ADVANCED CALCIUM-THIONYL CHLORIDE HIGH-POWER BATTERY

Periodic Technical Report

by

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**Title**: Advanced Calcium Thionyl Chloride High Power Battery

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**Subject Terms**: Calcium battery; thionyl chloride; conductivity; Viscosity; Raman spectra; Strontium; Barium shelf life; High Energy density battery.

**Abstract**: Recently we at TAU have made a breakthrough in the development of two advanced Ca-TC systems which have much better storage properties than the state-of-the-art Ca-SnCl_2 cell. This has been done by replacing the CaX_2 (X=AlCl_4) electrolyte by SrX_2 (type A), or BaX_2 (type B). The project's goals are to gain a better understanding of the electrochemistry of the advanced systems and to establish their safety and performance. In this first report we present preliminary results regarding the properties of these three electrolytes emphasizing the role of SO_2 in affecting their viscosity, conductivity and Raman spectra.
Introduction

Recently we, at TAU, have made a breakthrough in the development of two advanced Ca-TC systems (1,2,3) which have much better storage properties than the state-of-the-art Ca cell. These are: Ca/Sr(AlCl₄)₂-SOCl₂/C - (type A) and Ca/Ba(AlCl₄)₂-SOCl₂/C - (type B). Our modified (but not optimized) C-size hermetically sealed cell delivered 4.4 Ah after one month of storage at 70°C. This is 10-20% higher than the capacity of a fresh Li-SO₂ C-size cell.

The project's goals are to gain a better understanding of the electrochemistry of the advanced calcium-thionyl chloride system and to establish the safety and performance properties of optimized C-size hermetically sealed cells with the use of our proprietary art.

We expect that our advanced calcium battery will have 25-50% more capacity than a similar size Li-SO₂ battery. Our Ca-TC cell can be made vent-free and able to resist, with no rupture or leakage, abuse tests including forced discharge, charging, mechanical damage and short circuit (under certain conditions). Thus no limitations on air transportation are expected. Its shelf-life is expected to be 3-5 years at 20°C and its operating temperature range is -30 (or even -40) to 150-200°C, depending on the rate of discharge.

The Ca-TC cell has a working voltage equal to that of the Li-SO₂ cell. Thus, it can replace the Li-SO₂ battery with no problem. In addition it is expected to be less expensive than the Li-SO₂ technology.

We believe that our advanced Ca-TC technology, after being fully developed, can be used as the major power source for all portable electronic equipment in the army. It will give better performance, better safety and lower cost than is offered by the existing Li-SO₂ technology.
The proposed statement of work includes: study of the electrochemistry, safety, performance and storage properties of the state-of-the-art Ca/Ca(AlCl₄)₂-TC+SO₂/C system as a baseline system, and of our two advanced modified systems A and B. In modification A, we have changed the chemical composition of the Solid Electrolyte Interphase (SEI) of the calcium, and in modification B, we mainly changed the morphology and decreased the thickness of the SEI (1-3). We would like to accomplish a better understanding of the effects of SEI chemical composition, morphology and electrochemical properties on the performance, safety and storage properties of the Ca-TC sealed battery. The experimental techniques that will be used include conductivity measurements, Raman spectroscopy and viscosity measurements on the electrolytes; AC, SEM, micro-calorimetry, calorimetry of the electrochemical cells and cell components as well as storage, discharge and safety tests of sealed cells. The time frame is three years.

Experimental

All solutions were prepared and handled inside an argon-filled glove box. Riedel AR SrCl₂·6H₂O was vacuum dried at 130°C for 24h. It was mixed with AlCl₃ (Fluka Puriss)-SOCl₂ (Merck Zur Synthesis) solution to give the desired Sr(AlCl₄)₂ concentration. The resulting solution (with 10% excess of solid SrCl₂) was refluxed with calcium strips for 24h. The exact concentrations of Al and Sr were determined by atomic absorption (Perkin Elmer 403). The Al:Sr atomic ratio was found to be 2:1. Sulfur dioxide gas (Matheson 99.98%) was added to these solutions with the use of vacuum line. The final SO₂ concentration was determined from weight change. The solution conductivity was measured with the use of a four-platinum-electrode ampoule (shown in Fig.1) and El-Hama model TH 230 conductivity meter. This cell was designed to withstand a pressure of 10At. Sulfur dioxide was added directly
to the solution in the conductivity cell with the use of a vacuum line.

The viscosity of the solutions was measured with the use of a Lewis Viscosimeter (shown in Fig.2) over a temperature range of 10 to 70°C. A Rotaflo Teflon valve was attached to this viscosimeter and through it solution and SO₂ gas were introduced. The addition of SO₂ was accomplished with the use of a vacuum line.

Raman spectroscopy measurements were carried out (at Ben Gurion University with Prof. S. Efrima) with the use of glass ampoules similar in shape and size to the conductivity cells. The details of the Raman spectrophotometer: Coherent Innova Laser model 90/4; the excitation wave length was 514nm; Spex model 1403 monochromator, RCA type C31034 photomultiplier; "OSMA" - Optical Spectroscopic Multichannel Analyser; P.I. type ST120 detector; P.I. type ST120 Controller and IBM AT computer which controls "OSMA", reads and processes the data. The typical resolution of this system was 5 cm⁻¹.

AC measurements were conducted with the use of a home-made system which consists of an IBM PC-XT computer equipped with a Tecmar A/D board (TM40) and a home-made galvanostat. Frequency response range is 0.001 Hz to 10,000 Hz. The electrochemical cell consists of a hermetically sealed C-size SS cell with two G/M feedthroughs (one in the bottom and one in the cover) to which the calcium reference and working electrodes were attached. A round porous-nickel counter electrode was connected to the can.

RESULTS AND DISCUSSIONS

1. Electrolyte Properties
   a) Sr(AlCl₄)₂ - TC - SO₂ system.

This project is the continuation of many years of effort in our laboratory. Its goal is a better understanding of the conduction mechanisms
in TC/electrolytes and the effect on them of SO\(_2\) and temperature. In addition, we would like to form a data base which will help in optimizing the Ca-TG battery.

The effects of SO\(_2\) and temperature on the conductivity of 0.84M Sr(AlCl\(_4\))\(_2\)-TC solutions are shown in Fig. 3 (Ref.3). There is a pronounced effect of SO\(_2\) (up to a factor of 7 at low temperatures) on the conductivity.

In order to understand the reasons for this conductivity enhancement we conducted viscosity and Raman spectroscopy tests. The effects of SO\(_2\) and temperature on the viscosity of 0.84M Sr(AlCl\(_4\))\(_2\)-TC-SO\(_2\) solutions are shown in Fig. 4. It is interesting to note that increasing SO\(_2\) concentration from 0 to 10% does not significantly alter the solution viscosity. The conductivity corrected for the change in viscosity increases with the rise of SO\(_2\) concentration from 0 to 10% and does not change with further increase in SO\(_2\) concentration.

Raman spectra of 30% SO\(_2\)-TC-0.84M Sr(AlCl\(_4\))\(_2\) (Fig.5) taken at room temperature (Ref. 3) indicates the formation of a complex between SO\(_2\) and Sr\(^{++}\). The peak at 1140 cm\(^{-1}\) is assigned to SO\(_2\) while the peak at 1147 cm\(^{-1}\) is assigned to the Sr(SO\(_2\))\(_n\)\(^{++}\) complex. The Sr(SO\(_2\))\(_n\)\(^{++}\) peak height increases with SO\(_2\) concentration. It seems that the maximum value of n is three (Ref.3). These results indicate that the conductivity enhancement at low SO\(_2\) concentration is predominantly due to the formation of a larger SO\(_2\)-Sr\(^{++}\) complex ion (or an aggregate of of such ions) and at high concentration is due to the decrease in the viscosity of the electrolytes.

b) Ca(AlCl\(_4\))\(_2\), Ba(AlCl\(_4\))\(_2\)-TC-SO\(_2\) systems.

Preliminary results regarding viscosity and Raman spectroscopy measurements are reported here. The effect of SO\(_2\) on viscosity of 1M
Ca(AlCl₄)₂ can be seen in Fig. 6. The effect of 20% SO₂ on the viscosity of some Sr, Ca and Ba solutions can be estimated by comparing figures 7 and 8.

Raman spectra of 1M Ca(AlCl₄)₂ 30% SO₂-TC solution (Fig.9) indicate formation of a SO₂ complex as shown by the appearance of a shoulder or small peak at 1149 cm⁻¹.

Further results and discussions will be submitted in the next report.

2. AC MEASUREMENTS

The AC spectrum (Cole-Cole plot) for Ca/Ca(AlCl₄)₂ - SOCl₂ system has been previously measured in our laboratory (Ref. 4) over a frequency range of 40 Hz to 80 kHz. We have now extended these measurements to low frequencies - down to 0.001 Hz. A typical AC spectrum for the calcium-SEI electrode is given in Fig.10. The upper (positive) arc has a somewhat depressed shape. R₁ and R₂ increase with storage time but the ratio R₁/R₂ decreases. The upper arc is assigned to the SEI resistance while the lower one is probably associated with the ionic transference numbers in the SEI. The SEI resistivity (ρ) is, to a first approximation, calculated from \( \omega \) of the upper curve:

\[
\rho = \frac{1}{\omega \max \varepsilon \varepsilon_o}
\]

where \( \varepsilon_o \) and \( \varepsilon \) are the permittivity of vacuum and the dielectric constant of the CaCl₂ SEI respectively, (\( \varepsilon = 6 \)). The apparent thickness of the SEI (\( \ell \)) is calculated from:

\[
\ell = \varepsilon \varepsilon_o A
\]

where \( A \) = electrode area, and \( C \) = electrode capacitance. The characteristics of the Ca-SEI electrode in Ca(AlCl₄)₂-TC solutions are summarized in Table 1.
TABLE 1

<table>
<thead>
<tr>
<th></th>
<th>Meitav/Peled* (Ref. 4)</th>
<th>This Work **</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity, $\mu F/cm^2$</td>
<td>0.18</td>
<td>0.11</td>
</tr>
<tr>
<td>SEI app. thickness, $\AA$</td>
<td>490</td>
<td>485</td>
</tr>
<tr>
<td>Electrode resistance, $\Omega\cdot cm^2$</td>
<td>66</td>
<td>36</td>
</tr>
<tr>
<td>SEI resistivity ($\rho$), ohm cm</td>
<td>$1.3 \times 10^{10}$</td>
<td>$0.74 \times 10^{10}$</td>
</tr>
</tbody>
</table>

* Two months of storage in 0.9M Ca(AlCl$_4$)$_2$.
** One month of storage in 0.75M Ca(AlCl$_4$)$_2$.

3. **C-SIZE CELL ASSEMBLY**

Nine C-size Ca-TC cells have been assembled. They have 130 cm$^2$ of active electrode area and consist of: calcium anode pfizer 99.9% (0.5x210x40mm), porous carbon cathode (0.7x200x40mm), 0.9M Ca(AlCl$_4$)$_2$ + 7% SO$_2$. These cells will be tested during the next period.
4. **Research Plans for Remainder of the Contract Period.**

1. Baseline system (Ca(AlCl₄)₂ - TC).
   1.1. Complete the Raman and viscosity measurements for the Ca(AlCl₄)₂-SOCl₂-SO₂ system.
   1.2. Study the effect of SO₂ on the calcium-SEI electrode.
   1.3. Evaluate the properties of C-size baseline cells.
2. Study the electrochemistry of type A and B systems Sr(AlCl₄)₂-SOCl₂-SO₂ and Ba(AlCl₄)₂-SOCl₂-SO₂.
   2.1. Complete the Raman and viscosity measurements.
   2.2. Study the effect of SO₂ on the SEI calcium electrode.
   2.3. Evaluate the properties of C-size cells having type A electrolyte.

**REFERENCES**

1. Israel Pat. Appl. No. 77786, UK Pat. Appl. No. GB 2187590A.
2. E. Elster, R. Cohen, M. Brand, Y. Lavi and E. Peled.
3. E. Elster, R. Cohen, M. Brand, Y. Lavi and E. Peled
   J. Electrochem. Soc. in press.
Figure Captions

Fig. 1. Conductivity Cell.

Fig. 2. Lewis Viscometer.

Fig. 3. Conductivity of 0.84M Sr(AlCl₄)₂-SO₂-TC solutions vs. temperature.

Fig. 4. Viscosity of 0.84M Sr(AlCl₄)₂-SO₂-TC solutions vs. temperature.

Fig. 5. Raman spectrum of 0.84M Sr(AlCl₄)₂ in TC containing 30% (v/v) SO₂ at room temperature.

Fig. 6. Viscosity of 1M Ca(AlCl₄)₂-SO₂-TC solutions: 1-0% SO₂; 2-20% SO₂; 3-30% SO₂.

Fig. 7. Viscosity of MX₂-TC solutions, M = alkali metal, X = AlCl₄⁻:
1-0.84M BaX₂; 2-0.84M SrX₂; 3-1M CaX₂; 4-1.3M BaX₂; 5-1.3M SrX₂.

Fig. 8. Viscosity of MX₂-TC+20% (v/v) SO₂ solutions as in Fig. 7.

Fig. 9. Raman spectrum of 1M Ca(AlCl₄)₂-TC+30% (v/v) SO₂ at room temperature.

Fig. 10. An AC spectrum for Ca electrode in 0.75M Ca(AlCl₄)₂-SOCl₂ solution after four days of storage at room temperature.
Fig. 1. Conductivity Cell
Fig. 2. Lewis Viscometer
Fig. 3. Conductivity of 0.84M Sr\((\text{AlCl}_4)_2\)\(-\text{SO}_2\)-TC solutions vs. temperature.

A: 50% \text{SO}_2,  B: 40% \text{SO}_2,  C: 30% \text{SO}_2

D: 20% \text{SO}_2,  E: 10% \text{SO}_2,  F: 0% \text{SO}_2
Fig. 4. Viscosity of 0.84M Sr(AlCl₄)₂-SO₂-TC solutions vs. temperature.

A: 0% SO₂, B: 10% SO₂
C: 20% SO₂, D: 30% SO₂
Fig. 5. Raman spectrum of 0.84M Sr(AlCl$_4$)$_2$ in TC containing 30% (v/v) SO$_2$ at room temperature.
Fig. 6. Viscosity of 1M Ca(AlCl₄)₂-SO₂-TC solutions:
1-0% SO₂; 2-20% SO₂; 3-30% SO₂.
Fig. 7. Viscosity of $\text{MX}_2$-TC solutions, $M =$ alkali metal, $X = \text{AlCl}_4$: 1-0.84M BaX$_2$; 2-0.84M SrX$_2$; 3-1M CaX$_2$; 4-1.3M BaX$_2$; 5-1.3M SrX$_2$. 
Fig. 8. Viscosity of \( \text{MX}_2 - \text{TC} + 20\% \ (v/v) \ \text{SO}_2 \) solutions, as in Fig. 7.
Fig. 9. Raman spectrum of 1M Ca(AlCl₄)₂-TC+30% (v/v) SO₂ at room temperature.
Ca Electrode in Ca(AlCl₄)₂
area: 6-7 cm²; conc. = 0.7 M

Fig. 10. An AC spectrum for Ca electrode in 0.75 M Ca(AlCl₄)₂·SOCl₂ solution after four days of storage at room temperature.
To date no funds have been received from U.S. Army on this contract.

During this period we have already incurred expenses as per budget of this contract.
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