

## COMPARISON OF THE BEHAVIOR OF THE Li/SOCl<sub>2</sub> AND Ca/SOCl<sub>2</sub> SYSTEMS AT ELEVATED TEMPERATURES

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### Summary

The behaviors of Li/SOCl<sub>2</sub> and Ca/SOCl<sub>2</sub> systems at temperatures up to 200 °C were compared. The results indicate that at temperatures higher than 100 °C the electrical performance of the Ca/SOCl<sub>2</sub> system is inferior to the Li/SOCl<sub>2</sub> system as a result of excessive calcium anode corrosion either during storage or during discharge. The CaCl<sub>2</sub> surface layer consists of aggregates of crystallites of considerably smaller size than that of the LiCl on the lithium surface. The abnormally high resistance of the CaCl<sub>2</sub> surface layer determines the OCV value as well as the poor load voltage at higher temperatures. By contrast, the Li/SOCl<sub>2</sub> system exhibits lower self-discharge and good voltage stability at temperatures up to 200 °C.

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### Introduction

The feasibility of continuously discharging Li/SOCl<sub>2</sub> cells at temperatures higher than the melting point of the lithium anode (180.5 °C) has recently been demonstrated [1]. Thus, thermal runaway of the Li/SOCl<sub>2</sub> system is not caused by the existence of molten lithium, as it is kinetically protected in this state as well as in the solid state. Safe operation of Li/SOCl<sub>2</sub> cells at temperatures exceeding the melting point of the lithium metal was obtained by confining the molten lithium to prevent it from flowing either to the carbon current collector or to the positive terminal. An internal short circuit caused by molten lithium, at 200 °C for instance, may cause the cell temperature to rise to the limit where thermal runaway can occur. However, the shock and vibration conditions in practical applications at temperatures exceeding the melting point of lithium prevent its containment. Such applications exist on oil and geothermal energy drilling rigs. The use of a high melting point lithium-magnesium alloy [2] or calcium metal [3] as the negative electrode has recently been suggested for applications requiring

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operating temperatures higher than the lithium melting point. The possibility of using a calcium anode, with its high melting point of 838 °C, at temperatures above 180 °C has not been confirmed, mainly because of electrolyte leakage through the cell seal [3].

The purpose of this study is to compare the electrical performance of Ca/SOCl<sub>2</sub> with Li/SOCl<sub>2</sub> cells using LiAlCl<sub>4</sub> as the ionic conducting salt at temperatures up to 200 °C (approximately 120 °C above the boiling point of the cell electrolyte at atmospheric pressure).

## Experimental

Electrical discharge measurements were conducted in a number of specially designed, hermetically-sealed, C-size cells. The cell, with a thick-walled stainless steel case to withstand the high-pressure of a 1.2 M solution of LiAlCl<sub>4</sub> in SOCl<sub>2</sub> at 200 °C (at least 40 atm), was a low-rate version, with an internally located bobbin-type, carbon current collector [4]. The apparent surface area (25 cm<sup>2</sup>) and capacity (5.0 A h) were the same for both the lithium and the calcium anode. While lithium metal was pressed onto the stainless steel woven wire current collector, the calcium metal was spot welded to it. Both anode stacks were spot welded to the can through an exposed area of the woven wire current collector. The anode was separated from the cylindrical, PTFE-bonded carbon bobbin by two layers of non-woven glass separator. To prevent the free flow of molten lithium at temperatures above 180 °C, the carbon current collector was made longer than the lithium anode and was held tightly against it.

Rolled calcium metal (99.8%), 0.89 mm thick was obtained from Pfizer. It was first mechanically abraded to remove the oxide coating, degreased in dichloroethane, and annealed at 500 °C under an argon atmosphere for 2 h. It was then chemically treated with dilute nitric acid in dimethylformamide (DMF) until a bright, metallic surface was obtained, and finally rinsed in pure DMF according to the method of McManis *et al.* [5]. The calcium metal was analysed using a combination of inductive-coupled plasma (ICP) and atomic absorption spectroscopy (AA). The impurity concentrations (in wt.%) found were: 0.26, Mg; 0.14, Al; 0.003, Fe; <0.001, Ni; <0.001, Cu; 0.001 Na; 0.002, K; 0.011, Si. By comparison with the lithium metal used in the present work, calcium metal has appreciably higher concentrations of Mg, Al, and Si. A solution of 1.2 M LiAlCl<sub>4</sub> in thionyl chloride served as an electrolyte for both lithium and calcium cells. The lithium salt was preferred to the more conventional calcium salt since it has been reported [6] that an excess of SO<sub>2</sub> causes precipitation of CaCl<sub>2</sub> while turning the electrolyte acidic. Excess SO<sub>2</sub> is formed either during discharge or during thermal decomposition of SOCl<sub>2</sub> at elevated temperatures [1].

Each calcium specimen for scanning electron microscopy (SEM) was mounted onto a stainless steel screen and stored in an hermetically-sealed

stainless steel cell can. The configuration of the assembly and the experimental procedure for handling the specimens have been described previously [4].

## Results and discussion

Lithium/SOCl<sub>2</sub> and Ca/SOCl<sub>2</sub> systems can be discharged over a wide temperature range. The cells used were at least 2 months old. Prior to discharge, cells were equilibrated at the discharge temperature for 16 h. Both cell types were anode limited and had equal anode capacities of 5.0 A h and an equal apparent surface area of 25 cm<sup>2</sup> (C-size cells). Thus, the calcium anode thickness had to be 50% greater than that of the lithium anode. These constraints did not permit optimization of cell capacity.

Since the useful cell voltage ranged from 3.4 V to 2.0 V depending on system type, discharge temperature, and discharge rate, capacities were reported to a 2.0 V cut-off.

### *Effect of discharge temperature*

The effect which the discharge temperature has on the cell discharge characteristics in the 25 - 200 °C range can be seen in Figs. 1 and 2 for Li/SOCl<sub>2</sub> and Ca/SOCl<sub>2</sub> cells, respectively. The cells were discharged at 94 Ω, corresponding to approximately 1.3 mA cm<sup>-2</sup>. The capacities and corresponding capacity efficiencies relative to the theoretical anode capacity (5.0 A h) for both systems are summarized in Table 1.

The curves in Fig. 1 show that the Li/SOCl<sub>2</sub> system can operate efficiently within the 25 - 200 °C temperature range. The cells exhibit good voltage stability, and the load voltage remains practically constant between 25 °C and 175 °C. At 200 °C the operating voltage is slightly reduced from 3.4 V to 3.0 V, probably due to corrosion reactions [4]. By contrast, Fig. 2

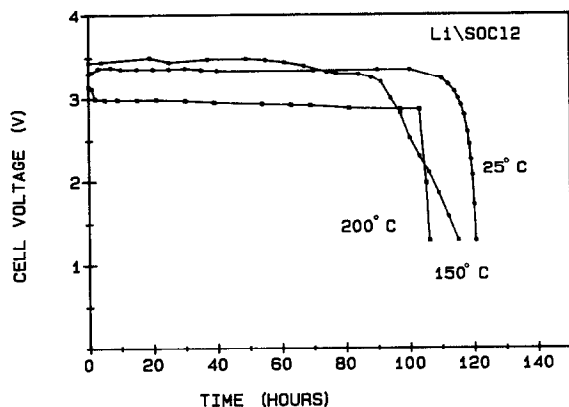


Fig. 1. Effect of discharge temperature on the discharge characteristics of C-size Li/SOCl<sub>2</sub> cells discharged at 94 Ω. The OCV of the cells is not shown.

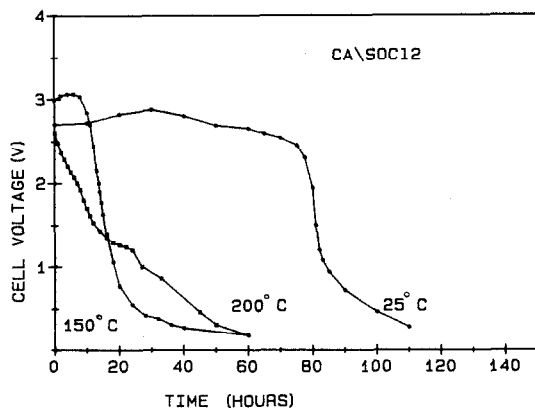


Fig. 2. Effect of discharge temperature on the discharge characteristics of C-size Ca/SOCl<sub>2</sub> cells discharged at 94 Ω. The OCV of the cells is not shown.

TABLE 1

Average capacity and coulombic efficiency (relative to anode capacity), at several temperatures, for Li/SOCl<sub>2</sub> and Ca/SOCl<sub>2</sub> cells discharged at 94 Ω

Discharge temperature (°C)	Li/SOCl <sub>2</sub>		Ca/SOCl <sub>2</sub>	
	Capacity (A h)	Efficiency (%)	Capacity (A h)	Efficiency (%)
25	4.2	84	2.4	48
150	3.8	77	0.45	9
175	3.9	78	0.44	8
200	3.4	68	0.19	4

shows severe degradation of the Ca/SOCl<sub>2</sub> system performance when discharging above 100 °C. The degradation includes capacity reduction from 2.4 A h at 25 °C to 0.4 A h at 150 °C, accompanied by a corresponding reduction in operating voltage and in voltage stability. There is no substantial capacity increase, even for a cut-off voltage as low as 0.5 V (Fig. 2). This capacity degradation at elevated temperatures may be due to a relatively high self-discharge which either consumes a significant amount of the available calcium metal, or forms a high resistance surface layer.

#### Effect of discharge rate

Typical discharge curves for the Ca/SOCl<sub>2</sub> system at 200 °C at 94 Ω and 700 Ω (corresponding to approximately 1 and 0.1 mA cm<sup>-2</sup>, respectively) are given in Fig. 3. Apart from a small increase in capacity at the higher load, the cell still exhibits a very low coulombic efficiency. Between 94 Ω and 700 Ω the highest capacity was only 0.33 A h at 150 Ω. Similar behavior was also recorded at temperatures of 150 °C and 175 °C.

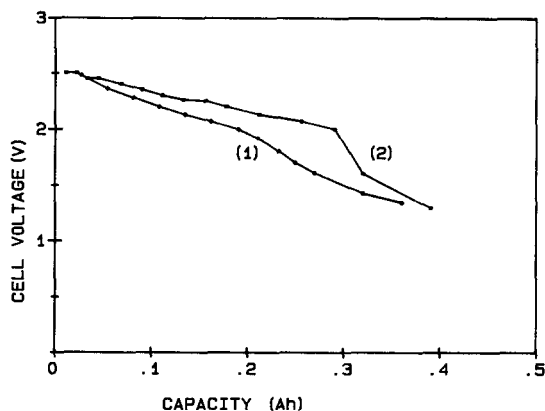


Fig. 3. Discharge curves at 200 °C for C-size Ca/SOCl<sub>2</sub> cells at (1) 94 Ω; (2) 700 Ω.

The almost constant discharge capacities of the Ca/SOCl<sub>2</sub> system at 150 - 200 °C over a wide range of loads indicate that self-discharge of the calcium anode, which consumes a significant portion of the anode, is the main cause of the low coulombic efficiency. The resistive nature of the anode passivation layer plays a secondary role. On the other hand, discharge of the Li/SOCl<sub>2</sub> cells at 700 Ω at 200 °C yields a similar capacity value (3.2 A h) to that obtained at 94 Ω, even though the discharge duration is about an order of magnitude longer. This shows the exceptionally low self-discharge rate of the Li/SOCl<sub>2</sub> system at 200 °C [4].

#### *Effects of storage at elevated temperatures*

To investigate the possible cause of capacity degradation in Ca/SOCl<sub>2</sub> cells at elevated temperatures, the open circuit voltages (OCV) of cells stored at 200 °C for extended periods were monitored. The OCV behavior of Ca/SOCl<sub>2</sub> and Li/SOCl<sub>2</sub> cells during storage at 200 °C is shown in Fig. 4. In less than 10 days the OCV of the Ca/SOCl<sub>2</sub> cells had fallen to zero, but, even after 30 days, no significant change in OCV was observed for Li/SOCl<sub>2</sub> cells. Analysis of the Ca/SOCl<sub>2</sub> cells with zero OCV showed that almost all of the calcium metal had been converted to a thick, mechanically loose, layer of CaCl<sub>2</sub>.

The extent of chemical corrosion of a calcium specimen, after storage in 1.2 M LiAlCl<sub>4</sub> in SOCl<sub>2</sub>, was determined from the decrease in quantity of Ca metal obtained by hydrolysis, followed by titration for Ca(OH)<sub>2</sub>. The Ca anode specimens used for this test had the same thickness as the anodes in the C-size cells and were mounted in a similar way. The extents of Ca corrosion after 150 days storage at 25 °C, and 1 day storage at 150 °C and 200 °C, are summarized in Table 2.

Table 2 shows that the calcium corrosion rate at 200 °C agrees well with the results of the OCV decay in Ca/SOCl<sub>2</sub> cells after 10 days at 200 °C (Fig. 4). In addition, Table 2 also indicates that within the experimental errors, the corrosion rates for Ca at 150 °C and at 200 °C are similar. A plausible

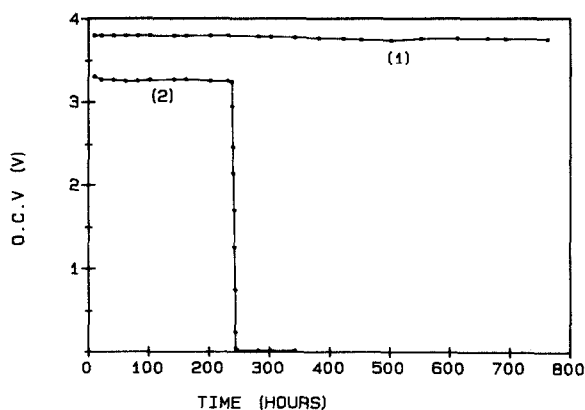


Fig. 4. Variation of open circuit voltage (OCV) values with storage time at 200 °C for (1) Li/SOCl<sub>2</sub> and (2) Ca/SOCl<sub>2</sub> cells.

TABLE 2

Corrosion rate of Ca specimen stored in 1.2 M LiAlCl<sub>4</sub>-SOCl<sub>2</sub>

Storage temperature (°C)	Storage time (days)	Ca lost per day (%)
25	150	<0.1
150	1	13
200	1	10

explanation for this unexpected result is that different electrolyte compositions prevail at the different elevated temperatures [4] due to the thermal decomposition of thionyl chloride at temperatures above 70 °C.

#### Temperature dependence of the OCV

The dependence of the open circuit voltage (OCV) of Li/SOCl<sub>2</sub> and Ca/SOCl<sub>2</sub> cells on storage at temperatures in the range -40 °C to 200 °C are given in Figs. 5 and 6, respectively. Readings were taken following at least 4 h stand at each temperature, starting at -40 °C.

In the lower temperature range, *i.e.*, -40 °C to +70 °C, Figs. 5 and 6 reveal that the OCV characteristics of the two systems are significantly different. For the Li/SOCl<sub>2</sub> system, the OCV decreases with increasing temperature. It has been suggested [1, 7] that the observed behavior is caused by the presence of low concentrations of impurities in the electrolyte which are more oxidizing than thionyl chloride, and by corrosion reactions of the lithium anode. While the corrosion reactions tend to reduce the OCV as the temperature increases, the impurities tend to increase it. Thus, for the Li/SOCl<sub>2</sub> system, at the lower end of the temperature range, the OCV is determined mainly by the presence of contaminants with higher oxidizing poten-

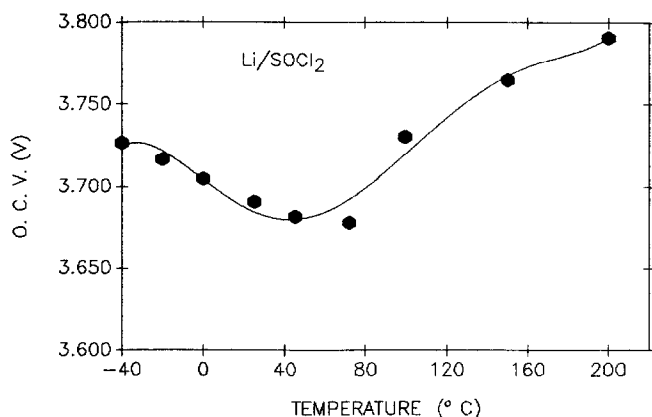


Fig. 5. Temperature variation of open circuit voltage (OCV) for Li/SOCl<sub>2</sub> cells.

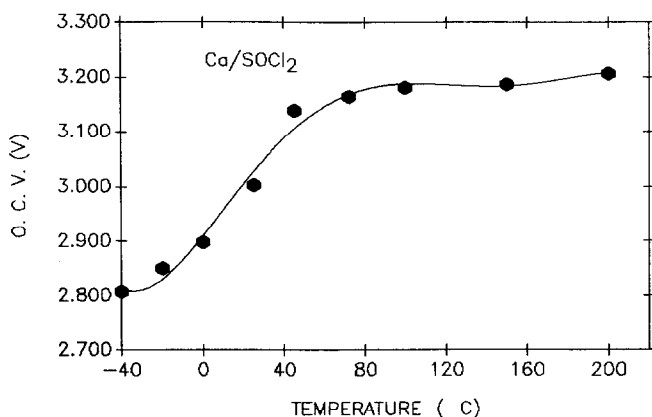
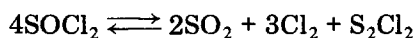


Fig. 6. Temperature variation of open circuit voltage (OCV) for Ca/SOCl<sub>2</sub> cells.

tial than thionyl chloride. The opposite trend found for the Ca/SOCl<sub>2</sub> system is a result of the extremely high resistance of the solid-electrolyte interphase (SEI) due to CaCl<sub>2</sub> corrosion deposits. The relatively steep positive slope of the OCV-temperature curve, and the nature of the electrochemical reaction, ruled out the possibility of an endothermic reaction for the Ca/SOCl<sub>2</sub> system.

At the high end of the temperature range (70 °C - 200 °C) it was shown [1] that the OCV behavior of the Li/SOCl<sub>2</sub> system is determined mainly by the presence of either S<sub>2</sub>Cl<sub>2</sub> or Cl<sub>2</sub> formed by the thermal decomposition of thionyl chloride;

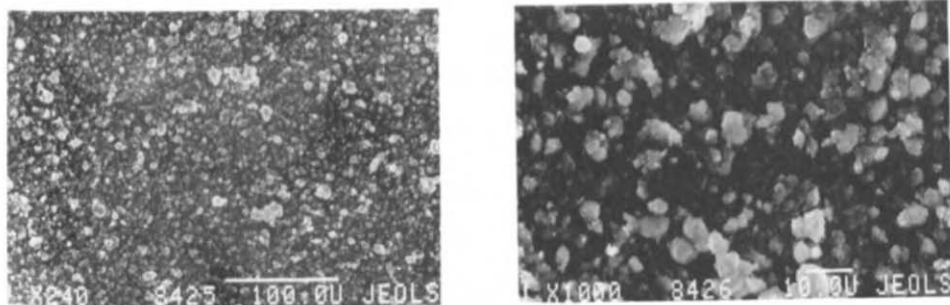


Within this temperature range, increasing the temperature results in an increase in the concentration of these species, which is responsible for increasing the OCV. The simultaneous increase of the anode corrosion rate offsets, to some extent, the OCV rate of increase.

This explanation is also valid for the Ca/SOCl<sub>2</sub> system, but the significantly lower value of the OCV increase between 70 °C and 200 °C (40 mV compared with 200 mV for the Li/SOCl<sub>2</sub> system) is due to the higher corrosion rates of the Ca/SOCl<sub>2</sub> system.

#### *Calcium surface morphology at elevated temperatures*

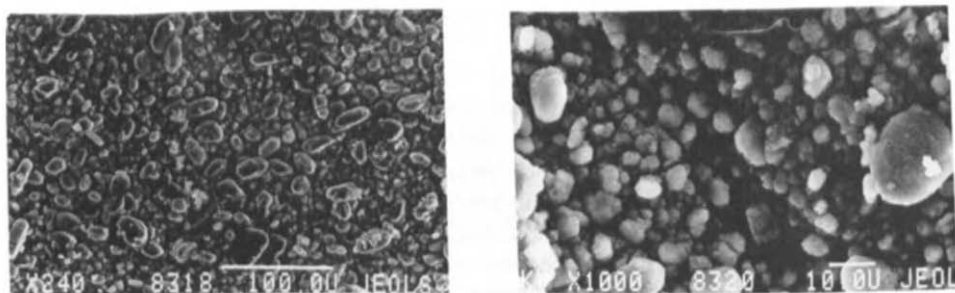
The influence of high storage temperatures (150 °C and 200 °C) on the morphology of calcium surfaces is shown by scanning electron micrographs (SEM photographs) in Figs. 7 - 9. The specimens were stored for 6 months at room temperature followed by one day at 150 °C or 200 °C.



(a)

(b)

Fig. 7. SEM photographs of Ca surface exposed to 1.2 M LiAlCl<sub>4</sub>-SOCl<sub>2</sub> for 6 months at RT. (a)  $\times 120$ , (b)  $\times 500$ .



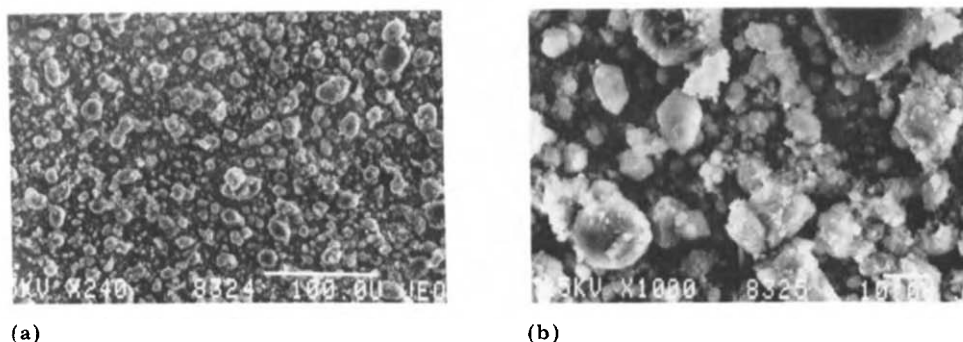
(a)

(b)

Fig. 8. SEM photographs of Ca surface exposed to 1.2 M LiAlCl<sub>4</sub>-SOCl<sub>2</sub> for 6 months at RT and 24 h at 150 °C. (a)  $\times 120$ , (b)  $\times 500$ .

Figures 7 - 9 show that the CaCl<sub>2</sub> layers are relatively uniform, and lack any pitting structure. The CaCl<sub>2</sub> crystals do not appear to be well-formed. This morphology differs from that reported earlier for lithium metal stored in an LiAlCl<sub>4</sub> electrolyte [4, 8], where well-defined crystals of larger size were reported. In fact, the calcium surface under  $\times 1000$  magnification appears to consist of aggregates of crystallites. Similar crystals were reported earlier by Staniewicz [9] for a Ca sample stored at 55 °C.





(a)

(b)

Fig. 9. SEM photographs of Ca surface exposed to 1.2 M  $\text{LiAlCl}_4\text{-SOCl}_2$  for 6 months at RT and 24 h at 200 °C. (a)  $\times 120$ , (b)  $\times 500$ .

As expected, storage of Ca at 150 °C and 200 °C produces crystals of larger size than crystals formed following storage at 25 °C. The average crystal size of samples stored at 200 °C, however, is, surprisingly, somewhat smaller than those stored at 150 °C. The same trend was reported earlier for the  $\text{Li/SOCl}_2$  system at temperatures higher than 100 °C [4], where it was suggested that a higher concentration of  $\text{SO}_2$  in the electrolyte, found at the higher temperature, was responsible for this phenomenon, since it had already been reported [8] that the presence of  $\text{SO}_2$  in the electrolyte tends to reduce crystal size.

## Conclusions

The  $\text{Ca/SOCl}_2$  system with  $\text{LiAlCl}_4$  as the conductive salt shows excessive calcium anode corrosion during storage and discharge at temperatures above 100 °C. Anode corrosion increases the cell internal resistance and results in short operating life and poor load voltage.

The  $\text{Li/SOCl}_2$  system, on the other hand, exhibits a lower self-discharge rate and good voltage stability even at temperatures up to 200 °C.

The use of an alloy based upon lithium [2] would seem to be more practical for applications at temperatures above 175 °C.

## Acknowledgement

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