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ADVANCED CALCIUM-THIONYL CHLORIDE HIGH-POWER BATTERY

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Periodic Technical Report

by

Professor E. Peled

Final Report

(May 1989 - May 1990)

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<p>In this phase we have demonstrated that $\text{Ca/SrX}_2 + 7$ or $20\% \text{SO}_2\text{-TC}^+$ cells (A7 and A20 types) can deliver at RT up to 5.5Ah at low rates and 4.4Ah at 0.9A. These cells have 10 to 80% more capacity than have commercial Li-TC and Li-SO₂ wound c-size cells. The improved A7 and A20 types cells lost almost no capacity after 4-5 weeks of storage at 70°C. The A20 type cell generates less heat at 20°C under OCV conditions than equivalent Li/TC cells, having the same electrode area, i.e. it has a longer shelf life.</p> <p style="text-align: right;">Abstract continued over the page....</p>			
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Abstract cont....

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The addition of P40 additive to $SrX_2 + TC + SO_2$ solutions decrease further the corrosion rate of calcium. The lowest corrosion rate found for solutions containing 20% SO_2 + 0.3% P40. Formulation of the SrX_2 -TC electrolyte with 20% SO_2 and 0.3% P40 (A20S type cell) found to have the following advantages: it increases shelf life, it increases cell capacity at high discharge rates and at low temperatures, it increases load voltage and Faradaic efficiency. A preliminary specification of A20S type Ca-TC cell is enclosed.

↖ Ten A20 c-size cells have been submitted for evaluation to the Power Sources division of LABCOM ETDL Ft. Monmouth. These cells successfully passed a one month 55°C storage test (at ETDL) with no loss of capacity (at 0.7A discharge rate).

↖ The improved shelf-life of calcium in BaX_2/TC solutions as compared to CaX_2/TC solutions results mainly from the difference in the solubility or reactivity of the CaO film in those two solutions. In CaX_2/TC solutions the oxide dissolves leaving the calcium with a $CaCl_2$ layer which does not provide the metal with good protection. In BaX_2/TC solutions, on the native CaO layer a $BaCl_2 + AlCl_3$ or Al_2O_3 layer is formed. This $BaCl_2 + AlCl_3 + Al_2O_3$ layer does not form when the oxide is missing from the surface. Therefore cleaned calcium in BaX_2/TC solution corrodes at the same rate as does calcium in CaX_2/TC solutions.

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Content

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Chapter 3: Effect of Additives on the Performance of the Ca/SrX₂ - SOCl_2 cell.

Chapter 4: Preliminary specifications of the AL20S type calcium/TC cell.

Introduction

This project is a continuation of contract No. DAJA45-88-C-0012 (12/87 - 12/88). Its goals are to gain a better understanding of the electrochemistry of the advanced Ca/TC battery systems, to establish their safety and performance, with the use of propriety art developed at TAU.

Summary of the results of the first year

(contract DAJA-45-88-C-0012)

This report contains four chapters. The calorimetric study of Ca/Sr(AlCl₄)₂-SOCl₂+7%(v/v)SO₂ C-size cells during constant-temperature discharge is reported in Chapter 1. Fresh and stored (70°C for four weeks) cells were discharged inside a dedicated home-made calorimeter on two loads: 9.4Ω and 4Ω at 30 and 50°C. The heat flow (W_T) of the cells (thermal power) during discharge was measured as a function of discharge time. There was no significant difference between fresh and stored cells with respect to heat generation during discharge.

There was no loss in capacity during the four weeks of storage at 70°C.

The following components of W_T were calculated and plotted against discharge capacity: W_S -thermodynamic; W_P -polarization; W_C -chemical. W_P was found to be the largest component of W_T . The maximum corrosion rate (I_c) of the calcium anode during discharge and its minimum Faradaic efficiency (ϵ) were calculated from W_C on the assumption that anodic corrosion is the major component of W_C . At 30°C, ϵ was about 0.9 while at 55°C it drops from 0.87 at 2 mAcm⁻² to 0.84 at 4 mAcm⁻². At 30°C the value of ϵ , is similar to that of ϵ of the SEI of the calcium, indicating a similar corrosion mechanism for the calcium anode (both under OCV conditions and under load).

Chapter 2 presents a calorimetric study of the baseline cell Ca/Ca(AlCl₄)₂-SOCl₂ + 7% (V/V)SO₂. The thermal power generated by the Ca/CaX₂ cells is similar to that of the Ca/SrX₂ cells at 30°C. However at 55°C, I_c , a of the Ca/CaX₂ cells is much higher. Thus the faradaic efficiency of the Ca/CaX₂ cells is similar or lower than that of the Ca/SrX₂ cells.

Chapter 3 presents the performance safety and storage properties of Ca/CaX₂ and Ca/SrX₂ cells.

The Ca/CaX₂ cell loses most of its capacity after 4 weeks of storage at 70°C. However, the Ca/SrX₂ cell loses only 0-15% of its capacity when discharged over the temperature range -30 to +60°C after being stored for 4 weeks at 70°C. Its voltage delay is 0-100 sec. at -20 and -30°C after such storage. It has no voltage delay at room temperature and above. Cells equipped with a glass separator and a vent may vent on forced discharge as a

result of overheating. The Ca/SrX_2 cell may be made safe and vent-free with the use of a Tefzel separator.

Chapter 4 presents a summary of the results regarding the properties of $\text{H}_2\text{SO}_4\text{-SO}_2\text{-TC}$ solutions ($\text{M}=\text{Ca, Sr, Ba}$) including Raman spectra, viscosity and conductivity data. We explain the effect of SO_2 and temperature on the conductivity and conduction mechanism.

CHAPTER 1: A 5.5 Ah Ca/Sr(AlCl₄)₂-SOCl₂ C-Size Cell

The calcium-thionyl chloride (TC) cell is considered as a safer alternative to high-power lithium cells.⁽¹⁻³⁾ There is a high probability that it can be developed⁽⁴⁾ as a safe, vent-free cell which will not rupture or leak over a wide range of abusive conditions. The major drawback of the Ca-TC cell has been rapid corrosion of the calcium anode (i.e. too short a shelf life). This high rate of corrosion in the CaX₂ (X=AlCl₄) electrolyte results from the fact that the CaCl₂ SEI does not provide the calcium anode with sufficient corrosion protection^(4,5). This problem has been successfully solved by replacement of the CaX₂ electrolyte by SrX₂ or BaX₂ electrolytes^(5,6). These substitutions improved both the morphology and chemical composition of the passivating layer which covers the calcium anode. The addition of SO₂ to the electrolytes affects the morphology of the passivating layer and further decreases the corrosion rate of calcium^(6,7). A calorimetric study⁽⁸⁾ of the Ca/SrX₂-SOCl₂ cell revealed that the Faradaic efficiency of the calcium anode is about 0.9 at 30°C, and that there is no loss of capacity after four weeks' storage at 70°C.

The goal of this work was to demonstrate that the Ca/SrX₂-TC cell can be developed, not only as a safe cell, but also as a premium long-life high-power cell with very high energy density.

Previous work^(4,8) has indicated that a) the Ca-TC cell generates excessive heat at high discharge rate especially at elevated temperatures, b) that the Faradaic efficiency decreases with current density and temperature. Thus we decided to increase the active electrode area from 150 cm² (4,5,7) to 200-220 cm² and in this way to reduce the current density. The effect of this change can be seen in Fig.1 and Table 1. Information on cell components and assembly can be found in Refs. 4,7 and 8. The "old" Ca/TC cell

in Fig.1 had 150 cm² electrode area and a 50μ thick Tefzel separator of 60% porosity (Scimat) while the "improved" Ca/TC cell had 200-220 cm² electrode area and a Tefzel separator of 80% porosity. Both cells had the same electrolyte - 0.84M Sr(AlCl₄)₂ + 7%(v/v)SO₂ (or 20% SO₂). The cells were discharged either at 30 or 55°C inside a home-made calorimeter (7,8), or at RT. The improved Ca/TC cell has about 30% more capacity than the "old" Ca/TC cell. At low discharge rates the improved Ca/TC cell has 10% and 80% more capacity than a wound SAFT Li/TC C-size cell and a wound Duracell C-size Li/SO₂ cell respectively. At 0.9A rate it has 50% more capacity than either of these cells.

The increase of SO₂ concentration from 7 to 20% (v/v) does not seem to have a major effect on the cell capacity at RT discharge, on the heat flux during discharge, or on the Faradaic efficiency. However, it significantly decreased the heat output (under OCV conditions), i.e. the self-discharge rate (Fig.2). It can be seen that, when adjusted to the difference in electrode area, the heat output of the "old" Ca/TC cell with 7% (v/v) SO₂ is similar or smaller than that of Li-TC cells. However, the improved Ca/TC cell with 20% SO₂ generates much less heat than do either the Li/TC (bobbin or wound) cell or the Ca/TC cell with 7% SO₂. This is in good agreement with the results of calcium corrosion tests⁽⁷⁾. Ca/TC cells with either 7 or 20% SO₂ performed very well in a 4-5 week 70° storage tests with minor loss in capacity (Table 1). Moreover, cells that were stored for 5 weeks at 70°C and an additional 10 months at RT (Fig.3) lost less than 2% capacity. This storage affects neither the Faradaic efficiency nor the heat generation rate during discharge. It caused a 0-70 mV voltage penalty at high discharge rates (Table 1).

To conclude, the improved Ca/SrX₂-SOCl₂+SO₂ cell has, at RT discharge, 10-80% more capacity than do commercial Li/TC and Li/SO₂ cells, it loses

almost no capacity after 4-5 weeks of storage at 70°C, and it generates less heat at 20°C under OCV conditions than equivalent Li/TC cells having the same electrode area, i.e. it has a longer shelf life.

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TABLE 1:

The Effect of SO₂ Concentration, RT and 70°C Storage and Electrode area on performance.

Code Cell El. area (cm ²)	[SO ₂] [%]	Storage Condition	load (Ω)	Average Voltage (V)	Discharge Temp. (°C)	Capacity (to 2V) (Ah)	W _T (W)	ε	
Q ₁₂ (150)	7	Fresh	4	2.56	55	3.7	1.2	84	ref.8
Q ₆ (150)	7	1	4	2.56	55	3.6	1.21	83	ref.8
Q ₁ (150)	7	2	6.6	2.55	55	3.8	0.59	85	
Q ₁₁ (150)	7	Fresh	9.4	2.39	30	3.4	0.49	88	ref.8
Q ₂₀ (150)	7	1	9.4	2.39	30	3.4	0.46	89	ref.8
Q ₁₈ (150)	7	2	9.4	2.35	30	3.34	0.46	88	
Q ₁₀ (150)	7	Fresh	4	2.30	30	2.2	1.1	88	ref.8
Q ₂ (150)	7	1	4	2.30	30	2.2	1.1	89	ref.8
S ₁₈ (200)	7	Fresh	4	2.40	30	3.7	1.1	89	
S ₂₀ (200)	7	4	4	2.33	30	4.0	1.1	89	
T ₁₃ (220)	20	Fresh	4.05	2.45	55	4.2	1.2	84	
T ₁₀ (220)	20	Fresh	3	2.45	RT	4.4			
T ₁₈ (220)	20	4	2.9	2.40	RT	4.05			
S ₁₇ (200)	7	Fresh	3	2.55	RT	4.4			
T ₄ (220)	7	Fresh	2.6	2.55	RT	4.2			
S ₁₉ (200)	7	3	113	2.76	RT	5.48			
T ₇ (220)	20	5	19.5	2.50	RT	5.0			
T ₁₇ (220)	7	5	42.5	2.61	RT	5.23			

1. 5 weeks at 70°C + 4 weeks at RT 4. 4 weeks at 70°C
2. 5 weeks at 70°C + 10 months at RT 5. 3 months at RT
3. 6 months at RT

Figure Captions

Fig.1. Plots of room temperature capacity vs current for different C-size cells: *-Improved $\text{Ca/SrX}_2\text{-SOCl}_2\text{+SO}_2$ cell; O-SAFT LSH14; Δ - $\text{Ca/SrX}_2\text{-SOCl}_2\text{+SO}_2$ "old" cell; -Duracell L028SH cell.

Fig.2. Comparison of 20°C heat output under OCV conditions of C-size or equivalent size lithium and calcium TC cells: 1-Li-TC, AA/2 size bobbin type 5 cm² electrode area, values were multiplied by 44 (from ref.9); 2-Li-TC, AA size bobbin type 14 cm² electrode area, values were multiplied by 15.7 (from ref.9); 3-Li-TC D-size wound cell, values were divided by 2 (from ref.10); 4- $\text{Ca/SrX}_2\text{-SOCl}_2 + 7\% \text{SO}_2$ 150 cm²; 5- $\text{Ca/SrX}_2\text{-SOCl}_2 + 20\% \text{SO}_2$, 220 cm².

Fig.3. Heat output measured at 20°C under OCV conditions of C-size $\text{Ca/Sr}^{++} + 7\% \text{SO}_2$ cells which have been stored for 5 weeks at 70°C.

FIG.1 COMPARISON BETWEEN C-SIZE CELLS

RT Discharge

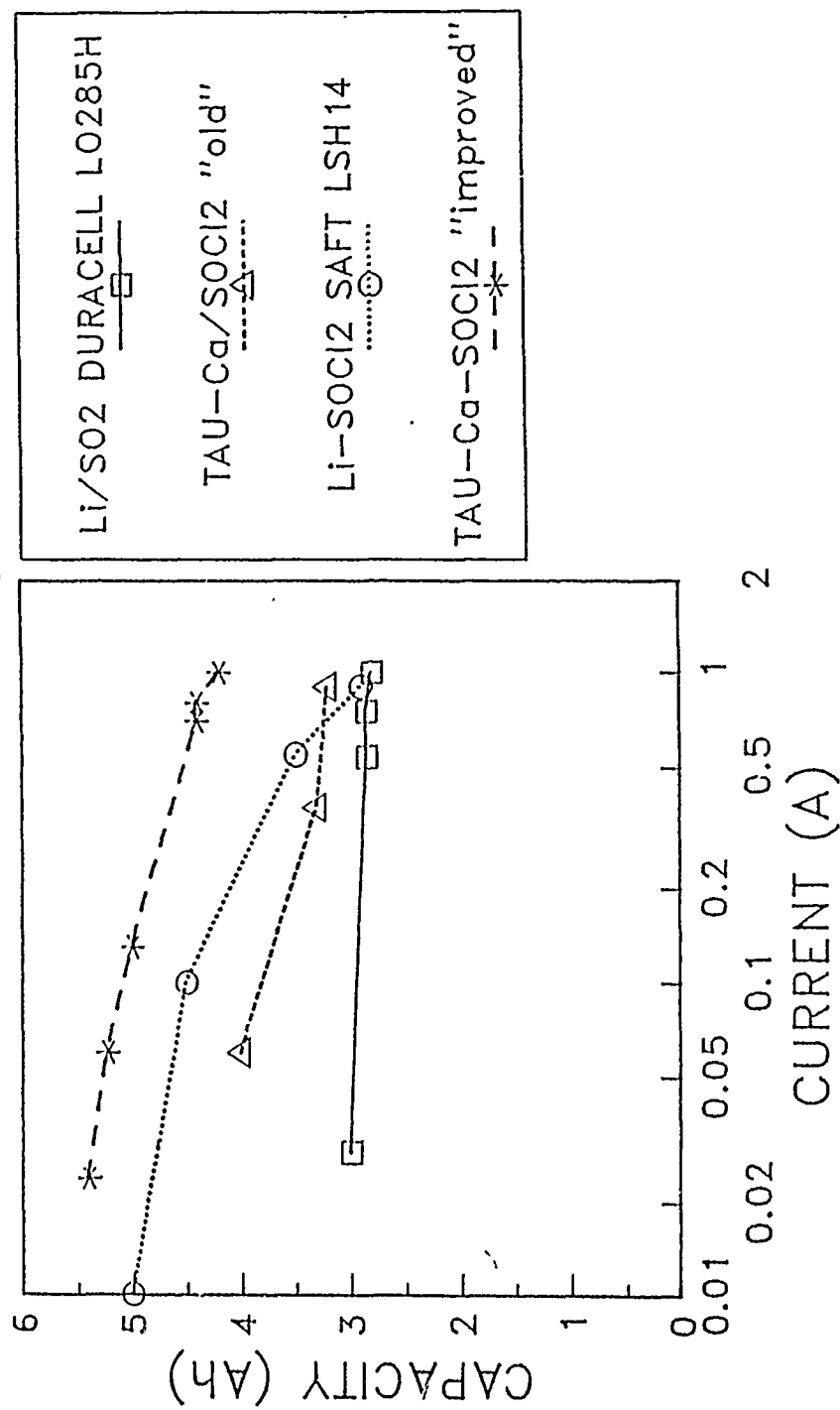


FIG.2 Heat Output of Wound Cells
C-size or Equivalent

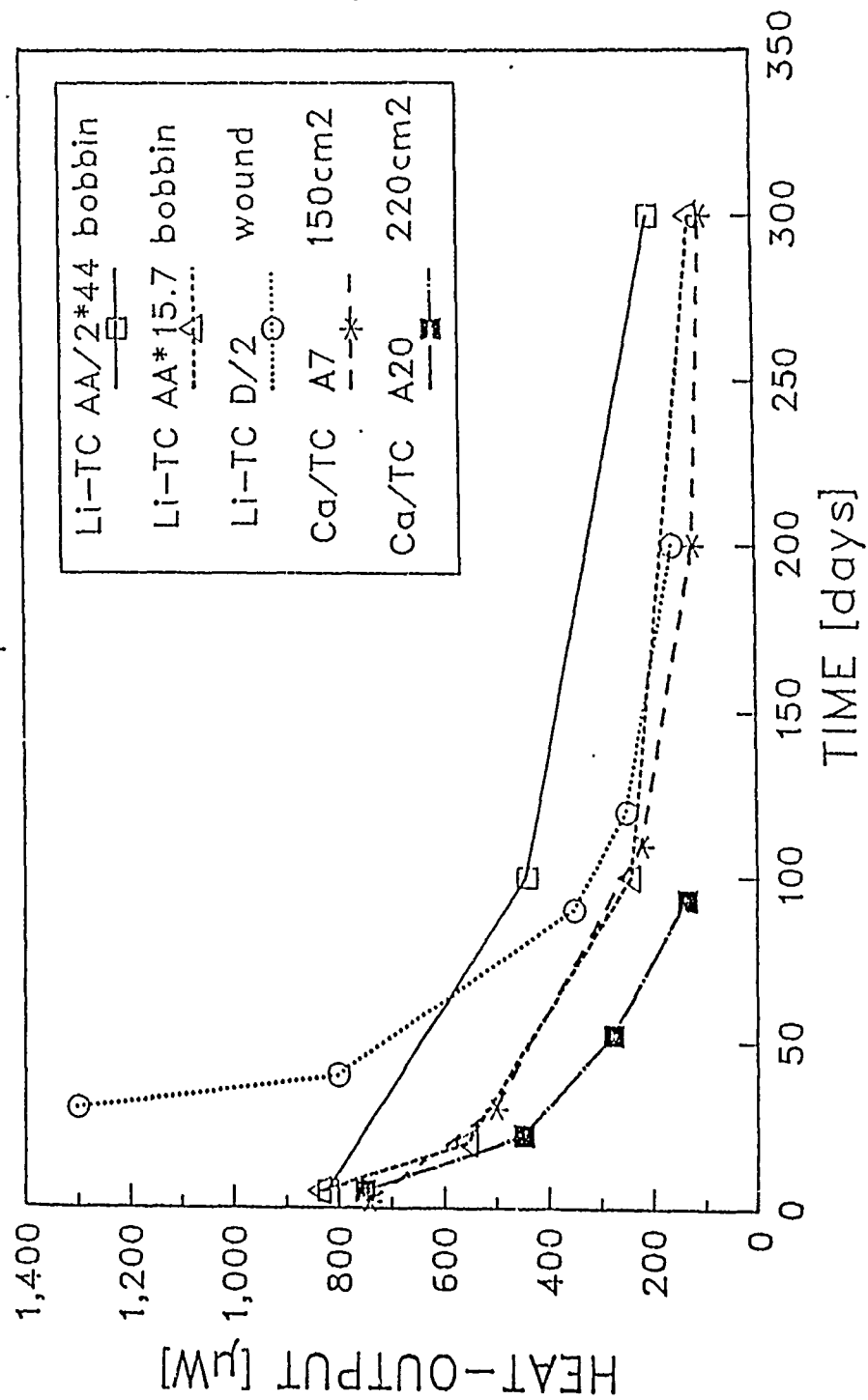
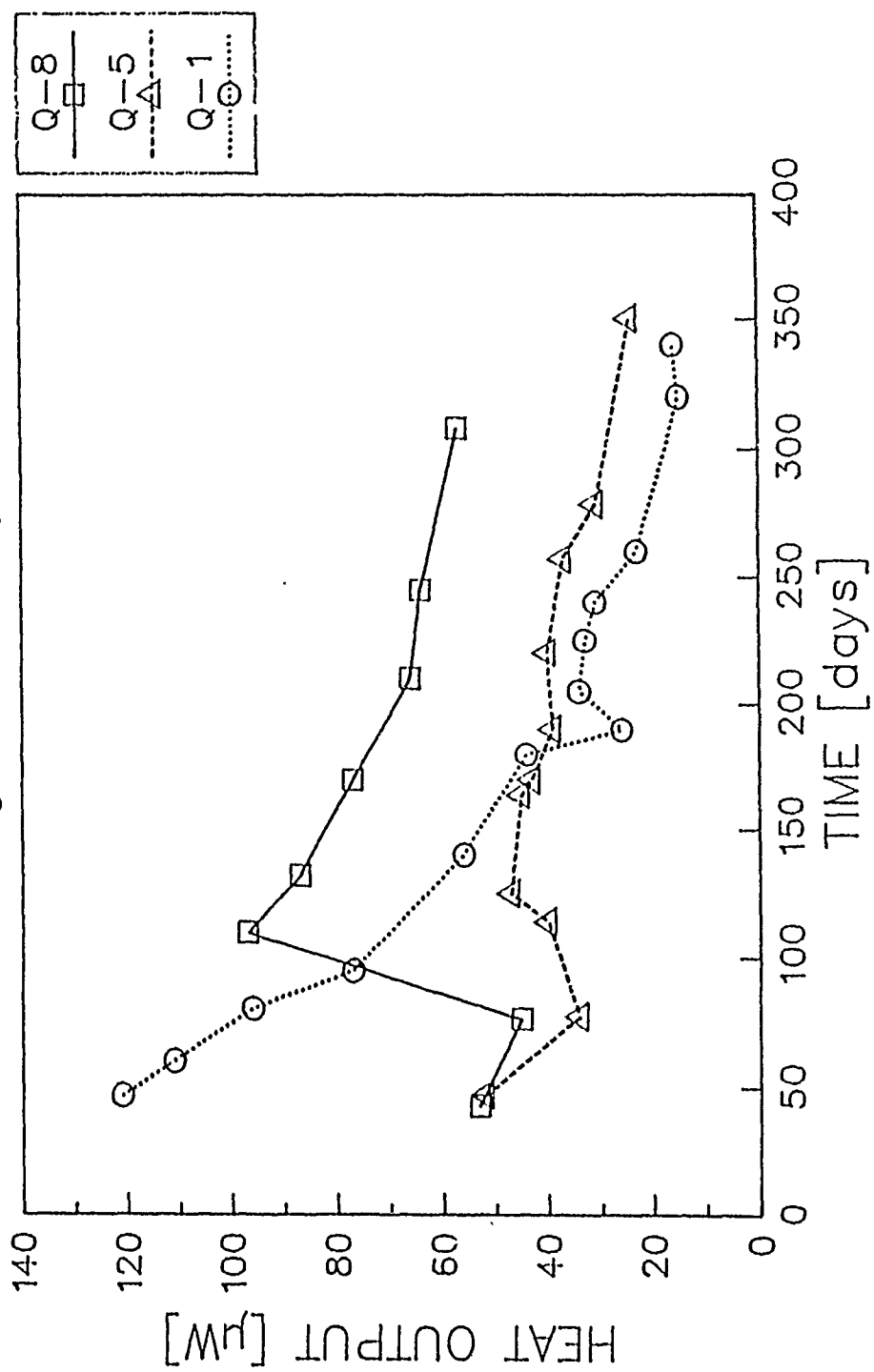


Fig. 3 Heat Output of Ca-TC A7 C-size cells
after storage of 28 days at 71C



CHAPTER 2: THE CHARACTERIZATION OF THE CALCIUM ELECTRODE IN

Ba(AlCl₄)₂/TC SOLUTIONS

2.1 INTRODUCTION

Efforts were being made in our laboratory to increase the shelf-life of calcium-thionyl chloride batteries, i.e. to decrease the corrosion rate of calcium in thionyl chloride solutions. The result of these efforts has been the development of two different systems. In one, the CaX₂ (X=AlCl₄) salt dissolved in the thionyl chloride was replaced with SrX₂ and in the other it was replaced by BaX₂ [1].

Calcium in the Ca/TC system is an SEI [2] electrode, and the solid electrolyte which covers the calcium metal governs the rate of the reaction between the metal and the thionyl chloride solution- the corrosion rate. Therefore changes in the corrosion rate following replacement of the electrolyte salt are connected to changes in the film.

As a result of previous studies it became clear that the native oxide film covering the calcium metal foil plays a greater and more complex role in determining the corrosion and performance characteristics of the calcium electrodes than has been believed up to now.

The goal of this work was to study the effect of surface treatment on the behavior of the film found in these thionyl chloride solutions.

Samples of calcium foil whose surface has been treated in various ways were examined:

Untreated calcium: calcium used as received,

Sandpapered calcium: calcium was abraded inside the glove box

with number 1 sandpaper,

Chemically cleaned calcium: calcium was immersed in 1% HCl in ethanol until its surface was shiny and immediately transferred into pure thionyl chloride in order to form CaCl_2 film. All these operations were carried out in the glove-box. Calcium metal used throughout this work was purchased from Pfizer and is from two batches: 1) batch 1983 (A)- 99.5% purity calcium strips, rolled in a non-controlled atmosphere room and shipped in mineral oil, 2) batch 1986 (B)- 99.5% calcium strips rolled in a glove box and shipped under argon.

This report summarizes the results obtained so far in the BaX_2/TC system .

2.2 CORROSION RESULTS

Corrosion of calcium strips in BaX_2/TC solutions was studied at elevated temperatures (71°C) and at RT. At 71°C this was done by measuring the amount of calcium remaining in the ampules, or the capacity remaining in C-size cells after storage. At RT the corrosion rate was measured during the storage period by a microcalorimeter with a 20.00°C bath temperature, and by measuring the remaining capacity in C-size cells at the end of the storage period.

2.2.1 Corrosion of calcium stored in ampules at 71°C.

Strips of untreated calcium and abraded calcium were prepared from batch A, and strips of untreated and chemically cleaned calcium were prepared from calcium batch B. The amount of calcium remaining after the storage period was determined by immersing the

calcium in water and titrating the resulting Ca(OH)_2 with HCl. The results are summarized in table 2-1. Calcium samples were stored simultaneously in CaX_2/TC for reference. The results of calcium stored in CaX_2 are also given in table 2-1. In each batch, samples of calcium which were not stored at all were titrated with HCl in order to determine the amount of CaO in the sample. Corrosion results shown in table 2-1 are corrected for the amount of oxide, that is they are based on the loss of calcium metal only.

2.2.1.1 CaX_2 solutions.

Examination of the results of storage in CaX_2 shows very high corrosion ($\approx 20 \mu\text{A}/\text{cm}^2$) for chemically cleaned calcium (batch B) i.e. calcium that was almost completely deprived of its native protective layer, which is probably oxide, and for abraded calcium (batch A), in spite of the film that seems to cover abraded calcium after annealing. Although the corrosion rate is similar for both these categories, the corrosion mechanism seems different. Abraded calcium samples of batch A were pitted over their whole surface. Cleaned calcium samples of batch B were slightly pitted on the periphery only, indicating homogeneous corrosion of the sample area.

Untreated calcium of batches A and B showed less corrosion than treated calcium. Batch B which had a thicker oxide layer (13 mg CaO in 100 mg sample in batch B compared to 5.3 mg CaO in 100 mg sample in batch A) had less corrosion.

2.2.1.2 BaX_2 solutions

Examination of the results of storage in BaX_2 solutions shows that samples of abraded calcium of batch A exhibit the lowest corrosion current in this set of experiments, with no significant

difference between untreated calcium covered by its native oxide film or abraded calcium covered with a thin oxide film. On the basis of four weeks at 71°C being equivalent to three years at RT, the result of $7\mu\text{A}/\text{cm}^2$ at 71°C is equivalent to $0.2\mu\text{A}/\text{cm}^2$ at RT.

Chemically cleaned calcium showed the highest corrosion rate. It is interesting to note that for cleaned calcium the corrosion rate is similar in CaX_2 and BaX_2/TC solutions.

2.3 SEM TESTS-MORPHOLOGY AND COMPOSITION OF THE FILM

Samples of treated and untreated calcium of batch B were stored in 0.75M BaX_2 for periods ranging from 1 hour to 10 months at RT and 28 days at 71°C. The morphology of the surface, and of cross sections was studied with the use of SEM equipped with an X-ray analyzer.

2.3.1 Chemically Cleaned Calcium.

The results are summarized in table 2-2. The atomic percentage of the elements is calculated on the assumption that the sum of the analyzable elements is 100%. The column "%total" in the table states the percent reflection of the surface relative to the reflection expected for the composition measured. A low %total may be due to an undetectable element (for the X-ray) on the surface or a surface which is not smooth.

Room temperature tests In samples stored at RT two regions could be observed. One was shiny, with the surface appearing as immediately after cleaning. The other seemed to be covered

with some layer. It was found that the samples were covered on both sides with a very thin chloride layer. This was concluded from high %total and excess calcium. Thus metallic calcium was measured together with the CaCl_2 layer. It is hard to tell how much of the small amount of chlorine is combined with Ba as BaCl_2 , and how much as CaCl_2 . If we assume that all the barium on the surface exists in the form of BaCl_2 , it seems that some regions remain as CaCl_2 with no barium at all, and some are enriched with barium. In areas that were richer in barium than the starting concentration of 0.1-0.2 atomic percent, there was also sulfur.

71°C tests In one month-71°C storage tests, two very distinct areas were found. A dark grey region and a higher white area surrounding it. The two areas are chloride areas. The grey one- a CaCl_2 layer, and the white one- a $\text{BaCl}_2/\text{CaCl}_2$ layer with more BaCl_2 than CaCl_2 . ($\text{Ba}:\text{Ca}=1.27$).

If we adopt the findings at RT that some areas become progressively enriched with barium and some are not, the results at 71°C show the same behavior. The reason may be that there are distinct anodic and cathodic areas. In the anodic areas calcium is dissolved, precipitating as CaCl_2 following migration of Cl^- through the CaCl_2 film. In the cathodic areas thionyl chloride is reduced, thus leaving some sulfur on the area. In these areas the concentration of BaCl_2 rises and BaCl_2 precipitates. After one month at 71°C there is much barium in this region, but almost no sulfur. It may be that sulfur is soluble at 71°C.

Aluminum was found at low concentrations (up to 3%) only in samples with low %total, i.e. surfaces that were not thoroughly

cleaned. In chemically cleaned samples there is no Al compound on the surface.

2.3.2 Untreated Calcium.

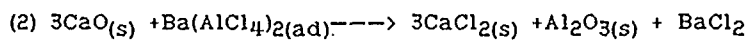
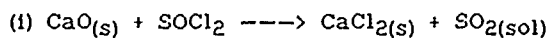
The results of the elemental analysis of untreated calcium (batch B) samples stored in BaX_2/TC solution at RT and at 71°C are summarized in table 2-3.

RT tests: The appearance of the samples is that of a plain surface with lumps of crystals on it. The amount of the crystals on the surface increases with the duration of storage in the solution until after 10 months of storage the whole surface is covered, and the analysis of a crystal and of average surface is similar.

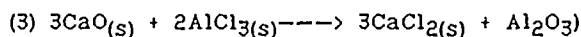
The elemental analysis shows that the surface is covered with a thin BaCl_2 layer together with an aluminum chloride and/or oxide. Because this layer is thin it is analyzed together with calcium metal beneath it. Crystals are thicker than the layer and therefore less calcium from underneath the layer appears. The %total increases with time indicating a slow decrease in the oxygen content of the layer. The percentages of Cl and Ba increase, while Ca percentage decreases. At the beginning of storage the amount of Cl fits $\text{BaCl}_2 + \text{AlCl}_3$. After a few days (2 days for crystals and 1 week for plain surface) the amount of Cl does not correspond to all the Al being in the form of AlCl_3 and it seems that some of the Al exists in a compound with an undetectable element, probably oxygen.

The CaO native film may react with the electrolyte

in two parallel ways; with thionyl chloride (1), and with adsorbed BaX_2 (2). Both reactions are thermodynamically feasible.



(Estimation of the the free energy change for reaction (2) was made using reaction (3))



It seems that two processes occur on the surface of calcium samples covered with CaO:

I) Reaction between CaO and thionyl chloride.

II) Reaction between the CaO and BaX_2 adsorbed on the surface.

This process occurs in two stages:

a) $\text{Ba}(\text{AlCl}_4)_2$ ($\text{BaCl}_2 \cdot \text{AlCl}_3$) precipitates on the surface.

b) Some of the AlCl_4^- reacts with the CaO and Ba^{++} to give $\text{CaCl}_{2(s)}$, $\text{Al}_2\text{O}_{3(s)}$ and $\text{BaCl}_{2(s)}$.

This reaction is very slow, as evidenced by a sample stored for 10 months at RT. On the surface the sample contained BaCl_2 (18%), CaCl_2 (5.6%), some AlCl_3 and a little Al_2O_3 with a very high total (85-91%). In a cross section it was revealed that under that layer existed a layer with a very low total (43-44%) with no Ba or Al, probably a CaO layer.

By processes a) and b) the surface is depleted of CaO but enriched with BaCl_2 , CaCl_2 , AlCl_3 and Al_2O_3 .

Barium content increases with time up to a maximum of 18 atomic percent after 10 months of storage at RT. Aluminum content on the surface reaches a maximum after one week of storage.

71°C tests: At 71°C Al content decreases with time of storage in all the areas and the %total increases. Areas rich in CaCl_2 do not contain Al (0.95% after 10 days of storage, 0.37% after 28 days of storage) and areas rich in Ba contain some Al, which decreases with time of storage at 71°C to 3% after 28 days. It seems that the oxide layer dissolves with time, and with it the Al-compound-containing layer. As $\text{CaO} + \text{Al}$ decrease with time, the surface is left with a quite pure CaCl_2 layer which does not provide good corrosion protection to the calcium. Corrosion sets in as for cleaned calcium and two distinct areas can be seen. One area becomes depleted of BaCl_2 with time (12% Ba after 10 days, 1-4% after 24 days and 0.5% after 28 days). The second area becomes enriched with BaCl_2 .

2.3.3 Summary of SEM-X-ray Results

In the elemental analysis the difference between samples that were cleaned and untreated samples is seen again. In chemically cleaned calcium, which was deprived of its oxide layer and given a CaCl_2 layer, the outer layer is CaCl_2 with some barium in part of the areas. The only observations of distinct amounts of barium and aluminum were found in the case of inadequately cleaned samples. In the cleaned samples there probably exist two areas: one which is enriched in barium and is the cathodic area and the other a pure CaCl_2 , the anodic area.

In untreated calcium, covered with an oxide layer, the CaO is quite stable. On top of it BaCl_2 and some compound of Al with Cl and probably O precipitate, forming round mounds of crystals. This process is homogeneous on the surface. Upon storage at 71°C, the

CaO reacts with the electrolyte, the situation becomes similar to that for chemically cleaned samples, and two areas are formed. The cathodic BaCl_2 area and the anodic CaCl_2 area.

2.4 AC RESULTS

AC measurements were made on untreated, abraded and chemically cleaned calcium electrodes with the use of hermetically sealed three-electrode cells in 0.75M BaX_2 solution.

The results show:

SEI Resistivity- Resistivity at 20 \pm 5°C after 10-100 days of storage ranges between 40×10^{10} - 200×10^{10} $\Omega \cdot \text{cm}$. Abraded electrodes have the highest resistivity, untreated have lower resistivity and cleaned electrodes the lowest.

SEI Thickness- Two electrodes that were stored in a glove-box for more than a month between cell assembly and filling showed a relatively thick SEI of about 200-500Å. All other electrodes had SEI thickness ranging between 20 to 75Å from the first day of filling. From the ac results the importance of the oxide covering the calcium is obvious. In the case of cleaned calcium there is a rise in the resistivity during the first 20 days of storage. Afterwards the resistivity remains constant but a decrease in the thickness occurs, resulting in a decrease in the resistance. Untreated and abraded electrodes show a common behavior. An SEI is formed with a constant thickness and increasing resistivity. The resistivity of these electrodes is much higher than that of the cleaned calcium.

In corrosion tests, as well, the results for untreated and abraded calcium were similar, while corrosion of cleaned calcium was much

higher. This parallel behavior suggests a connection between high ionic resistivity and low corrosion. Corrosion depends upon the electronic resistivity (R_e), and the connection between R_i (ionic resistivity) and corrosion suggests that in these cases the building of a layer with higher R_i and higher R_e occurs.

2.5 SUMMARY

The improved shelf-life of calcium in BaX_2/TC solutions as compared to CaX_2/TC solutions results mainly from the difference in the solubility or reactivity of the CaO film in those two solutions. In CaX_2/TC solutions the oxide dissolves leaving the calcium with a $CaCl_2$ layer which does not provide the metal with good protection. In BaX_2/TC solutions, on the native CaO layer a $BaCl_2+AlCl_3$ or Al_2O_3 layer is formed. This improves the corrosion resistance of the passive layer. This $BaCl_3+AlCl_3+Al_2O_3$ layer does not form when the oxide is missing from the surface. Therefore cleaned calcium in BaX_2/TC solution corrodes at the same rate as does calcium in CaX_2/TC solutions.

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Table 2-1: Summary of corrosion results for calcium stored in CaX_2/TC and BaX_2/TC solutions in ampules at 71°C.

Calcium Batch treatment	electrolyte	storage time (days)	weight loss of metal (%)	corrosion current ($\mu\text{A}/\text{cm}^2$)
A, untreated	CaX_2 1M	24	18±3	14±2
B, untreated	CaX_2 0.75M	28	17±2	11±1
A, abraded	CaX_2 1M	24	22±5	21±5
B, chem. clea.	CaX_2 0.75M	28	24±3	20±3
A, untreated	BaX_2 1M	24	10±3	8±2
A, abraded	BaX_2 1M	24	8±2	7±2
B, chem. clea.	BaX_2 0.75M	28	24±1	21±1

A: batch 1983, published before in [1], B: batch 1936

Elemental analysis for chemically cleaned Ca
in Ba(AlCl₄)₂/TC solutions

period	1hour mat	1hour shiny	1 day dark	1 day shiny	2 days	1 week	1month	1month 71C grey	white
Al	0.15	0.08	0.38	0.03	0.05	0.00	3.0	0.07	6.40
Cl	7.76	1.34	14.30	1.15	9.00	2.80	29.6	59.80	65.0
Ca	91.40	98.50	84.40	98.50	30.00	97.00	69.5	39.70	15.0
Ba	0.34	0.04	0.39	0.14	0.20	0.07	5.3	0.25	19.0
S	0.30	0.03	0.39	0.00	0.40	0.07	1.9	0.04	0.13
Total	87.00	90.00	72.00	90.00	78.00	88.00	73.0	87.00	87.0

Table 2-2: Elemental analysis results for chemically cleaned calcium stored in BaX₂/TC solution at RT and 71°C.

Table 2-3: Elemental analysis results for untreated calcium stored in BaX2/TC solution at RT and 71 °C.

	1hour	24hours	48hours	48h	1week	1week	1month	10months	10d71	1month71			
		crystal	crystal	surface	crystal	crystal	surface	crystal	surface	grey	white		
Al	1.90	5.70	3.8	1.10	16.40	4.40	7.1	14.60	7.4	0.95	6.5	2.97	0.37
Cl	8.40	17.90	18.0	6.20	48.70	14.00	33.0	43.00	61.4	62.00	60.6	58.80	64.70
Ca	87.00	71.20	71.5	91.20	20.70	77.60	8.2	4.29	8.4	24.00	5.5	5.30	34.20
Ba	1.50	4.10	5.0	1.00	10.80	2.89	5.3	8.70	18.1	12.00	26.5	32.50	0.47
S	0.44	0.72	1.0	0.33	2.73	0.73	2.4	4.50				0.20	0.00
Total	100.00	66.00	71.0	70.00	76.00	72.00	34.0	71.00	85.0	86.00	86.0	88.00	89.00

Untreated Calcium in BaX2 Solutions

Chapter 3

Effect of Additives on the Performance of a High Power Calcium/SrX₂-SOCl₂ Cell.

A part of this work has been presented at the 34th IPSS Cherry Hill, N.J.

June (1990)

Abstract

There is a growing need for a "super- power" battery which can continuously deliver 100 W/kg (about 2A for a C-size lithium cell).

It was previously found that the heat generation rate during discharge of Ca/TC cells is the factor which limits its deliverable power.

Two ways to increase the rate of capability of a C-size $\text{Ca/Sr(AlCl}_4)_2$ - TC cell have been evaluated:

- a) introduction of additives in order to minimize cell heating (this work):
- b) self air cooling of the battery during discharge (ref. 14).

The addition of a combination of SO_2 and P40 additive to the electrolyte was found to increase both the Faradaic efficiency and V_L , thus decreasing cell heating by 10-20%. The decrease of electrolyte concentration together with the addition of SO_2 and P40 improved cell performance at -30°C .

Introduction

The increasing interest in safe, high-power high-energy density batteries has encouraged research on the calcium/TC battery system (1-12). Calcium/TC cells have shown better safety features than have high power lithium cells (4,7). They successfully passed charge, forced discharged, short circuit, and nail penetration abuse tests. The enhanced safety of the calcium/TC cells results from the high melting point of the calcium anode and from the difficulty in plating metallic calcium (strontium or barium) from TC-MX_2 solutions ($\text{M}=\text{Ca, Ba, Sr}$; $\text{X}=\text{AlCl}_4$). The major drawback of the calcium/TC cell has been rapid corrosion of the calcium anode (i.e. too short shelf life). This problem has been successfully solved by the replacement of the CaX_2 electrolyte by SrX_2 or BaX_2 electrolytes (7, 11). These substitutions change the morphology, the chemical composition and properties of the SEI which covers the calcium anode. The addition of SO_2 to the electrolyte was found to

be beneficial (4-6, 8, 10-12) with respect to both storage capability and performance. With the use of small laboratory glass cells, it was found that the voltage and the discharge capacity of carbon cathodes could be dramatically improved by fabricating porous cathodes from a blend of high- and low-surface area carbon blacks (5). However this improvement was not so striking in the case of real D-size cells (9).

The C-size calcium/ SrX_2 -TC cell has recently been optimized for RT applications in our laboratory (8). It delivers 5.5Ah at low rates and 4.4Ah at about 0.9A, i.e. it has 50-80% more capacity (at RT) than has a similar size SAFT Li/ SO_2 (L028SH) cell. Moreover these cells have been stored for up to five weeks at 70°C plus an additional 10 months at RT with less than 5% loss in capacity. Their heat generation rate, as measured under OCV conditions, is smaller than that of equivalent size wound Li-TC cells (8), thus they have a lower self-discharge rate.

Wade et al have recently published results which contradict ours (9). This group has tested experimental D-size Ca/ SrX_2 -TC+ SO_2 cells, made by SAFT, employing cathodes made from a blend of high- and low-surface- area carbon blacks. The maximum capacity at RT and 1A discharge rate was only 5.6Ah for fresh cells and 0 to 5Ah for cells that were stored for 14 weeks at RT. These cells completely failed the 1 month storage test at 55°C. The authors concluded that the performance of these experimental SAFT Ca/TC cells was considerably poorer than that typically observed for Li/ SO_2 cells, and that cells shelf life is less than 10 months.

The authors apparently attribute the poor results to the combination of the electrolyte and the type of carbon cathode. However it seems to us that the major reason for the poor performance and especially for the high rate of self discharge is entirely different. We think that the can material is responsible for these problems. The can material was not specified in the

Wade paper. However in the SAFT presentation (6) it was mentioned that their can material is nickel plated cold-rolled steel (and not stainless steel as is the case of most commercial Li/TC batteries). The results of Wade et al proved that Ni-plated cold-rolled steel should not be used as can material for Calcium/TC cells.

We recently found (10) that the heat generation rate during discharge of Ca/TC cells is larger than that of wound Lithium cells, and, under certain conditions is the factor which limits the deliverable power of the cell. There are two major contributions to this - a polarization heat (W_p) and chemical heat (W_c) which results from rapid corrosion of the anode (low Faradaic efficiency) especially at high current densities and high temperatures.

The goal of this work were: 1) to evaluate a way of increasing the rate capability of the Ca/SrX₂-TC cell with the use of additives in order to minimize cell heating (W_p and W_c). 2) to optimize the cell for -30°C applications.

Experimental

In this work two groups of C-size cells, described in references 8 and 10, were used as a test vehicle. One group had 150 cm² electrode area and a 50μ thick Tefzel (Scimat) separator of 60% porosity; the other group had 200-220 cm² electrode area and a 50μ thick Tefzel separator of 80% porosity. The electrolyte was 0.84M SrX₂ in TC with either 7 or 20% (v/v) SO₂. The SS can and cover were Hudson commercial components. The cells were discharged on a resistive load either at 30°C or 55°C inside a homemade calorimeter (10), or at RT. To the electrolyte of some cells 0.3% P40 additive was added.

Results and Discussion

Effect of Additives on Performance and Storage Capability

Ampule corrosion tests

Our previous findings (15) regarding corrosion of Calcium in 0.84M $\text{Sr X}_2 + \text{SO}_2$ solutions were (Table 1a):

1. The calcium as received from the manufacturer contains only 92% metallic calcium and the rest is CaO.
2. The new batch, 0.4mm thick, which has been rolled in an uncontrolled atmosphere contains a lot of CaO in the bulk of the metal.
3. Calcium that was sandpapered corrodes faster than calcium covered with a thick native oxide layer.
4. No stress corrosion was found. Calcium strips which were sandpapered and twisted a full two turns showed no higher corrosion than plain strips.
5. The corrosion rate of the "new" 0.4mm thick calcium is similar to that of the sandpapered "old" 0.5mm calcium, i.e. it is higher than that of the native oxide covered "old" calcium.
6. SO_2 affects the morphology of the passivating layer of calcium which is formed in TC solutions.
7. The corrosion rate decreases with the addition of SO_2 to the solutions. At 20% SO_2 it is about one half of that in SO_2 free solutions.

Table 1B summarizes (16) the effects of P40 and SO_2 on the corrosion rate of calcium at 70°C. It has been found that the addition of either SO_2 (tested in the range 0-20%(V/V)), or 0.3% P40 additive to the electrolyte, decreased the corrosion rate of calcium strips. The corrosion rate of calcium decreased by about 50% with increase of SO_2 concentration from 0 to 20%. The lowest corrosion rate, 4% per month at 70°C, was measured for the combination of 0.3% P40 additive and 20% SO_2 . The corrosion rate measured for the basic system 0.84M SrX_2 , was 11-12% per month. On the basis of this low corrosion rate a

RT shelf life of about 10 years can be predicted for the A20S type cells (formulated with 0.84M $\text{SrX}_2 + 20\% \text{SO}_2 + 0.3\% \text{P40}$).

Discharge tests

Most of the discharge tests were carried out on a 4 ohm load inside a home-made calorimeter (10) at either 30 or 55°C. The results are summarized in Tables 2 and 3. The heat generation rate during discharge (W_T) measured by the calorimeter, has three components (10,13): Polarization (W_P), entropic (W_S) and chemical (W_C) [1].

$$W_T = W_P + W_S + W_C \quad [1]$$

W_C was calculated from equation 1 as described in references 10 and 13. The Faradaic efficiency ϵ can be calculated from W_C (10) or with the use of equation [2], (13) on the assumption that anodic corrosion is the major component of W_C (10, 13).

$$\epsilon = \frac{V_H}{V_L - W_T/I} \quad [2]$$

where V_H is the thermoneutral voltage of the Calcium/TC cell ($V_H = 3.73 \text{ V}$ (10)) and V_L is the voltage under load. Although the tests have not yet been completed, some conclusions can be drawn. Two sets of tests are reported in Tables 2 and 3. Table 2 summarizes the test results with 150 cm^2 electrode area A7 type cells which contain 0.84M $\text{SrX}_2 + 7\% \text{SO}_2$ electrolyte. Some of them, (A7S type), also contain 0.3% P40 additive. Some cells have been stored for four weeks at 70°C.

At 55°C discharge tests, both types, A7 and A7S (Fig. 1, Fig. 2), fresh and stored, delivered $3.7 \pm 0.1 \text{ Ah}$ on 4 ohms load (about 0.65A). Thus both types lost no capacity on storage. The addition of 0.3% P40 additive caused the following: a 40mV increase in V_L , a 10-20% decrease in W_T and a 25-45%

decrease in W_C . As a result the Faradaic efficiency rose from 83-84% to 87-90%.

At 30°C discharge test storage for four weeks at 70°C, the capacities of both types of cells were not affected. However, with the addition of 0.3% P40 the results were: an 50% increase in capacity (Fig. 3), 150mV increase in V_L , 20% decrease in W_T and 50% decrease in W_C . Thus the Faradaic efficiency rose from -88 to -92%. Discharge tests at RT were limited in number but we can see that storage of A7S type cell for four weeks at 70°C caused 20% loss in capacity.

It is very important to note that in all tests V_L was not affected by the 70°C storage period.

Table 3 summarizes discharge tests on cells having 200-220 cm² electrode area and 7 or 20% SO₂ (A7 and A20 type cells). Some cells also contained 0.3% P40 additive (A7S type cells). Some cells have been stored for four weeks at 70°C plus additional six months at RT. The quality of the calcium foil used for fabrication of batches S (from S17 to S20) .pl67 and T in this set of tests was poor. It contained only about 90% metallic calcium. The rest (10%) was probably CaO which was incorporated into the bulk of the calcium foil during the rolling process. Although the storage conditions in this set of experiments is more severe than the previous one and the anode purity is lower, (Table 2) it can be seen that A20 and A7S type cells lost only less than 10% capacity during this storage period. It seems that the addition of 0.3% P40 additive makes the cell more immune to problems arising from the impurity in the anode and to severe storage conditions.

A stored A7S type cell delivered 4.5 Ah at about 0.6A at 55°C (Fig. 4). Its V_L was 2.5 V, only 0.1V lower than that of a good fresh cell (S-1, Table 2). A stored A20 type cell (Fig. 4) delivered at 55°C only 3.9 Ah at 2.25V

which is 0.2V lower than the V_L value of a fresh A20 type cell (T-13, Table 3). A stored A7S type cell (T-20, Table 2) had at 30°C only 70 mV penalty in V_L versus an unstored good cell (S-3, Table 2).

The effects of 0.3% P40 additive on W_T , W_C and ϵ of fresh and stored 200 cm² cells (Table 3) are very similar to those found for the 150 cm² cells (Table 2).

Discharge tests of AL20S type cells at -30°C

A7 type C-size cells having 130 cm² electrode area delivered (7), at -30°C on a 10 ohm load, 1.9-2 Ah (to a cut-off voltage of 1.5V). However similar cells that had 50μ thick Tefzel separator of 60-80% porosity did not function adequately at -30°C. It was found, with the use of a reference electrode, that the largest overvoltage at -30°C falls on the calcium anode. It was concluded that the combination of high electrolyte viscosity and the small pores of the Tefzel separator is responsible for this high overvoltage. Thus it was decided to reduce electrolyte concentration from 0.84M to 0.75M and to add P40 additive. Table 4 summarizes preliminary results of discharge tests of AL20S type cells formulated with 0.75M SrX₂ + 20% SO₂ + 0.3% P40 electrolyte, 220 cm² electrode area, 80% porosity 50μ thick Tefzel separator. The decrease of electrolyte concentration, the addition of 20% SO₂ and 0.3% P40 additive to the electrolyte improved cell performance at -30°C. Cell capacity at about 0.2 to 0.6A (Fig. 5) rose to 2.8 - 3 Ah (to 1.5V cutoff voltage). However, cell operating voltage is still low, about 1.9V at 50% DOD, and needs to be increased. RT capacity of this cell (type AL20S) is similar to the previous types (A7 and A20).

Conclusions

Formulation of the SrX_2 -TC electrolyte with 20% SO_2 and 0.3% P40 additive was found to have the following advantages: It increases the shelf life by at least a factor of two, it increases cell capacity at high discharge rates and low temperatures, it increases V_L by 40 to 250 mV, it increases Faradaic efficiency and it decreases W_T by 10-20%. On the basis of ampule corrosion tests a RT shelf life of about 10 years can be predicted for the A20S type cell.

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Table 1A

Ampule corrosion tests of calcium in 0.84M SrX_2 - TC - SO_2 solutions. Storage
4 weeks at 70°C.

[SO_2] % V/V	Type of Sample*	Corrosion Rate** (%/month)
0	A	0.5
0	B	11
0	C	10
10	A	3
10	B	12
10	C	11
20	A	1
20	B	6
20	C	4

* A: Calcium strip covered with a thick native oxide layer

B: Calcium strips that were sandpapered

C: Calcium strips that were sandpapered and twisted two full turns.

** Each result is an average of two - three tests.

Table 1B

Ampule Corrosion tests of calcium in 0.84M SrX_2 - SO_2 - TC solutions with and without 0.3% P-40 additive. Storage period - four weeks at 70°C.

[SO_2] (% V/V)	P40 Additive	Corrosion rate (%)/month
0	-	11
0	+	6.5
10	-	10
10	+	5
20	-	6
20	+	3.5

Table 2

Discharge tests on 150 cm² Calcium/TC C-size A7 type cells Electrolyte: 0.84M

SrX₂ + 7% SO₂; load 4 ohms.

Cell Code	Cell Type	Stor. 4W at 70°C	Dis. Temp.	Dis.* Volt. (V)	W _T * (W)	W _C * (W)	ε* (%)	Capac. to 2V (Ah)
Q-12	A7	-	55	2.56	1.2	0.44	84	3.7
S-1	A7S	-	55	2.6	1.1	0.35	87	3.7
Q-6	A7	+	55	2.56	1.21	0.47	83	3.6
S-6	A7S	+	55	2.6	1.0	0.25	90	3.8
Q-10	A7	-	30	2.3	1.21	0.47	88	2.2
Q2	A7	+	30	2.3	1.1	0.25	89	2.2
S-3	A7S	-	30	2.45	0.95	0.22	92	3.2
S-5	A7S	+	30	2.40	1.0	0.25	92	3.2
P-1**	A7	-	RT	2.7				3.2
R-14	A7S	-	RT	2.7				3.7
S-4	A7S	+	RT	2.7				3.0

* At 50% DOD; ** 3 Ohm load; S in cell type stands for 0.3% P40 additive

Table 3

Discharge tests on 200 cm² Calcium/TC C-size cells. Electrolyte 0.84M SrX₂ + 7 or 20% SO₂, load - 4 Ohms (low quality calcium).

Cell	Elec- trolyte	So ₂	Stor. Cond.	Dis. Temp. (°C)	Dis.* (Volt.) (V)	W _T * (W)	W _C * (W)	ε (%)	Capac. (Ah)
T-13	A20	20	1	55	2.45	1.2	0.3	84	4.2
T-8	A20	20	2	55	2.25	1.1	0.23	89	3.9
T-16	A7S	7	2	55	2.5	1.1	0.27	88	4.5
T-6	A20	20	3	55	2.5	1.01	0.25	90	4.2
X-8	A20	20	4	55	2.51	1.2	0.3	85	5.02
S-18	A7	7	1	30	2.32	1.1	0.2	88	3.7
T-20	A7S	7	2	30	2.38	1.0	0.2	92	3.5
T-11	A20	20	1	30	2.25	1.1	0.22	89	4.2

* At 50% DOD

Storage conditions:

1) Fresh

2) 4 weeks at 70°C + 6 months at RT

3) One year at RT

4) Three weeks at 55°C

Table 4

Discharge tests on 200 cm² Calcium/TC C-size cells. Electrolyte 0.75M SrX₂ + 20% SO₂ + 0.3% P40, (type AL20S).

Cell Code	Discharge Temp. (°C)	Load (Ω)	Discharge\$ Voltage (V)	Capacity (Ah)
Z-7	-30	3.1	1.90	2.9*
Z-6	-30	4.9	1.80	2.8*
Z-5	-30	9.8	1.90	3.0*
Z-2	RT	3.1	2.78	4.4**

* to 1.5 cutoff voltage; ** to 2V cutoff voltage;

\$ At 50% DOD

Fig.1

Discharge plot for a fresh 150 cm² Ca/TC "C"-size cell type A7S at 55°C (in a calorimeter), 4Ω load.

Fig.2

Discharge plot for 150 cm² Ca/TC "C"-size cell type A7S at 55°C (in a calorimeter) after 4 weeks storage at 70°C, 4Ω load.

Fig.3

Discharge curves for 150 cm² Calcium/TC "C"-size cells (in calorimeter) at 30°C on 4Ω load. Q10 - A7 type; S3 - A7S type

Fig.4

Discharge plots for 200 cm² Calcium/TC "C"-size cells at 55°C (in calorimeter) after 4 weeks storage at 70°C, 4Ω load. T16 - A7S type; T8 - A20 type.

Fig.5

Discharge curve for 200 cm² Calcium/TC c-size cell type AL20S at -30°C, 4.9Ω load.

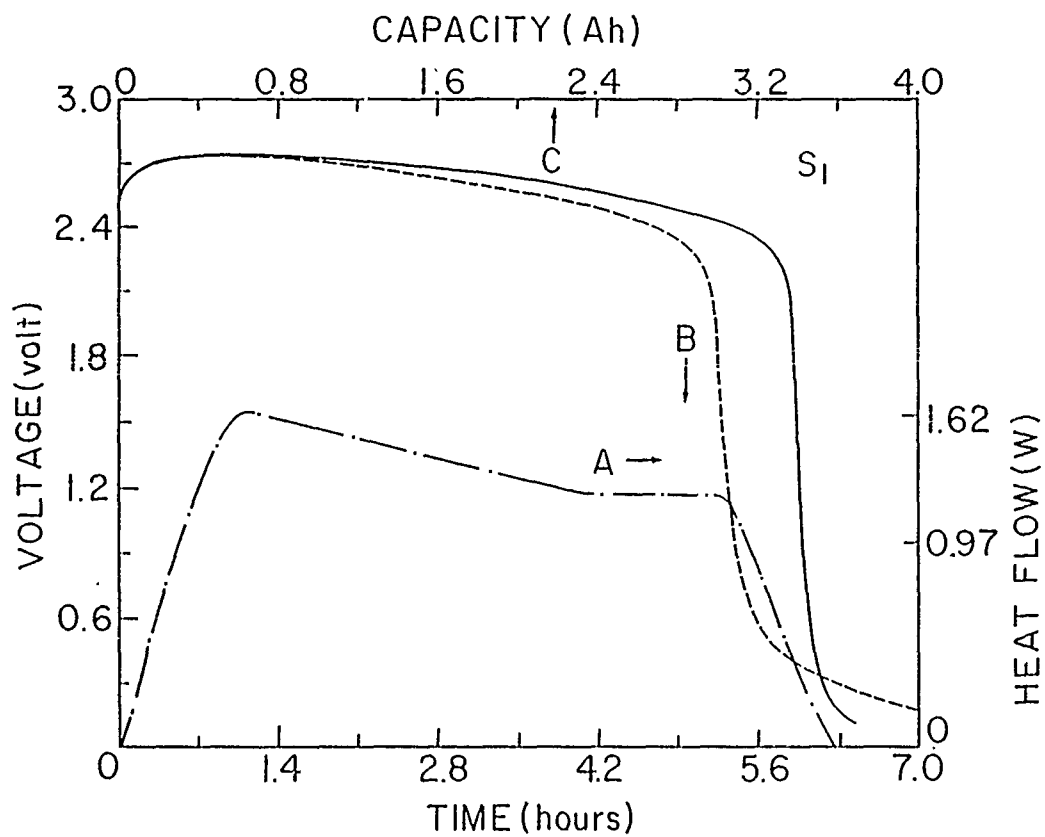


Fig.1

Discharge plot for a fresh 150 cm² Ca/TC "C"-size cell type A7S at 55°C (in a calorimeter), 4Ω load.

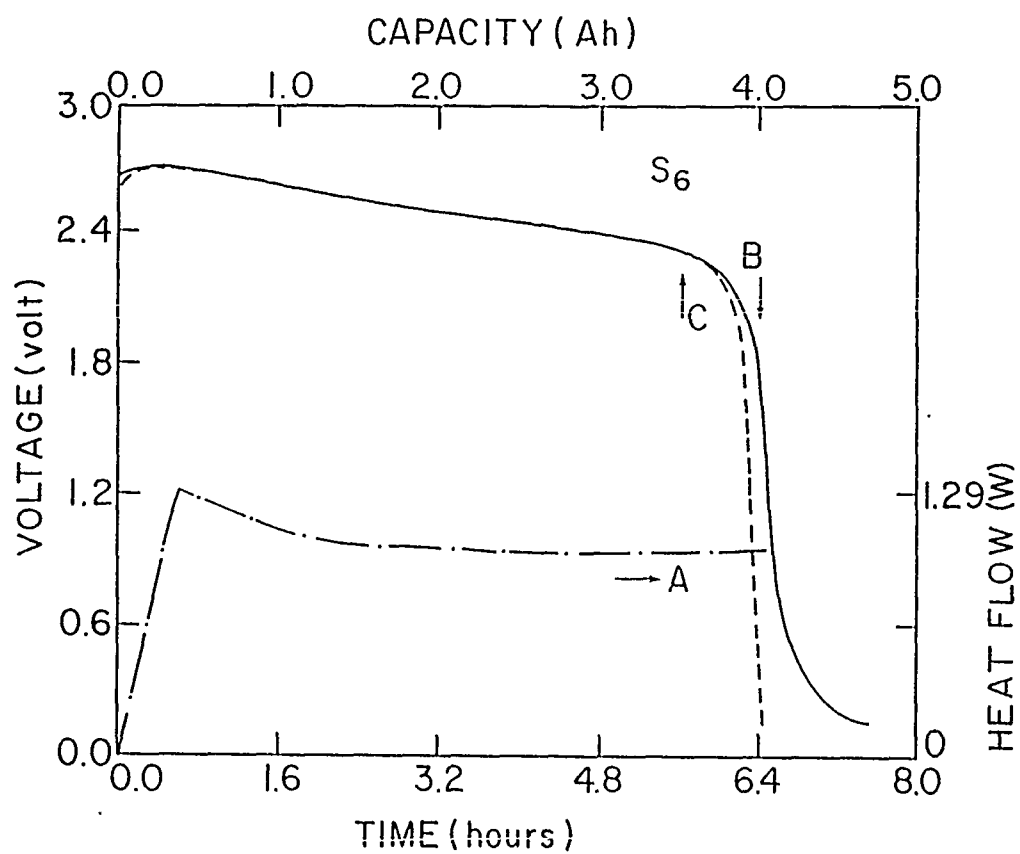


Fig.2

Discharge plot for 150 cm^2 Ca/TC "C"-size cell type A7S at 55°C (in a calorimeter) after 4 weeks storage at 70°C , 4Ω load.

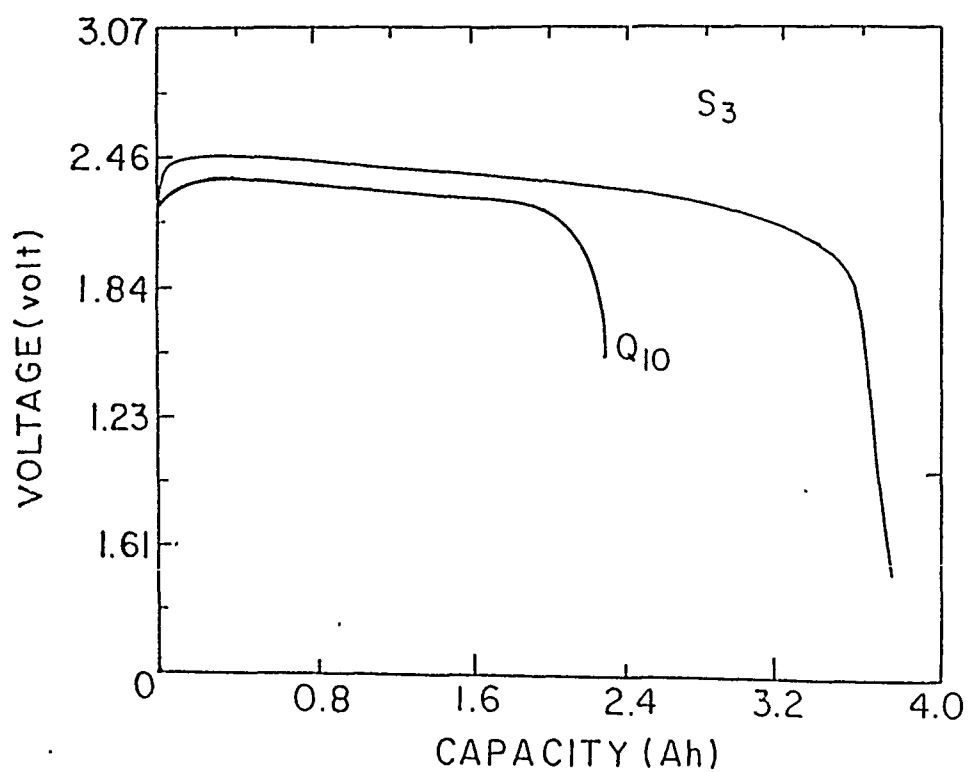


Fig.3

Discharge curves for 150 cm² Calcium/TC "C"-size cells (in calorimeter) at 30°C on 4Ω load. Q10 - A7 type; S3 - A7S type

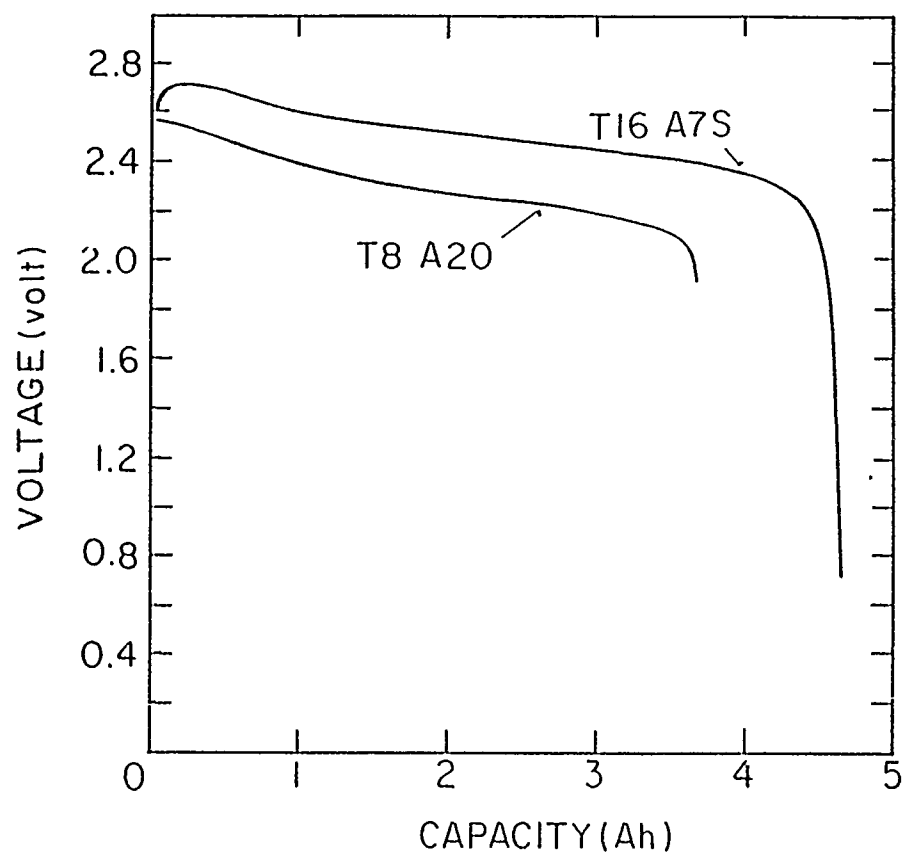


Fig.4

Discharge plots for 200 cm² Calcium/TC "C"-size cells at 55°C (in calorimeter) after 4 weeks storage at 70°C, 4Ω load. T16 - A7S type; T8 - A20 type.

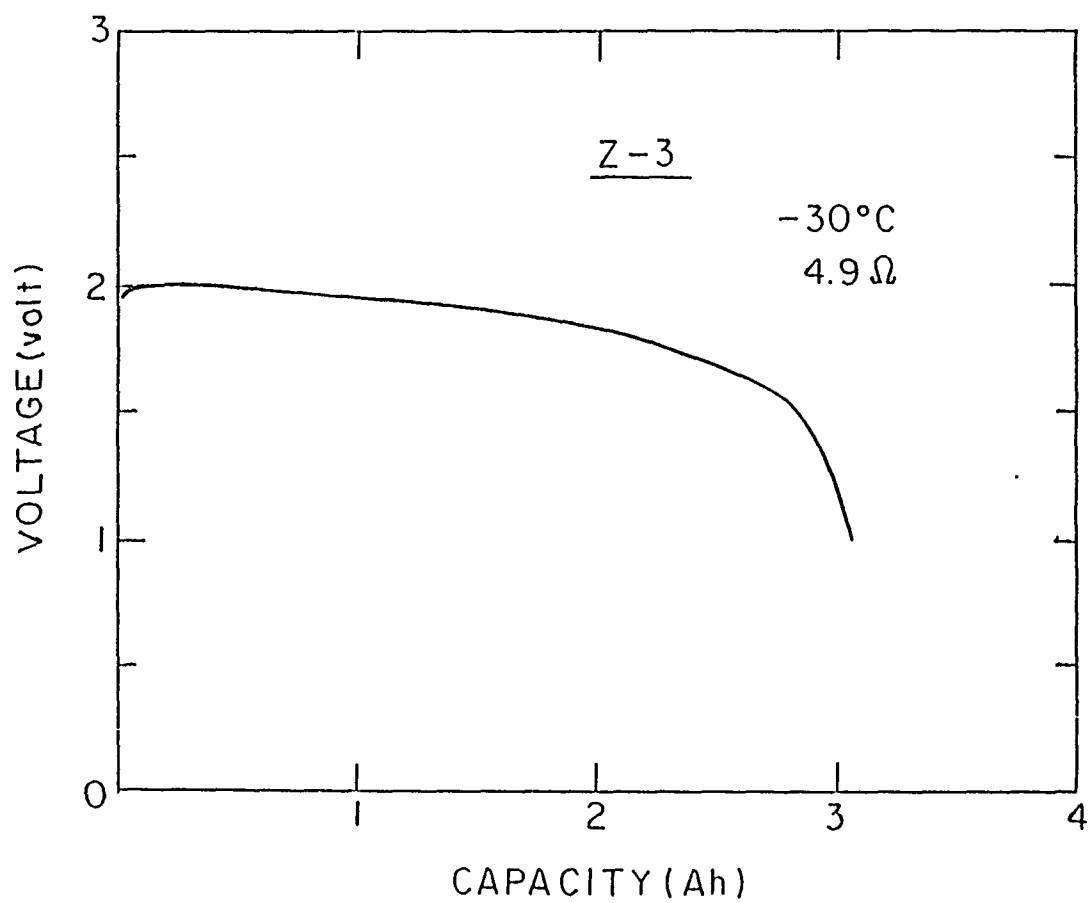


Fig.5

Discharge curve for 200 cm² Calcium/TC c-size cell type AL20S at -30°C,
4.9Ω load.

Chapter 4

Calcium/Thionyl Chloride (Ca/Tc)/Primary Cell

Cell Type: AL20S, Size C (for high rate applications)

Rating 3.2 Volts 5.5 Ah

Tel Aviv University

Preliminary specifications 1/8/90

Physical Specifications

Weight: 56 gr

Dimension: Diameter 25 mm, height 50 mm.

Cell has SS container and is hermetically sealed using glass to metal seal.

It has no venting device (however such a device can be incorporated in the cell).

Electrical Specifications

Voltage:

Nominal 3.15 \pm 0.15V

Average 2.75V at 0.0002-0.025A; 2.5V at 0.1-0.9A.

Final 2.0V

Rated capacity:

25°C; 5.0Ah at 100 mA (5.5Ah at 0.2 to 25 mA)

Storage: (% of rated capacity)

1 year at 21°C > 95%

1 month at 55°C > 95%

1 month at 70°C > 90%

Electrical Performance

Temperature (°C)	AV. Current (A)	AV. Voltage+ (V)	Capacity (Ah)
55	0.3 - 0.6	2.5	4.4
RT (Ca. 25)	0.9	2.5	4.2
RT (Ca. 25)	0.1	2.5	5.0
RT (Ca. 25)	0.0002** - 0.025	2.75	5.5
-20	0.1	2.5	3.0*
-30	0.1 - 0.6	1.8	3.0 (to 1.5V)
200***	0.05	3.3	1.2

+ At 50% DOD

* With a glass separator

** Capacity was predicted from microcalorimetric tests

*** HT version

Operating Conditions

Safety:

This cell has no venting device (all high power lithium cells have a venting device). Limited number of safety tests indicated that this cell does not leak or vent under the following abuse tests: Short circuit, charge at 0.5A to a voltage limit of 10V, force discharge at 0.5A to a voltage limit of 10V, heating to 200°C, partial compression (tested so far with a medium power version only).

Discharge Rate:

The AL20S cell is specially designed for high rate applications. It can deliver up to 4A current pulses. Discharge above 0.8A (at RT) should be intermitted to prevent overheating. Actual temperature rise of the cells depends on battery (or cells) thermal insulation, current and discharge