

AD-A211 856

DTIC FILE COPY

R&D 5899A-CH-01

(2)

ADVANCED CALCIUM-THIONYL CHLORIDE HIGH-POWER BATTERY

Periodic Technical Report

by

Prof. E. Peled

First Periodic Report

(May 1989 - July 1989)

United States Army

EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY

London England

CONTRACT NUMBER DAJA45-89-C-0013

Ramat, Tel-Aviv University Authority for Research  
and Industrial Development Ltd.

Approved for Public Release; distribution unlimited

The research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. This report is intended only for the internal management use of the Contractor and the U.S. Government.

DTIC  
ELECTE  
AUG 30 1989  
D S D

8 28 93

## REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release Distribution unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		4. PERFORMING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Ramat-TA Univ. Auth. for App. Res. and Ind. Dev. Ltd.	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) 32 University Street, Ramat Aviv, Tel-Aviv 61392, ISRAEL		7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U.S. Army European Research Office	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAJA45-89-C-0013	
8c. ADDRESS (City, State, and ZIP Code) 223/231 Old Marlbone Road London NW1 5TH ENGLAND		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Advanced Calcium Thionyl Chloride High Power Battery			
12. PERSONAL AUTHOR(S) Prof. Emanuel Peled			
13a. TYPE OF REPORT 1st Periodic Report	13b. TIME COVERED FROM 15/5/89 TO 15/7/89	14. DATE OF REPORT (Year, Month, Day) 1989/7/15	15. PAGE COUNT 15
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Calcium thionyl chloride battery, performance, shelf life, corrosion of calcium, characteristics of passive layers. High Energy density battery. SEI, calorimetry.
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) 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-SOCl <sub>2</sub> cell. This has been done by replacing the CaX <sub>2</sub> (X=AlCl <sub>4</sub> ) electrolyte by SrX <sub>2</sub> (type A), or BaX <sub>2</sub> (type B). The project's goals are to gain a better understanding of the electro-chemistry of the advanced systems and to establish their safety and performance.  Abstract cont.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

In this phase we improved significantly the cell performance. An improved C-size A7 type cell delivers 4.4 Ah at 0.9 A rate and room temperature which is 50% more than similar size commercial lithium cells have. The SAFT LSH14 lithium-thionyl chloride and the Duracell LO28SH lithium-SO<sub>2</sub> cells have at this rate only 2.9 and 2.7 Ah respectively. During one year of storage at room temperature the heat generation rate of 150 cm<sup>2</sup> C-size A7 type cells decreased to a level of 60-70 μW. A cell lost 0.3 Ah after this storage period. The effect of several parameters on the corrosion rate of calcium in TC solutions was studied. Preliminary results indicate: SO<sub>2</sub> decreases corrosion, there is no stress corrosion due to twisting of Ca foils, the native oxide layer helps in preventing corrosion, Ca foils as received contain only about 90% metallic calcium. The role native calcium oxide layer plays depends on the type of electrolyte used.

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, which have been developed at TAU, and to establish their safety and performance.

Summary of the results of the first year

(contract DAJA45-88-C-0012)

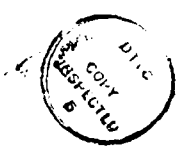
This report contains four chapters. The calorimetric study of Ca/Sr(AlCl<sub>4</sub>)<sub>2</sub>-SOCl<sub>2</sub>+7%(v/v)SO<sub>2</sub> C-size cells during constant-temperature discharge is reported in Chapter 1. Fresh and stored (70°C for four weeks) cells were discharged inside a dedicated home-made calorimeter on two loads: 9.4Ω and 4Ω at 30 and 55°C. The heat flow (W<sub>T</sub>) 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<sub>T</sub> were calculated and plotted against discharge capacity: W<sub>S</sub>-thermodynamic; W<sub>p</sub>-polarization; W<sub>c</sub>-chemical. W<sub>p</sub> was found to be the largest component of W<sub>T</sub>. The maximum corrosion rate (I<sub>c</sub>) of the calcium anode during discharge and its minimum Faradaic efficiency (ε) were calculated from W<sub>c</sub> on the assumption that anodic corrosion is the major component of W<sub>c</sub>. At 30°C, ε was about 0.9 while at 55° it drops from 0.87 at 2 mAcm<sup>-2</sup> to 0.84 at 4 mAcm<sup>-2</sup>. At 30°C the value of ε, is similar to that of t<sub>i</sub> 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(AlCl<sub>4</sub>)<sub>2</sub>-SOCl<sub>2</sub> + 7% (V/V)SO<sub>2</sub>. The thermal power generated by the Ca/CaX<sub>2</sub>

J  
J  
J  
=



Availability Codes	
Dist	Avail and/or Special
A-1	

cells is similar to that of the Ca/SrX<sub>2</sub> cells at 30°C. However at 55°C, I<sub>c,a</sub> of the Ca/CaX<sub>2</sub> cells is much higher. Thus the faradaic efficiency of the Ca/CaX<sub>2</sub> cells is similar or lower than that of the Ca/SrX<sub>2</sub> cells.

Chapter 3 presents the performance, safety and storage properties of Ca/CaX<sub>2</sub> and Ca/SrX<sub>2</sub> cells.

The Ca/CaX<sub>2</sub> cell loses most of its capacity after 4 weeks of storage at 70°C. However, the Ca/SrX<sub>2</sub> 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<sub>2</sub> 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 MX<sub>2</sub>-SO<sub>2</sub>-TC solutions (M=Ca,Sr,Ba) including Raman spectra, viscosity and conductivity data. We explain the effect of SO<sub>2</sub> and temperature on the conductivity and conduction mechanism.

#### Preliminary performance of an improved C-size cell (type A7)

In the previous reports we predicted that the Ca/TC cell will have 25-50% more capacity than a similar size Li-SO<sub>2</sub> cell has. In this research phase we achieved this prediction. We reduced the thickness of the anode from 0.5 to 0.4mm and that of the cathode from 0.7 to 0.5 mm. This way the electrode area rose from 150 to 200-220 cm<sup>2</sup>. The separator is 60% porous 50μ thick Tefzel foil (Scimat). The electrolyte is 0.84M Sr(AlCl<sub>4</sub>)<sub>2</sub>-TC with either 7 or about 20% (v/v) SO<sub>2</sub>. We have built 10 cells 5 with 7% SO<sub>2</sub> (type A7) and 5 with about 20% SO<sub>2</sub> (type A20). Four cells were discharged, two at RT and two at 30°C inside a calorimeter which has been described in the previous report.

The results are summarized in Table 1 and in Figs. 1 to 4.

Comparing the performance of the 150cm<sup>2</sup> cells to that of the 200cm<sup>2</sup> cells we can see the following:

At constant temperature discharge (30°C) and on 4Ω load the capacity increased from 2.2 Ah to 3.55-3.7 Ah and the average discharge voltage also increased by 50mV. The heat generation rate (thermal power) of the cells was not affected.

At RT on 3Ω load (0.8-0.9A) discharge, capacity rose from 3.2 Ah to 4.4 Ah. The maximum can's temperature decreased from 67 to about 50°C. The increase of SO<sub>2</sub> concentration from 7 to about 20% (v/v) does not seem to affect the capacity and cells' heating under these discharge conditions. However there is about 50mV loss in the average discharge voltage. This was previously found by B. Staniewicz et.al [33rd IPSS P.144 (1988)].

Table 2 shows the performance comparison of our improved C-size A7 type cell to two commercial systems. At about 0.9A room temperature discharge our Ca/TC A7 type cell delivers over 50% more capacity than have either the Li/TC LSH14 SAFT cell or Li/SO<sub>2</sub> LO28SH Duracell cell.

On the basis of these results it is expected that a D size Ca/TC cell of our technology will deliver about 10 Ah at 2A rate at RT.

#### Calcium purity problem

The purity of Pfizer bulk calcium is higher than 99.8%. However when it is rolled down to a thin foil it is contaminated by its oxide. Calcium foils as received contain only about 90% metallic calcium and the rest is CaO. Our previous calcium foils have been produced and rolled by Pfizer inside a glove box. However we run out of these batches and cells of (S<sub>17</sub>-S<sub>21</sub>) and T batches were assembled from calcium foils which were rolled down to 0.4mm in a regular room. The main difference between the previous calcium batches and the

present one is that previously most of the CaO was on the surface of the Ca foil while in the case of the last batch (rolled outside glove box) most of the CaO seems to be embedded in the bulk of the calcium. The question is to what extent this difference will affect the electrochemistry of the calcium and the characteristics of the cell.

#### Cell storage for a year at RT

Cells P-9 and P-4 have been stored at room temperature for over one year. Their heat output and OCV were measured at 20°C (Figs. 5 and 6). The OCV decreased from about 3.0V to 2.9V after 100 days and rose again to about 3.2V after 400 days. The heat output continuously decreased from about 800 $\mu$ w for fresh cells to about 60-70 $\mu$ w after 400 days. From the integral on the heat output it can be calculated that the capacity loss in one year was smaller than 0.5 Ah. Most of it 0.4 Ah was lost in the first 4 months. Cell P-4 was discharged at RT on 55 $\Omega$  load and yielded 3.7 Ah. A fresh cell of this batch yielded 4 Ah at the same rate of discharge.

#### Calcium corrosion tests - preliminary results

The goal of this set of experiments was to study the effect of SO<sub>2</sub> concentration, mechanical stress, type of calcium and paper sanding of the surface of the calcium, on the corrosion rate. The calcium strips were sealed in glass ampoules containing 0.84m Sr(AlCl<sub>4</sub>)<sub>2</sub>-TC-SO<sub>2</sub> solutions. These ampoules were stored for 28 days at 70°C. After this storage period, part of the calcium strips were taken for SEM tests and the other part was titrated to determine the content of the metal. Our preliminary findings are:

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

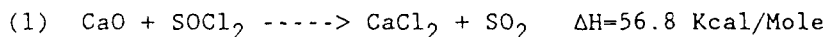
atmosphere contains a lot of CaO in the bulk of the metal.

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<sub>2</sub> 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<sub>2</sub> to the solutions. At 20% SO<sub>2</sub> it is about one half of that in SO<sub>2</sub> free solutions.

The influence of the native oxide layer on the characteristics of calcium electrodes.

The calcium metal foil (Pfizer, 99.8%) has a native oxide film 30-50 $\mu$ m when received from the manufacturer. Recently we became aware that this film plays a greater and more complex role than has been thought of before in determining the corrosion and performance characteristics of the calcium electrodes.

The CaO reaction with TC (1) is thermodynamically favored.



It was found that the rate of reaction (1) depends on the type of the metal ion (M) (M= Ca<sup>++</sup>, Sr<sup>++</sup>, Ba<sup>++</sup>) in the thionyl-chloride (TC)/M(AlCl<sub>4</sub>)<sub>2</sub> solution. Therefore we began a comprehensive study of the role of the oxide passive film on the behavior and properties of calcium electrodes.

In this study we use microcalorimetry, SEM + X-ray fluorescence analysis and AC technique to characterize untreated calcium electrodes and calcium electrodes from which the oxide layer was removed in several ways.

The following subjects are being investigated:

- a) The rate of exchange of the oxide layer to a chloride layer
- b) The rate of exchange of the Ca<sup>++</sup> in this layer with Sr<sup>++</sup> or Ba<sup>++</sup>.
- c) The changes in the morphology of the film.
- d) The changes in the thickness and resistivity of the film as a result of the changes discussed in a), b) and c).
- e) The correlation between the nature of the film and the shelf-life of the calcium battery.

All the experiments are now in progress.

TABLE 1

## Effect of Electrode Area on the Performance of a C-size Cell

Electrolyte: A7-0.84M  $\text{Sr}(\text{AlCl}_4)_2^+$  7%  $\text{SO}_2$ 

Cell Code	Elect. area ( $\text{Cm}^2$ )	Average Voltage (V)	Average Current (A)	Capacity 2V cut-off (Ah)	$W_{T,a}$ heat flow at 50% DOD (W)	Max. Temp. of can ( $^{\circ}\text{C}$ )
$Q_{10}^*$	150	2.3	0.58	2.2	1.1	-
$S_{18}^*$	200	2.35	0.59	3.7	1.1	-
$T_2^*$	220	2.35	0.59	3.55	1.1	-
$P_1^{**}$	150	2.8	0.93	3.2	-	67
$S_{17}^{**}$	200	2.65	0.88	4.4	-	49
$T_{10}^{**+}$	200	2.6	0.81	4.4	-	51

\* Discharge inside the calorimeter at  $30^{\circ}\text{C}$ .

\*\* RT discharge.

+ Electrolyte: 0.84  $\text{Sr}(\text{AlCl}_4)_2^+$  20%  $\text{SO}_2$ .

## TABLE

Comparison of Performance of C-size Cells of Different Technologies at RT and 0.9A\*

Technology	Cell Code	Ah	Average Voltage
Ca/TC (TAU)	Laboratory Prototype A7	4.4	2.65
Li/TC** (SAFT)	LSH14	2.9	3.2
Li/SO <sub>2</sub> ** (Duracell)	10285H	2.7	2.7

\* It is equivalent to at least 2A for D size cell.

\*\* Information was taken from manufacturers' brochures.

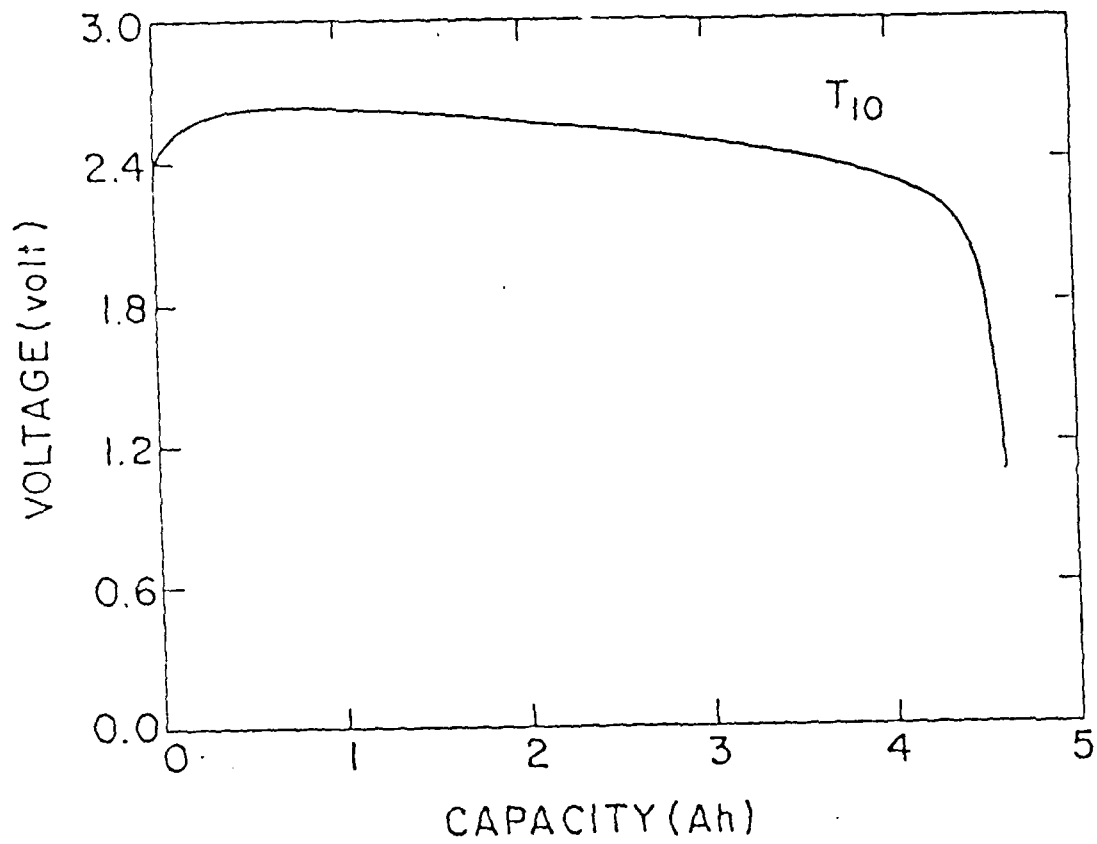


Fig. 1 Room temperature, discharge curve of C-size Ca/0.84M SrX<sub>2</sub>-TC + 20% (v/v) SO<sub>2</sub> cell (T<sub>10</sub>), 200 cm<sup>2</sup>, 3.2 Ω load.

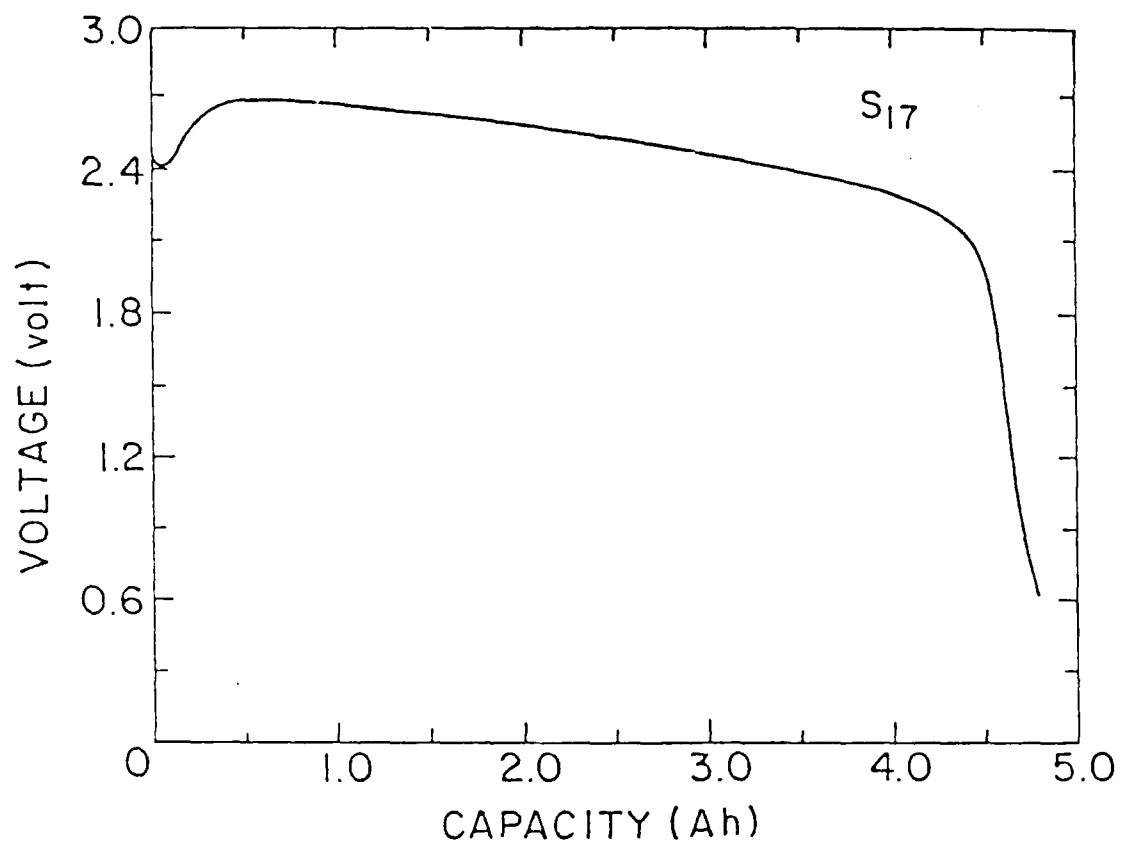


Fig. 2 Room temperature, discharge curve of C-size Ca/0.84M SrX<sub>2</sub>-TC + 7% (v/v) SO<sub>2</sub> cell (S<sub>17</sub>), 200 cm<sup>2</sup>, 3.0 Ω load.

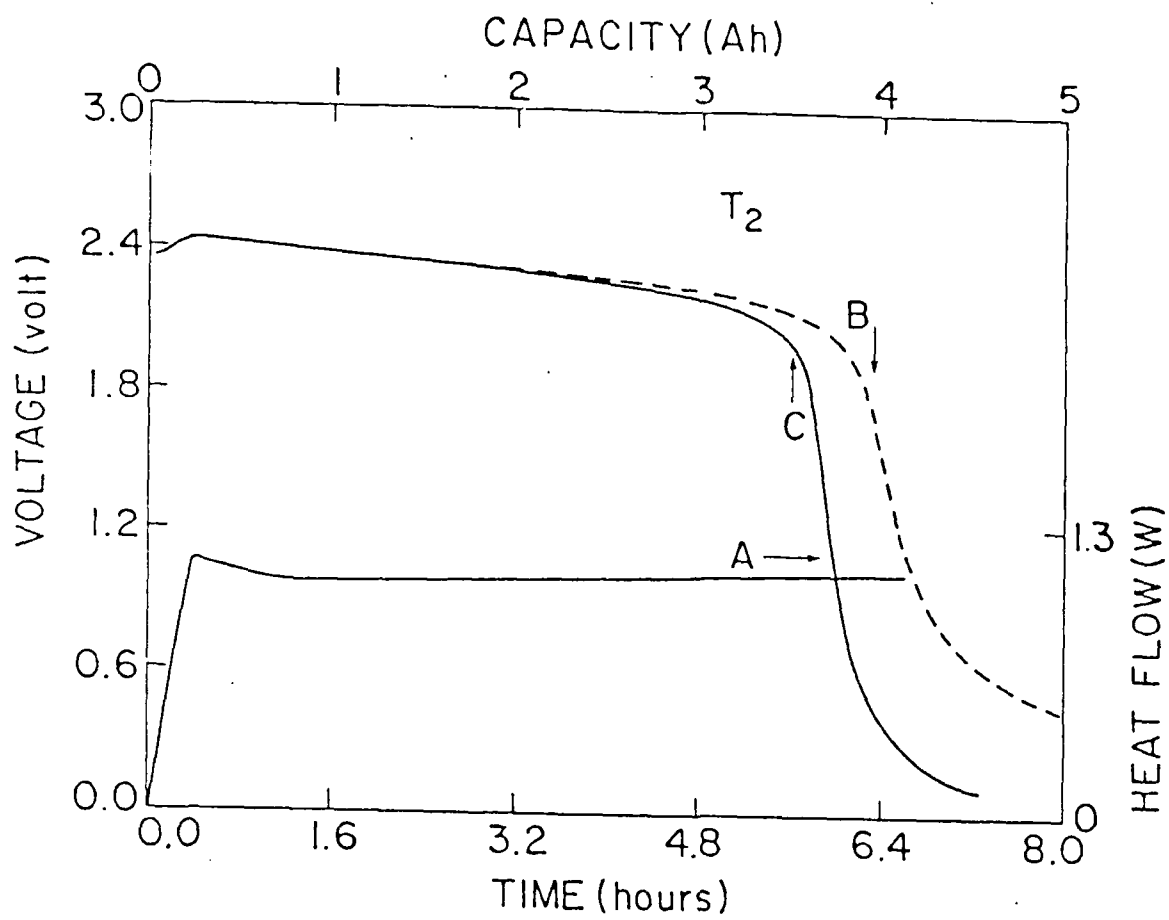


Fig. 3a Discharge (lines B and C) and calorimetric (line A) curves of C-size Ca/0.84M SrX<sub>2</sub>-TC + 7% (v/v) SO<sub>2</sub> cell. T<sub>2</sub> fresh, 4.05 Ω load, 30°C, 220 cm<sup>2</sup>.

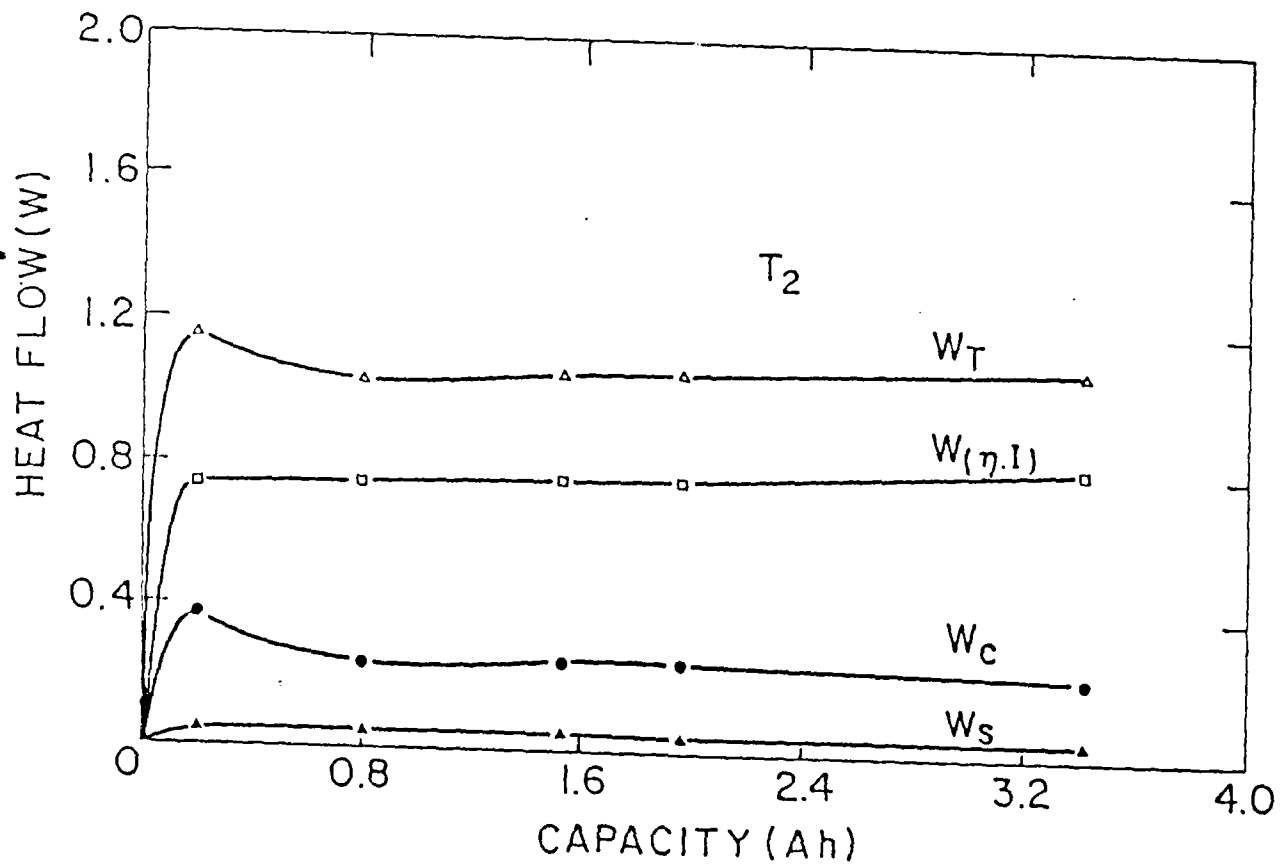


Fig. 3b Plots of  $W_T$  (total heat flow),  $W_p$  (polarization),  $W_c$  (chemical) and  $W_s$  (thermodynamic), for cell  $T_2$ , vs. discharge capacity.

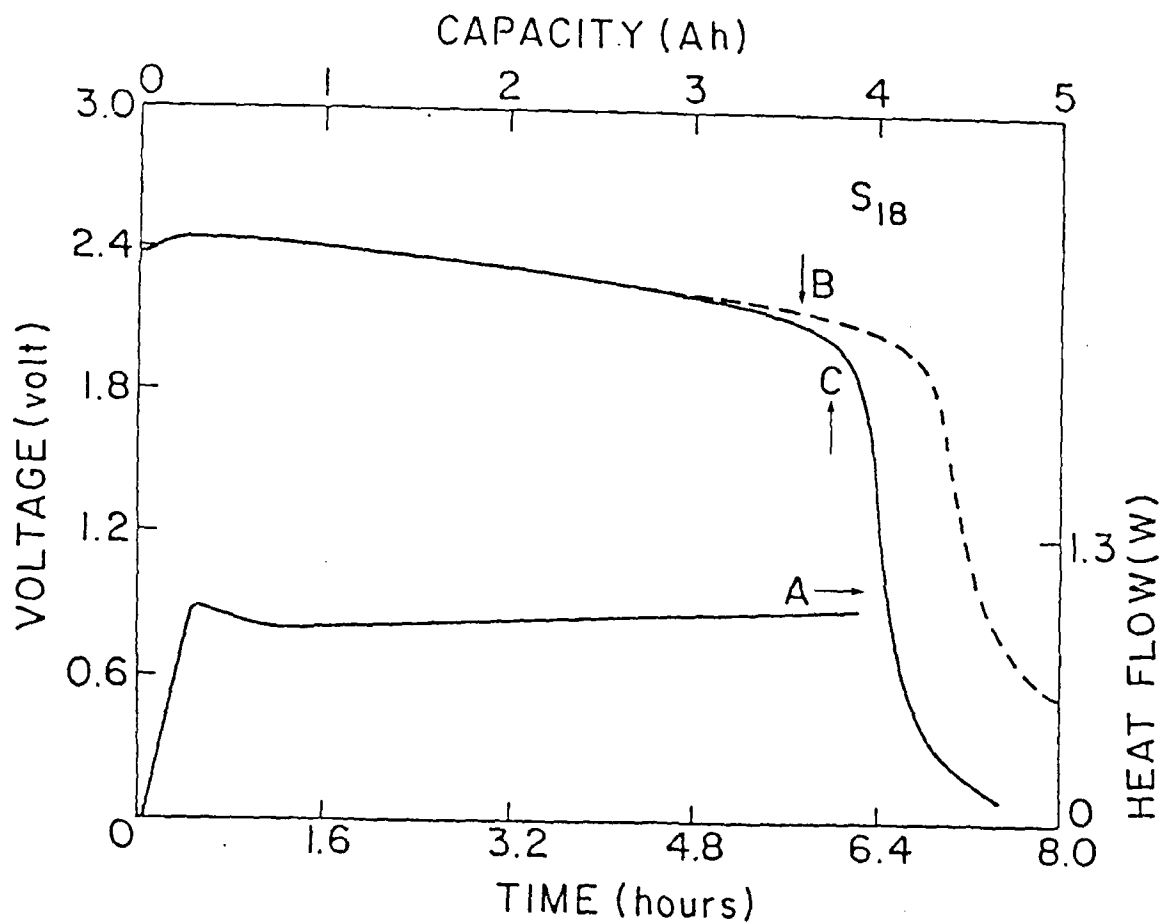


Fig. 4a Discharge (lines B and C) and calorimetric (line A) curves of C-size Ca/0.84M SrX<sub>2</sub>-TC + 7% (v/v) SO<sub>2</sub> cell. S<sub>18</sub> fresh, 4.05 Ω load, 30°C, 200 cm<sup>2</sup>.

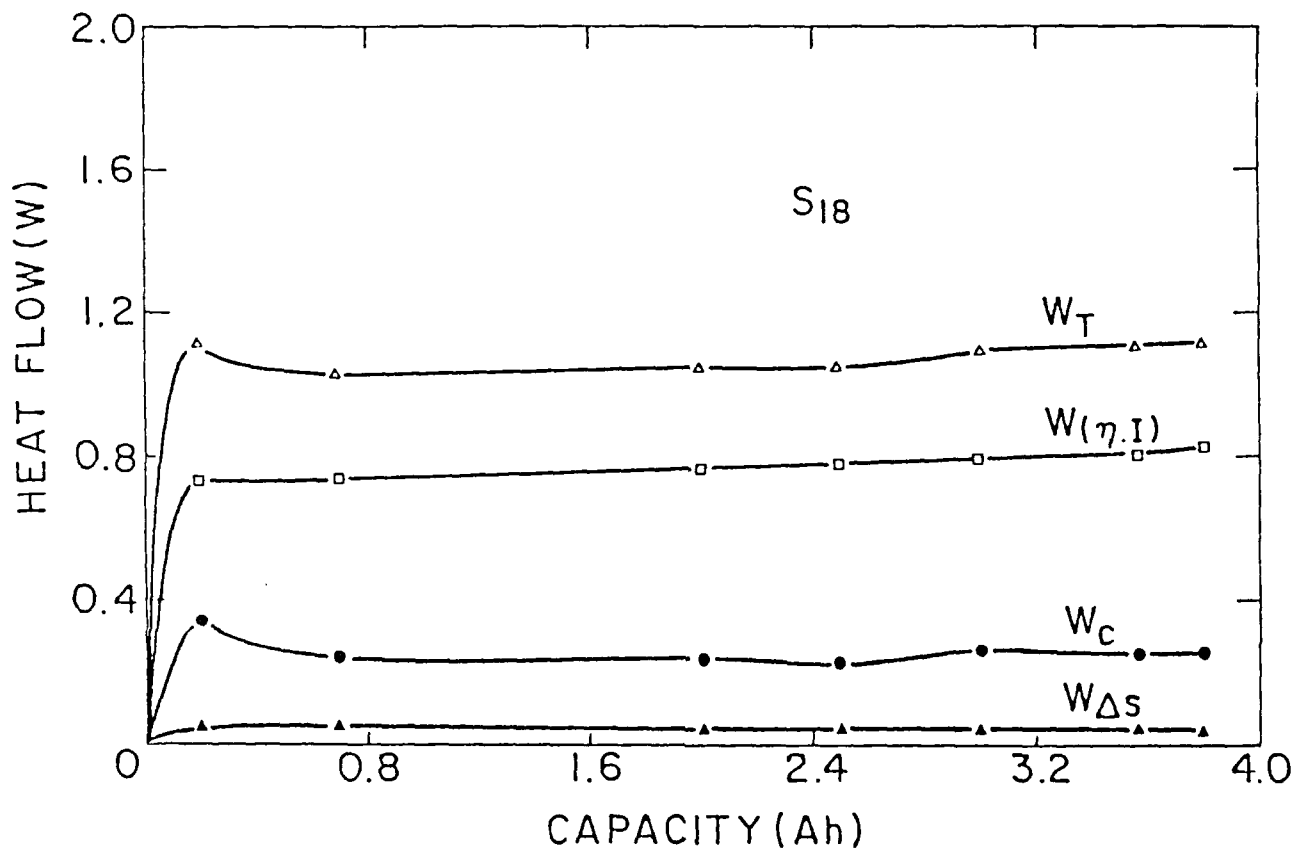


Fig. 4b Plots of  $W_T$  (total heat flow),  $W_p$  (polarization),  $W_c$  (chemical) and  $W_s$  (thermodynamic), for cell  $S_{18}$ , vs. discharge capacity.