(1)

Advanced Calcium Thionyl Chloride High Power Battery

Periodic Technical Report

R/D-5899-CH-01-2

by

Professor E. Peled
Sackler Faculty of Exact Sciences, School of Chemistry
Tel-Aviv University, Tel-Aviv, ISRAEL 69978

Second Periodic Report
February 1988 - June 1988

United States Army
EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY
LONDON, ENGLAND

CONTRACT NUMBER DAJA45-88-C-0012
Ramot, 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.

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for Public Release
Distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Ramot-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
DAJA45-88-C-0012

8c. ADDRESS (City, State, and ZIP Code)
223/231 Old Marlebone 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
2nd ~~1st~~ Periodic Report

13b. TIME COVERED
FROM 88/2/23 TO 88/6/24

14. DATE OF REPORT (Year, Month, Day)
88/7/25

15. PAGE COUNT
38

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Calcium battery, thionyl chloride, conductivity-Viscosity Raman spectra, Strontium, Barium shelf, life, High Energy density battery.

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~~ (Calcium Thionyl Chloride) systems which have much better storage properties than the state-of-the-art Ca-$SOCl_2$ 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.

(continued on reverse page)

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE (Include Area Code)

22c. OFFICE SYMBOL

DD Form 1473, JUN 86

Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

A

Abstract continued

In this report we present results regarding the properties of MX_2-SO_2-TC solutions (M = 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. We studied the effect of 70°C storage on performance of the baseline (C-size) cell. A fresh cell delivered, at room temperature, 3.4 Ah and 3.2 Ah on 10 and 4 ohm load respectively. It lost 20% and 55% or more capacity after two and four weeks of storage at 70°C, much more than type A cell. Short circuit, heavy load and reversal tests of type A cells ended with no cell venting or leaking. Ampule corrosion tests of calcium foils in type A electrolyte reveal 0.5-3% corrosion after four weeks of storage at 70°C. This indicates that a room temperature shelf life of more than ten years is feasible for type A system.

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: $Ca/Sr(AlCl_4)_2-SOCl_2/C$ - (type A) and $Ca/Ba(AlCl_4)_2-SOCl_2/C$ - (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 $Li-SO_2$ C-size cell.

The projects' goals are to gain a better understanding of the electrochemistry of the advanced calcium-thionyl-chloride systems 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 has a similar size $Li-SO_2$ battery. Our Ca-TC cell can be made vent free and resists, 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 the same working voltage that has the $Li-SO_2$ cell. Thus, it can replace the $Li-SO_2$ battery with no problem. In addition it is expected to be less expensive than the $Li-SO_2$ 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 $Li-SO_2$ technology.

The proposed statement of work includes: study of the electrochemistry, safety, performance and storage properties of the state-of-the-art

$Ca/Ca(AlCl_4)_2$-TC+SO_2/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 of the electrolytes; AC, SEM, microcalorimetry, 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.

Summary of the First Periodic Report (December 1987-February 1988)

In this report we described the experimental techniques including: preparation of solutions, conductivity and viscosity measurements, Raman spectroscopy measurements, AC measurements and C-size assembly.

The viscosity, conductivity and Raman spectra of 0.84M SrX_2-SO_2-TC ($X=AlCl_4$) solutions were reported. A comparison has been made between the viscosity of CaX_2, SrX_2 BaX_2 with and without SO_2 added. The Raman spectrum of 1M $Ca(AlCl_4)_2$ -30% SO_2-TC solution was presented. A preliminary AC spectrum of Ca electrode in 0.75M CaX_2-TC solution was also reported.

RESULTS AND DISCUSSIONS

1. Electrolyte Properties

This project is the continuation of many years of effort in our laboratory. Its goal is to have a better understanding of the conduction mechanisms in TC-electrolytes and the effect that SO_2 and temperature have upon them. In addition, we would like to form a data base which will help in optimizing the Ca-TC battery.

The effects of SO_2 and temperature on the conductivity of 0.84M $Sr(AlCl_4)_2$-TC solutions was previously reported (Ref.3). There is a pronounced effect of SO_2 (up to a factor of 7 at low temperatures) on the conductivity.

The viscosity of the MX_2-TC solutions rises significantly with the decrease of temperature and with the increase of MX_2 concentration. At room temperature it is about 1.5-2 cp for dilute MX_2 solutions and about 6-8 cp for 1.3M MX_2 solutions. However, at $10^{o}C$ it is about 3 cp for dilute MX_2 solutions and 8-14 cp for 1.3M MX_2 solutions. For high MX_2 concentration at $-30^{o}c$ it may reach 30 cp or more.

During cell discharge the electrolyte concentration rises by 20 to 40%. The exact change depends on cell design. In addition, during cell discharge, the concentration of SO_2 is built up. It may reach 30% (V/V) at the end of the discharge for a cell that contains no SO_2 to start with. We choose to study the effect of SO_2 and temperature on the viscosity and conductivity of 0.84M MX_2 and 1.3M MX_2 as the first concentration seems to be an optimal one (as the first choice) and the last one is the maximum predicted electrolyte concentration at the end of the discharge. Actually we believe that the optimal electrolyte concentration should be in the range 0.7M to 1.0M MX_2 depending on the applications.

The effects of SO_2 and temperature on the conductivity of 1.3M SrX_2-SO_2-TC solutions are shown in Fig.1 (Ref.3). At the temperature range -40 to +100°C the conductivity of solutions containing 0 to 30% (V/V) SO_2 increases monotonously with temperature. The conductivity also increases with the concentration of SO_2, however the most pronounced effect is at 10 to 20% SO_2.

The effects of SO_2 and temperature on the conductivity of 0.84M BaX_2-SO_2-TC and 1.3M BaX_2-SO_2-TC solutions are shown in Figs. 2 and 3. The general behaviour is similar to that in Fig.1. However, at high SO_2 concentrations the curves cross each other at about 80°C. In 1.3M BaX_2 solutions the most pronounced SO_2 effect is at the 10% level. The 40% SO_2 line in Fig.2 shows a broad peak at about 20°C.

These and previously reported results (3,5) indicate that: a) at room temperature and 30% SO_2 the conductivity increases in the order: $CaX_2 > SrX_2 > BaX_2$; b) at lower SO_2 concentrations the order is $CaX_2 > BaX_2 > SrX_2$.

The effects of SO_2 concentration and temperature on the viscosity of 1.3M SrX_2-SO_2-TC solutions are shown in Fig.4. Both, addition of SO_2 and increasing the tempearture cause a decrease in the viscosity of the solution. Similar phenomena were found for 0.84M BaX_2 (Fig.5), 1.3M BaX_2 (Fig.6) and 0.7M CaX_2 solutions (Fig.7).

The values of the apparent energy of activation for viscosity are collected in Table 1. It changes with the type of cation and with salt-concentration, but it changes very little with SO_2 concentration.

In order to find out if SO_2 increases conductivity, only because of its effect on the viscosity of the solutions, we plotted the normalized conductivity (σ_N) vs. temperature (Figs. 8,9,10,11). These plots are equivalent to Walden Product plots

$$\sigma_N = \frac{\sigma \times \eta_{\text{electrolyte}}}{\eta_{\text{solvent}}}$$

$$\text{Walden Product} = \lambda \cdot \eta_{\text{electrolyte}} = Kr$$

η = viscosity, r = radius of the solvated ion,

λ = molar conductivity of the ion

Walden product, $\lambda\eta$ (or normalized conductivity) should be independent of temperature, to the extent that the radius of the solvated ion is constant over the range of the temperature considered.

The normalized conductivity is about constant for 0.84M BaX_2 and SrX_2 10-30% SO_2 solutions, indicating no major change in solvation radius at 10-30% SO_2. However, it does change going from 0% to 10% SO_2 indicating that at 10% SO_2 the Ba^{++} and Sr^{++} ions are close to have their maximum solvation number.

Above 1M MX_2 σ_N changes both with temperature and with SO_2 concentration indicating a change in solvation number. The maximum change of σ_N was found at the range 0-10% SO_2 for 1.3M BaX_2 (Fig.10) and at the range 10-20% SO_2 for 1.3M SrX_2 (Fig.9) indicating that m in $M(SO_2)_m{}^{++}$ is larger for Sr^{++} than for Ba^{++}.

The normalized conductivity is much too high for the low dielectric constant solvents, for example at 10°C it is 60-100mS/cm. It is in the order of that for aqueous solutions. In addition, the Stokes radius is unreasonably small, for example the one calculated for 1.3M SrX_2-20% SO_2 solution (σ - 11mS/cm, η -6cp) is about 1Å only. All these and the fact that, in a certain temperature and concentration range, we found a negative apparent energy of activation for conductivity, indicate a pronounced contribution of a non-Stokesian relay-type (hopping) mechanism of conductivity.

SO_2 affects conductivity in two ways: a) It decreases viscosity. b) It increases the ionic radius and thus leads to a higher dissociation constant and a larger hopping distance in the relay-type conductivity mechanism.

Temperature affects conductivity in several opposing ways: It decreases viscosity and thus enhances Stokesian conductivity. It reduces the size of the ionic aggregates (Eq.2) and thus may cause a shift from solvent-separated ionic aggregates (Eq.1) to intimate ionic aggregates (Eq.3). This reduces the dissociation constants of the uncharged ionic aggregates (Eq.3) and in addition should shorten the hopping range (Eq.4).

1. $2XIIMIIX \rightleftharpoons MIIX^+ + XIIMIIXIIX^-$

2. $XIIMIIX \xrightarrow{T} XMX$

3. $2XMX \leftrightharpoons MX^+ + MX_3^-$

4. $XM^+ + XMX \rightarrow XM^+ \underset{\curvearrowleft}{\cdots} XMX \longrightarrow XMX + MX^+$

II-stands for a solvent molecule

As previously reported we are using Raman spectroscopy technique for collecting information on possible interactions between TC, SO_2 and the electrolyte salts. Fig.12 shows a spectrum of 30% SO_2 in TC with no salt added. The peak at 1140 cm^{-1} is assigned to "free" SO_2 and the broad one at 1230 cm^{-1} is assigned to TC. Raman spectra of MX_2-SO_2-TC (M=Ca,Ba,Sr) show peak or shoulder at 1147 to 1153 cm^{-1} (Figs.13 and 14 and Figs. 5 and 9 First Periodic Report). The height of this peak or shoulder increases with the concentration of both SO_2 and MX_2 and is therefore assigned to the $M(SO_2)_m^{++}$

complex. No effect of SO_2 on $AlCl_4^-$ bands was found. In the case of SrX_2 and CaX_2 solutions it was possible to measure its height while in the case of BaX_2 solutions it was not because there was no clear separation between the two neighboring peaks.

In order to quantitatively analyze a Raman spectrum there is a need to use an internal reference. We used the free SO_2 peak as an internal reference and plotted the ratio:

Nor.I-I(free SO_2)/[SO_2] x I (bonded SO_2)

vs. SO_2 concentration (Fig.15). It seems that in both systems (lines 1 and 2) there is an inflection point at about 3M SO_2. This may indicate that the SO_2 solvation number for Ca^{++} and Sr^{++} is about 3. These results support our previously mentioned conclusions that the SO_2-conductivity enhancement is in part due to the formation of large solvated ionic aggregates.

2. Discharge tests

a) Baseline system

A few years ago we used 9010 glass for the G/M seal and a hole in the cover as a filling port. We encountered problems of leaks through the G/M seal and around the filling port. Therefore we replaced this cover assembly by a new cover made by Fusite using a standard Hudson cover to which a Fusite G/M eyelet with a 435 glass was welded. This G/M eyelet contained 52 alloy tube which was used as a filling port. This modification completely eliminated the leak problem.

The baseline C-size cells have about 130 cm^2 electrode area and a 0.1mm thick glass separator. Their electrolyte is 0.9M $Ca(AlCl_4)_2$ + 7% (V/V) SO_2.

The effect of 70°C storage on their 10 ohm room temperature discharge is shown in Fig.16. A fresh cell delivered 3.4Ah. After two weeks of storage at 70°C the cell lost 20% of its original capacity while after four weeks of storage it lost more than half of its capacity and had a 0.3V lower discharge voltage. At a higher discharge rate the capacity loss is more severe (Fig.7). On 4 ohm load at room temperature a fresh cell delivered 3.2Ah. After two weeks of storage the cell lost 30% of its capacity and about 0.3V in discharge voltage. After four weeks of storage the cell died (lines 3a,3b, Fig.17).

The difference in the storage properties of the baseline cell and a type A cell can be seen in Figs. 18 and 19. After four weeks of storage the best baseline cell delivered, on 10 ohm load, about 1.6Ah while type A cell delivered 3.2Ah. At -30°C and on 10 ohm load (Fig.19), a fresh baseline cell delivered 20% more capacity than a fresh type A cell. However, type A cell lost no capacity after four weeks of storage at 70°C (curves A and B, Fig.19).

3. <u>Microcalorimetry of Cells</u>

The 20°C heat output of several cells was measured vs time of storage at room temperature (Fig.20). The old version baseline cells exhibited heat output peak (curves 1 and 2). Due to equipment problems we were not able to test the new version cell during the first 35 days, thus we do not know yet if it has or has not a heat output peak. However, its heat output is less than half of that of the old version cell. This improvement may result from a better hardware and from the additon of 7%(V/V) SO_2.

The heat output of a type A cell is even smaller and reached about $250\mu W$ after 100 days of storage.

4. **Discharge tests of type A cells**

We built 22 type A cells and started testing them. These cells contain a 60% porous 50μ thick Tefzel (SCIMAT) separator instead of the glass separator that has been used before. In addition their active electrode area is about 150 cm^2 (instead of 130 cm^2).

At room temperature they delivered (Fig.21) 4Ah on 60 ohm load and 3.2Ah on 3 ohm load (about 0.9A). In order to demonstrate their rate capability we discharged a cell on 1 ohm load in intermittent regime - 5 minutes on and 5 minutes off (Fig.22). Average cell voltage was 2.3V, i.e. it was discharged at 2.3A (15 $mAcm^{-2}$). It delivered 1.5Ah to a cut-off voltage of 2V. Its skin temperature rose to a maximum of 90°C.

5. Safety tests of A type cells

A fresh A type cell was short circuited on 0.1 ohm load (Fig.23). Its short circuit current rose to a maximum of 8.5A and its skin temperature reached a maximum of 125°C. It seems that the decay of the short circuit current results from a partial melting of the Tefzel separator.

A heavy load test ended in a similar way. A cell was discharged continuously on 1 ohm load. Its skin temperature rose to 125°C (Fig.24) and the cell died. Up to this point the cell delivered 0.9Ah at about 2.4A.

A forced discharge test is described in Fig.25. This cell was forced discharged at 0.25A with a reverse voltage limitation of 10V. After 60 minutes into reversal the current started to decline. The skin temperature of the cell reached a maximum of 80°C.

It should be noted that in these three safety tests no cell vented or even leaked.

6. Ampule corrosion tests

The goal of this test was to find out the effect of SO_2 on the corrosion rate of calcium in 0.84M SrX_2-SO_2-TC solutions at 70°C. Prior to this test we analyzed the calcium content of Pfyzer 99.5% calcium foils by acid titration. We found out that fresh calcium foils contain 98±0.5% calcium and the rest is probably oxygen. However, calcium foils that have been stored in the glove box for several weeks contain only 93.5±0.5% calcium.

Calcium strips have been stored with the electrolyte in sealed glass ampoules for four weeks at 70°C. Then they were titrated with HCl and the total amount of calcium metal and CaO (if existed) was calculated.

The loss of calcium was then calculated taking into account the average oxide content of the calcium strips prior to its immersion into the solution. Preliminary results are summarized in Table 2.

It can be seen that the corrosion rate of calcium is very low - only 1-3% per month at 70°C. The lowest values were found for 0, 7.5 and 20% SO_2 and the highest for 10% SO_2. More tests are in progress to find out if the SO_2 effect is significant. In any case, these preliminary results indicate that Type A cell may have a very long shelf life of more than ten years.

7. Research Plans for Remainder of the Contract Period

1. Baseline system ($Ca(AlCl_4)_2$ - TC).

1.1. Complete the report on Raman and viscosity measurements for the $Ca(AlCl_4)_2-SOCl_2-SO_2$ system.

1.2. Study the effect of SO_2 on the calcium-SEI electrode.

1.3. Complete the evaluation of the properties of C-size baseline cells.

2. Study the electrochemistry of type A and B systems $Sr(AlCl_4)_2-SOCl_2-SO_2$ and $Ba(AlCl_4)_2-SOCl_2-SO_2$.

2.1. Complete the report on Raman and viscosity measurements.

2.2. Study the effect of SO_2 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. Proceedings of the 172nd Electrochemical Soc. Meeting, Honolulu 1987.

3. E. Elster, R. Cohem, M. Brand, Y. Lavi and E. Peled. J. Electrochem. Soc. in press.

4. A. Meitav and E. Peled, Electrochimica Acta, in press.

5. R. Cohen, J. Kimel, E. Elster, E. Peled, 4th International Meeting on Lithium Batteries, Vancouver, Canada, May 1988.

6. E. Peled, E. Elster, R. Cohen, J. Kimel and Y. Lavi, 33rd IPSS, Cherry Hills, NJ., June 1988.

TABLE 1.

APPARENT ENERGY OF ACTIVATION FOR VISCOSITY (X = $ALCL_4$)

SOLUTION	Ea kcal/mol
1.2M CaX_2, 0-30% SO_2	4.6
1.3M SrX_2, 0-30% SO_2	5.4
1.3M BaX2, 0-30% SO_2	3.2
1 M CaX_2, 0-30% SO_2	3.8
0.7M CaX_2, 0-30% SO_2	2.9
0.84M SrX_2, 0-30% SO_2	2.7
0.84M BaX2, 0-30% SO_2	3.0

TABLE 2.

Ampule corrosion test of calcium foils stored for four weeks at 70°C in 0.84M SrX_2-TC-SO_2 solutions.

	SO_2 concentration % ($^v/_v$)	Weight of Ca foil before storage (mg)		Calculated weight after storage (mg) (from titration)	Ca corrosion loss (%)
		with oxide	Corr.for oxide		
1.	0	132	123.4	122.9	0.4 ±0.4
2.	7.5	144	134.7	133.7	0.7 ±0.5
3.	10	155	107.5	104.3	3.0 ±0.5
4.	20	118	110.3	109	0.6 ±0.5

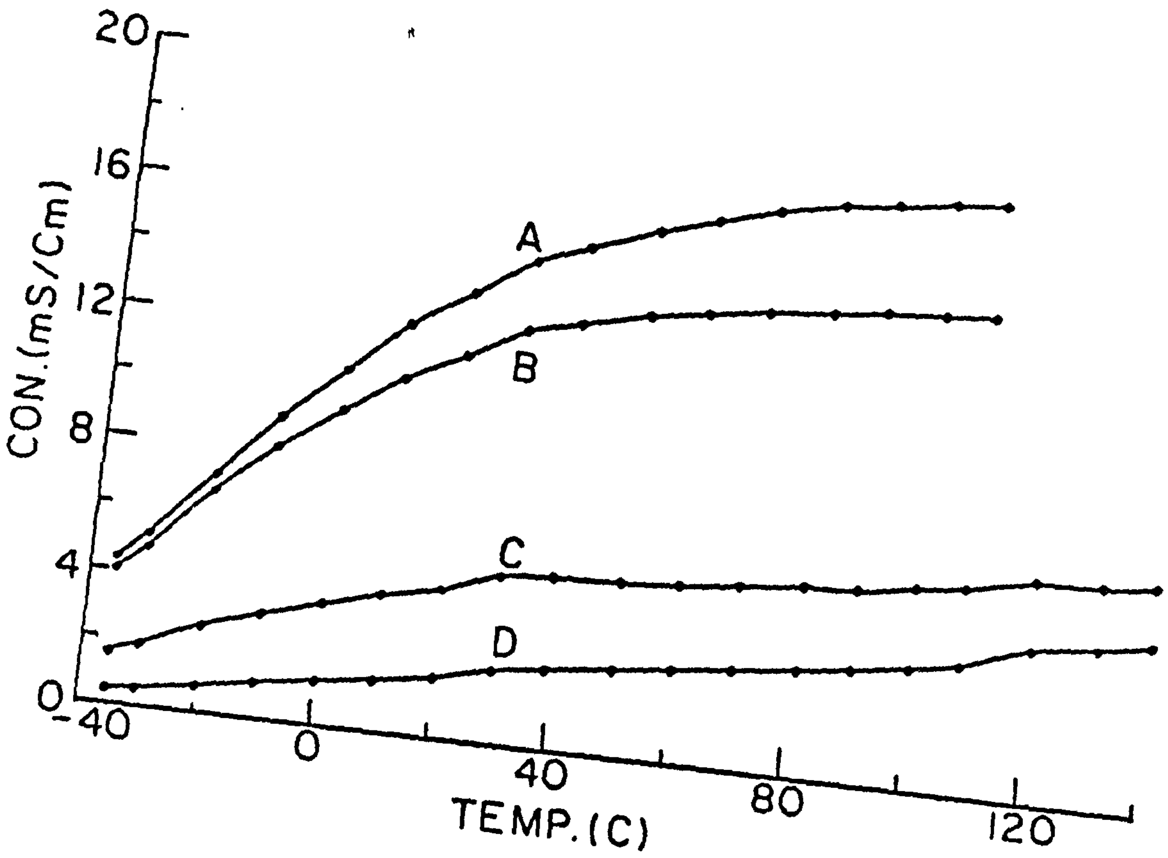

Fig. 1 Conductivity of 1.3M SrX_2-TC-SO_2 solutions vs. temperature. SO_2 volume percent: A-30; B-20; C-10; D-0.

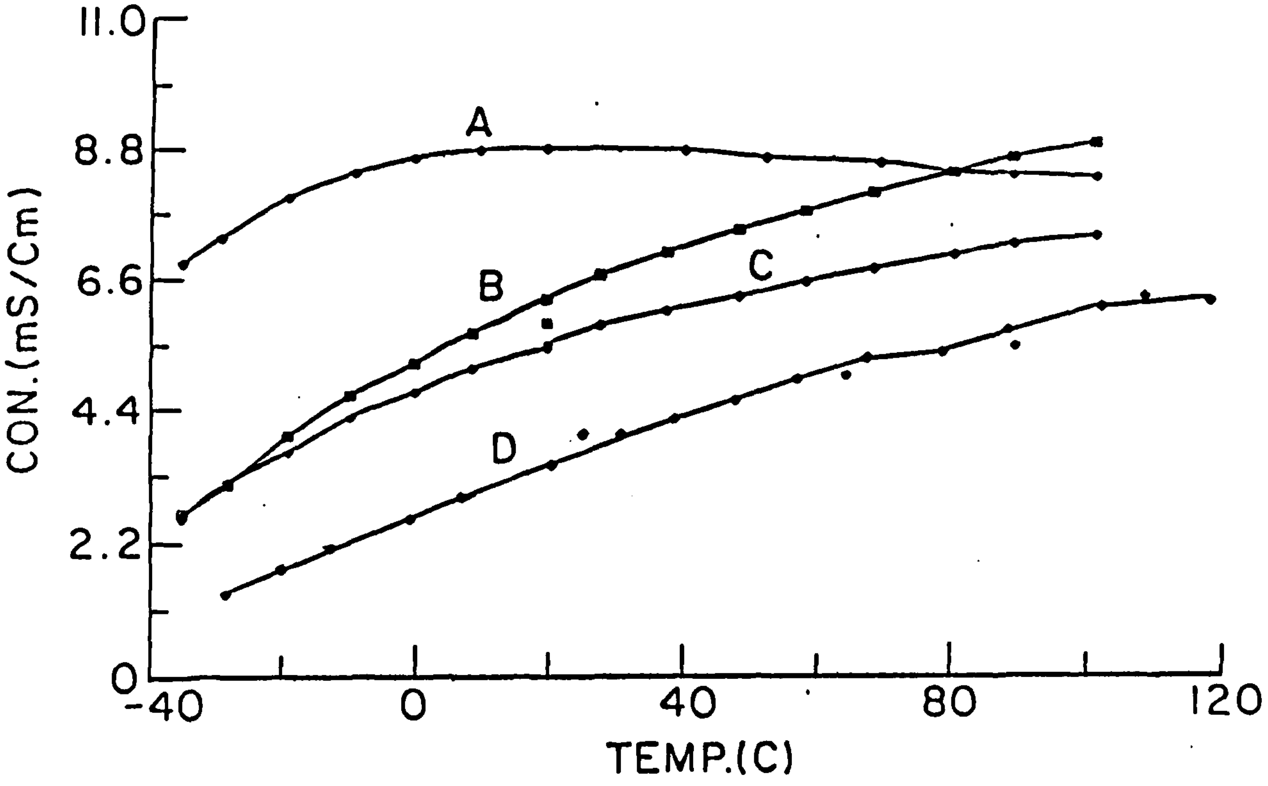

Fig. 2 Conductivity of 0.84M BaX_2-TC-SO_2 solutions vs. temperature. SO_2 volume percent: A-40; B-20; C-10; D-0.

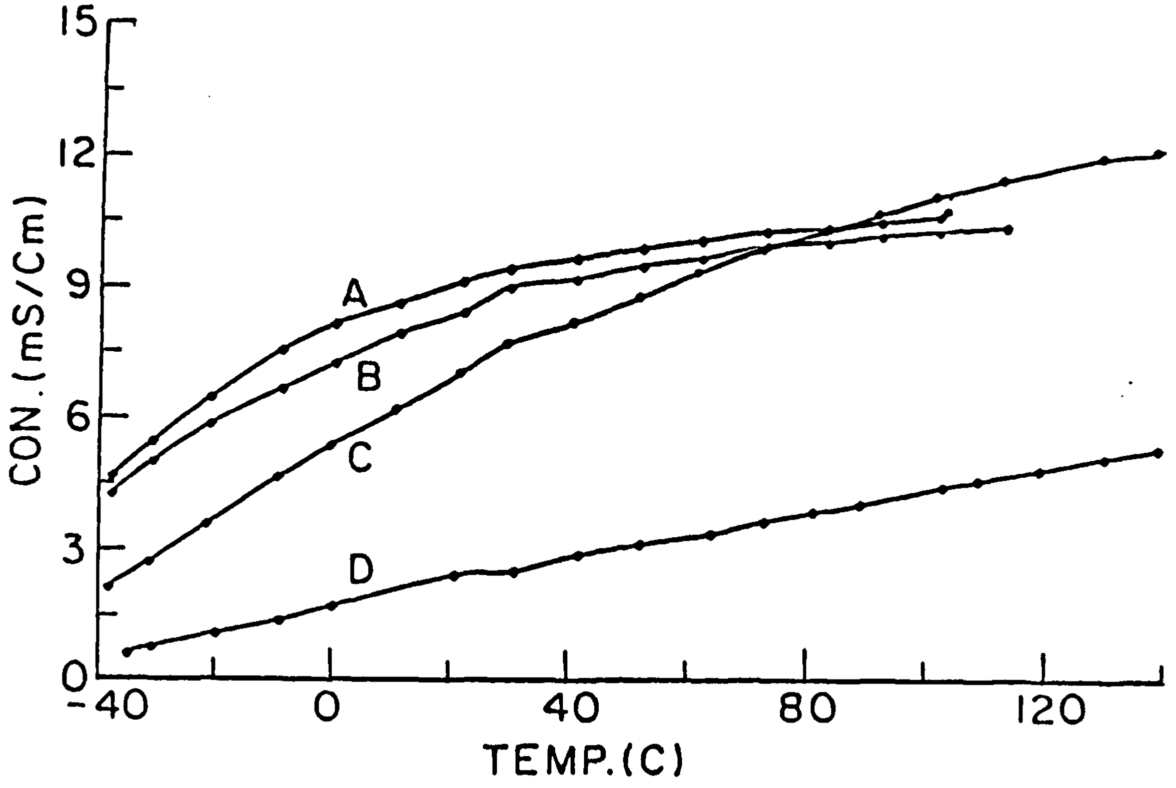

Fig. 3 Conductivity of 1.3M BaX_2-TC-SO_2 solutions vs. temperature. SO_2 volume percent: A-30; B-20; C-10; D-0.

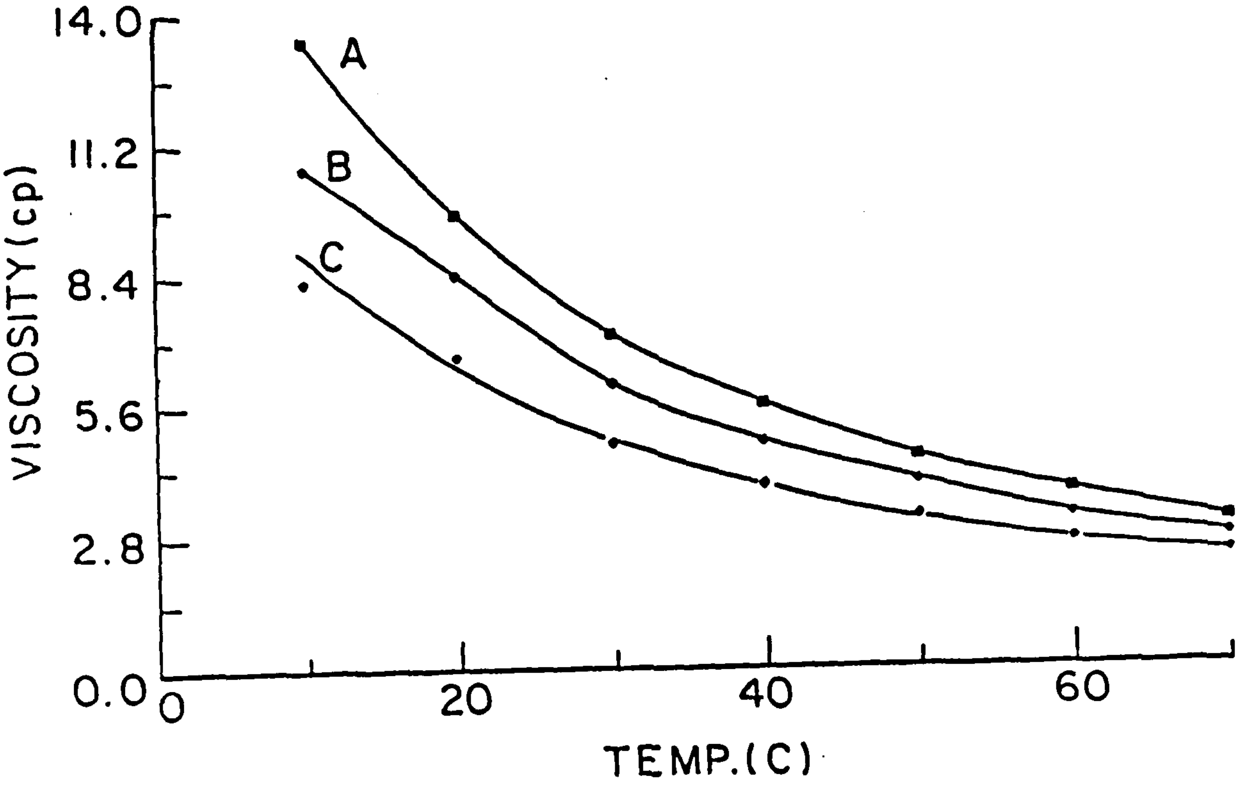

Fig. 4 Viscosity of 1.3M SrX_2-TC-SO_2 solutions vs. temperature.
SO_2 volume percent: A-0; B-10; C-20.

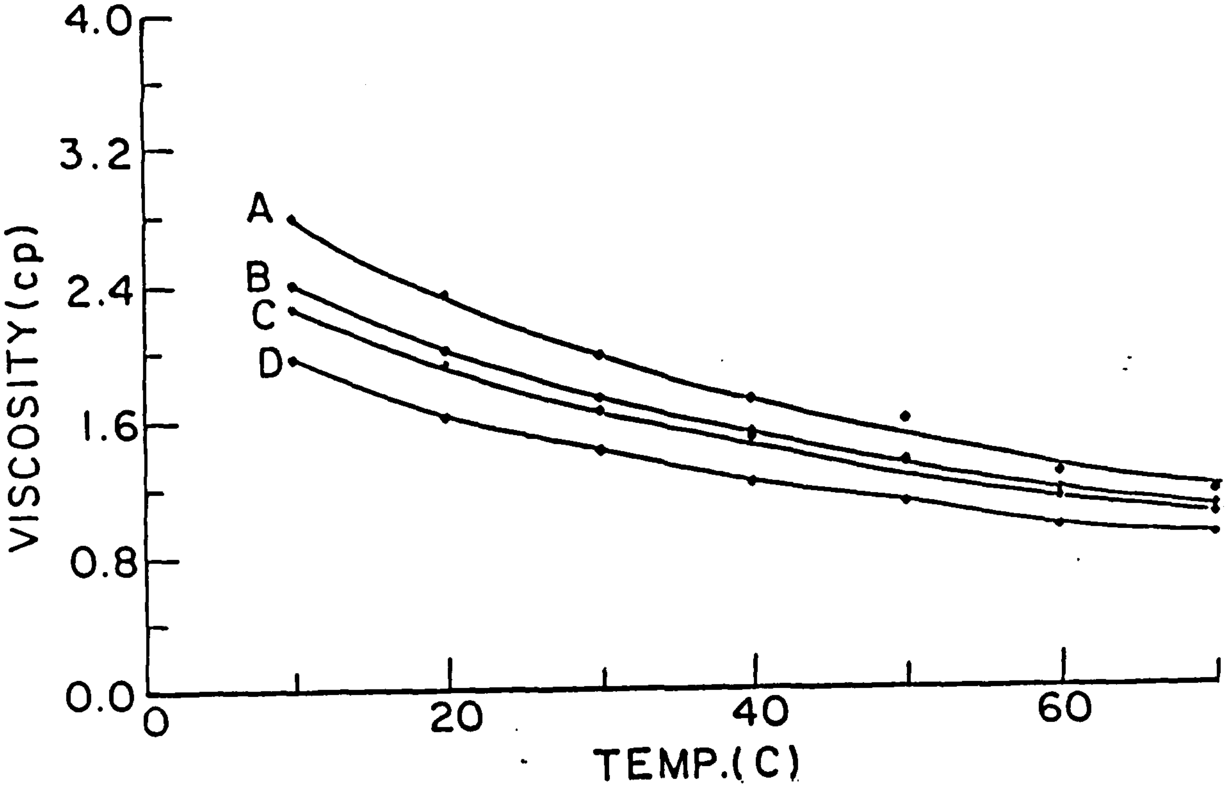

Fig. 5 Viscosity of 0.84M BaX_2-TC-SO_2 solutions vs. temperature. SO_2 volume percent: A-0; B-10; C-20; D-30.

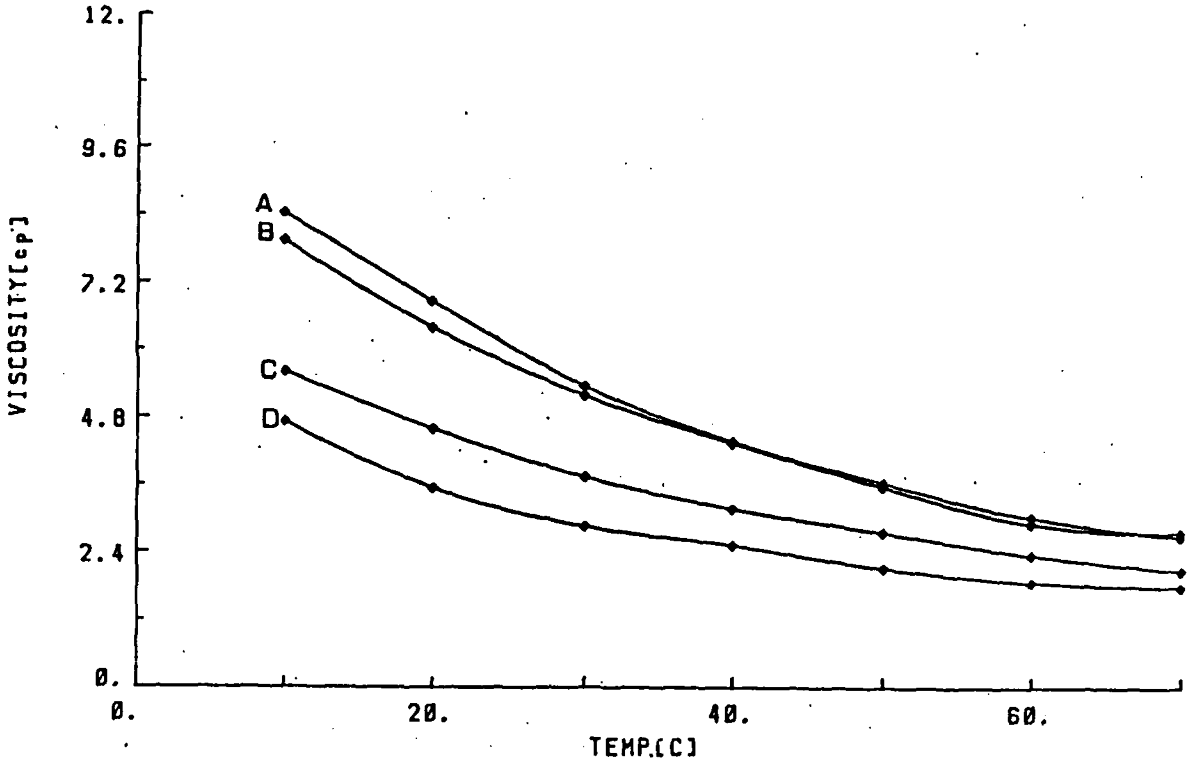

Fig. 6 Viscosity of 1.3M BaX_2-TC-SO_2 solutions vs. temperature

SO_2 volume percent: A-0; B-10; C-20; D-30

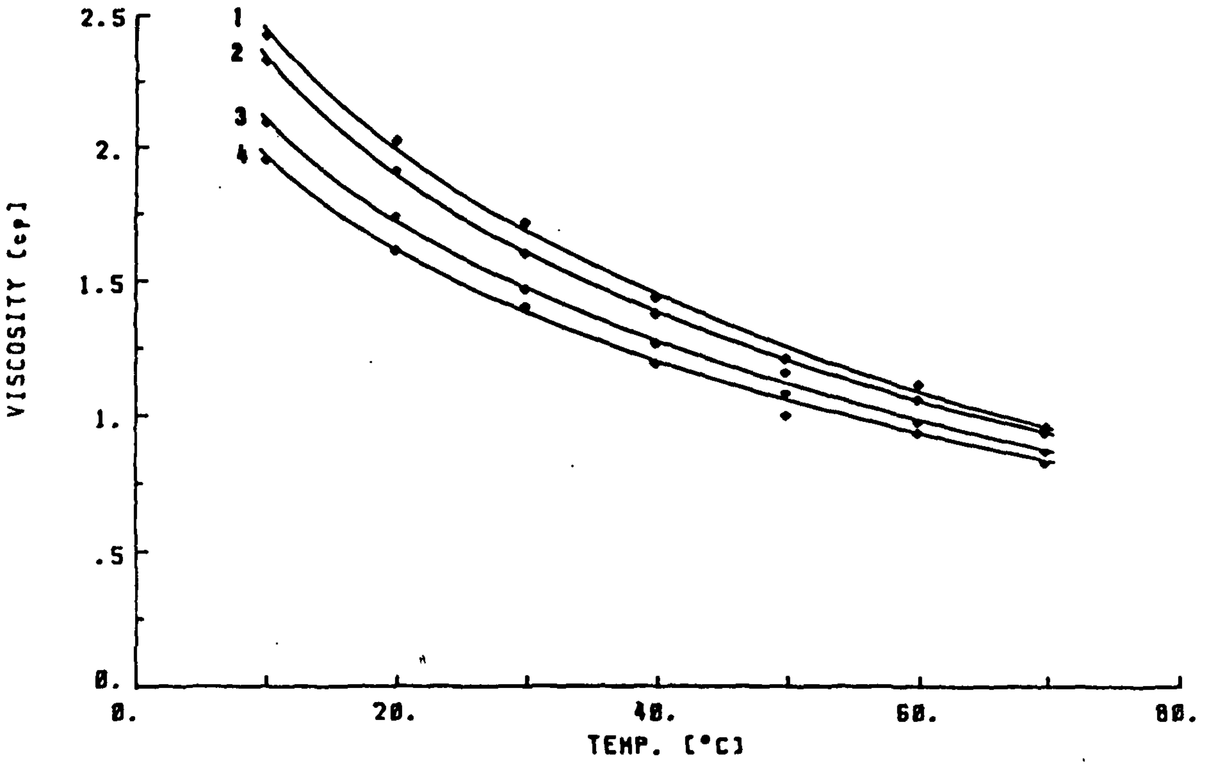

Fig. 7 Viscosity of 0.7M $Ca(AlCl_4)$-TC-SO_2 solutions vs. temperature. SO_2 volume percent:
1 = 0%, .2 = 10%, 3 = 20%, 4 = 30%.

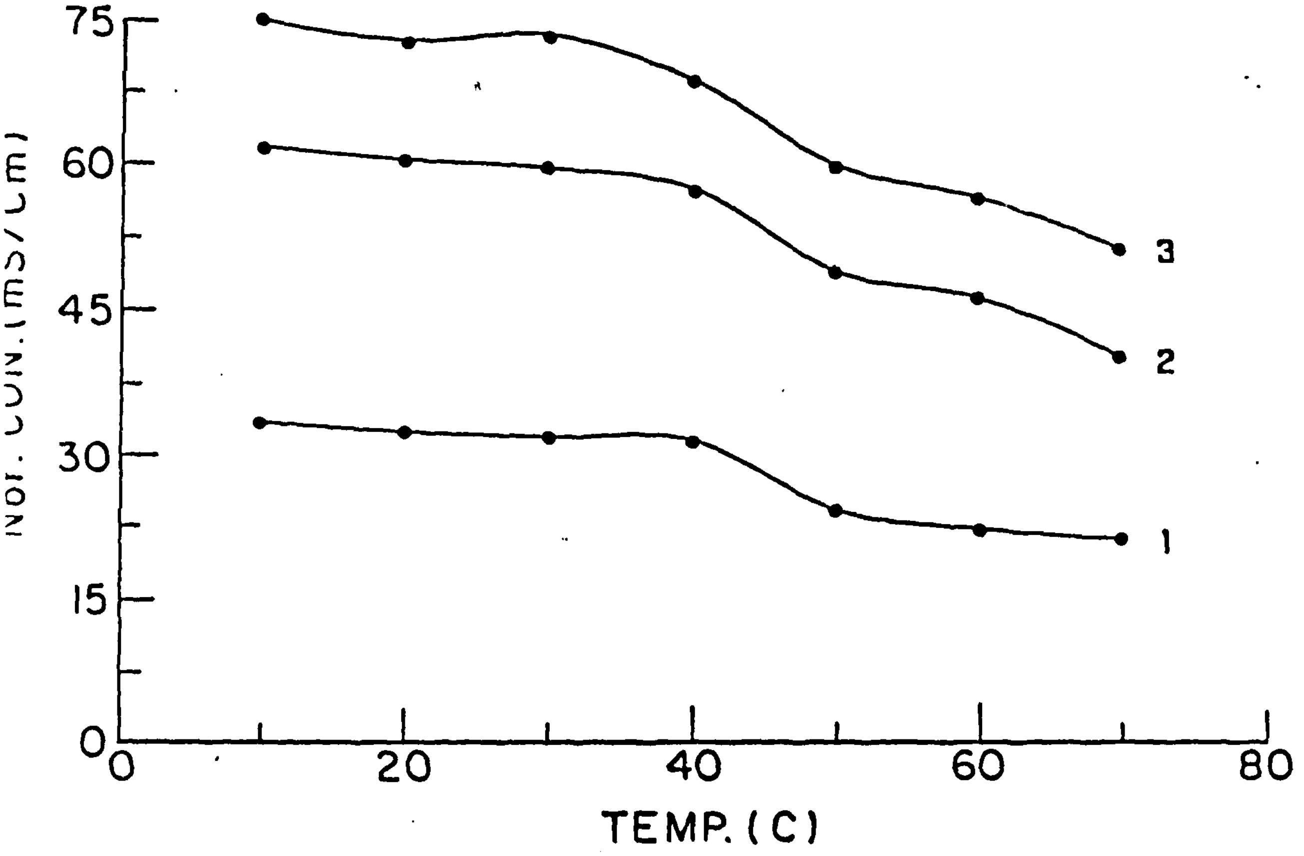

Fig. 8 Normalized conductivity of 1M CaX_2-TC-SO_2 solutions vs. temperature. SO_2 volume percent: 1-0; 2-20; 3-30.

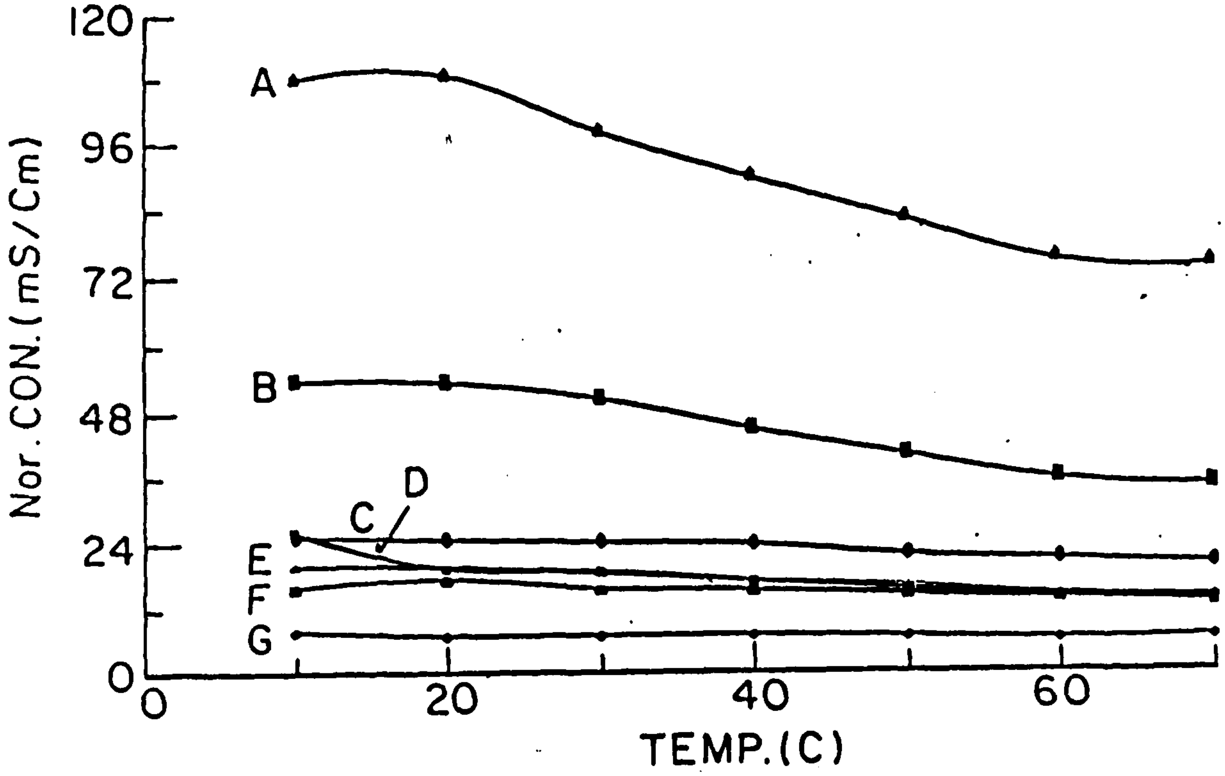

Fig. 9 Normalized conductivity of SrX$_2$-TC-SO$_2$ solutions vs. temperature.

A to C 1.3M SrX$_2$, SO$_2$ volume percent: A-20; B-10; C-0.

D to G 0.84M SrX$_2$, SO$_2$ volume percent D-30; E-20; F-10; G-0.

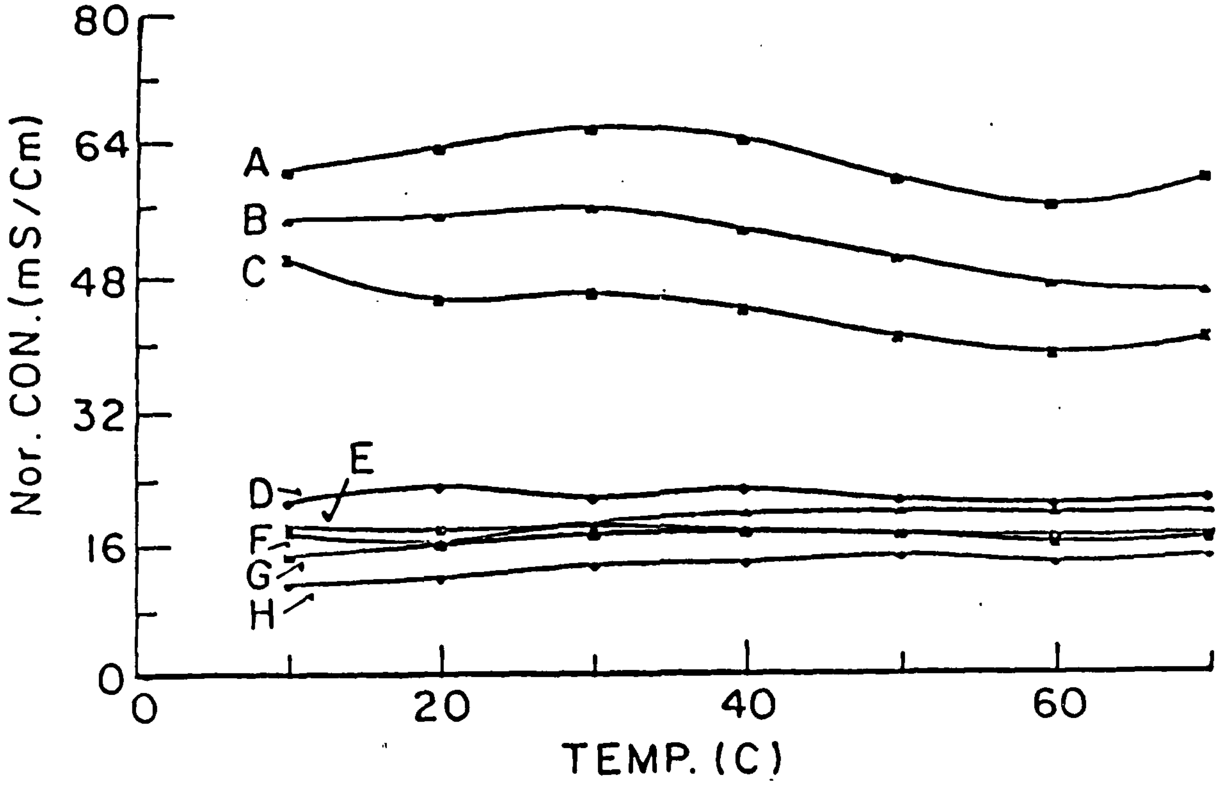

Fig. 10 Normalized conductivity of BaX_2-TC-SO_2 solutions vs. temperature. A to D 1.3M BaX_2, SO_2 percent: A-30; B-20; C-10; D-0. E to H 0.84M BaX_2, SO_2 volume percent E-30; F-20; G-10; H-0.

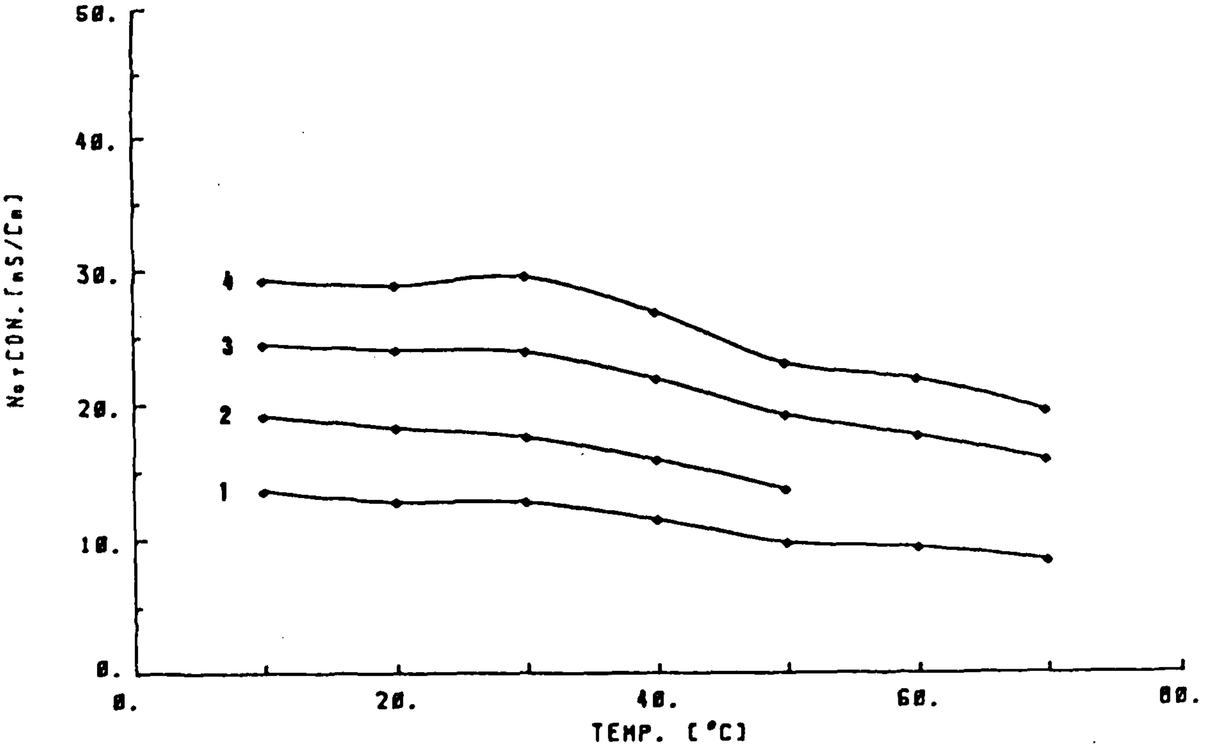

Fig. 11 Normalized specific conductivity of 0.7M $Ca(AlCl_4)$-TC-SO_2 solutions vs. temperature. SO_2 volume percent: 1 = 0%, 2 = 10%, 3 = 20%, 4 = 30%.

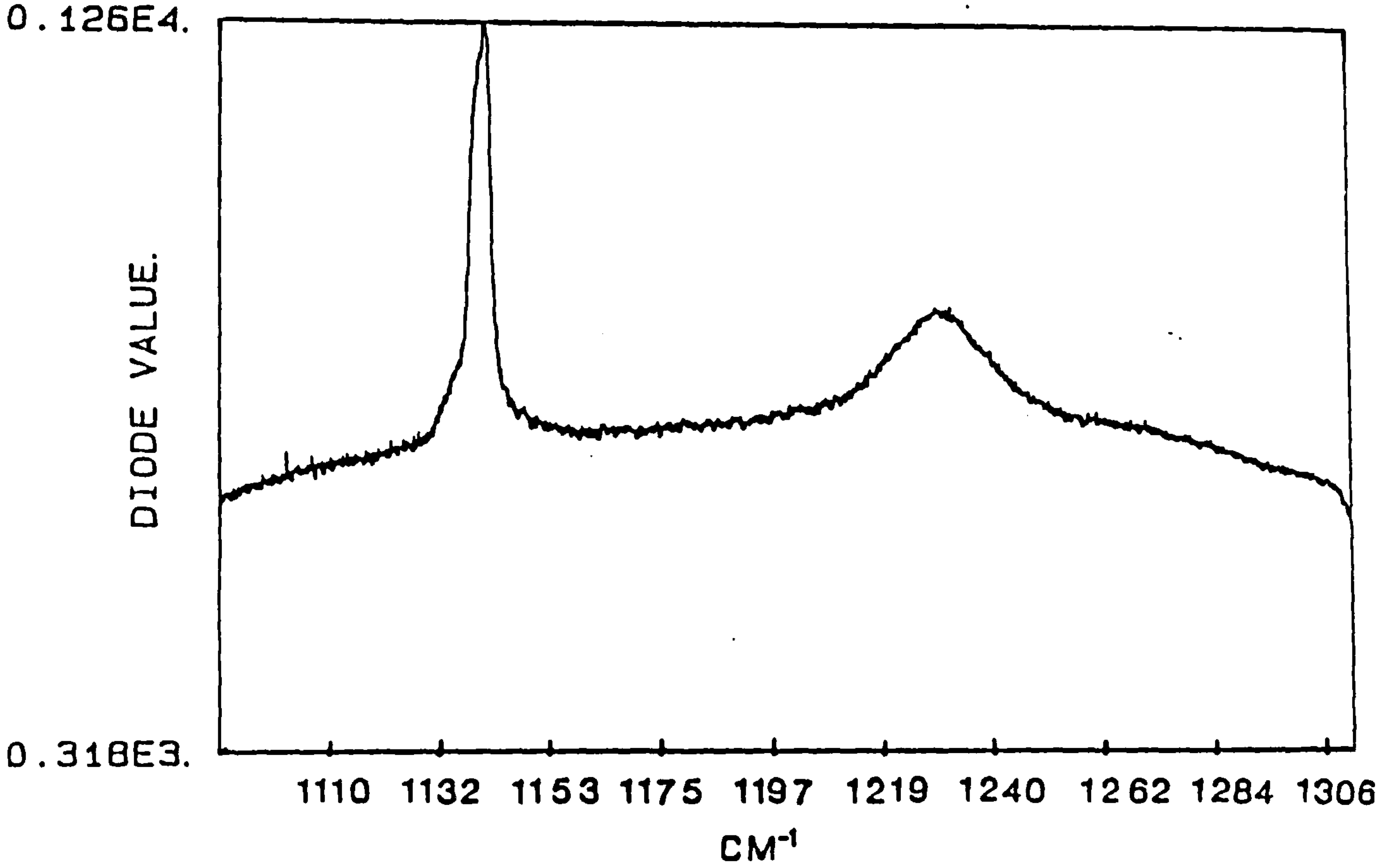

Fig. 12 Raman spectrum of TC-30% (v/v) SO_2. The peak at 1140 cm^{-1} is assigned to SO_2 and that at 1130 to TC.

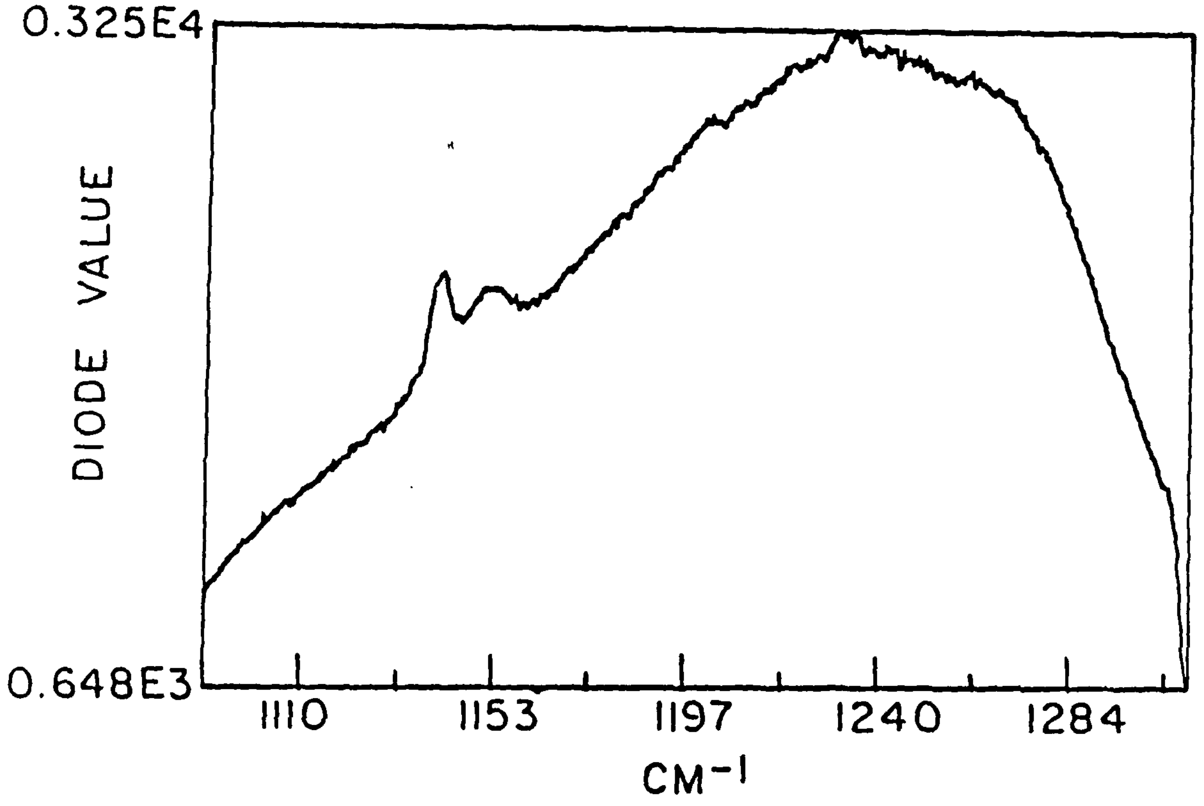

Fig. 13 Raman spectrum of 1.3M CaX_2·TC 50% (v/v) SO_2 solution.

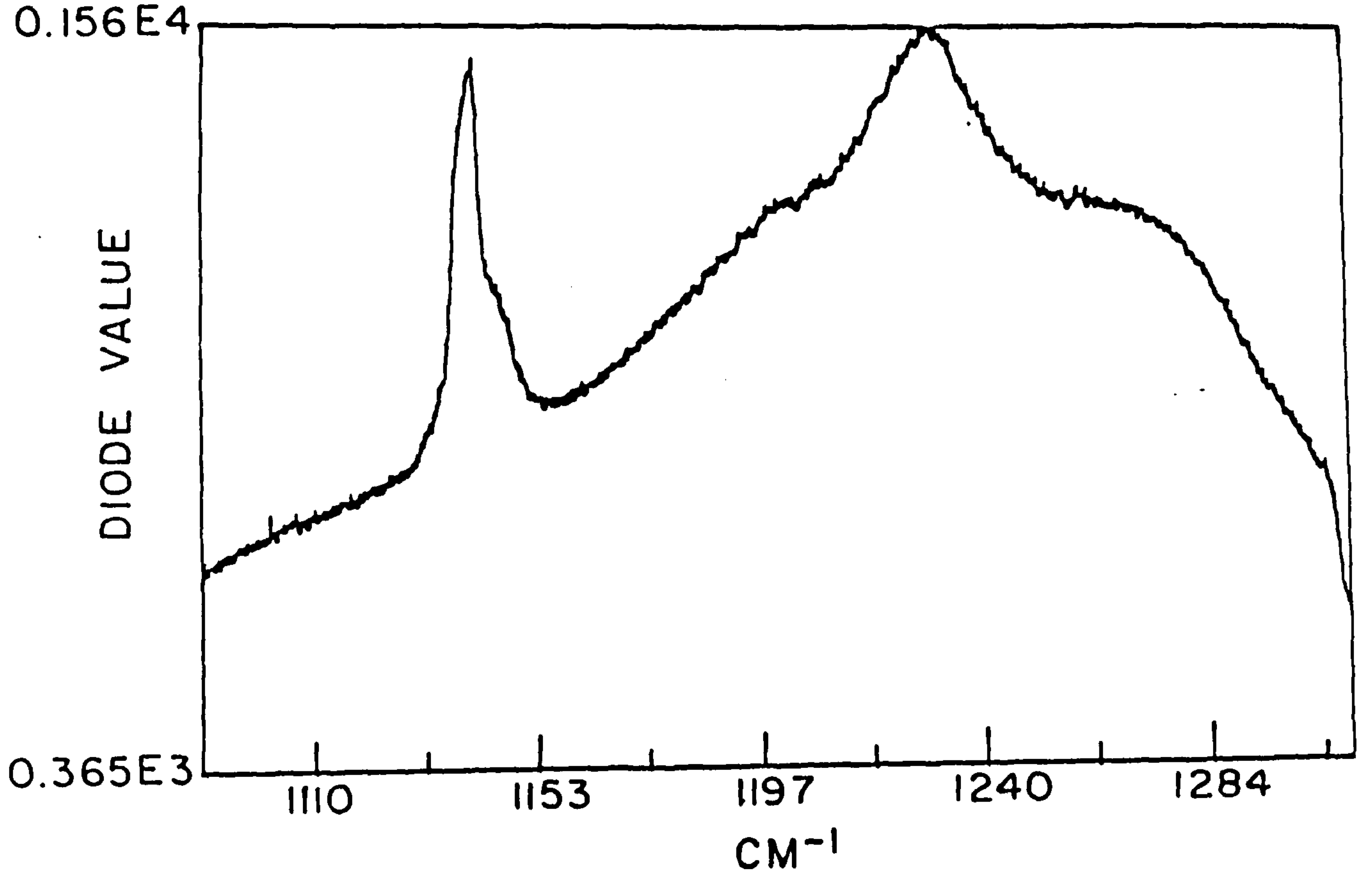

Fig. 14 Raman spectrum of 0.84M BaX_2-TC 30% (v/v) SO_2 solution.

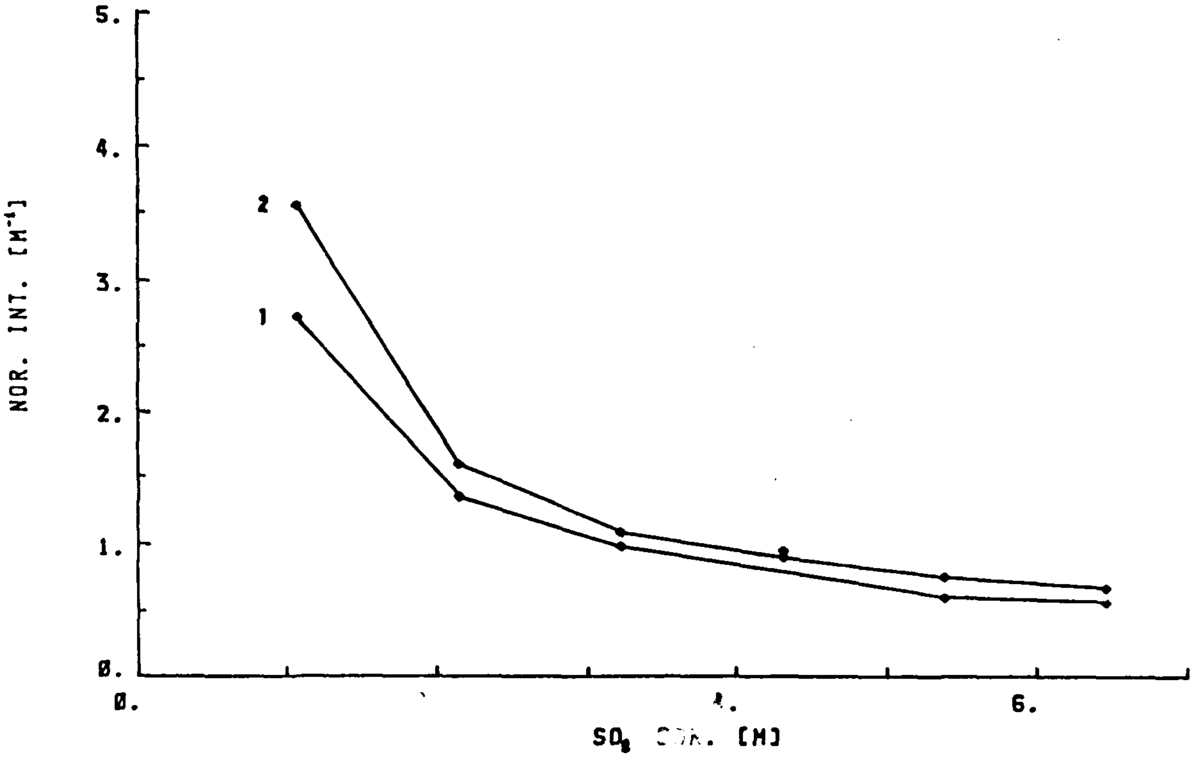

Fig. 15 A plot of normalized intensity of the free SO_2 peak divided by the intensity of the bonded SO_2 peak vs. SO_2 concentration. 1 - 1M CaX_2; 2 - 0.84M SrX_2.

$$\text{Nor.I} = \frac{\text{I (free } SO_2)}{[SO_2] \times \text{I(bonded } SO_2)}$$

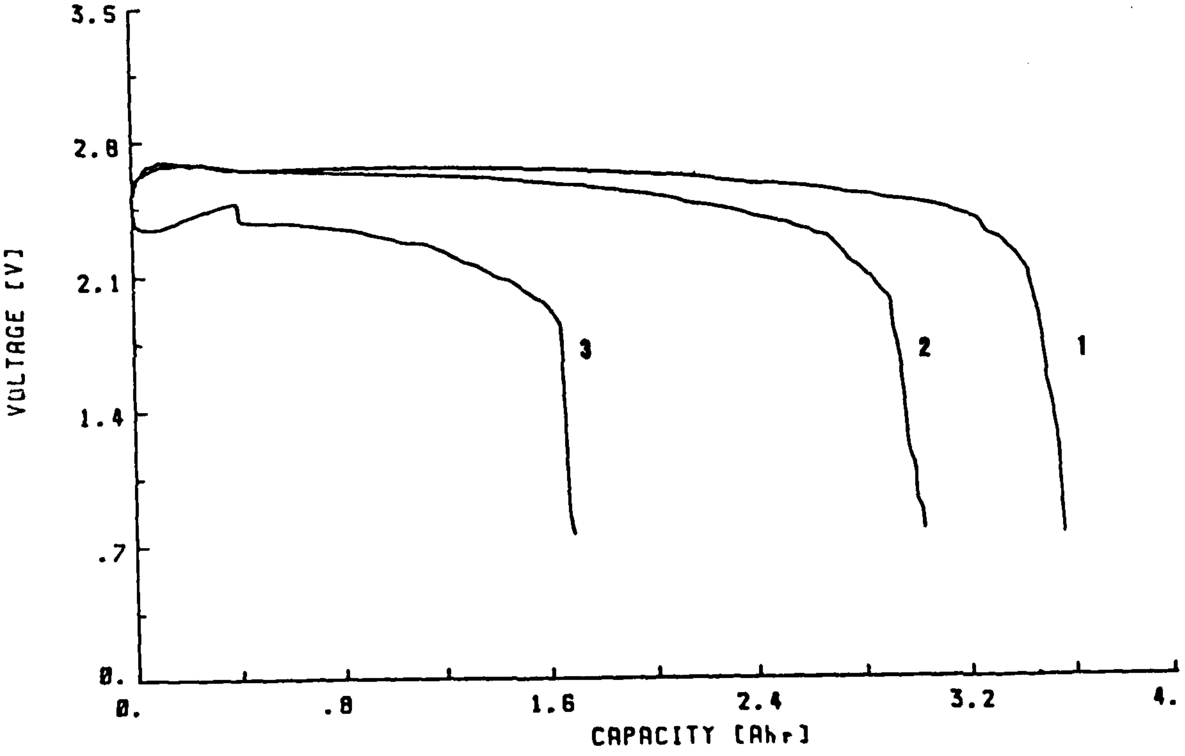

Fig. 16 Discharge curves of Ca/TC C-size cells containing 0.9M $Ca(AlCl_4)_2$ + 7% (V/V) SO_2. 1 = a fresh cell, 10Ω (260 mA); 2 = after 2 weeks of storage at 70°C, 10.1Ω (250 mA); 3 = after 4 weeks of storage at 70°C, 10.1Ω (230 mA).

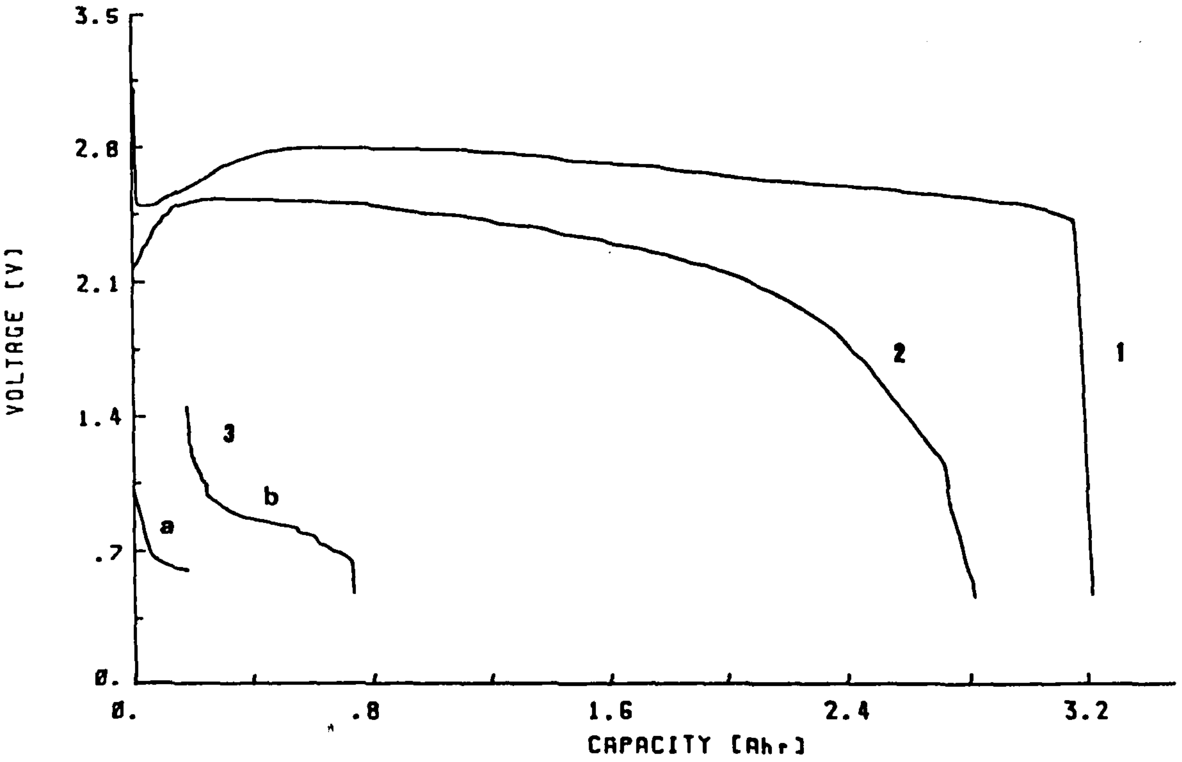

Fig. 17 Discharge curves of Ca/TC C-size cells containing 0.9M $Ca(AlCl_4)_2$ + 7% (V/V) SO_2. 1 = a fresh cell, 4.6Ω (570 mA); 2 = after 2 weeks of storage at 70°C, 4.1Ω (560 mA); 3 = after 4 weeks of storage at 70°C, a = 4Ω, b = 10Ω.

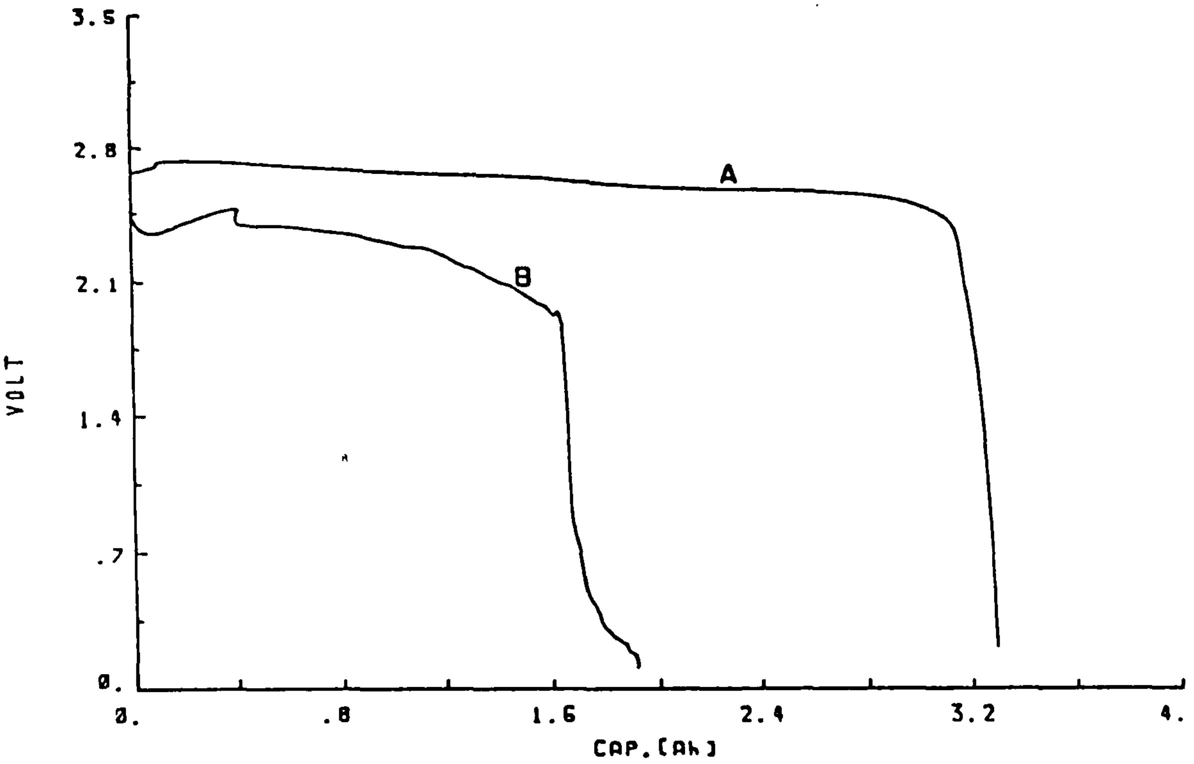

Fig. 18 Discharge curves at RT, after 4 weeks storage at 70°C, 10Ω Load. A: 0.84 M $Sr(AlCl_4)_2$ + 7% SO_2
B: 0.9 M $Ca(AlCl_4)_2$ + 7% SO_2

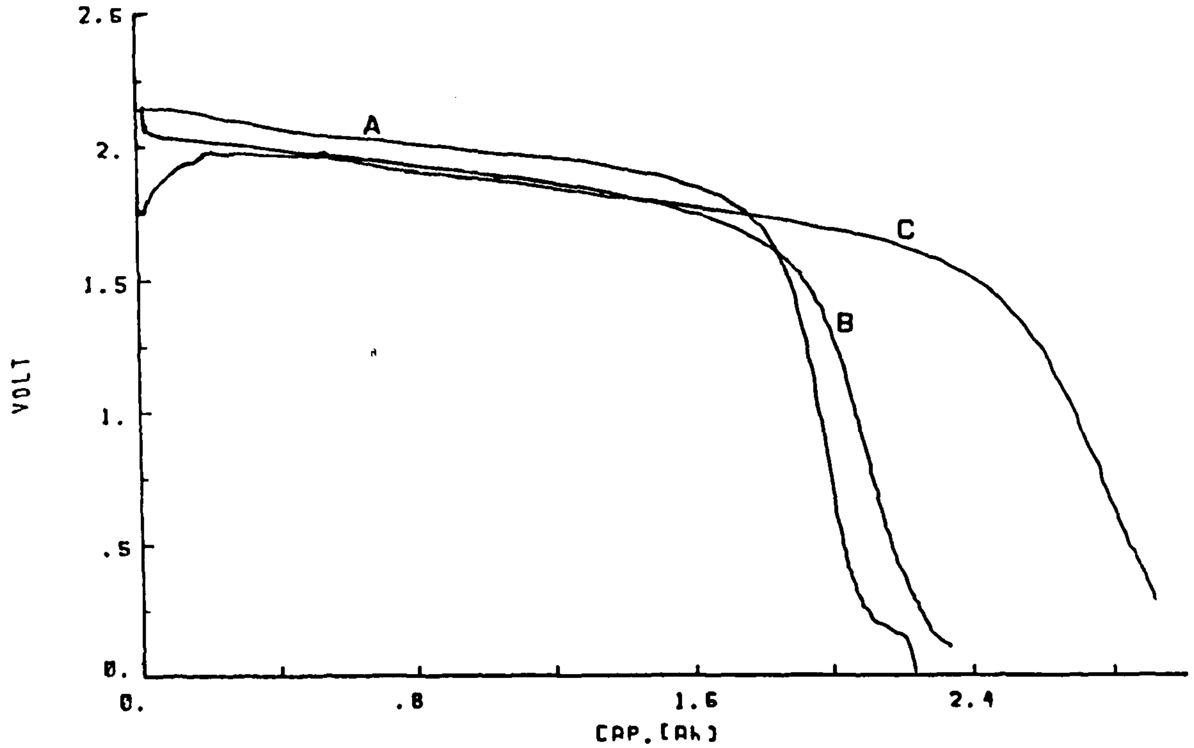

Fig. 19 Discharge curves at -30°C, 10Ω Load. A,B: 0.84 M $Sr(AlCl_4)_2$ +7% SO_2; A-fresh; B-stored cell. C: 0.9 M $Ca(AlCl_4)_2$ + 7% SO_2

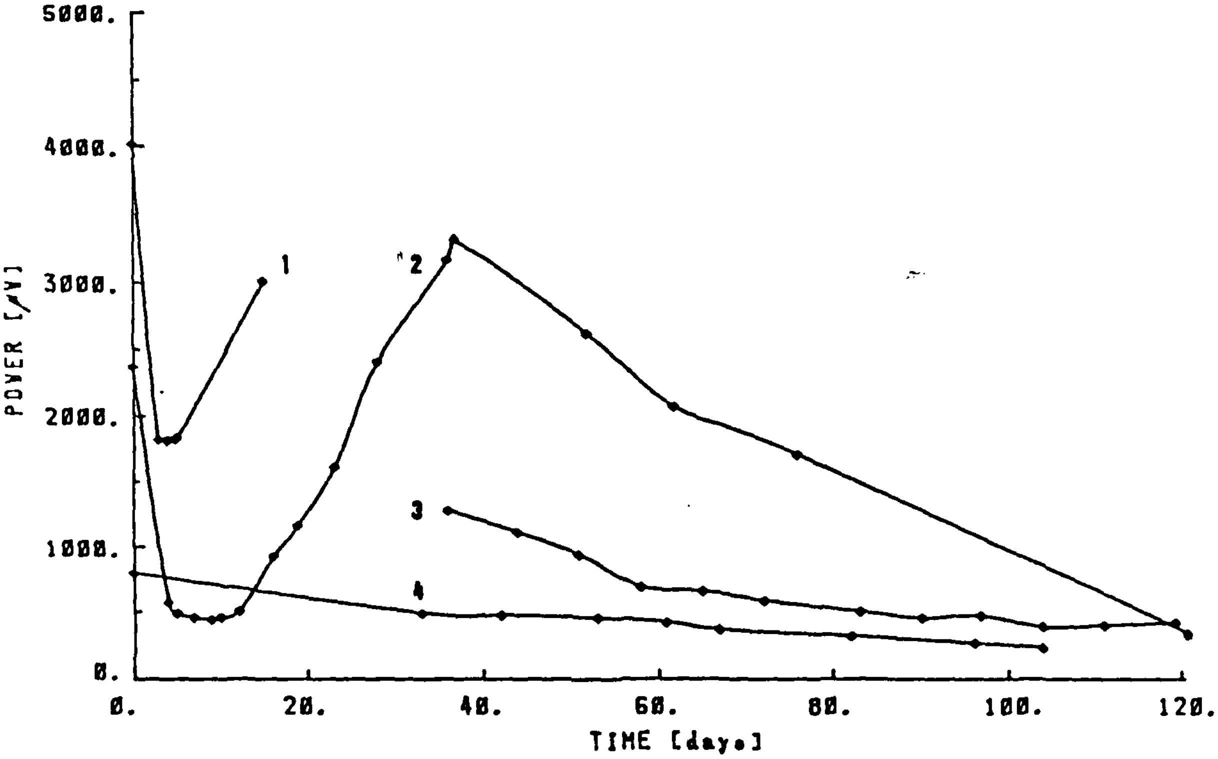

Fig. 20 Heat output of Ca/MX_2-TC C-size cells containing:
1,2 - 0.7M CaX_2 (old version); 3 - 0.9M CaX_2 + 7% (V/V) SO_2;
4 - 0.84M SrX_2 + 7% (V/V) SO_2

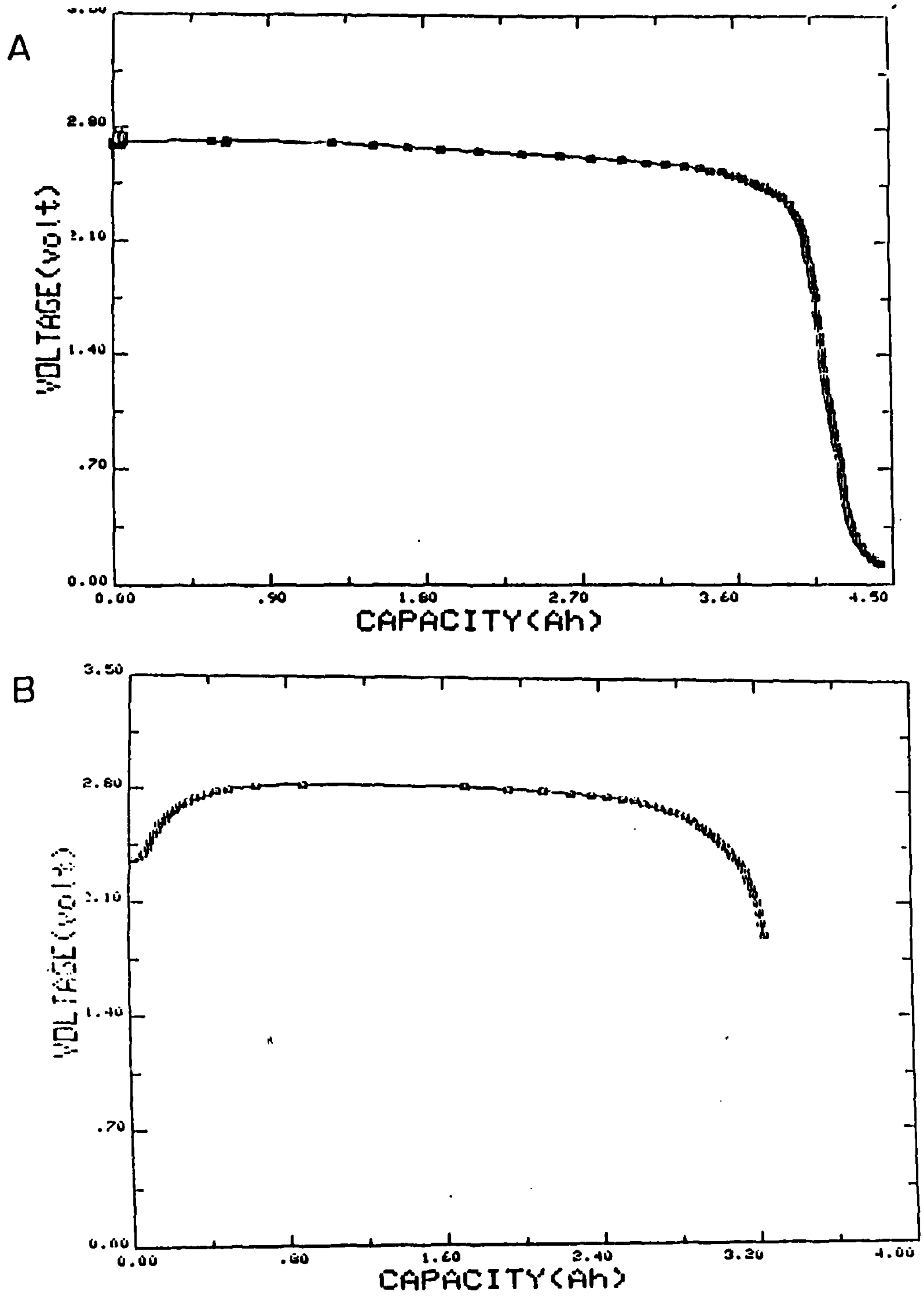

Fig. 21 Discharge curve of C-Cell SrX_2+7%SO_2 with tefzel separator A:40mA B:0.9A

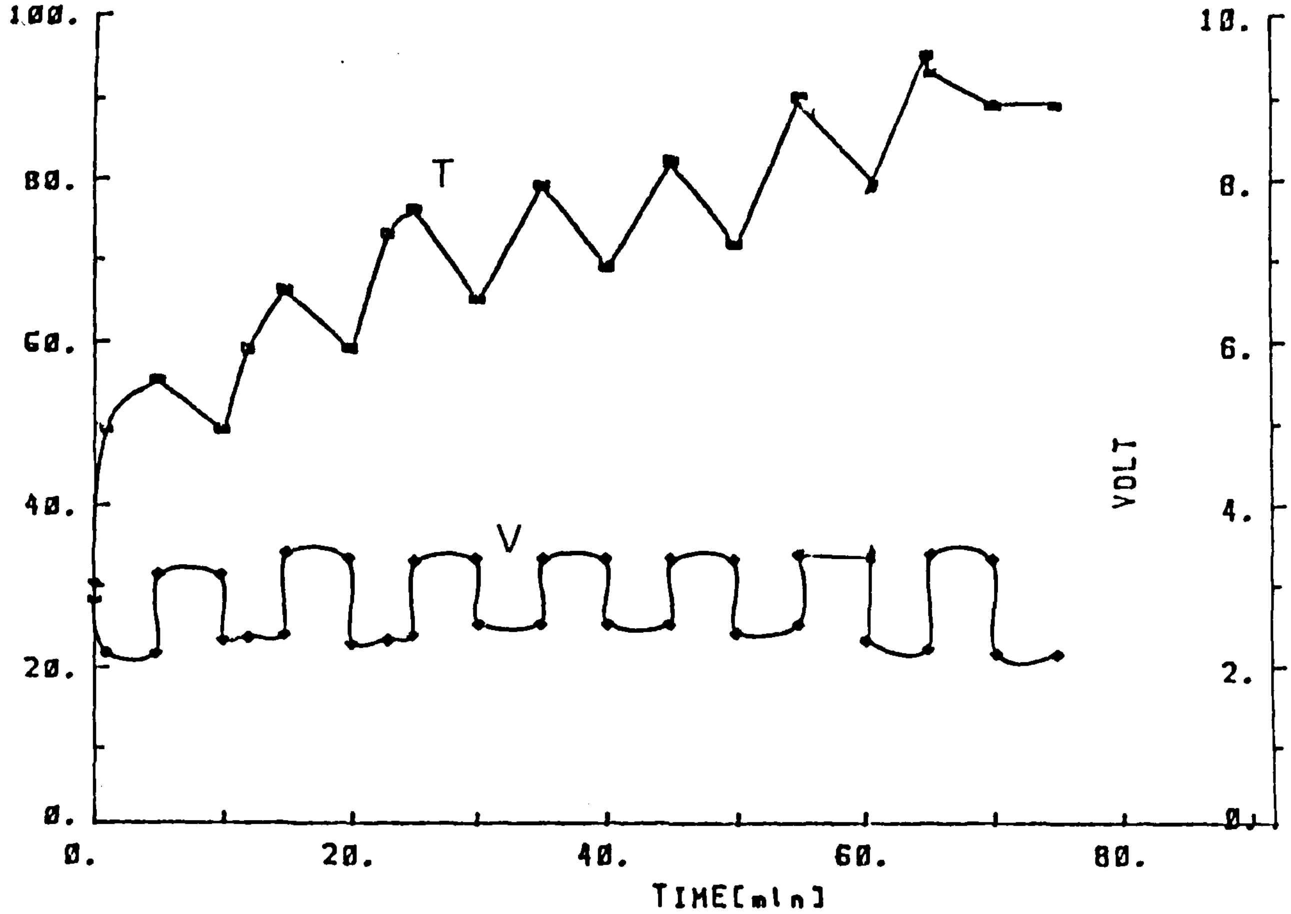

Fig. 22 Heavy load discharge (1Ω), 5min. on 5 min off of C-Cell $SrX_2+7\%SO_2$ with tefzel separator

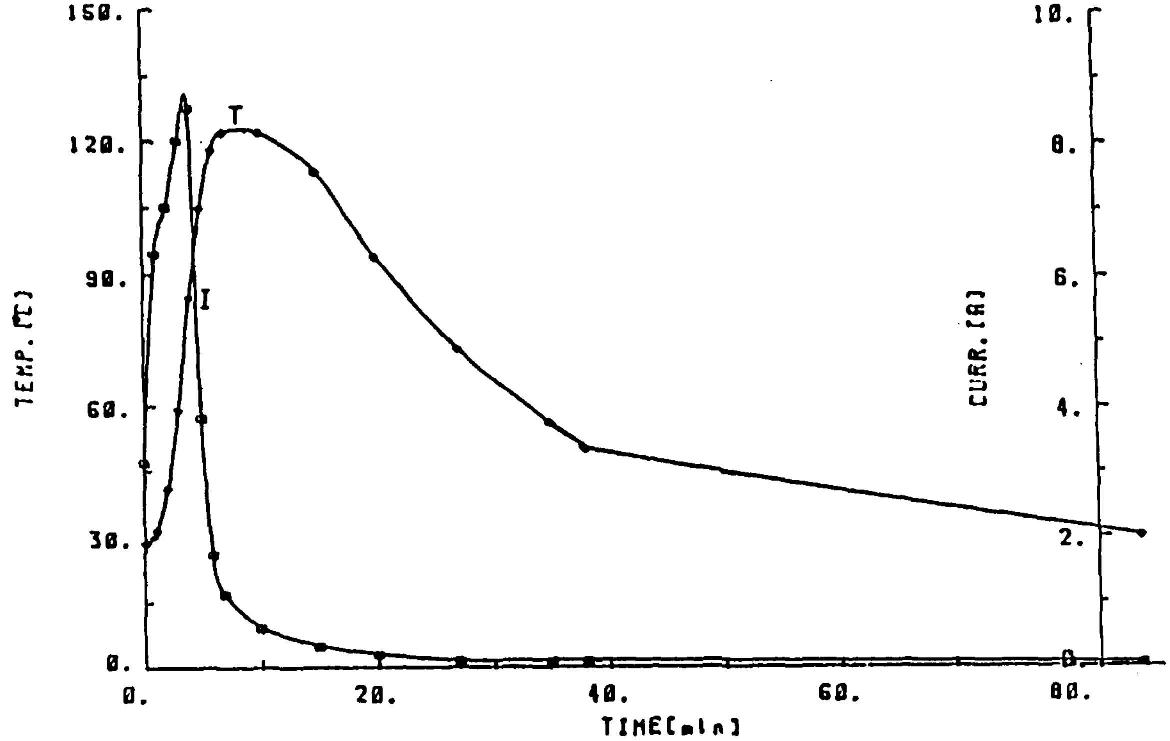

Fig. 23 Short circuit test of 0.84 M $Sr(AlCl_4)_2$ + 7% SO_2 C-cell, 0.1Ω Load.

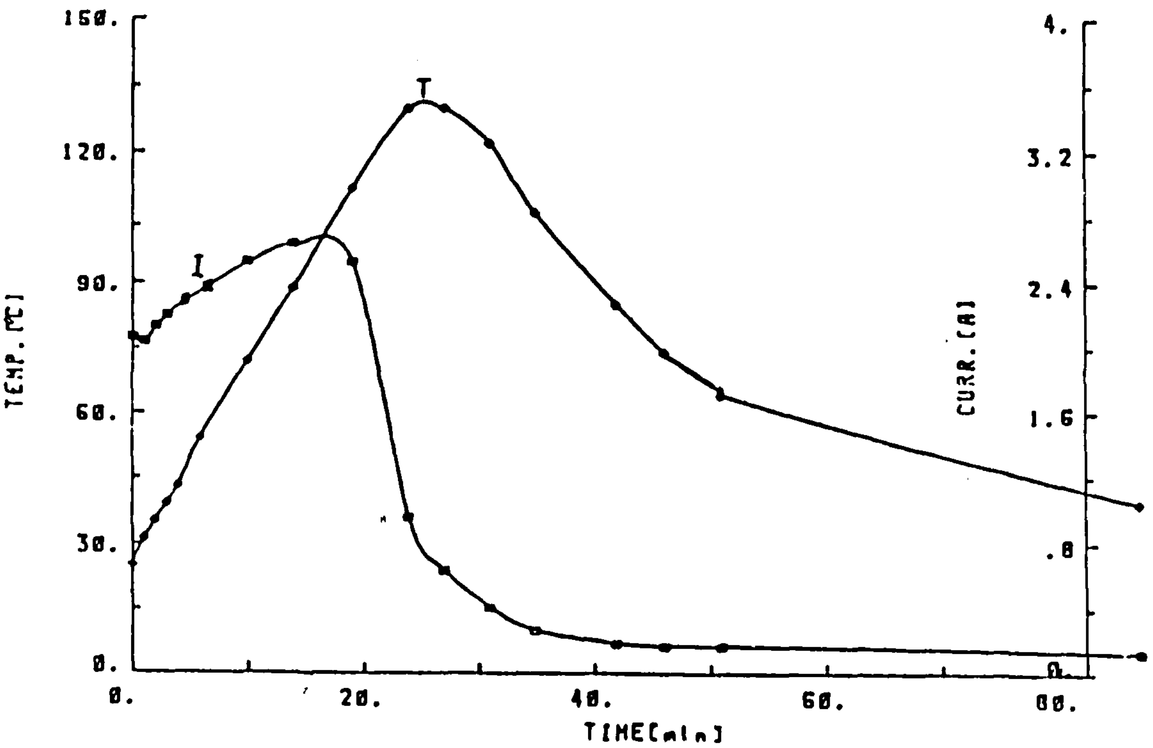

Fig. 24 Heavy load discharge test of 0.84 M $Sr(AlCl_4)_2$ + 7% SO_2 C-cell, 1Ω Load.

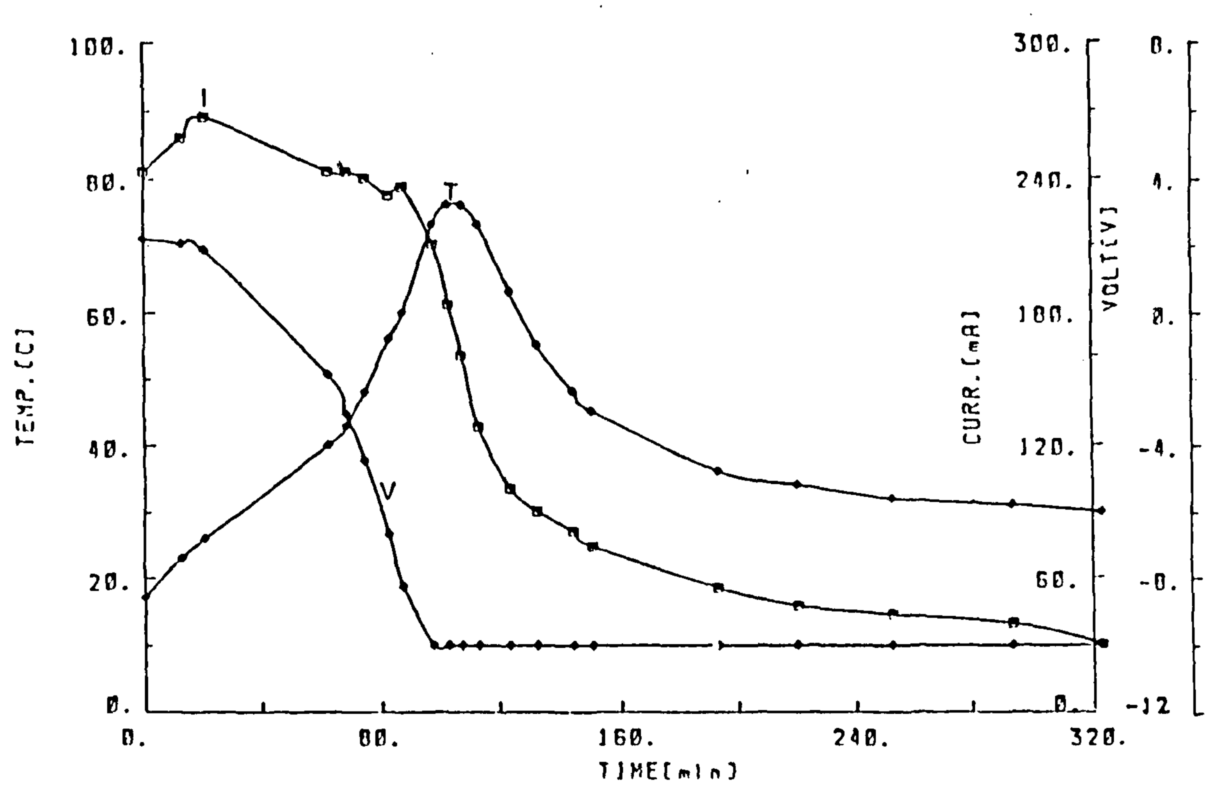

Fig. 25 Forced discharge test of 0.84 M $Sr(AlCl_4)_2$ + 7% SO_2 C-cell