again over a period of 1 min to 2.0 V. Average load voltages were approximately 2.1 V. Capacities for the times that cells operated above 2.0 V were approximately 3.35 A h. These cells, discharged at -30 °C, had lost approximately 40% of their capacity compared with those at 25 °C. These results, obtained in an air circulating bath, are worst case results. They reflect the actual cell performance which would take place at -30 °C.

*(ii) Discharge of cells stored for four months at RT**(a) RT discharge*

Table 2 shows that cells stored for 14 weeks at RT and then discharged at 1 A had poor and variable capacities. At the onset of discharge, the potential rapidly fell to a low value then rose to a value above 2.0 V. During discharge, these cells showed frequent voltage dips towards 0 V which resembled cell shorting. The exact reason for these voltage excursions is not known.

TABLE 2

Summary of performance tests on D-size cells stored for 14 weeks at RT then discharged at 1 A at RT

Start voltage (V)	Low voltage (V)	Time to 2.0 V (s)	A h capacity
2.71	1.99	<2	0.01
2.70	2.36	—	4.18
2.74	2.39	—	5.09
2.71	1.77	<5	2.88
2.70	2.47	—	4.01
2.85	2.37	—	3.07

(b) -30°C discharge

Table 3 shows performance data for cells stored for 4 months at room temperature and then discharged at -30°C , at either 0.5 A or 1.0 A. Many of these cells exhibited startup delays. Two cells vented under the 0.5 A discharge. One cell vented while the cell potential was at 1.78 V, the other cell vented when it was driven into reversal; venting occurred at -9.8 V. Capacities for these cells were no better than 3 A h.

TABLE 3

Summary of performance tests of D-sized cells stored for 4 months at RT and discharged at -30°C

Load current (A)	Start voltage (V)	Low voltage (V)	Time to 2 V (s)	A h capacity	Comments
0.5	2.74	2.50	—	0.98	Vented at 1.78 V
0.5	2.81	2.55	—	3.06	Vented 3 h after being driven below 2.0 V. Potential at -9.8 V
0.5	2.78	2.52	—	2.73	
0.5	2.45	1.70	8	2.23	
0.5	2.43	1.74	(9 h)	—	Potential never reached 2.0 V.
1.0	2.50	1.10	36	3.03	Ran 2 h past 2.0 V to -9.6 V. No incident.
1.0	2.46	1.40	—	—	
1.0	2.46	1.59	15	2.58	
1.0	2.47	1.70	15	0.60	
1.0	2.46	1.58	15	2.73	Ran 1.5 h past 2.0 V to -9.9 V. No incident.

(iii) Discharge of cells stored for two months at RT and one month at 55 °C.

(a) RT

A generally accepted rule of thumb is that 1 month storage at 55 °C is approximately equivalent to 8 months of RT storage. Thus, tests of cells stored for two months at RT followed by one month at 55 °C corresponds to the equivalent of 10 months storage at RT. Seven cells stored under these conditions had low and varied OCVs. Three of these cells could not support 1 A loads when discharged at RT; potentials fell to below 1.0 V or even to negative potentials. Under a 2 A drain, only one of the 4 other cells had any capacity, and that cell gave only 1.1 A h to a 2.0 V cutoff. Potentials of the other three cells rapidly fell below 0 V. Our results show that Ca/SOCl₂ cells, prepared as described, do not have a projected shelf life greater than 10 months.

Conclusions

D-size calcium-thionyl chloride cells fabricated with (i) Sr(AlCl₄)₂-based electrolyte containing 20% added SO₂ and (ii) carbon cathodes made from a blend of high- and low-surface-area carbons, have poor capacities, even under low drains, at both room temperature and -30 °C. They appear to have a shelf life of less than 10 months.

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