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HIGH EFFICIENCY LITHIUM-THIONYL CHLORIDE CELL

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Electrolyte properties in Li/SOCl₂ systems are found to contribute significantly towards the cathode overpotential. Cathodes doped with catalysts greatly minimized the activation polarization throughout the operating temperatures.

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ABSTRACT

This report briefly summarizes the objectives of the program on Contract DAAK20-81-C-0381 and the activities carried out during the period of April 9, 1981 to July 9, 1981.

The main objectives are to evaluate the polarization characteristics of Teflon bonded carbon electrodes in the Li/SOCl_2 system and to improve cathode performance at high discharge rates and low operating temperatures (-40°F to 32°F). During the report period, we have studied the half-cell polarization and discharge performance characteristics of Li/SOCl_2 cells with and without improved cathodes. In addition, the effect of catalysts on cyclic voltammograms and electrolyte viscosity and conductivity relationships with operating temperature have been examined.

Electrolyte properties in Li/SOCl_2 systems are found to contribute significantly towards the cathode overpotential. Cathodes doped with catalysts greatly minimized the activation polarization throughout the operating temperatures.

I. INTRODUCTION

The Li/SOCl₂ system (1-4) has the potential to be one of the best primary batteries having combined characteristics of high rate and high energy density capability, long shelf-life and wide operating temperature range. However, many of these advantages have not been fully derived. The operating capabilities of Li/SOCl₂ batteries are limited, to a large extent, by the Teflon bonded porous carbon electrode commonly used as a cathode. Cell failure at high discharge rates and/or low operating temperatures has, as one of its main causes, the high cathodic overpotential resulting from non-uniform current distribution over the porous electrode.

The porous carbon cathode, where the reduction of SOCl₂ occurs, has a limited capacity for retaining solid lithium chloride as it precipitates in the pore structure. As the lithium chloride accumulates, the porosity of the electrode is reduced to where mass transport, particularly of the cathode depolarizer, can no longer be maintained at a rate sufficient to support the required current density. When this happens, polarization becomes excessive and denotes the end of useful battery life.

At high rate discharges and low operating temperatures, the cathode polarization problem becomes very severe. Analysis of the porous electrode showed that, at high rate discharges, only a small part of the available surface participates in the electrochemical process.

Cathode polarization and the reaction zone thickness strongly depend on electrode reactions, cathode thickness and composition. Minimization of the effects of these variables on overpotential is essential in order for Li/SOCl₂ batteries to be viable electrochemical devices for many of the high rate/low temperature applications.

The objectives of this program, therefore, are to:

- a) Evaluate the polarization characteristics of Teflon-bonded porous carbon cathodes.
- b) Improve cathode performance at high discharge rates and low operating temperatures.

Polarization characteristics will be determined as a function of cathode thickness, composition and density, applied current density and temperature (-40°F to 75°F). Several experimental techniques such as half-cell measurements, discharge performance characteristics, impedance measurements and cyclic voltammetry studies will be employed to evaluate the extent of each variable's contribution to the cathode polarization.

Improvement in cathode performance will be made by the use of electrocatalyst. Three catalysts to be employed in this program (5) have shown marked improvements in both cell voltage and cathode capacity. They are,*

Catalyst A = Cobalt Phthalocyanine monomer, CoPc

Catalyst B = Iron Phthalocyanine monomer, FePc

Catalyst C = Polymeric Cobalt Phthalocyanine, (CoPc)_n

During the first quarter of this program, we evaluated the cathode overpotential by examining the half-cell measurements and discharge performance of our baseline cathode containing with and without catalyst B and catalyst C. In addition, the effect of catalyst A and B on cyclic voltammograms at different electrode surfaces and the effect of temperature on the electrolyte (1.0M LiAlCl₄/SOCl₂ and 1.5M LiAlCl₄/SOCl₂) conductivity and viscosity have been studied.

* Patents pending

II. EVALUATION OF CATHODE OVERPOTENTIAL

A. INTRODUCTION

The overpotential of an electrode system is defined as the difference between the measured potential under working conditions and the thermodynamic potential. Both physical and chemical processes taking place at the electrode interphase influence the extent of overpotential, commonly referred to as polarization.

The voltage of an electrochemical cell during discharge is given by the open circuit voltage (OCV) minus all the resistance and polarization losses throughout the cell. Thus, for cell discharge

$$E_D = OCV - i\sum R - \sum \eta_c - \sum \eta_a \quad (1)$$

where,

i = applied current

$\sum R$ = sum of electrolyte, electrode and lead resistance

$\sum \eta_c$ = sum of concentration polarization at both electrodes

$\sum \eta_a$ = sum of activation polarizations at the anode and cathode

Concentration polarization is anticipated to be severe in the Li/SOCl₂ system at low operating temperatures. Poor electrolyte conductivity and high viscosity contribute severely to the diffusion rate of the depolarizer. Furthermore, LiCl precipitation in the pore structure adversely affects both IR drop and concentration polarization. Both half-cell measurements and discharge characteristics should enable an evaluation of the magnitude of concentration polarization.

Activation polarization arises from the irreversibility of both chemical and electrochemical processes taking place. Therefore, the electron transfer processes and hence the discharge rate influence the activation overpotential. It is known that SOCl₂ reduction proceeds smoothly at porous carbon cathodes

at low discharge rates. High discharge rates are achieved (5) only at cathodes doped with electrocatalysts. Therefore, our approach to improve cathode performance by electrocatalysis should minimize the activation polarization.

Ohmic overpotential arises from the non-uniformity of current distribution over the porous electrode. In addition, electrolyte conductivity and viscosity and LiCl precipitation in pore structure contribute to this overpotential. Therefore, IR drop, which is directly proportional to the applied current, has a severe effect on the Li/SOCl₂ cell potential.

All three types of overpotential contribute to cathode polarization in a Li/SOCl₂ system. The magnitude of each type depends on the operating temperature, electrolyte conductivity and viscosity. During the program, attempt will be made to understand and evaluate each type.

B. LABORATORY CELL MEASUREMENTS

1. Experimental

Cathodes. Our baseline cathode contains 95% Shawinigan Acetylene Black (100% compressed grade) and 5% Teflon-6. The standard cathode fabrication process is summarized in Figure 1.

Our best improved cathodes contain either iron phthalocyanine monomer, FePc or polymeric cobalt phthalocyanine, (CoPc)_n. FePc is soluble in the electrolyte therefore, it is dissolved in the electrolyte before cells were activated. (CoPc)_n is impregnated onto carbon from a concentrated H₂SO₄ solution by diluting with ice water. The material was washed thoroughly with distilled water and dried at 160°C. This catalyst-carbon mix was then heat treated between 500-700°C in an inert atmosphere to activate the catalyst. The heat treated catalyst is not soluble in SOCl₂ electrolytes. Cathodes are fabricated according to standard procedure. The final cathode composition is 5% (CoPc)_n, 90% SAB and 5% Teflon-6.

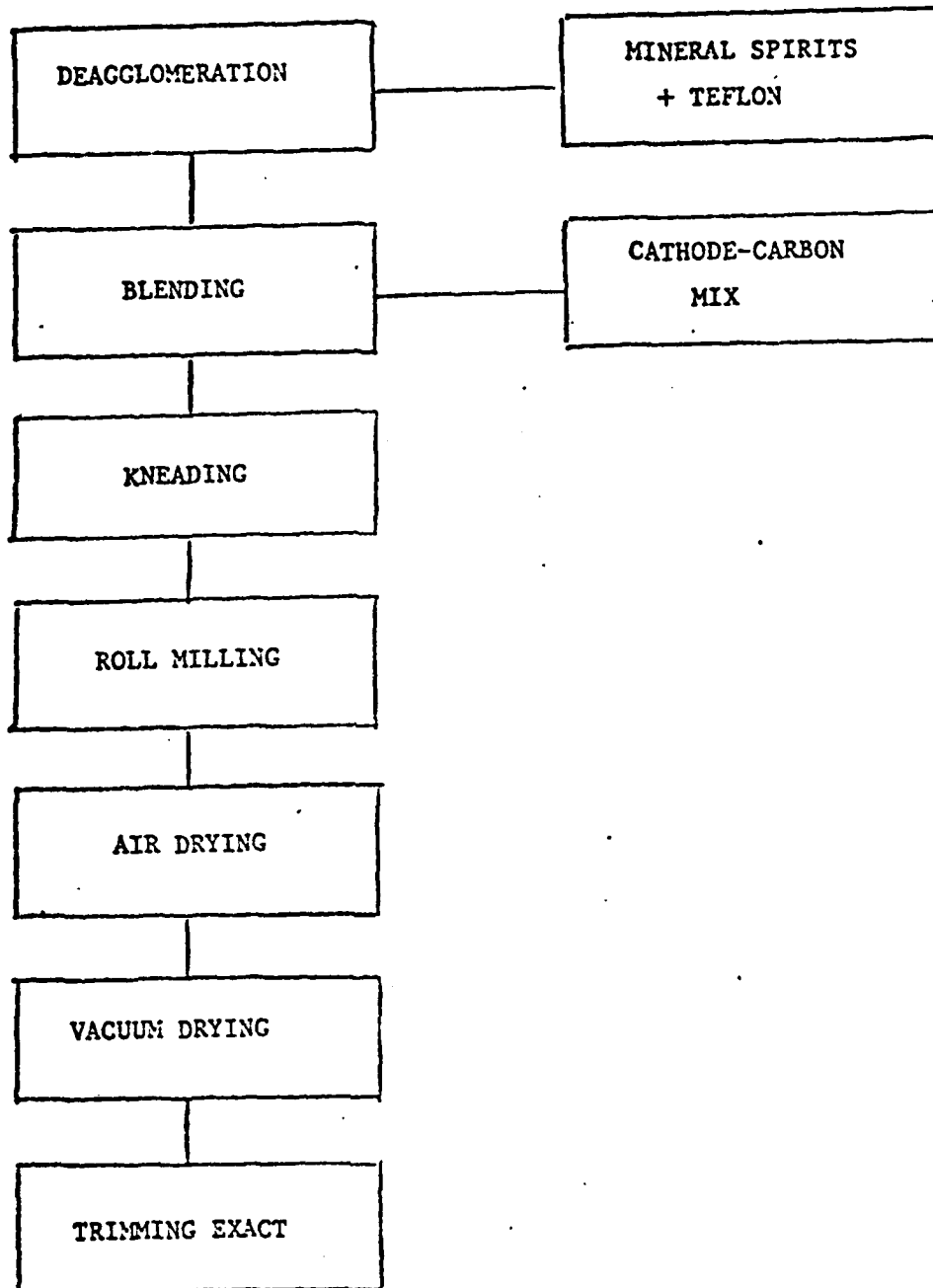


Figure 1. Flow Diagram of Cathode Fabrication Process. Workability of the process not restricted to specific carbon type. Rolling incurs excellent mechanical integrity on the cathode.

Electrolytes. 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte is manufactured by dissolving required AlCl_3 and LiCl salts in thionyl chloride. Commercial AlCl_3 , (Fluka-grade), LiCl (MCB) and SOCl_2 (MCB-TX535) are used without further purification.

Laboratory Cell. The laboratory cell used for both polarization and discharge characterization experiments is a sealed electrochemical fixture (Figure 2) containing a basic cell structure of two plate prismatic electrodes (Figure 3), one Teflonated carbon electrode and one lithium anode, both pressed onto nickel grid current collectors.

The cathode is 0.5" (wide) x 1.0" (high) x 0.024" (thick)*, the anode (0.01" thick) has the same apparent surface area (0.5" x 1.0"). Two layers of 0.005" thick each Manning Glass separators are used. All cells were activated at ambient temperature using 2 cc of electrolyte. Low temperature experiments were carried out after placing them at the operating temperature for 2 hours. Experiments were carried out in duplication at ambient temperature, +32°F, 0°F and -20°F.

2. Half-cell Measurements. Three types of cathodes were examined for their polarization behavior at -20, 0, 32 and 75°F. They are (1) baseline cathode (2) FePc catalyzed cathode and (3) $(\text{CoPc})_n$ doped cathode. The potential dependence of current is determined by measuring steady-state electrode potential relative to a lithium reference electrode at various controlled currents. At low applied currents (<5 mA/cm²), 2-5 minutes of time was needed to reach steady state, whereas less than a minute was needed at higher applied currents.

In Figures 4-7, the polarization characteristics of three electrodes at operating temperatures of 75, 32, 0 and -20°F were compared. With catalyzed cathodes, the cathode polarization is reduced significantly. FePc catalyzed cathode has the lowest polarization. The decrease in voltage loss with catalyzed cathodes is due mainly to the lowering of activation polarization associated with SOCl_2 adsorption and electron transfer processes.

The electrode polarization becomes severe in all types with lowering of operating temperatures. Furthermore, the limiting currents decrease with decreasing temperatures. This could be attributed to both LiCl precipitation in pore

* The results plotted in Figures 16 and 17 were achieved with 0.028" thick cathodes.

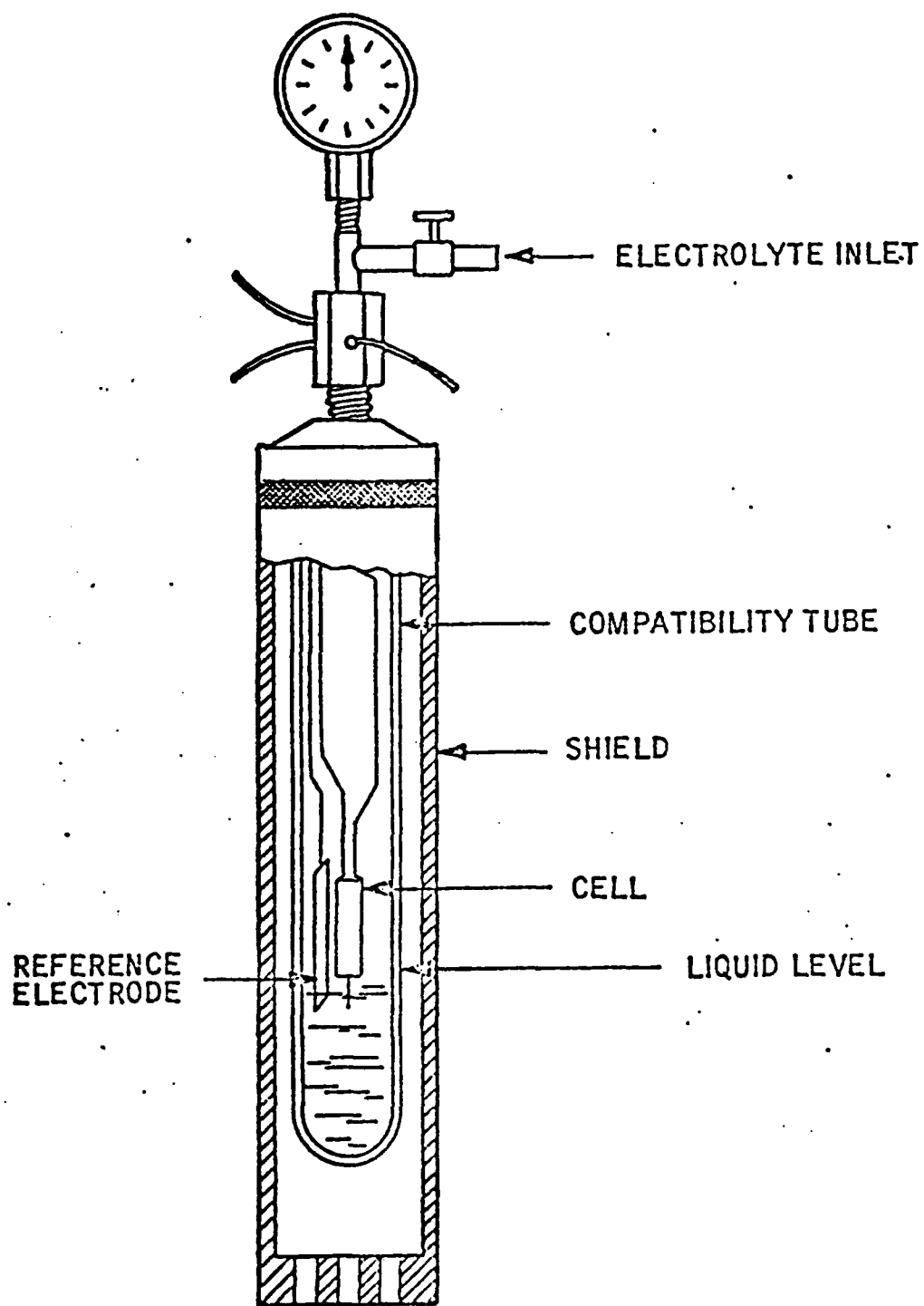


Figure 2. Laboratory Cell. Employed to examine the hypotheses on electrolyte and cathode behavior.

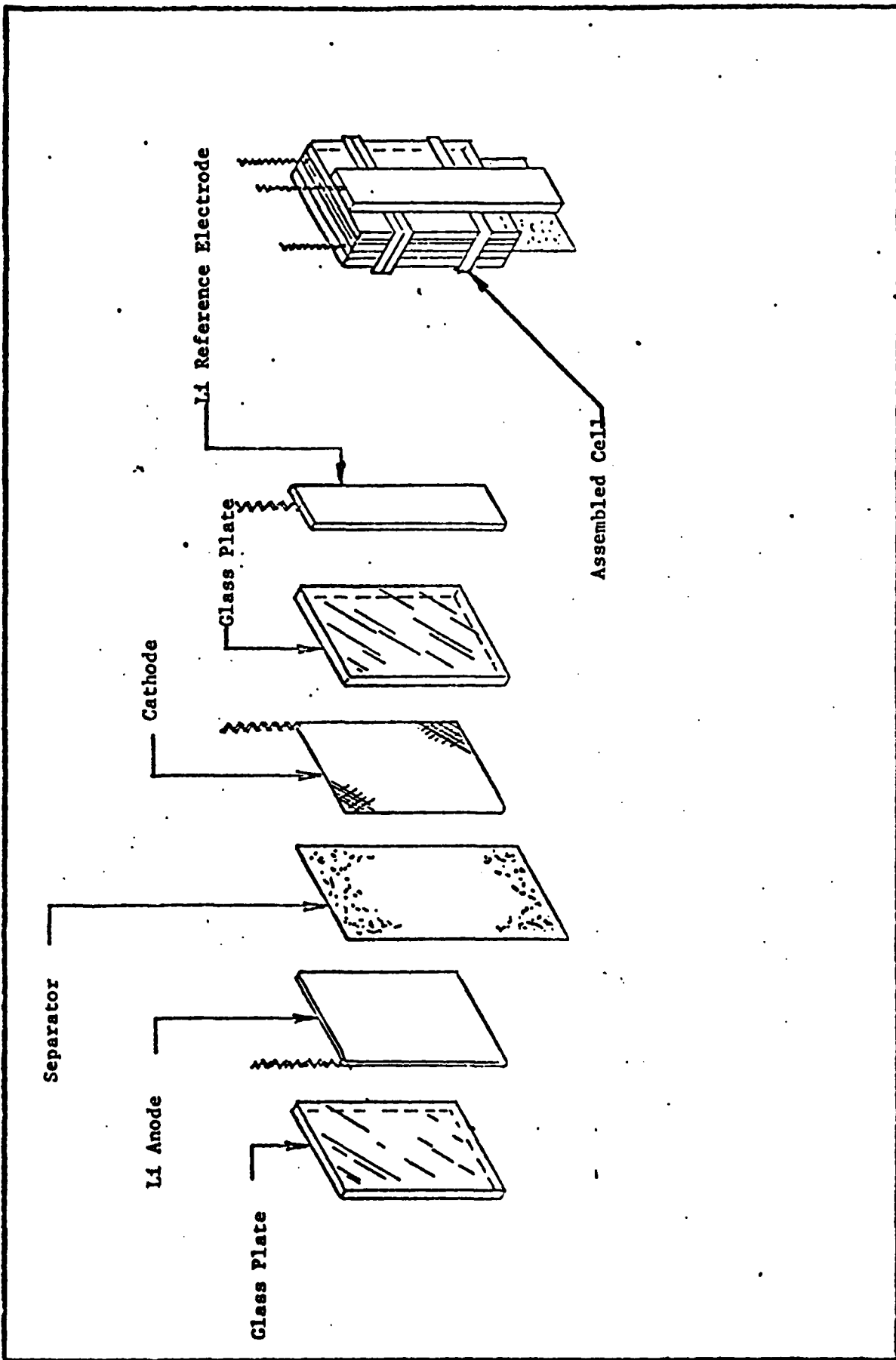


Figure 3. Details of Two-Plate Laboratory Cell.

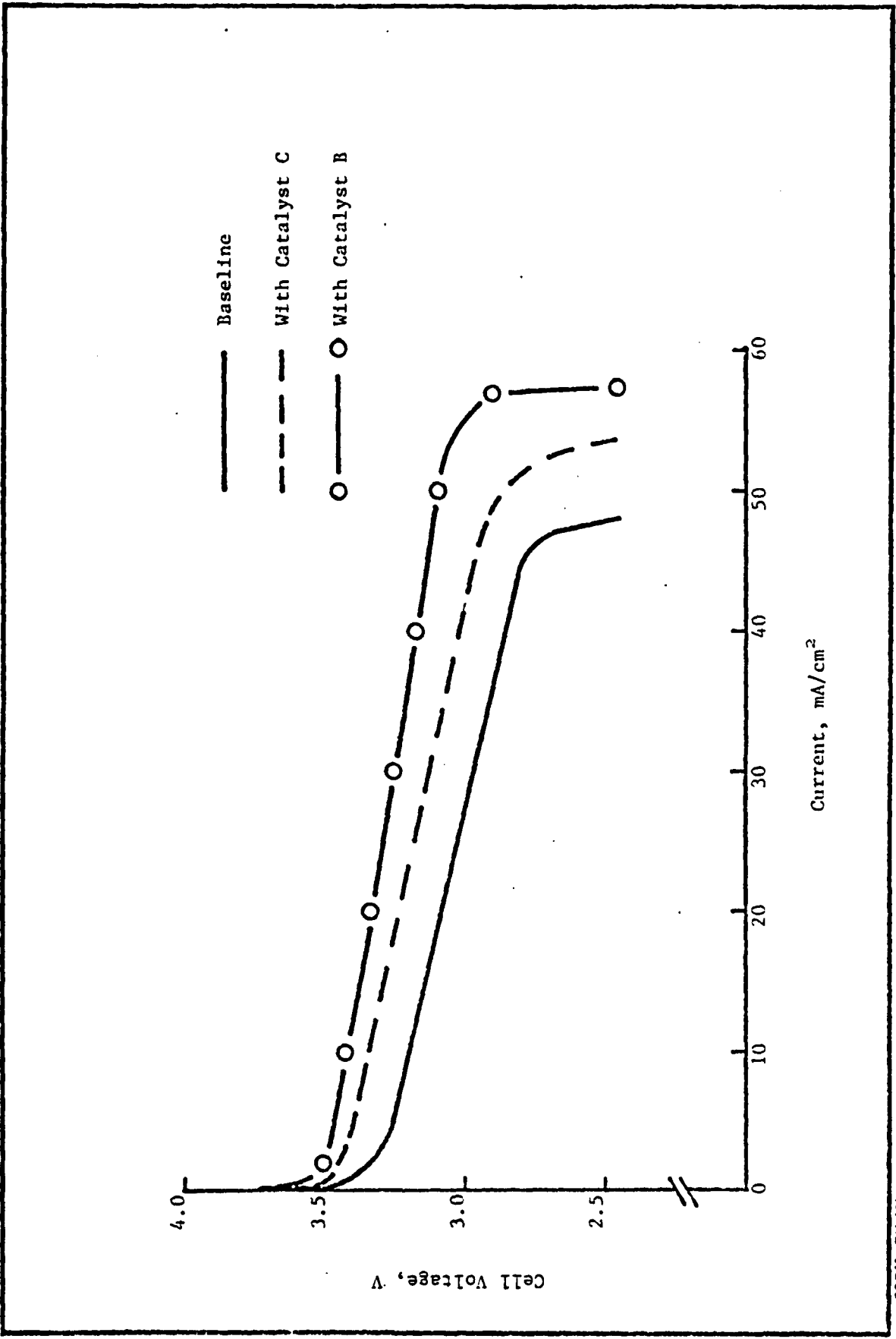


Figure 4. Polarization Characteristics of I₂/SOCl₂ Laboratory Cells at 75°F

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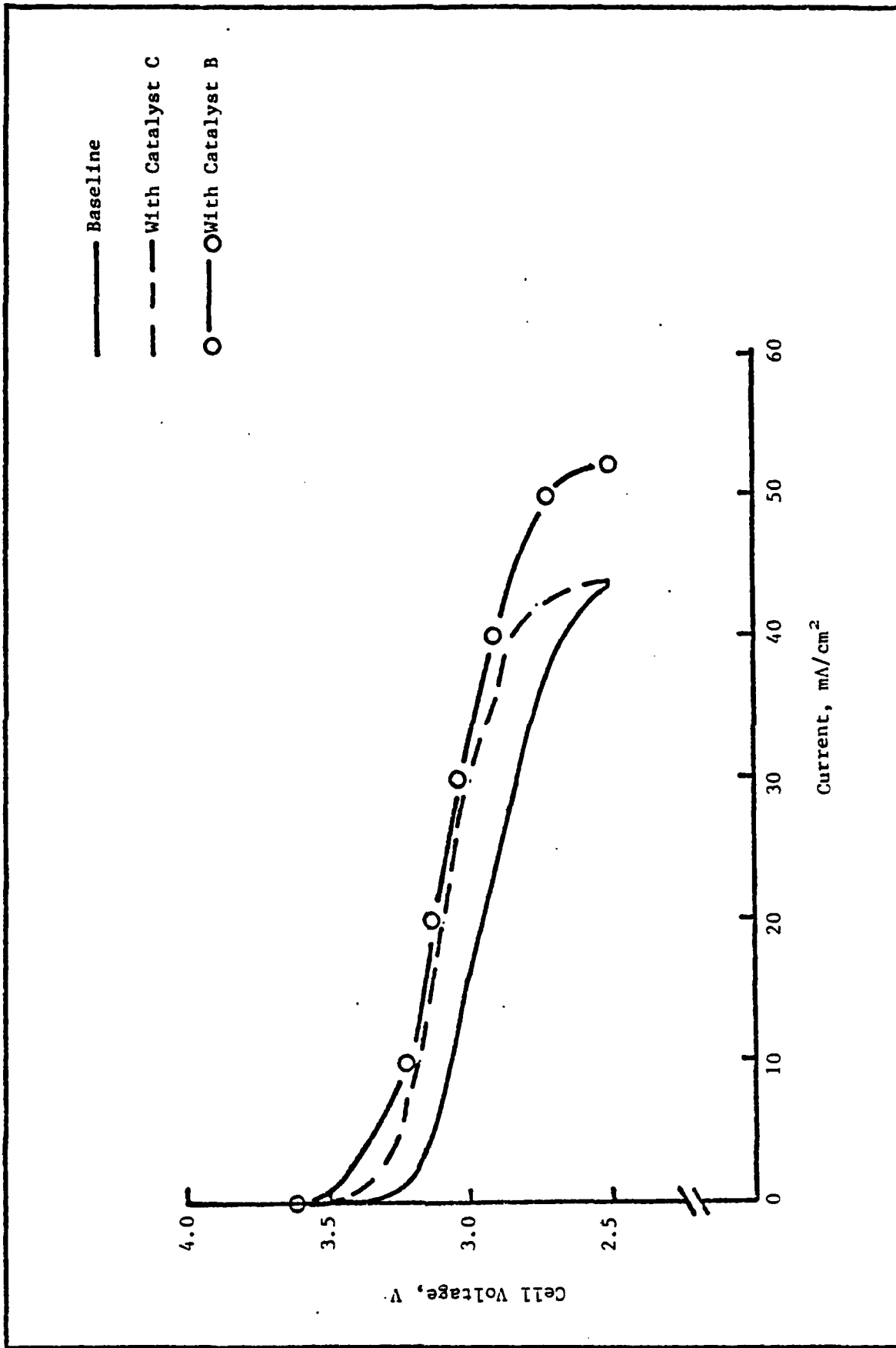


Figure 5. Polarization Characteristics of H₂/SOCl₂ Laboratory Cells at 32°F

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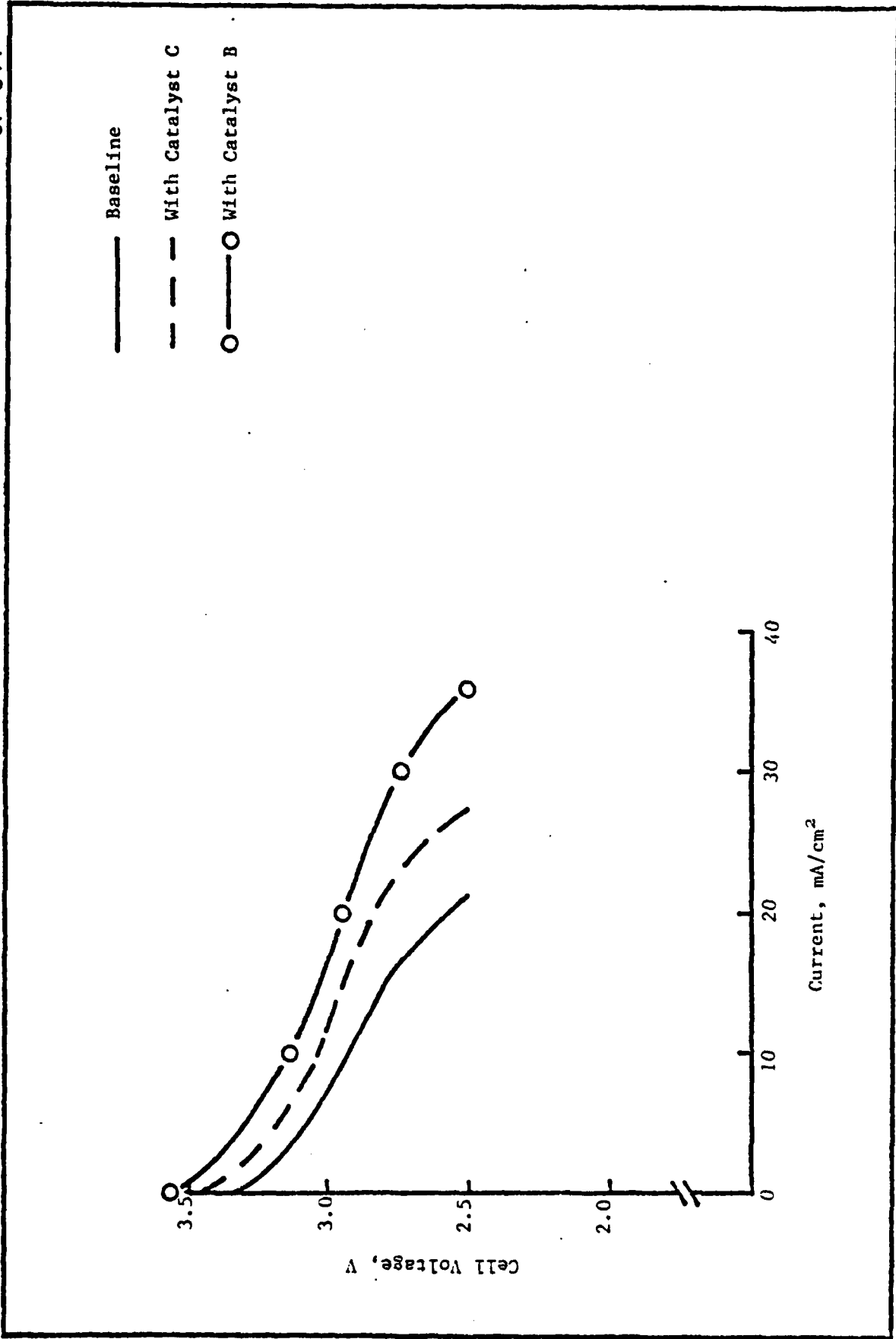


Figure 6. Polarization Characteristics of Li/SOCl₂ Cells at 0°F.

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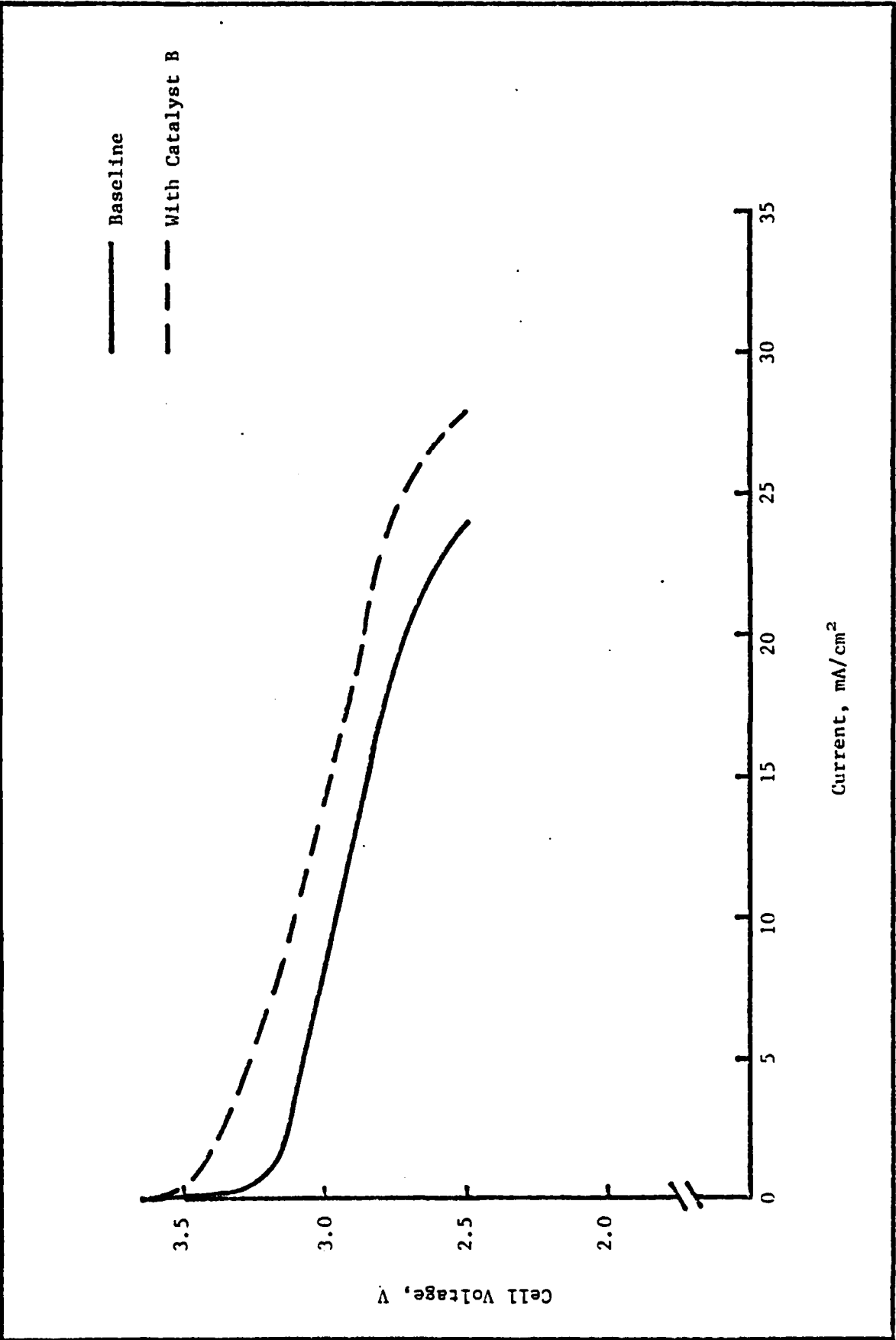


Figure 7. Polarization Characteristics of Li/SOCl₂ Cells at -20°F

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structure and mass transport problems associated with poor electrolyte conductivity and high electrolyte viscosity.

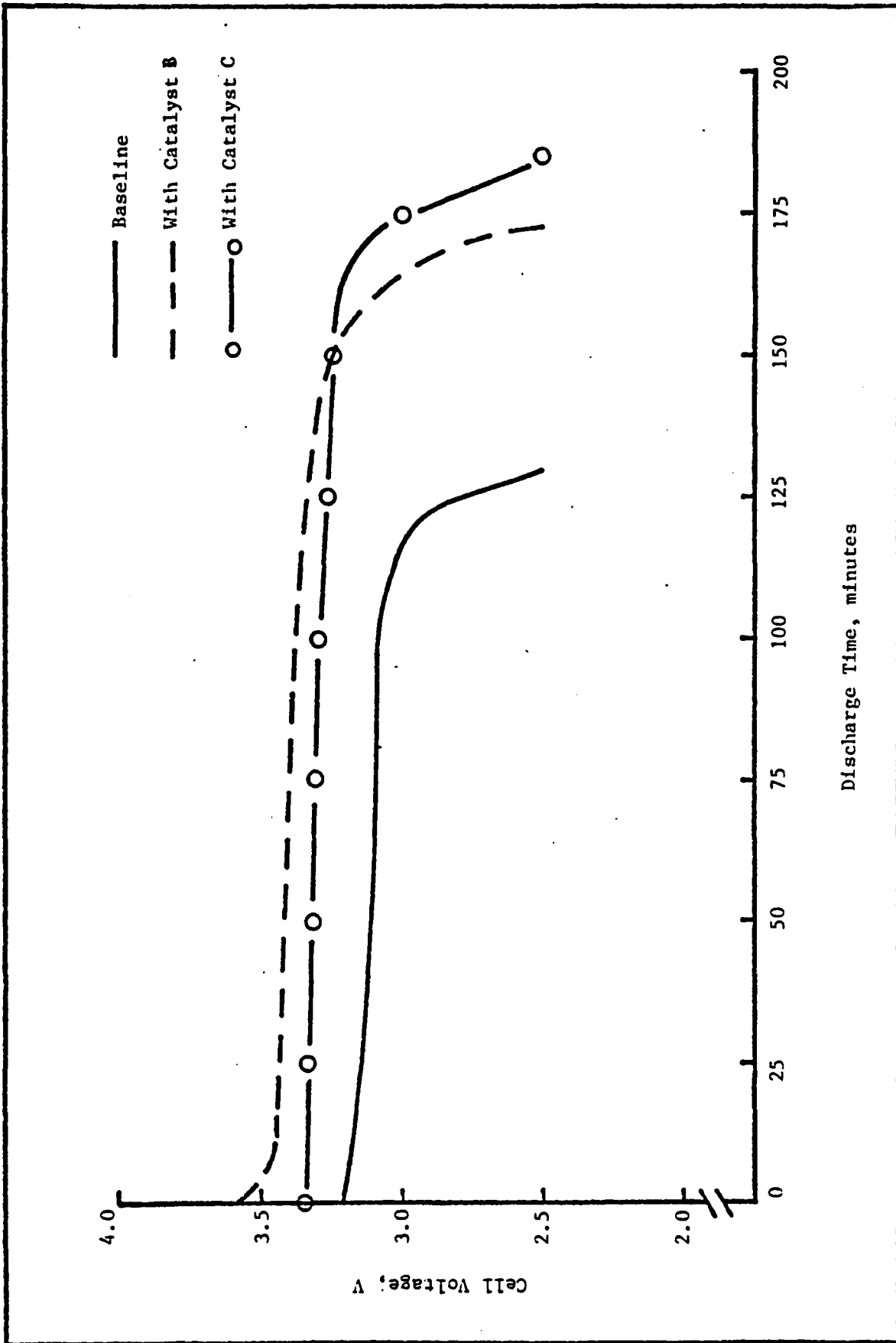
At all operating temperatures studied, higher limiting currents are achieved with catalyzed cathodes. The improvement for FePc catalyzed cathode is around 25% more than that of baseline cathode. In both cases, the same electrodes were employed. Therefore, the increase in the limiting currents might be an indication of a modified cathode reaction mechanism.

3. Discharge Characteristics. The objectives of laboratory cell measurements are to evaluate the discharge characteristics at low operating temperatures and also to analyze the discharged cathodes for reaction zone thickness and product characterization. During the first quarter, only discharge behavior of all three types of cathodes at discharge rates of 10 and 20 mA/cm² were examined. Cells were discharged with constant current loads using a Hewlett-Packard DC current source (#6181B). The data was gathered with a Fluke 2240B datalogger. All experiments were duplicated and in most cases, the results are reproducible.

In Figures 8-11, the discharge characteristics of laboratory cells with three different electrodes at 75, 32, 0 and -20^oF were plotted. At all temperatures, the catalyzed cathodes improved both cell voltages and discharge times. However, at low temperatures, the overall performance of FePc catalyzed cells is superior to cells with (CoPc)_n doped cathodes.

At 20 mA/cm² discharge rates, shown in Figures 12-14, the improved performance of Li/SOCl₂ cells with catalyzed cathodes is similar to that achieved at 10 mA/cm² discharges. Similar results are also obtained at 5 mA/cm² at -20^oF as shown in Figure 15. Further experiments at -20 and -40^oF are planned in the second quarter research work.

It is apparent from the discharge performance data in Tables 1 and 2 that the significantly longer discharge times achieved with catalyzed cathodes are attributed to changes in both reaction mechanisms and reaction zone thickness. At ambient temperature, similar improvements in both cell voltage and discharge performance are observed through a wide range of discharge rates as shown in Figures 16 and 17, respectively.



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Figure 6. Discharge Characteristics of Li/SOCl₂ Laboratory Cells at 10 mA/cm² and 75°F.

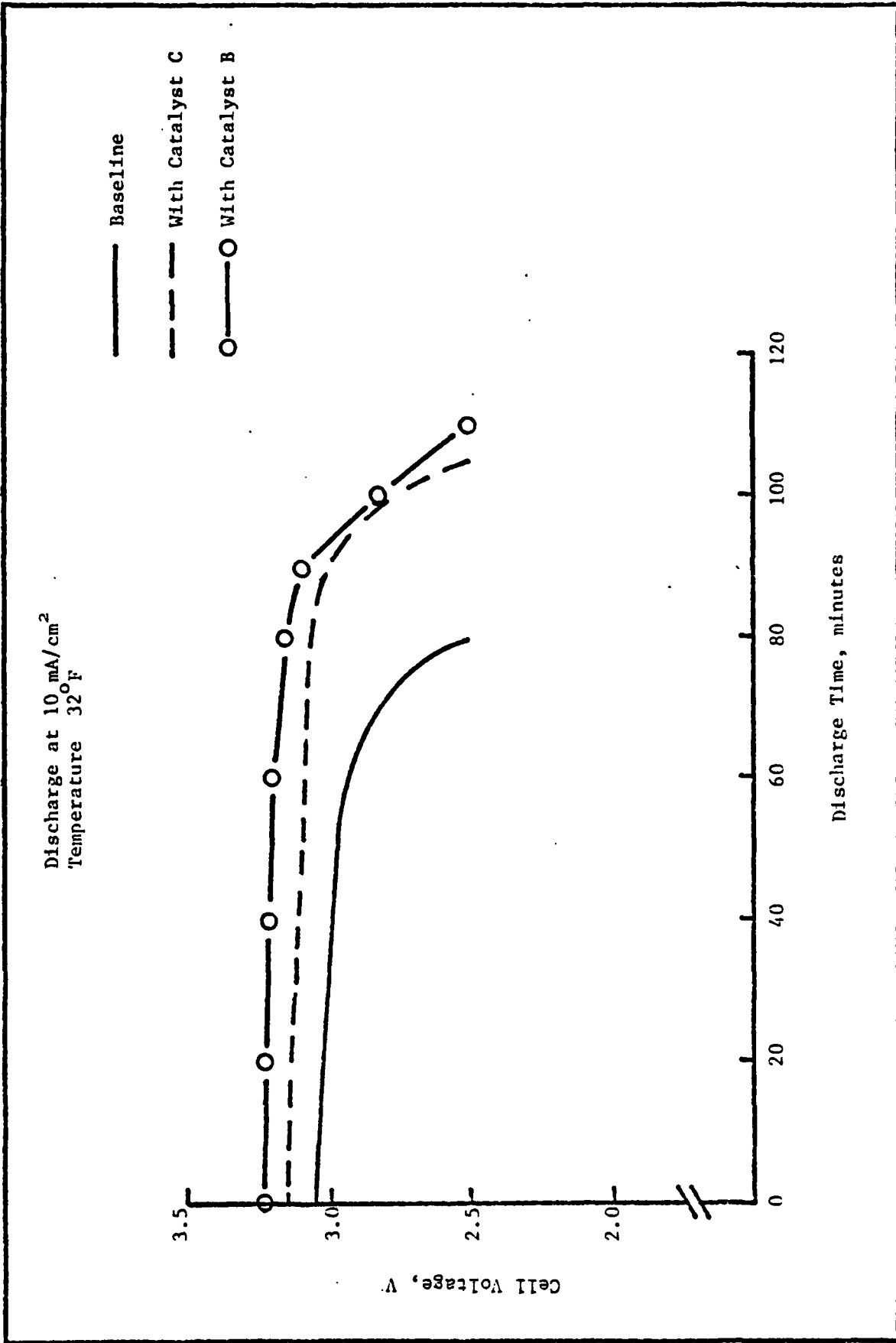


Figure 2. Discharge Characteristics of Li/SOCl₂ Laboratory Cells at 10 mA/cm² and 32°F.

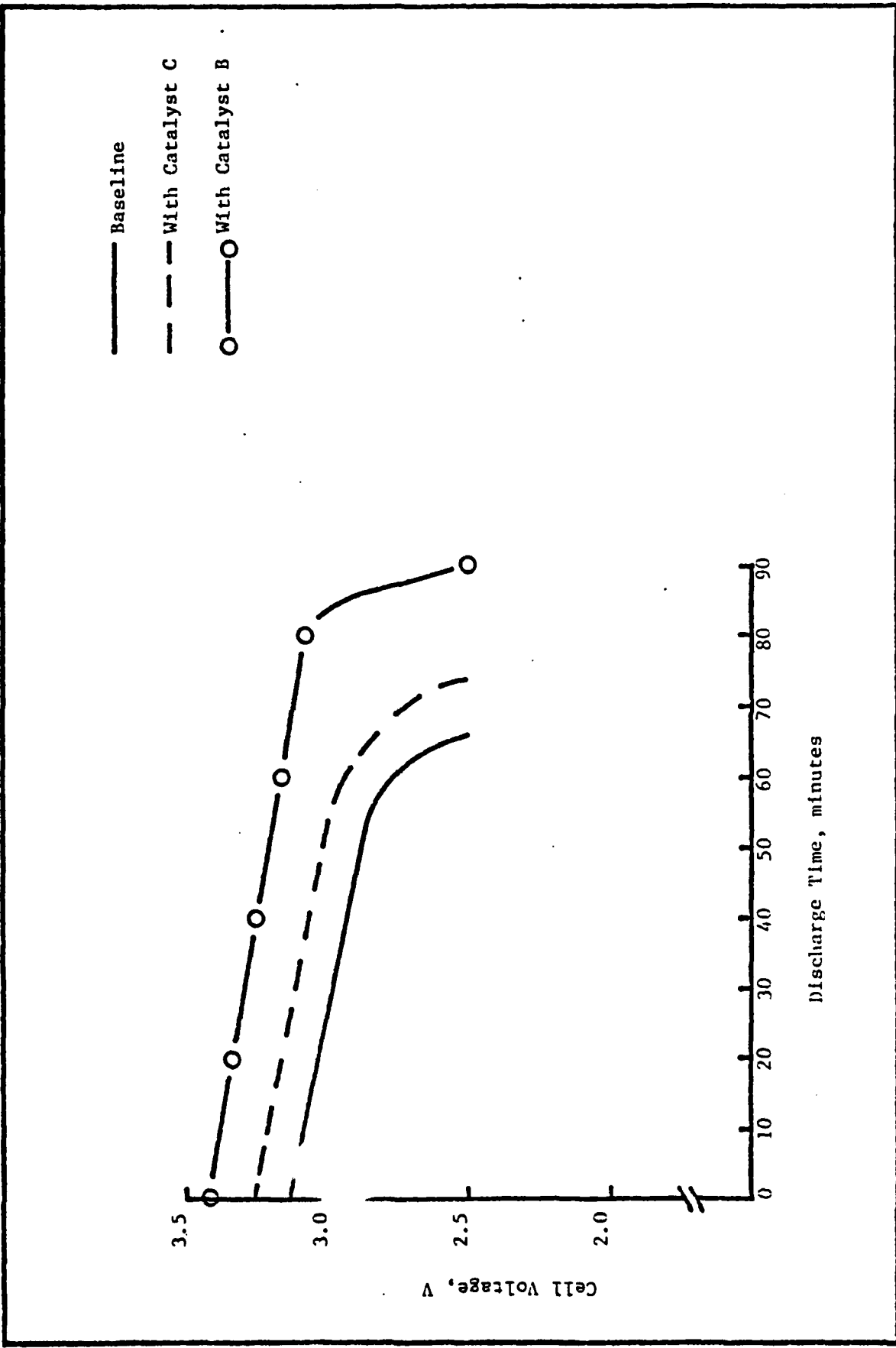
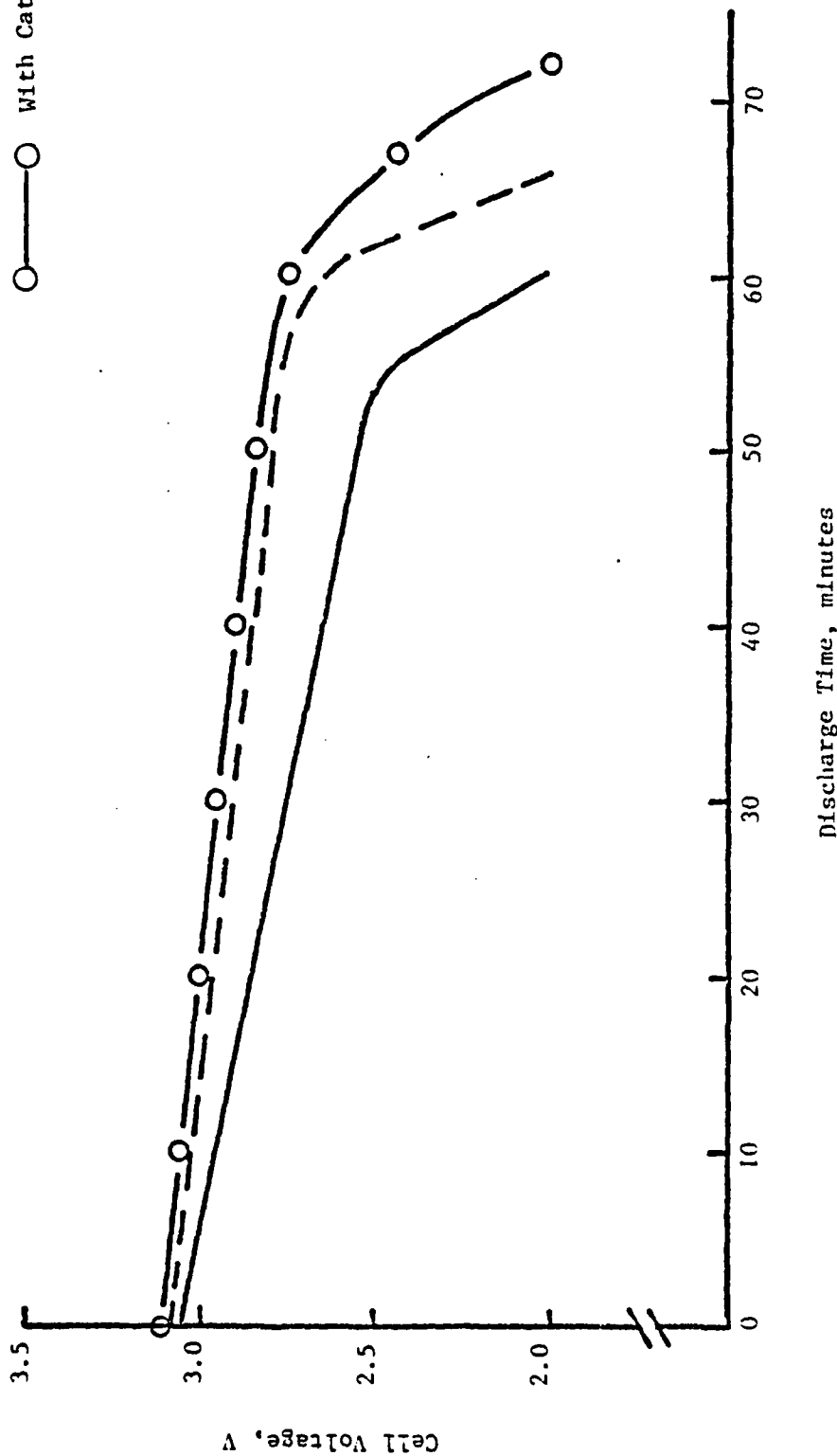


Figure 10. Discharge Characteristics of Li/SOCl₂ Laboratory Cells at 10 mA/cm² and 0°F.

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Discharge at 10 mA/cm²
Temperature -20°F

— Baseline
- - - With Catalyst C
○ With Catalyst B

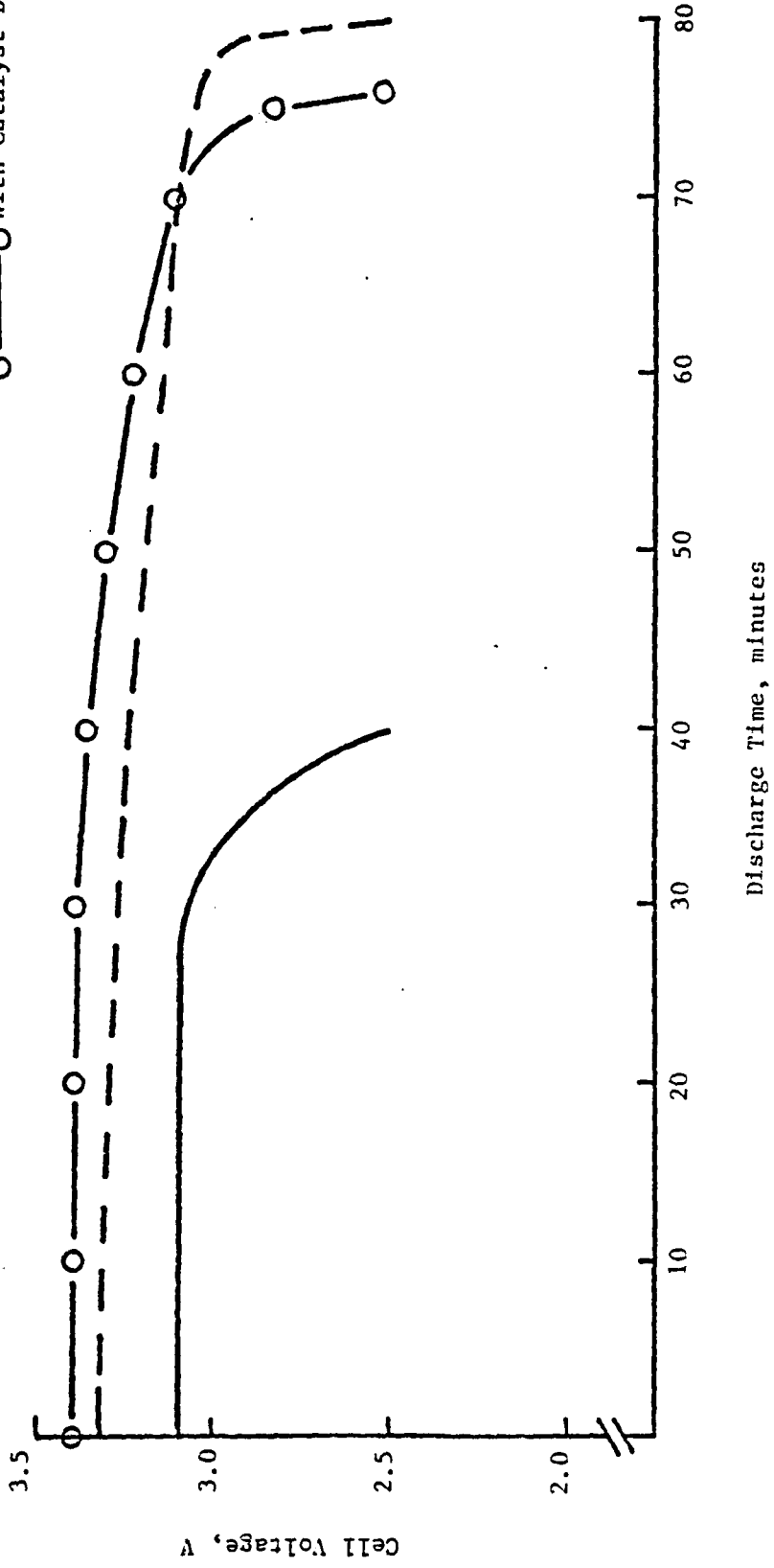


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Figure 11. Discharge Characteristics of Li/SOCl₂ Laboratory Cells at 10 mA/cm² and -20°F

Discharge at 20 mA/cm²
Temperature 75°F

- Baseline
- - - With Catalyst C
- With Catalyst B

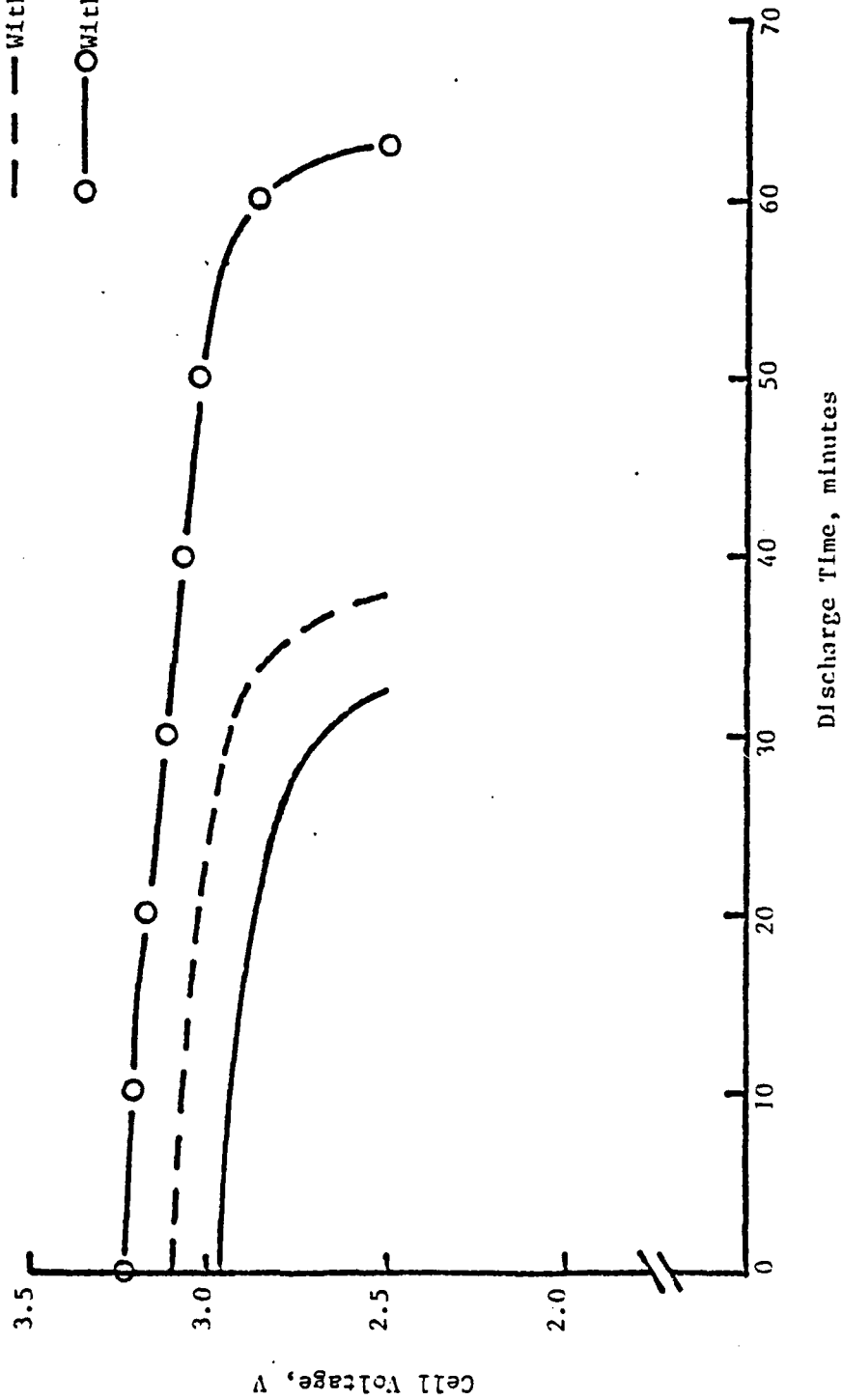


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Figure 12. Discharge Characteristics of Li/SOCl_2 Laboratory Cells at 20 mA/cm² and 75°F

Discharge at 20 mA/cm²
Temperature 32°F

— Baseline
- - - With Catalyst C
○—○ With Catalyst B

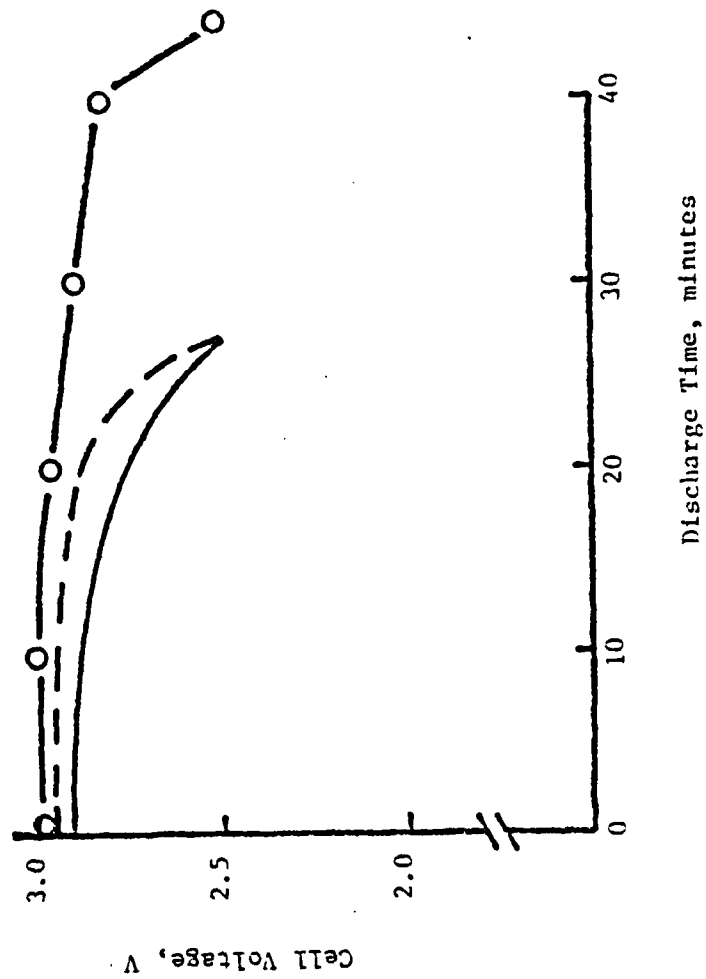


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Figure 13. Discharge Characteristics of Li/SOCl₂ Cells at 20 mA/cm² and 32°F.

Discharge at 20 mA/cm²
Temperature 0°F

- Baseline
- - - With Catalyst C
- With Catalyst B

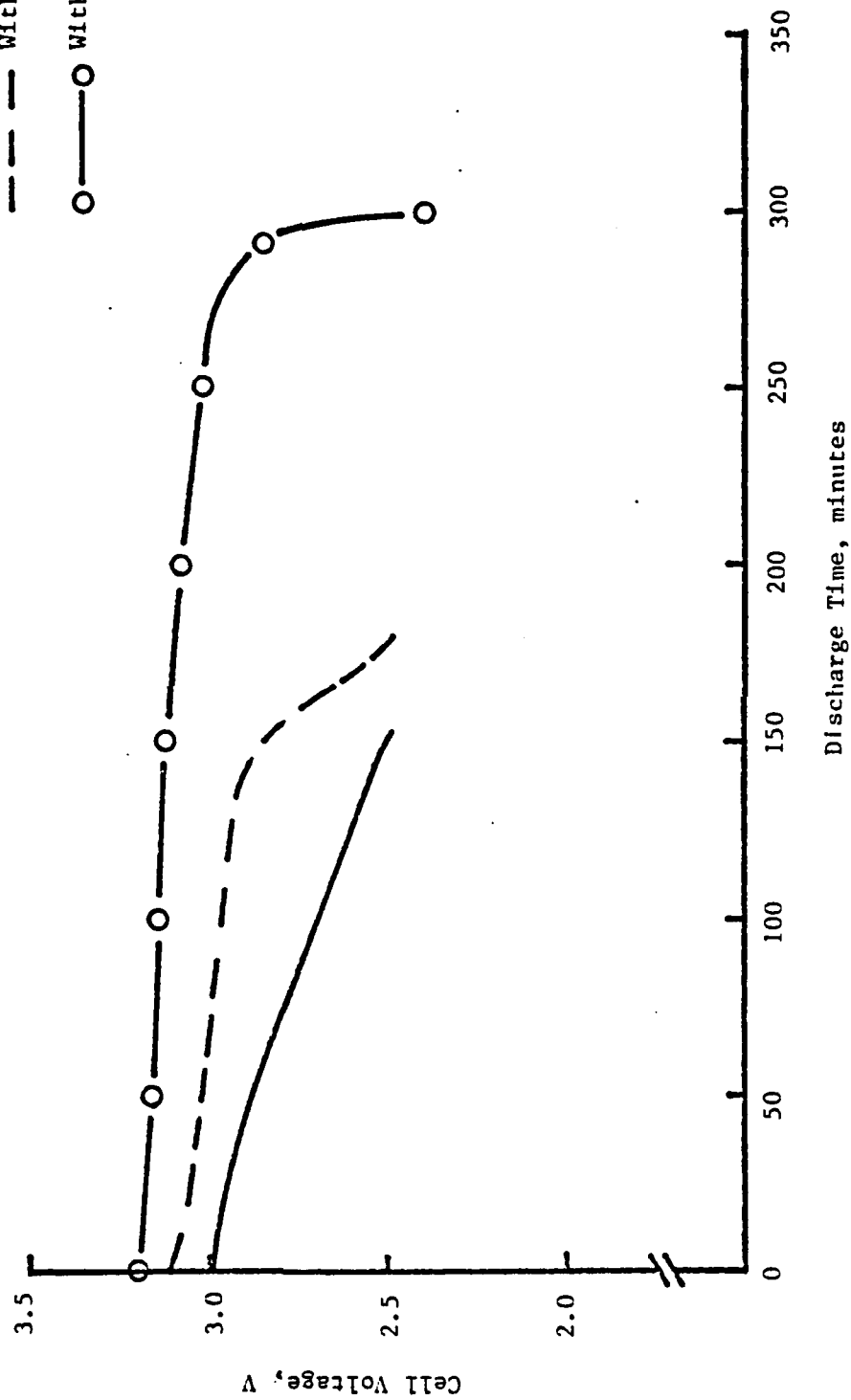


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Figure 14. Discharge Characteristics of i1/SOCl2 Laboratory Cells at 20 mA/cm² and 0°F.

Discharge at 5 mA/cm²
Temperature. -20°F

— Baseline Cathode
- - - With Catalyst C
○—○ With Catalyst B



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Figure 15. Discharge Characteristics of Li/SOCl₂ Laboratory Cells at 5 mA/cm² and -20°F

Table 1. Discharge Characteristics of Li/SOCl₂ Cells at 10 mA/cm² in 1.5M LiAlCl₄/SOCl₂.

Temp. °F	Baseline Cathode		With Catalyst B		With Catalyst C	
	Avg. Cell Voltage, V.	Discharge Time, min.	Avg. Cell Voltage, V.	Discharge Time, min.	Avg. Cell Voltage, V.	Discharge Time, min.
75	3.11	125	3.41	162*	3.30	180
32	3.01	85	3.20	135	3.12	105
0	2.99	60	3.21	89	3.06	86
-20	2.80	55	2.89	76	2.90	64

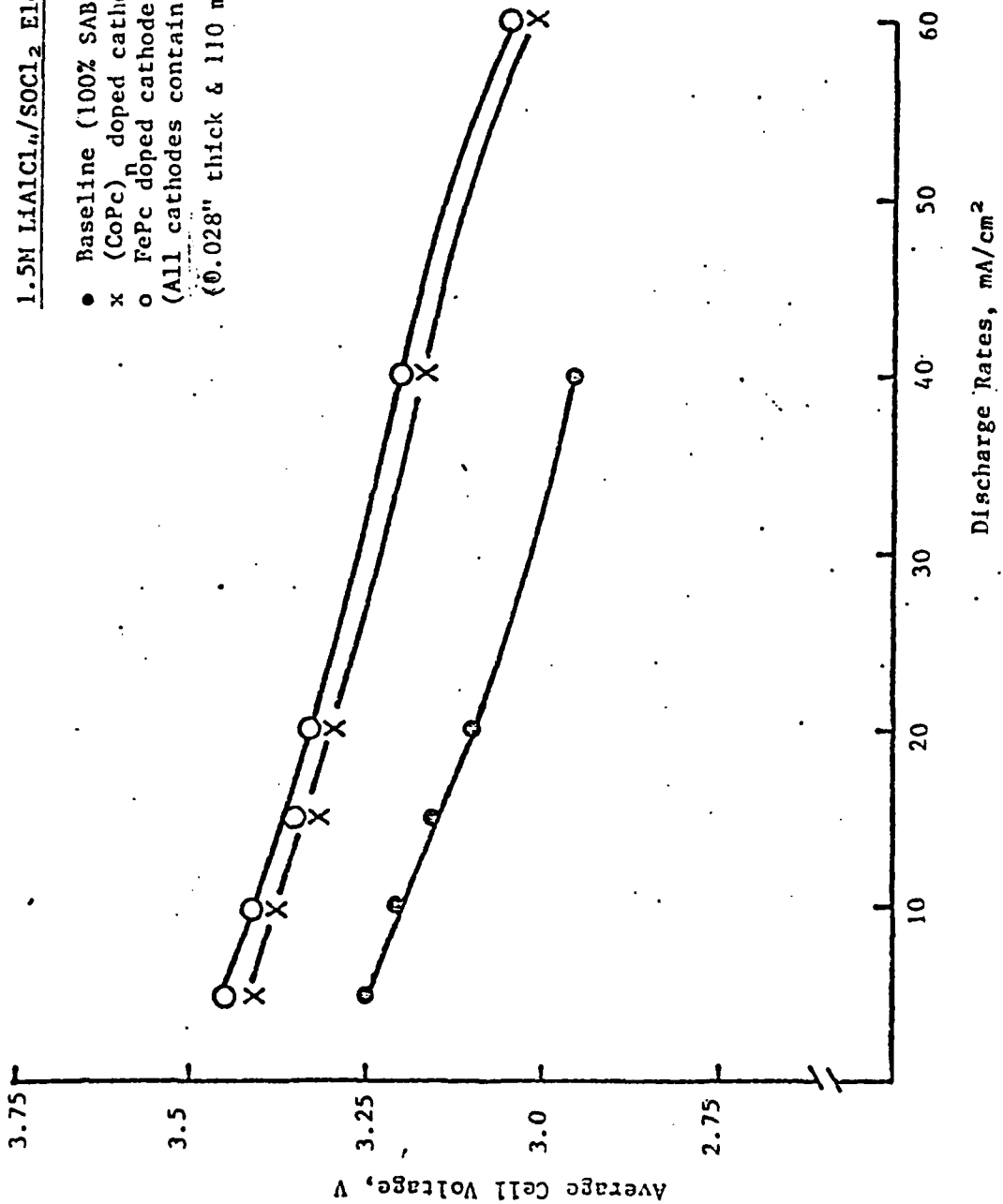
* Low value is attributed to variation in cathode thickness and cell assembly technique.

Table 2. Discharge Characteristics of Li/SOCl₂ Cells at 20 mA/cm² in 1.5M LiAlCl₄/SOCl₂

Temp. °F	Baseline Cathode		With Catalyst B		With Catalyst C	
	Avg. Cell Voltage, V.	Discharge Time, min.	Avg. Cell Voltage, V.	Discharge Time, min.	Avg. Cell Voltage, V.	Discharge Time, min.
75	3.09	40	3.35	77	3.29	70
32	2.94	30	3.11	66	3.02	38
0	2.84	28	3.03	35	2.90	28

1.5M LiAlCl₄/SOCl₂ Electrolyte

- Baseline (100% SAB)
 - x (CoPc)_n doped cathode
 - o FePc doped cathode
- (All cathodes contain 5% PTFE)
 (0.028" thick & 110 mg mix weight)



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Figure 16. Average Discharge Voltage of Li/SOCl₂ Cells versus Discharge Rate at 72 F

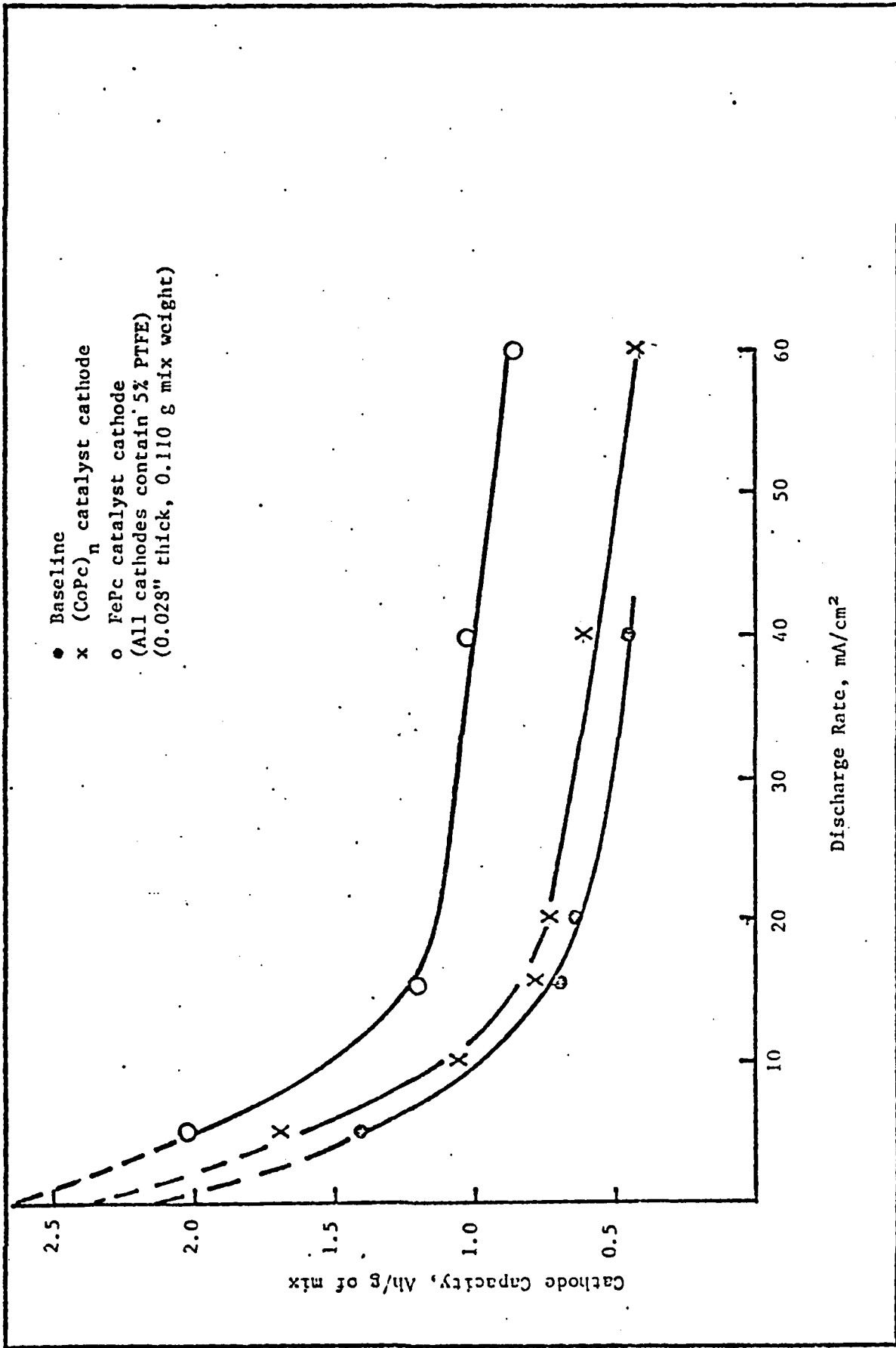


Figure 17. Discharge Performance of Li/SOCl₂ Cells with 1.5M LiAlCl₄/SOCl₂ at 72°F (2.5V cutoff)

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C. KINETIC AND MECHANISTIC STUDIES

Reaction mechanisms of SOCl_2 reduction at porous carbon cathodes have been proposed to involve free radical intermediates, although there is a considerable disagreement on the overall reaction mechanisms. Since both the reaction mechanisms and reaction products contribute to the performance of a battery, it is desirable to understand these two important factors. It is planned to employ during the program period both cyclic voltammetry and rotating disc electrode techniques to better understand the reaction mechanism of SOCl_2 reduction at cathodes doped with and without catalysts. In this report, we present the preliminary results obtained in cyclic voltammetry.

Thionyl chloride from MCB was refluxed over lithium metal and distilled twice and the solvent was stored at 0°F . 1M $\text{LiAlCl}_4/\text{SOCl}_2$ solution was made an hour before it was used. A conventional electrochemical cell with three electrodes was employed. Pressure annealed pyrolytic graphite ($A=0.178\text{ cm}^2$), polycrystalline carbon ($A=0.178\text{ cm}^2$), glassy carbon ($A=0.44\text{ cm}^2$) and platinum ($A=0.178\text{ cm}^2$) were used as working electrodes. All working electrodes were sealed in Teflon rods. At the end of each cyclic voltammogram, the electrodes were cleaned employing normal techniques to produce reproducible surfaces. The reference and counter electrodes were made freshly by pressing lithium foil onto nickel grids. The cyclic voltammetric studies were carried out in a dry room using Princeton Applied Research Model 170 Electrochemistry System.

In Figure 18, the effect of sweep rate on cyclic voltammograms at pressure annealed pyrolytic graphite electrode in 1.0M $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte at 75°F is shown. Both peak height and position change with sweep rate as anticipated. Similar behavior was also observed with catalyst B. However, the peak height increased and the peak position moved toward more positive potential with the catalyst. In both cases, a linear relation between peak height and square root of sweep rate was observed (Figure 19), indicative of a diffusion controlled system. Similar behavior was also observed at platinum electrode (Figure 20) and glassy carbon electrode (Figure 21).

At low operating temperatures, the electrolyte viscosity and conductivity strongly influence the peak positions. The change in peak height should

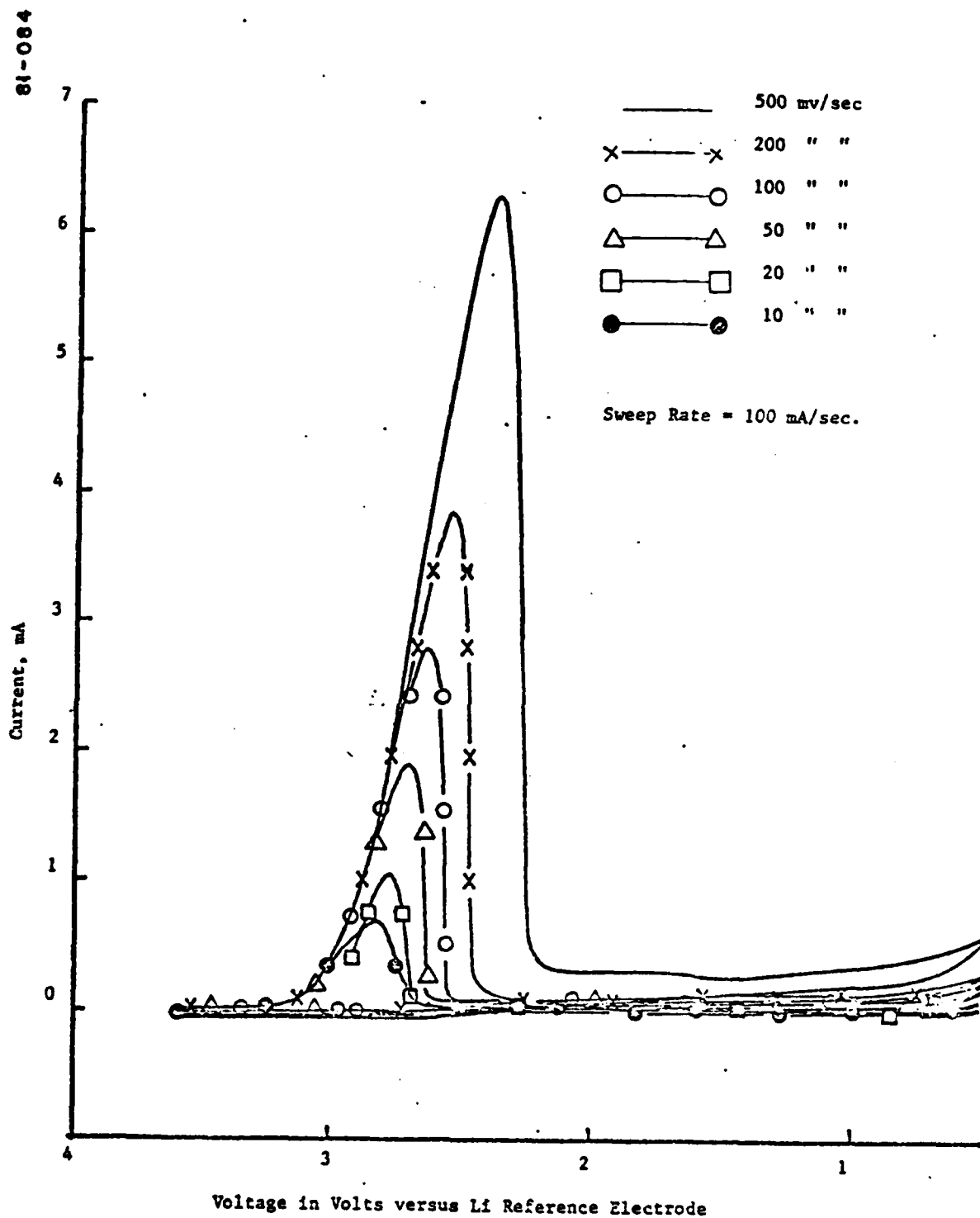
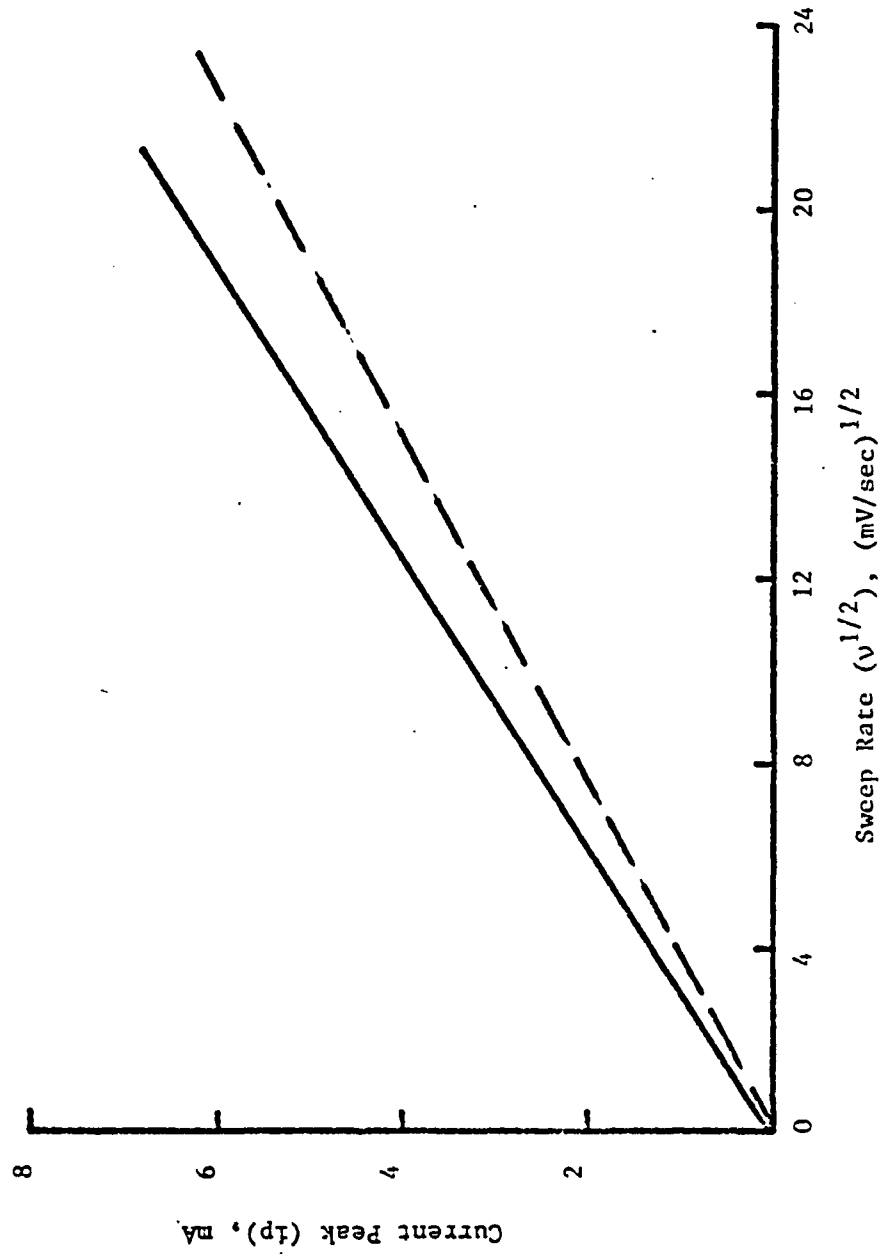


Figure 18. Effect of Sweep Rate on Cyclic Voltammograms at Pressure Annealed Pyrolytic Graphite Electrode ($A=0.178 \text{ cm}^2$) in $1.0M \text{ LiAlCl}_4/\text{SOCl}_2$ Electrolyte at 75°F .

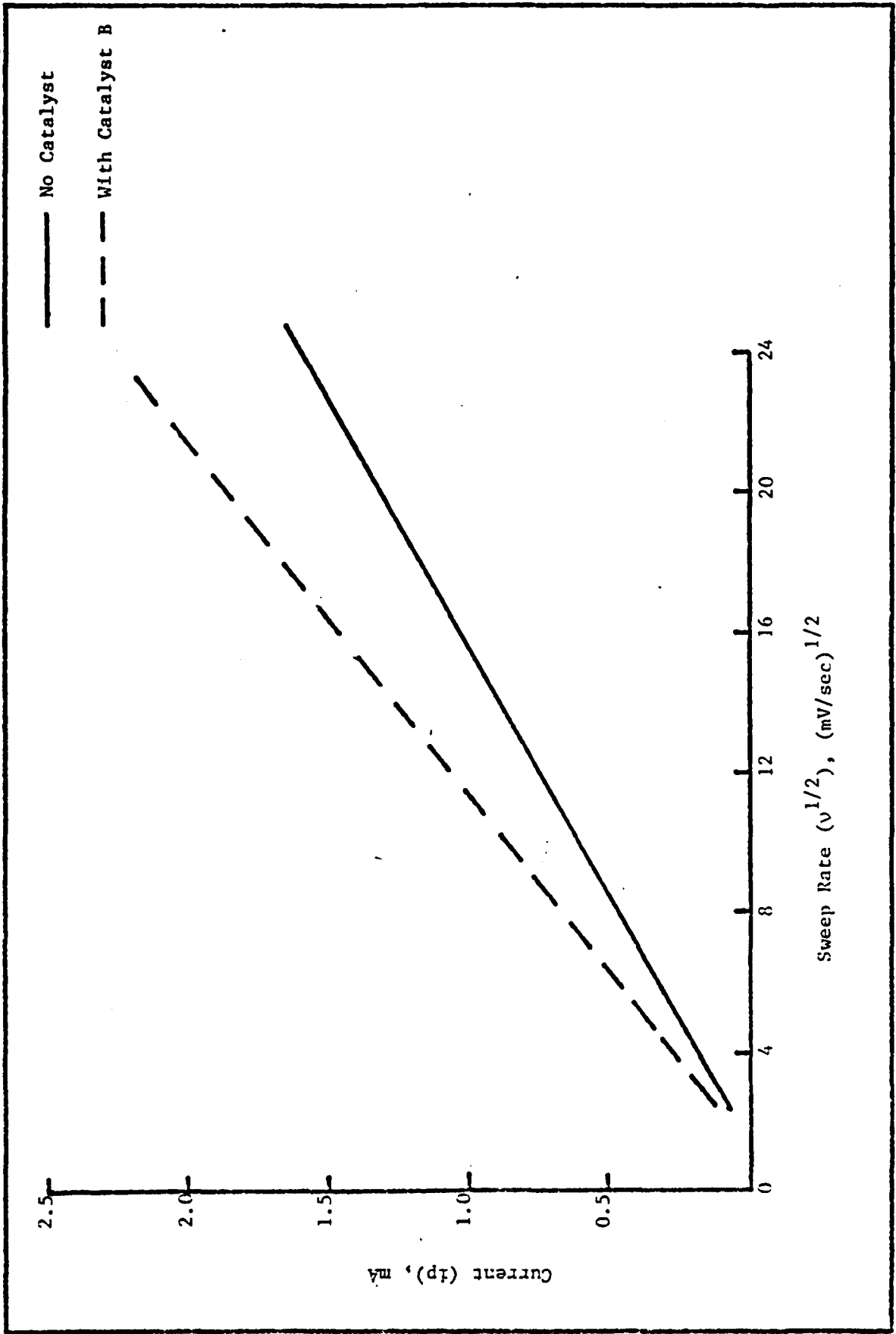
— With Catalyst B
- - Without Catalyst



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Figure 19. Current Peak Height (i_p) versus Square Root of Sweep Rate ($v^{1/2}$).
Pressure Annealed Pyrolytic Graphite ($\Lambda=0.178 \text{ cm}^2$) in 1M $\text{LiAlCl}_4/\text{SOCl}_2$
at 75 $^\circ\text{F}$.

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Figure 20. Current peak height (i_p) versus Square Root of Sweep Rate. Pt electrode ($A=0.178 \text{ cm}^2$) in 1M $\text{HAlCl}_4/\text{SOCl}_2$ at Ambient Temperature.

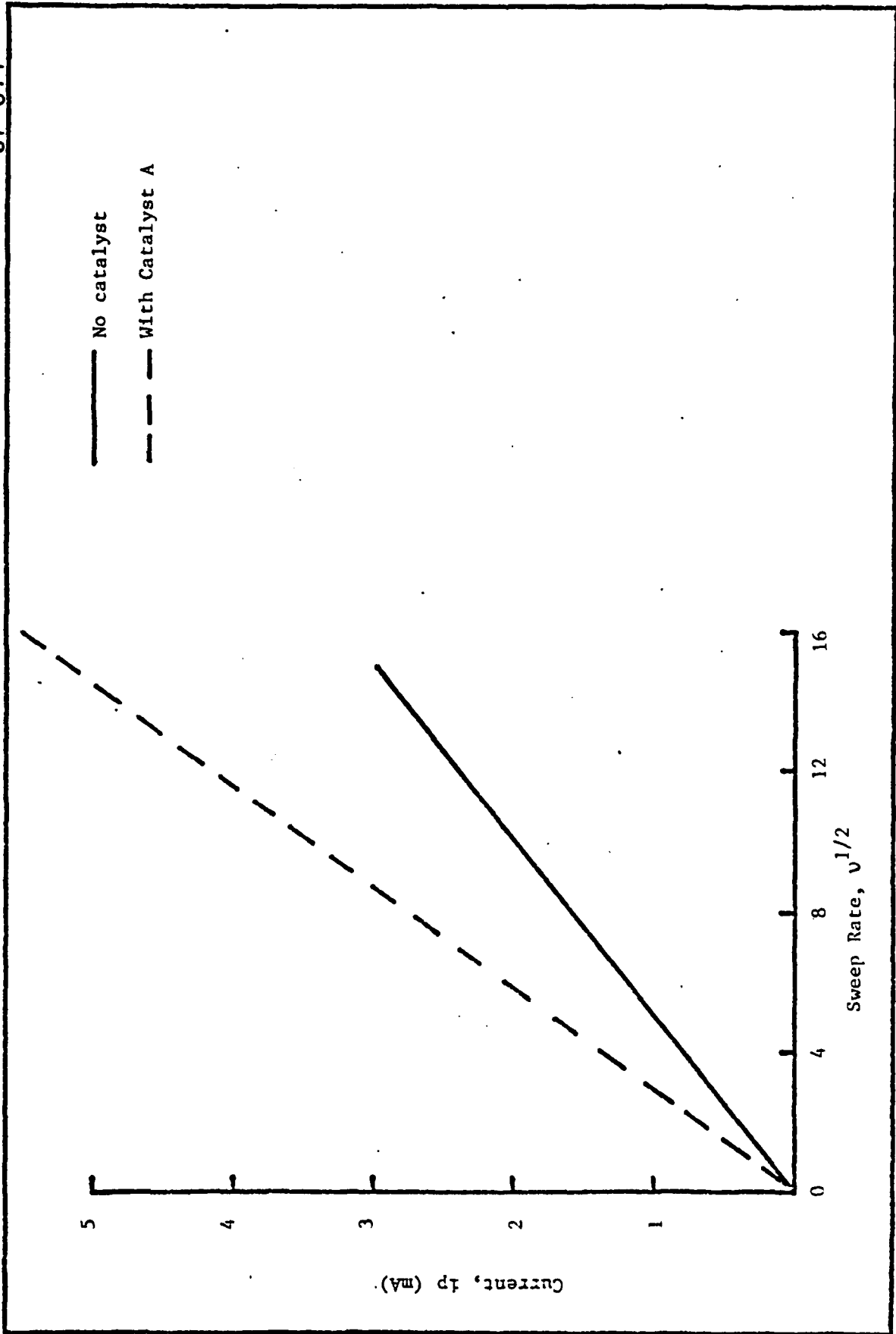


Figure 21. Current Peak Height (i_p) versus Square Root of Sweep Rate, Glassy Carbon Electrode (0.44 cm^2) in $1M \text{ LiAlCl}_4/\text{SOCl}_2$ at 32°F .

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indicate the extent of electrolyte influence on the rate capability of an electrode. In Figures 22 and 23, the effect of temperature on SOCl_2 reduction peak position and peak height in cyclic voltammograms at polycrystalline carbon electrodes in 1.0M $\text{LiAlCl}_4/\text{SOCl}_2$ containing with and without FePc catalyst are shown. In both cases, the reduction peak decreases in operating temperature. This decrease can be attributed directly to the electrolyte properties which influence the diffusion coefficients.

The reduction peak height with and without catalyst showed a linear relationship with reciprocal temperature. The energies of activation derived from $\ln I_p$ vs $1/T$ relationship from Figures 22 and 23 are 1.83 and 1.65 Kcals, respectively. Such small change in activation energies indicates that the cathode performance is strongly influenced by electrolyte properties. The peak shift toward more negative potential with decrease in temperature is observed only with baseline cathodes. No such shift is found with catalyzed cathodes. This could be due to changes in activation polarizations.

D. IMPEDANCE MEASUREMENTS

Determination of cell internal resistance and charge transfer resistance is essential in determining the sources of electrode overpotential. Since both the electrolyte physical properties and cathode structure and its reaction contribute to the polarization, we will evaluate both these important factors. In this report, we present the effect of temperatures on the electrolyte conductivity and viscosity.

Our starting electrolyte for this program is 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$. Improvements to achieve higher conductivity and lower viscosity are needed for better mass transport properties at low operating temperatures. Therefore, conductivity and viscosity measurement between -40°F and 77°F were made for both 1.0M and 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$ so as to compare these variables on the electrolyte composition.

1. Conductivity. Conductivity measurements were made employing a General Radio Impedance Comparator Bridge and Jones type conductivity cell having

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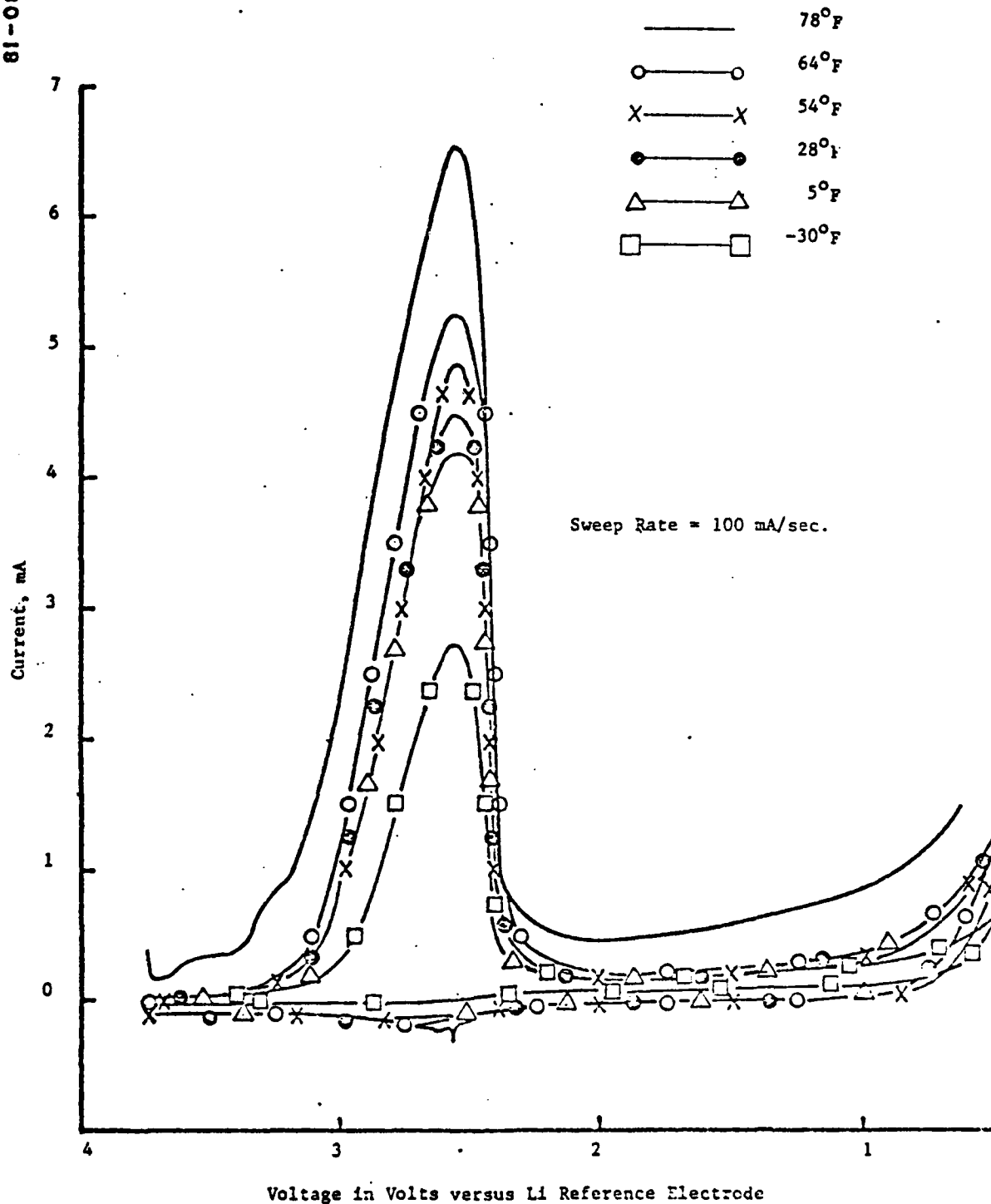


Figure 22. Effect of Temperature on Cyclic Voltammograms at Polycrystalline Carbon Electrode in 1.0M LiAlCl₄/SOCl₂ Electrolyte Containing FePc Catalyst.

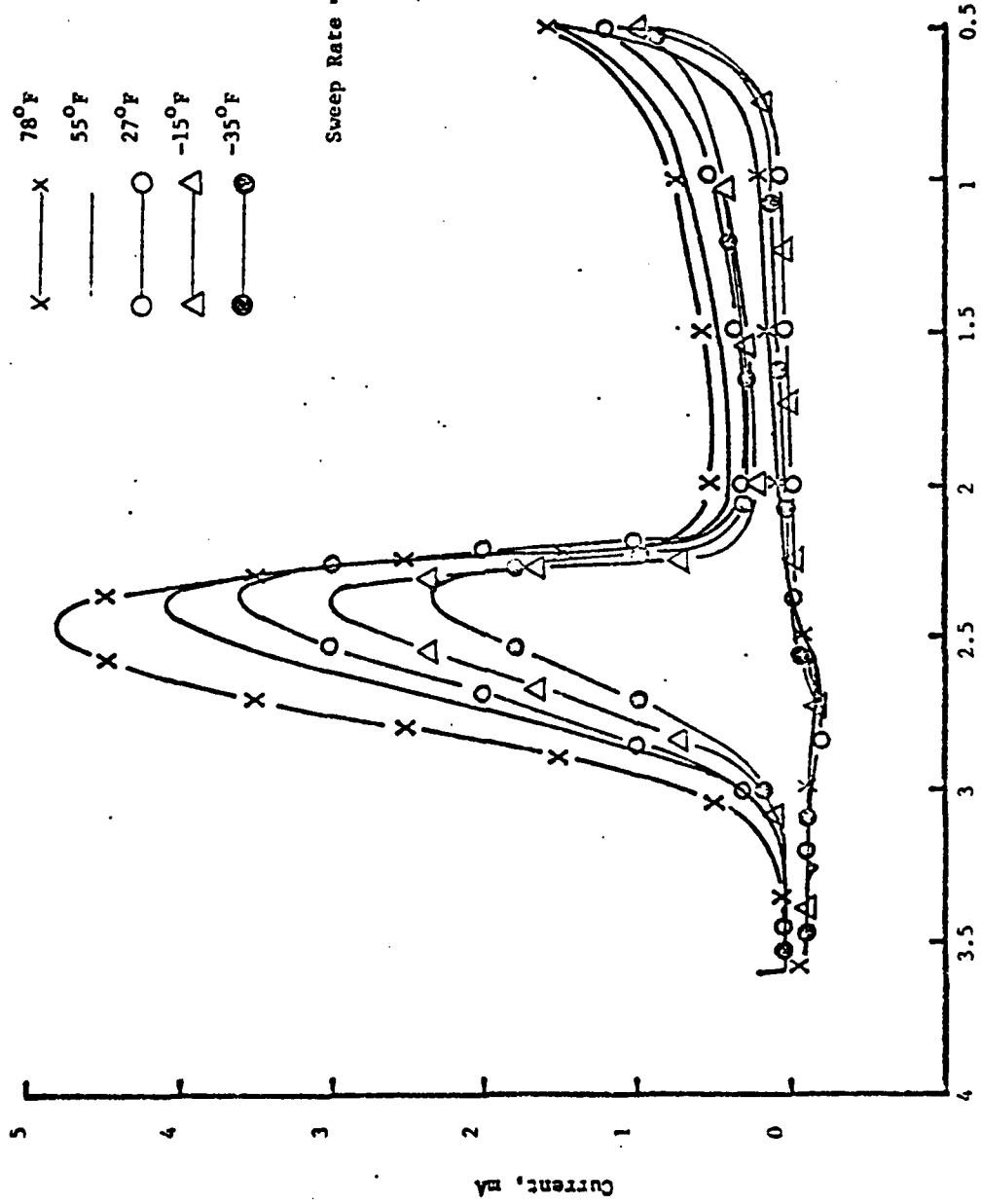


Figure 23. Effect of Temperature on Cyclic Voltammograms at Polycrystalline Carbon Electrode ($A=0.178 \text{ cm}^2$) in 1.0M $\text{LiAlCl}_4/\text{SOCl}_2$ Electrolyte.

bright platinum electrodes. The electrodes were cleaned with chromic acid cleaning solution, washed thoroughly with distilled water and finally dried before each experiment. The cells were calibrated at 25°C with KCl solutions, and are used to duplicate experiments. The cell constants are 114.63 and 130.50 cm⁻¹.

Resistance R measurements of the electrolyte solutions were made at 10 KHz over the temperature range. From the resistance value, the specific conductance, L_s in ohm⁻¹ cm⁻¹, were calculated from the standard equation:

$$L_s = \frac{L}{AR}$$

where,

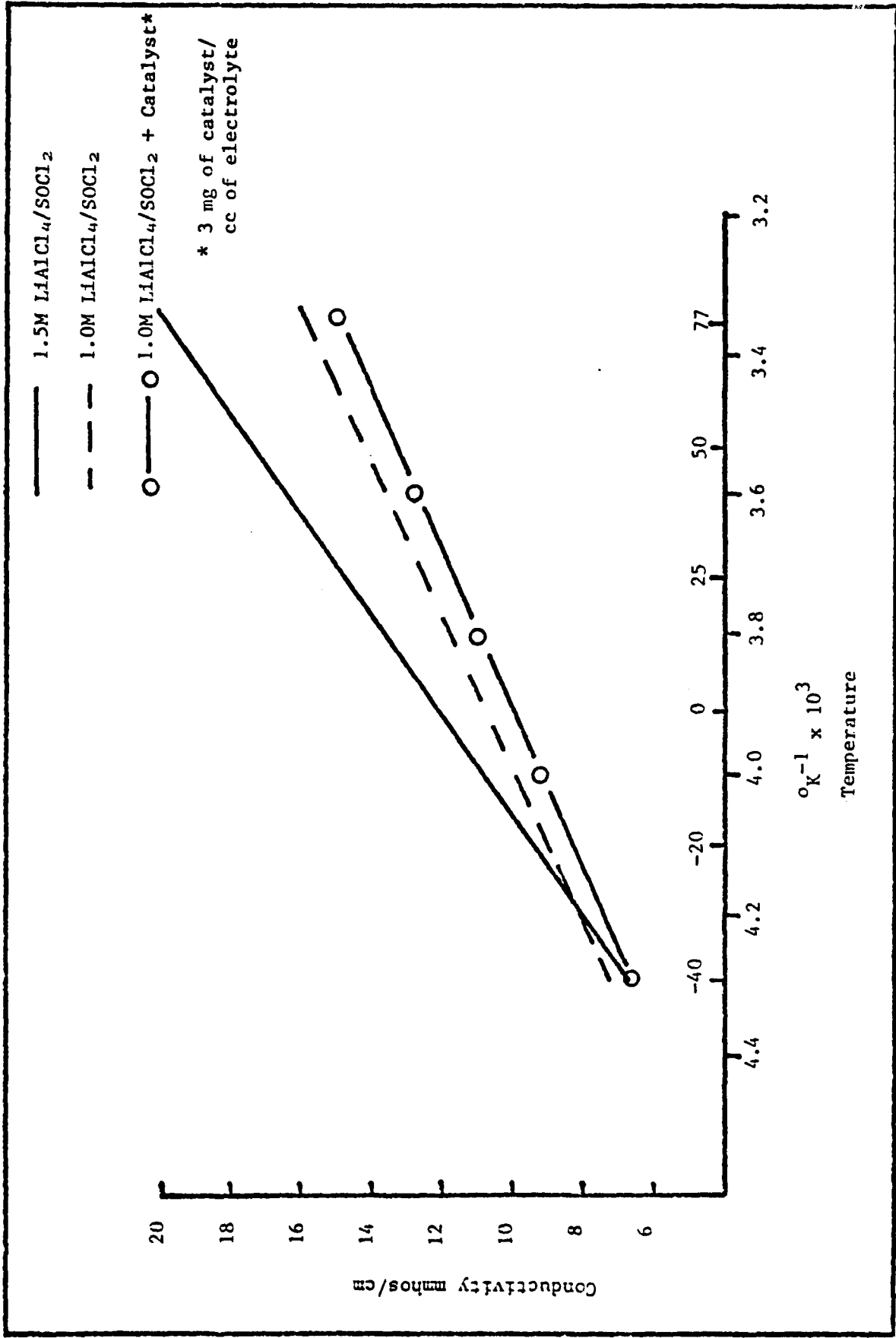
L = Electrode separation

A = Electrode area, cm²

The temperature dependance of specific conductance of electrolyte is shown in Figure 24. The conductivity of 1.5M LiAlCl₄/SOCl₂ is higher than that of 1.0M LiAlCl₄/SOCl₂. Furthermore, addition of catalyst decreases the conductivity slightly throughout the temperature range studied.

2. Viscosity. Viscosity measurements were made employing Cannon-Zhukov capillary type viscometers calibrated with deionized water at 25°C. Measurements between -40°F and 77°F were carried out in a Conrad/Missimer environmental chamber. The temperatures were read with a Doric thermocouple temperature indicator. Viscometer flow times were measured with a Precision Scientific Timer giving readings to 0.1 second.

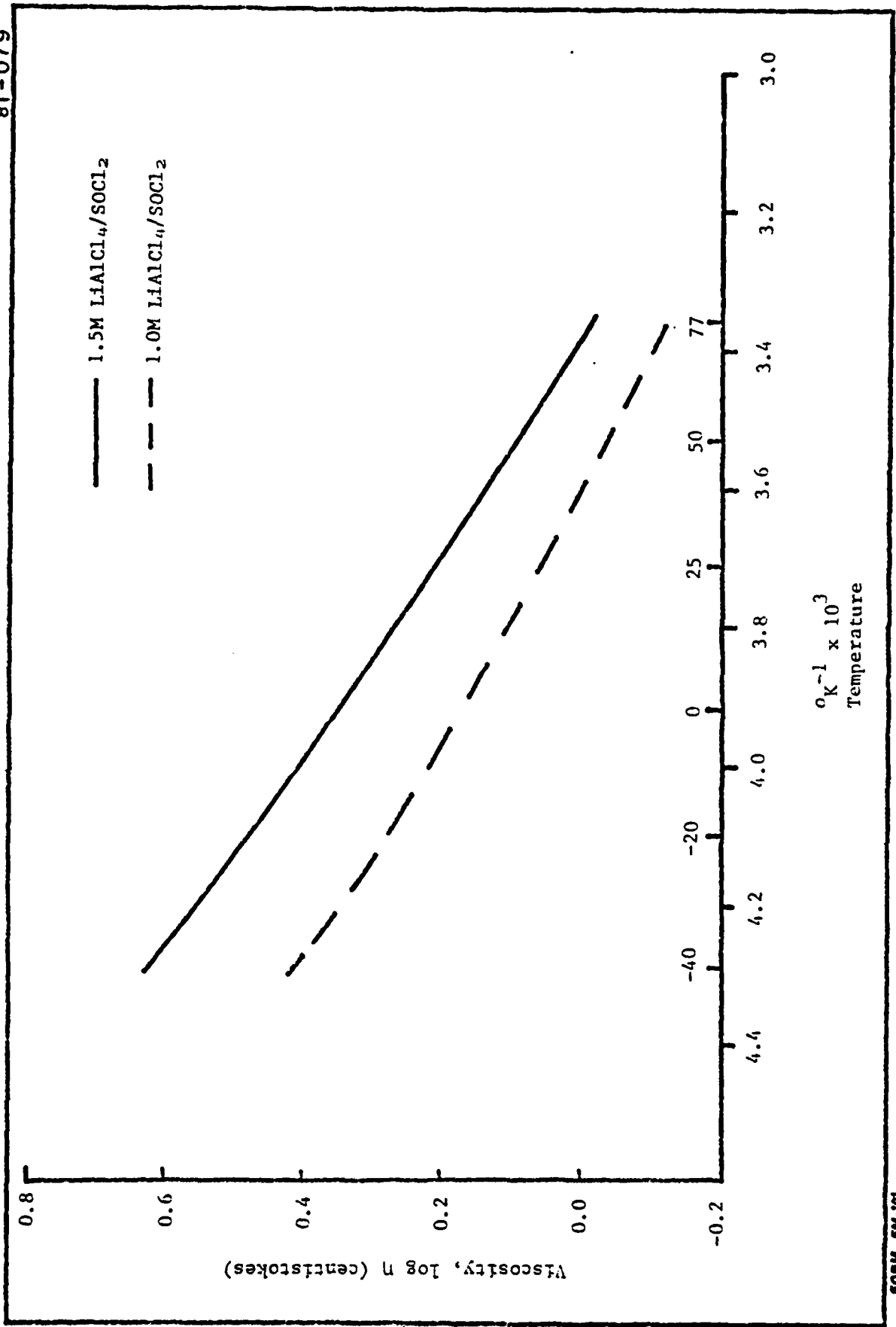
The viscosity versus temperature data are plotted in Figure 25. An Arrhenius temperature dependancy of viscosity was observed if one considers the break at low temperature due to temperature management difficulties. The increase in viscosity with decrease in temperature is much severe with 1.5M LiAlCl₄/SOCl₂ than with 1.0M LiAlCl₄/SOCl₂. Such an effect influences the conductivity as observed in Figure 24.



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Figure 24. Effect of Temperature on the Conductivity of LiAlCl₄/SOCl₂ Electrolyte

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Figure 29. Effect of Temperature on LiAlCl₄/SOCl₂ Electrolyte Viscosity

III. SUMMARY AND FUTURE WORK

Half-cell measurements and discharge characteristics of Li/SOCl₂ cells have been studied at -20, 0, 32 and 78^oF. The cells contain our best baseline cathode and cathodes doped with catalyst such as FePc and (CoPc)_n. Effect of catalyst and temperature on cyclic voltammograms have been examined. The temperature dependancy of electrolyte viscosity and conductivity were evaluated.

Initial results indicate that the physical properties of electrolyte greatly contribute to the cathode overpotential at high discharge rates and low operating temperature. Catalyst doped cathodes drastically reduce the activation polarizations. Furthermore, both SOCl₂ reduction mechanism and reaction zone thickness are modified at catalyzed cathode.

During the next quarter, further half-cell measurements and discharge performance of Li/SOCl₂ cells at -20 and -40^oF will be examined. Effect of electrode rotation on the kinetics of SOCl₂ reduction will be studied. Cathode performance improvements will be made by systematically evaluating the catalyst distribution techniques and cathode thickness and density.

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