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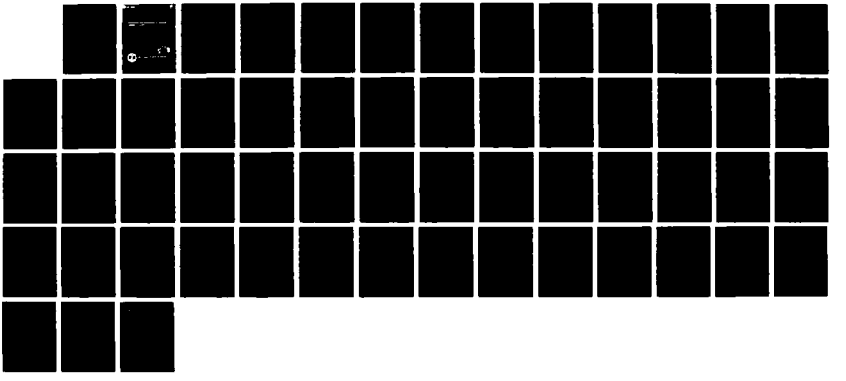

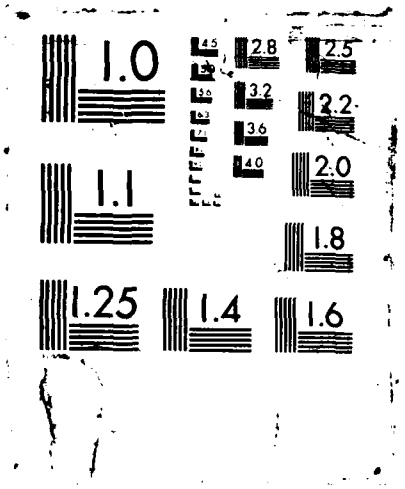
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NSWC TR 87-184

PREPARATION AND DEVELOPMENT OF ADVANCED BATTERY CATALYSTS

BY W. P. KILROY (NSWC)
K. M. ABRAHAM AND M. ALAMGIR (EIC)

RESEARCH AND TECHNOLOGY DEPARTMENT

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New catalysts which improve the discharge performance of Li/$SOCl_2$ cells have been identified. These catalysts were obtained by thermal treatment of acetylene black carbon doped with the precursors, $Co(NO_3)_2$, manganese phthalocyanine (MnPc) or vanadium phthalocyanine oxide (VOPc). The latter two materials appear to be superior to many catalysts presently available for use in Li/$SOCl_2$ cells. Compared with uncatalyzed cells, MnPc-containing cells showed a 60% increase in cell capacity and a 10% increase in cell voltage at room temperature. VOPc-containing cathodes increased the cell capacity by 50% and cell voltage by 10% under the same conditions. The use of VOPc also resulted in significant improvements in cell performance at low temperatures, e.g., at -30°C.

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FOREWORD

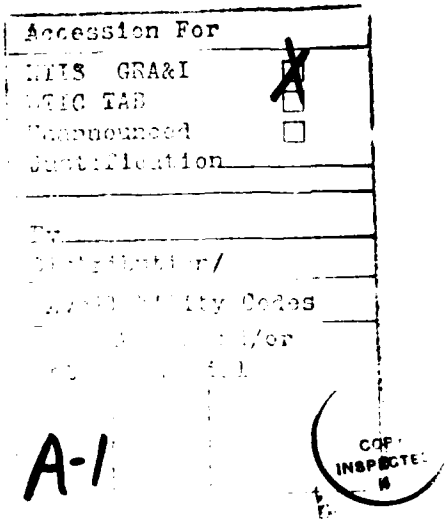
This interim report describes some initial studies to evaluate new catalytic materials to improve the performance of high energy density, active lithium batteries.

This work is part of a collaborative effort between NSWC and EIC Laboratories to understand the fundamental mechanism of electrocatalysis in Li/$SOCl_2$ cells to improve their overall safety and to increase their performance to meet operational requirements of new Navy mine batteries.

Funding for this effort was provided by the Office of Naval Technology High Energy Battery Technology Project (Mines Block), and the NSWC Navy Small Business Innovative Research Program.

Approved by:

WILLIAM T. MESSICK, Acting Head
Materials Division



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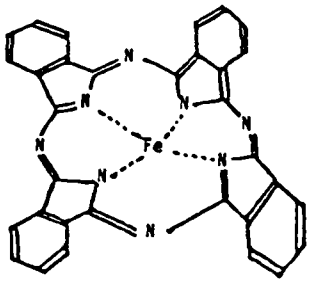
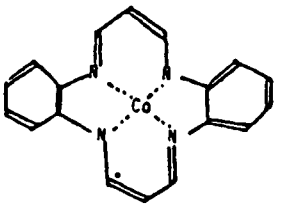
CHAPTER 1

INTRODUCTION

The search for catalysts to improve the discharge performance and safety of the $Li/SOCl_2$ cell is being actively pursued at NSWC. Data available to date[1-7] indicate that the power capabilities of the $Li/SOCl_2$ cell can be improved to varying degrees in the presence of cathode catalysts. A variety of materials, when incorporated in the carbon cathode or added to the electrolyte, have been found to increase cell discharge potentials and provide higher capacities at high rates. Some of these materials include finely divided Pt,[5] Cu powder,[6] metal phthalocyanine and related macrocyclic complexes,[1,2,4] and tetracyanoethylene and acetylacetonate complexes of Co and Fe.[7] Two of the most promising catalysts have been the Fe-phthalocyanine (FePc) complex, I,[4] and the Cobalt-dibenzotetra-azaannulene (Co-TAA) complex, II.[1,2]



I, Fe-phthalocyanine



II, Cobalt-dibenzotetraazaannulene

Despite empirical observations of improved discharge behavior and better safety characteristics of $Li/SOCl_2$ cells containing cathodes doped with catalysts, our present understanding of the mechanism of electrocatalysis in this cell is inadequate. This lack of knowledge of the mechanism is evident in the following explanations given by different researchers concerning the discharge mechanism of catalyzed $Li/SOCl_2$ cells.

- Doddapaneni[4] initially suggested that FePc changes the mechanism of the $SOCl_2$ discharge reaction and that the increased capacity was due to the reduction of SO_2 to $Li_2S_2O_4$. However, no analytical work was carried out to verify this. Additional quantitative work is required to support this claim.

- Walsh and Yaniv[2] suggested that the discharge mechanism in Co-TAA catalyzed cells is different from that in the uncatalyzed cells. They maintained that the final discharge products are LiCl, solvated Li_2O, and S, and since no SO_2 is formed according to this mechanism, the cells are safer. However, little analytical data were presented to substantiate this claim. Our studies on the discharge products from Co-TAA

catalyzed $Li/SOCl_2$ cells showed no evidence of Li_2O upon analysis by X-ray diffraction and FTIR spectroscopy.[1] The X-ray diffraction pattern of discharged cathodes showed LiCl and S. FTIR analysis of the gaseous products from discharged cells showed that SO_2 is a discharge product in Co-TAA catalyzed cells. Additional analyses are needed to quantitatively determine the discharge products and resolve these different findings.

Clearly, the present understanding of the mechanism of electrocatalysis in $Li/SOCl_2$ and related cells is poor. Because of the lack of understanding of the mechanism of catalyst-assisted discharge reactions, systematic design of catalysts for the $Li/SOCl_2$ cell cannot be accomplished without additional studies.

The eletrocatalytic activity of CoO, Co_3O_4, or Co towards the reduction of $SOCl_2$ was investigated to see if the actual catalyst species in the Co-TAA or CoPc impregnated cathodes might be one or more of these oxides, or finely divided Co. In the preparation of Co-TAA- or CoPc-catalyzed carbon cathodes, carbon black containing the complexes is heat treated at 500 to 600°C.[2,4] At these temperatures, the metal macrocyclic complexes undergo decomposition giving off volatile organic fragments.[9-11] The residues left behind have been claimed to have varying compositions. It is believed that Co-TAA decomposes in a stepwise fashion when heated. At ~400°C, Co-TAA gives off hydrogen to form what appears to be a polymeric material. At higher temperatures, e.g., ~550°C, a substantial loss of carbon and hydrogen along with some nitrogen occurs. At about 800°C there is evidence of complete decomposition of Co-TAA to give metallic cobalt as the residual product. Cobalt oxide (CoO) is also believed to be a component of the residue obtained from the decomposition of Co-TAA. The latter apparently is formed by the reaction of the initially-formed, finely-divided Co with oxygen.

Knowledge of the actual composition of the catalyst is important. Oxides are less expensive and easier to prepare than macrocyclic complexes. Certain limitations of the present transition metal complex catalysts, such as their instability in $SOCl_2/LiAlCl_4$ or poor high temperature storability of cells, may be overcome with improvements brought about by the knowledge of the actual composition of the catalyst species. It is believed that some of these limitations arise from reactions associated with the organic moiety in the complex. Therefore, eliminating the organic moiety from the catalyst center may result in overall improvements in cell performance.

CHAPTER 2

EXPERIMENTAL

Our scheme for preparing catalyzed carbon cathodes involved treatment of acetylene black carbon with appropriate precursors followed by heat treatment at various temperatures. The chemical reactions that were used to deposit cobalt oxides and finely divided Co in the carbon are depicted in equations (1-4).

$$CoCO_3 \xrightarrow{500°C} CoO + CO_2 \quad (1)$$

$$3Co(NO_3)_2 \xrightarrow{400°C} Co_3O_4 + 6NO_2 + O_2 \quad (2)$$

$$Co_2(CO)_8 \xrightarrow{\sim 200°C} 2Co + 8CO \quad (3)$$

$$Co_4(CO)_{12} \xrightarrow{200°C} 4Co + 12CO \quad (4)$$

Three transition metal phthalocyanine complexes have also been evaluated. These are cobalt phthalocyanine (CoPc), manganese phthalocyanine (MnPc), and vanadium phthalocyanine oxide (VOPc). All these metal complexes are commercially available and their synthesis is rather straightforward. In addition, we have attempted to prepare Co-TAA by simpler synthetic routes and evaluate its catalytic performance.[12]

The precursors used for preparing cobalt oxide-catalyzed cathodes were $Co(NO_3)_2$ and $CoCO_3$. Acetylene black carbon was first doped with the precursors and then sintered at various temperatures prior to fabricating the electrodes. $Co(NO_3)_2$ was incorporated into the carbon in an aqueous medium. Solutions in water containing required amounts (5, 10, and 20 w/o) of $Co(NO_3)_2$ were mixed well with carbon, dried at 100°C and the mixture was heat treated at 400 or 900°C under flowing argon.

In order to incorporate $CoCO_3$, a slurry of $CoCO_3$ in ethanol/H_2O was mixed with carbon, dried at 100°C and then sintered, in argon, at 500 or 900°C.[13]

Teflon-bonded carbon electrodes were made with doped cathodes. The Li/$SOCl_2$ laboratory cells used for these studies consisted of a cathode sandwiched between two Li anodes (15 mil thick) pressed onto Ni screens. The cells were filled with 4.0 ml, 1.8M $LiAlCl_4/SOCl_2$ electrolyte solution and were truly carbon-limited. A Li strip was also incorporated into the cell as a reference electrode. Typically, the cathodes were 3.5 cm x 3.0 cm x 0.10 cm, and the geometric surface area was 21 cm^2. The cells were discharged galvanostatically.

CHAPTER 3

RESULTS AND DISCUSSION

Discharge results obtained with $Co(NO_3)_2$ catalyzed cells are summarized in Table 1. The capacity in an uncatalyzed cell, hereafter referred to as baseline cell, at 10 mA/cm^2 at room temperature corresponded to a carbon utilization of 1.36 Ah/g. Figures 1 through 14 illustrate discharge behavior of the doped cells compared to a baseline cell whereas Tables 1 through 6 show the capacity normalized (Ah/g carbon) to account for the varying masses of carbon used in each cell. Cathodes containing 5% $Co(NO_3)_2$, sintered at 400°C, and those first dipped in a $Co(NO_3)_2$ solution followed by a heat treatment at 130°C show evidence of catalytic activity. In Cell No. 1, containing 5 percent $Co(NO_3)_2$-doped cathode, the carbon utilization was 1.59 Ah/g or a 17 percent improvement over the uncatalyzed cell. It appears that the catalytic activity is extremely sensitive to the thermal treatment of the carbon. Figures 1 and 2 compare the behavior of the $Co(NO_3)_2$ doped cells with the baseline cathodes. The $Co(NO_3)_2$-doped cathodes, whether sintered at 400 or 900°C, showed no catalytic activity at -30°C as illustrated in Figure 3. A close examination of the data for Cells 3 and 4 in Table 1 shows that the apparent lack of catalytic activity in cathodes doped with 10 percent and 20 percent $Co(NO_3)_2$ may be due to a decrease in th. total available $SOCl_2$ at the electrode active sites, because the excess catalyst begins to occupy significant fractions of pore volume. The mass-transport in the cathode is impeded as cha..els are blocked. The observed capacities of Cells 3 and 4 agree with this explanation because the capacity of Cell 3 is ~85 percent and that of Cell 4 is ~77 percent of the capacity of Cell 1. The decrease in capacity in each cell corresponds approximately to the amount of catalyst added beyond 5 percent.

The behavior of the carbon electrodes that were dipped in $Co(NO_3)_2$ solution followed by dr;ing at 130°C is illustrated in Figure 4. These electrodes exhibit higher voltages than the electrodes sintered at 400°C, and their capacities are similar to those sintered at 900°C.

A comparison of the behavior of $Co(NO_3)_2$-containing electrodes heat treated at 400 and 130°C, presented in Figures 1 and 4, suggest that in the latter case the active species probably is $Co(NO_3)_2$ itself while in the former case it is an oxide, probably Co_3O_4. Although the capacity of the cathode is increased as a result of Co_3O_4 doping, the cell discharge potential remains the same as that in the baseline case. When $Co(NO_3)_2$ itself is the active catalyst species, the cell discharge voltage is slightly enhanced while the capacity of the cathode shows a decline.

Further studies of these electrodes, especially with respect to optimization of the amount of $Co(NO_3)_2$ and the sintering temperature, are warranted because of the promising results from $Co(NO_3)_2$ doping. This will be carried out in future studies.

TABLE 1. DISCHARGE RESULTS FOR $Li/SOCl_2$ CELLS CONTAINING $Co(NO_3)_2$-DOPED CATHODES
[DISCHARGE CURRENT IS 210 mA (10 mA/cm^2)]

Cell No.	Weight Percent of $Co(NO_3)_2$	Carbon Sintering Temperature, °C	Discharge Temperature, °C	Mid-Discharge Voltage, V	Capacity** mAh	Capacity** Ah/g
1	5	400	20	3.04	686	1.59
2	5	400	-30	2.35	406	0.97
3	10	400	20	2.99	406	1.35
4	20	400	20	2.98	470	1.23
5	20	400	-30	2.18	343	0.93
6	5	900	20	3.08	500	1.16
7	5	900	20	3.10	562	1.22
8	5	900	20	3.10	504	1.16
9	10	900	20	3.09	420	0.95
10	*	130*	20	3.13	349	0.90
11	*	130*	-30	2.35	309	0.77

*Finished cathodes dipped in 7% solution followed by drying at 130°C.
**Capacity in cells without catalyst = 1.36 Ah/g.

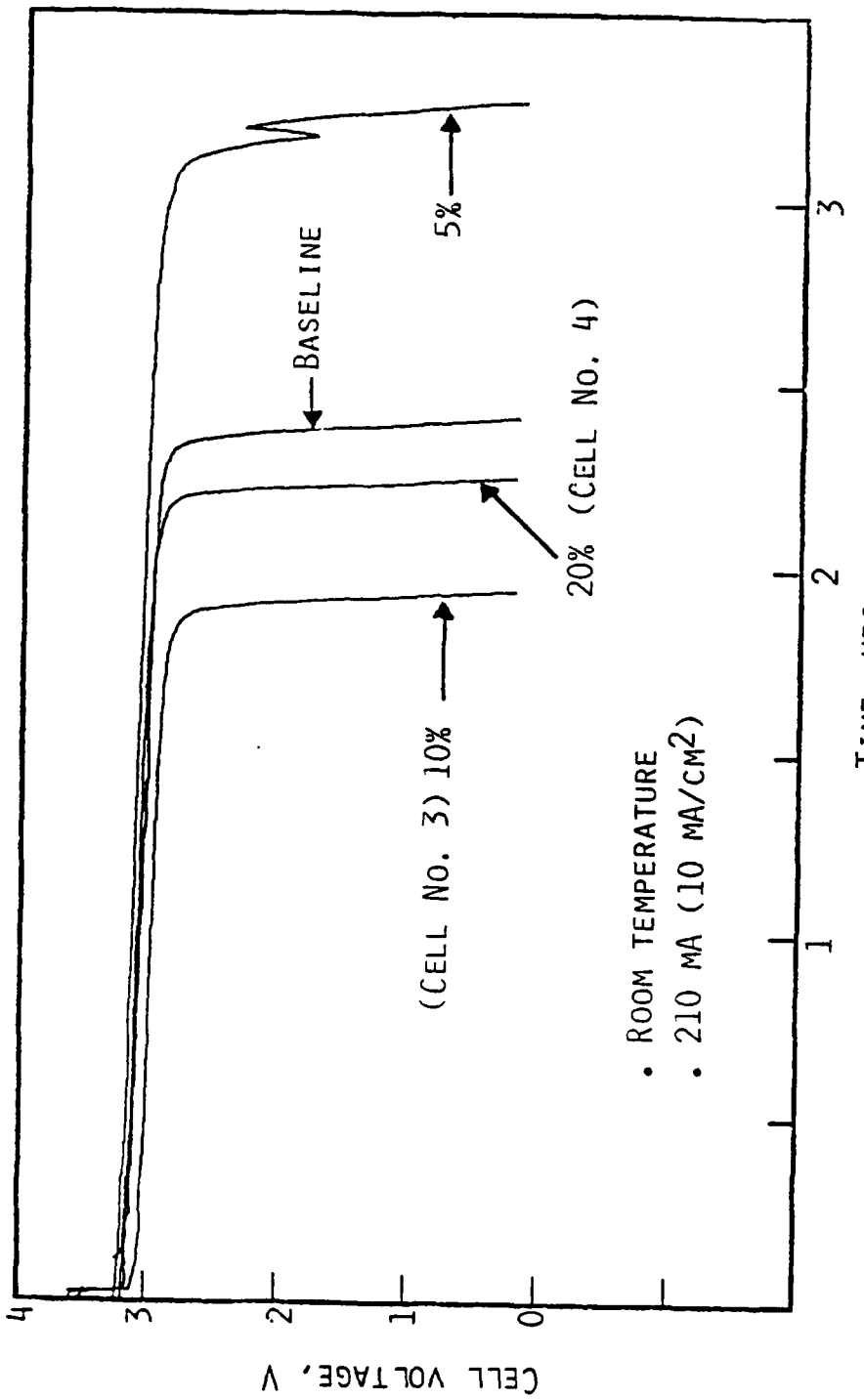


FIGURE 1. DISCHARGE PLOTS OF LABORATORY $Li/SOCl_2$ CELLS CONTAINING $Co(NO_3)_2$-DOPED CATHODES, HEAT-TREATED AT 400°C, AND BASELINE CATHODE

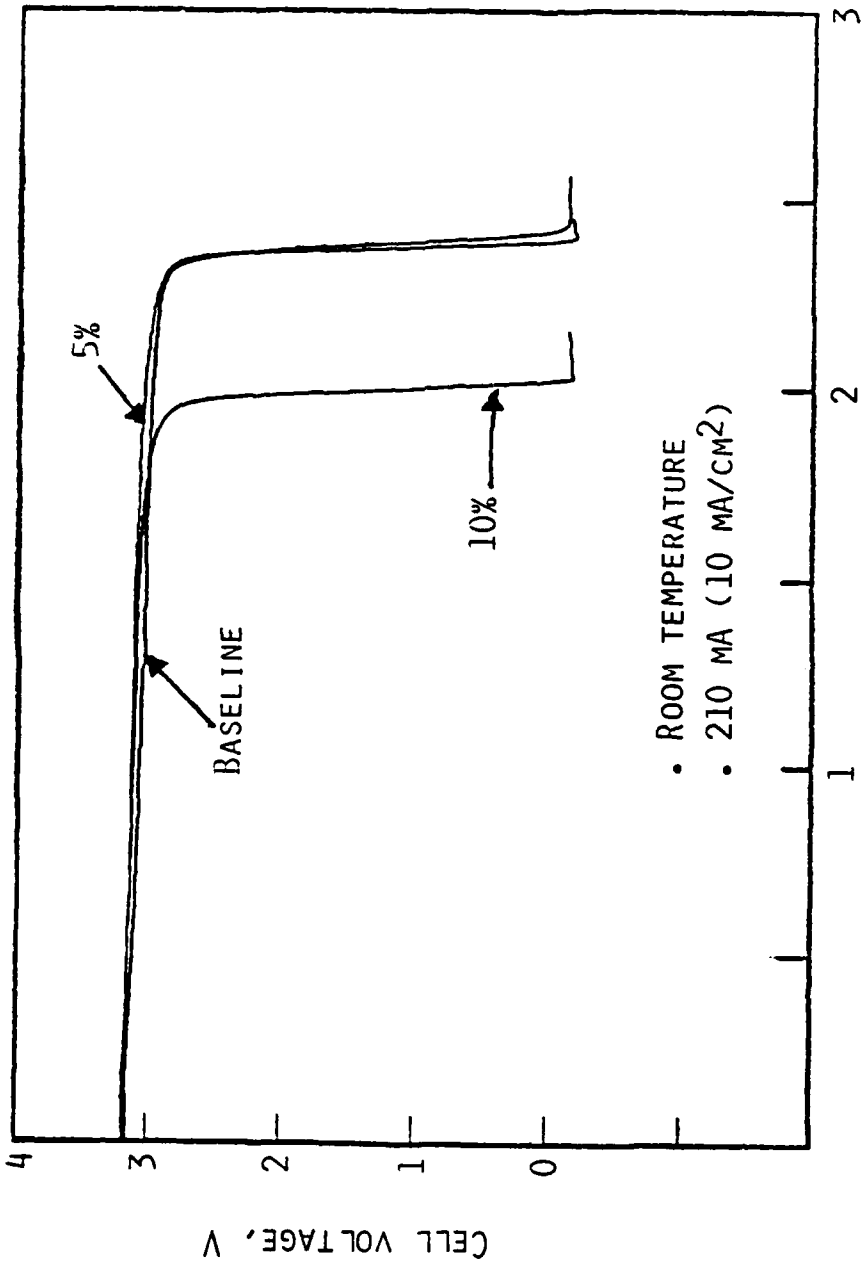


FIGURE 2. DISCHARGE PLOTS OF LABORATORY $Li/SOCl_2$ CELLS CONTAINING $Co(NO_3)_2$-DOPED CATHODES, HEAT-TREATED AT 900°C, AND BASELINE CATHODE

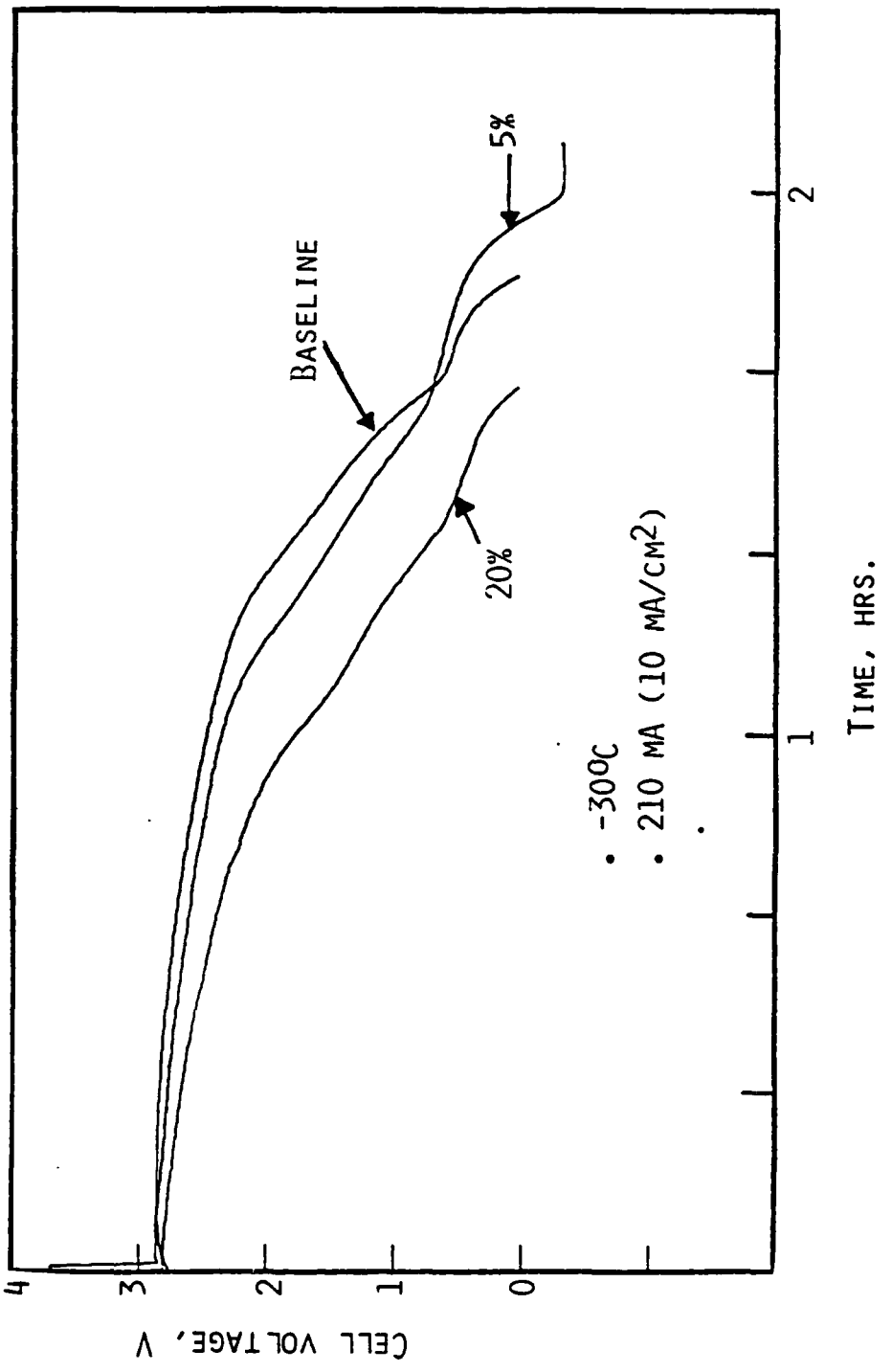


FIGURE 3. DISCHARGE PLOTS OF LABORATORY $Li/SOCl_2$ CELLS CONTAINING $Co(NO_3)_2$-DOPED CATHODES, HEAT-TREATED AT 400°C, AND BASELINE CATHODE

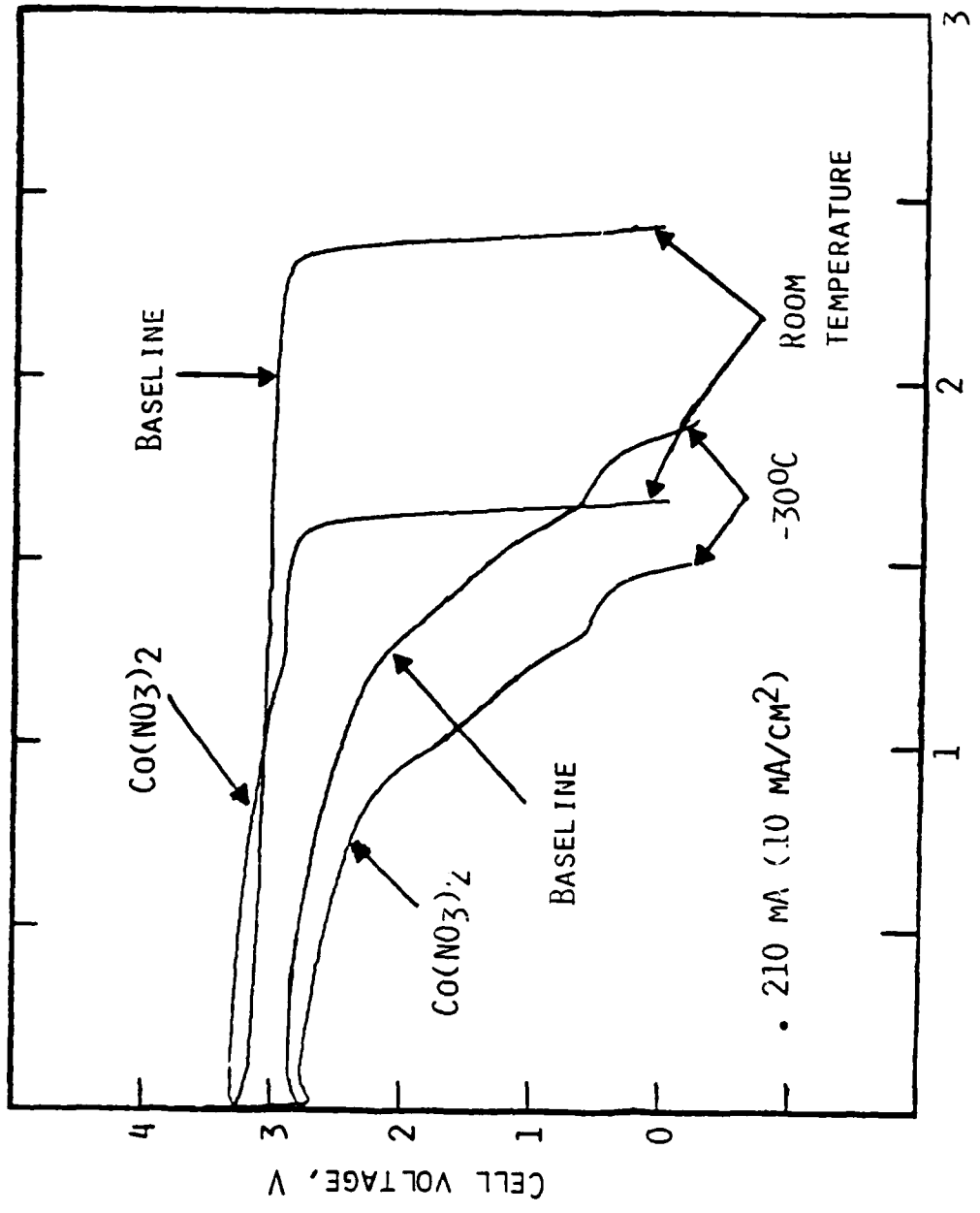


FIGURE 4. DISCHARGE PLOTS OF LABORATORY Li/$SOCl_2$ CELLS CONTAINING CATHODES DIPPED IN 7% $Co(NO_3)_2$ SOLUTION AND DRIED AT 130°C, AND BASELINE CATHODE

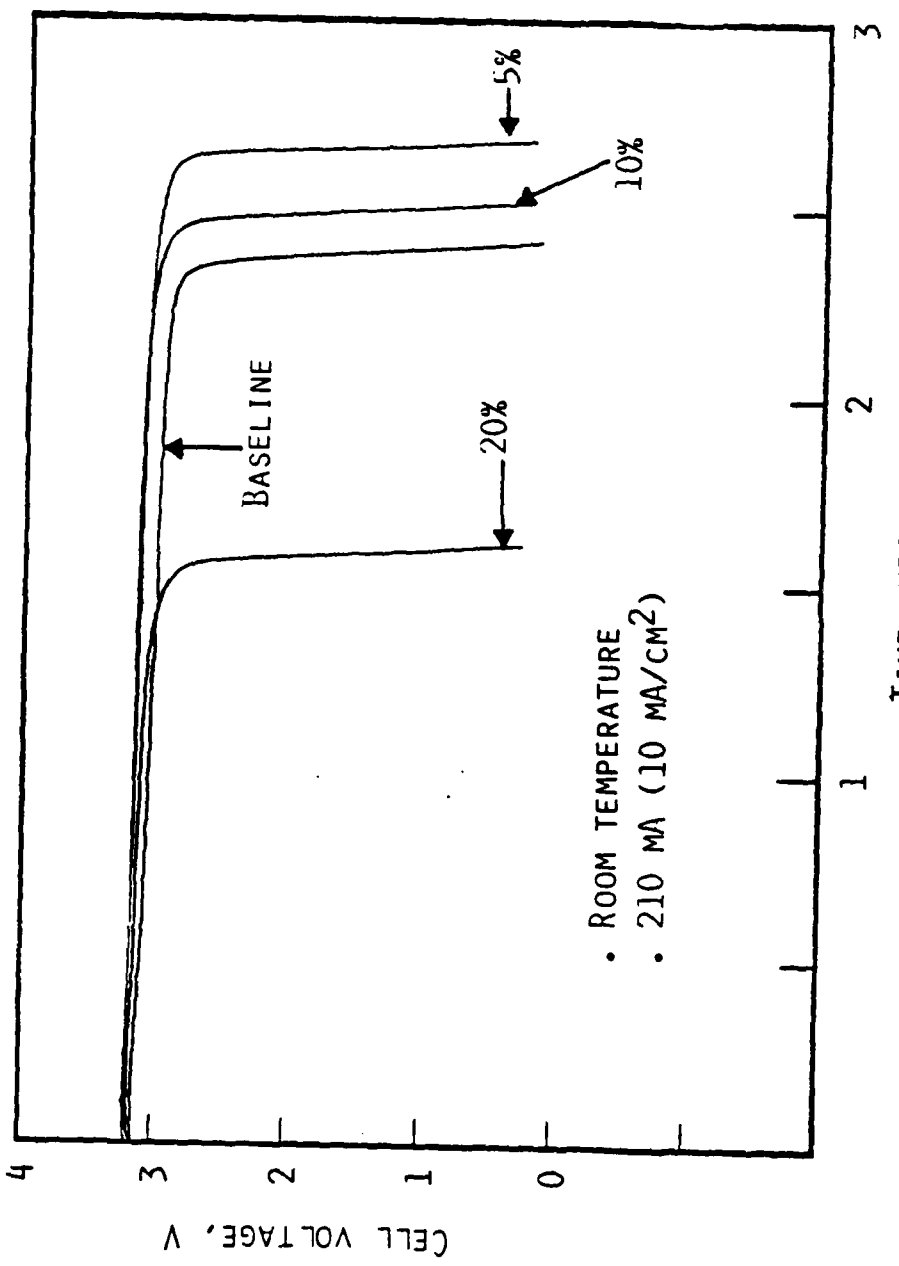


FIGURE 5. DISCHARGE PLOTS OF LABORATORY $Li/SOCl_2$ CELLS CONTAINING $CoCO_3$-DOPED CATHODES, HEAT-TREATED AT 900°C, AND BASELINE CATHODE

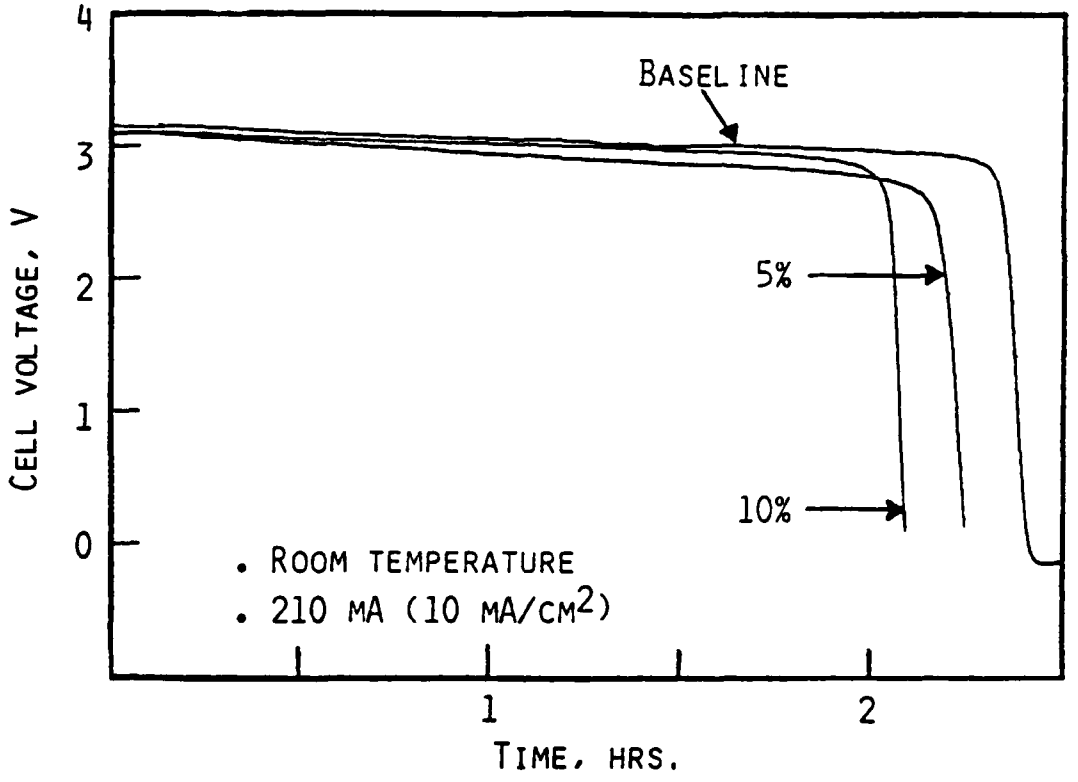


FIGURE 6. DISCHARGE PLOTS OF LABORATORY $Li/SOCl_2$ CELLS CONTAINING $CoCO_3$-DOPED CATHODES, HEAT-TREATED AT 500°C, AND BASELINE CATHODE

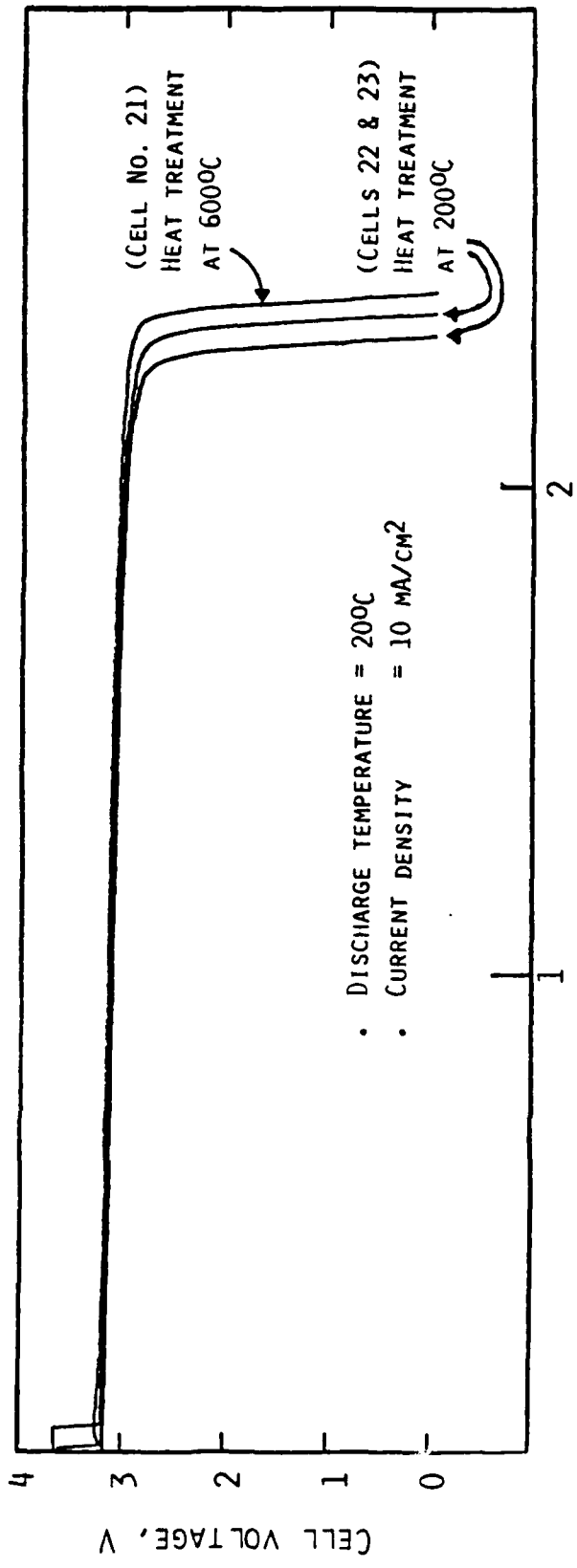


FIGURE 7. DISCHARGE PLOTS OF LABORATORY $Li/SOCl_2$ CELLS CONTAINING 5 w/o $Co_2(CO)_8$ AS A CATHODE DOPANT WITH DIFFERENT HEAT TREATMENTS

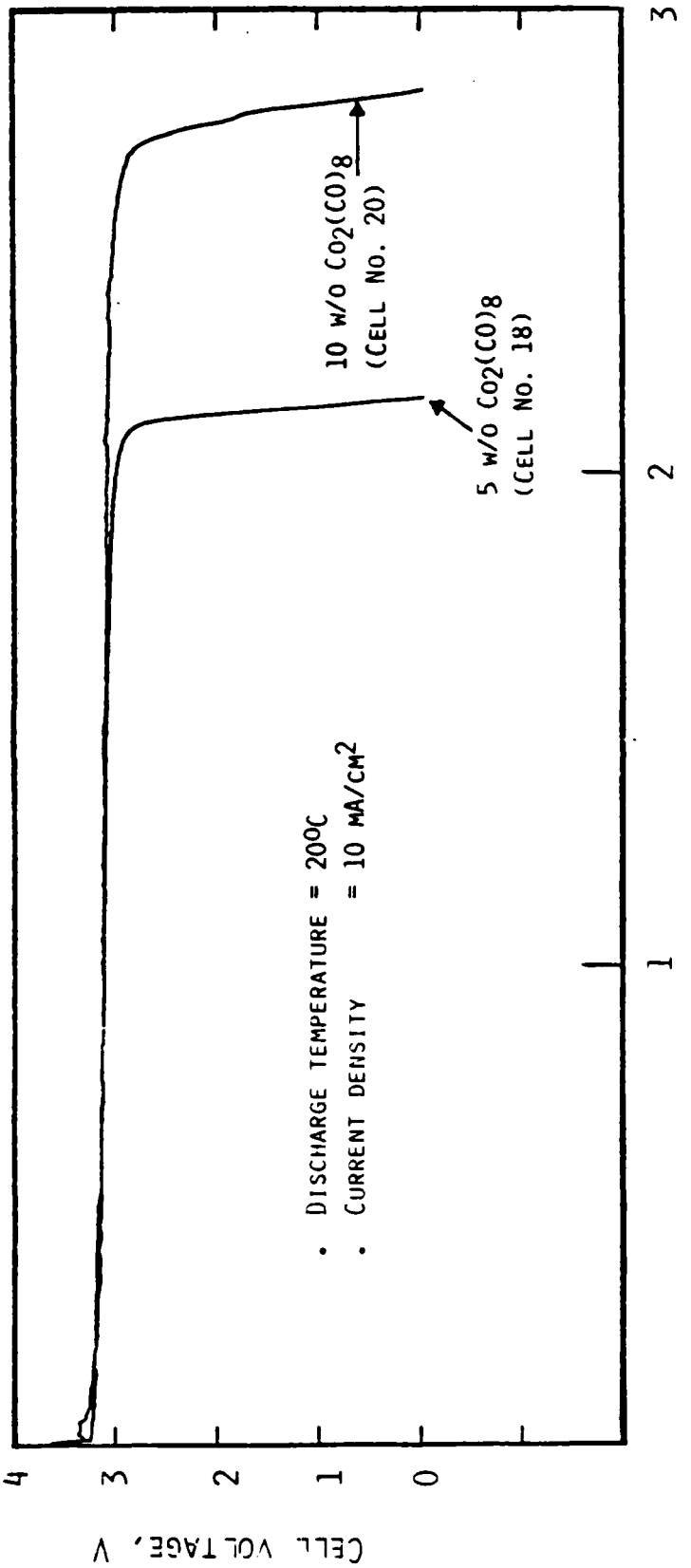


FIGURE 8. DISCHARGE PLOTS OF LABORATORY Li/$SOCl_2$ CELLS CONTAINING $Co_2(CO)_8$, SINTERED AT 300°C, AS CATHODE DOPANT

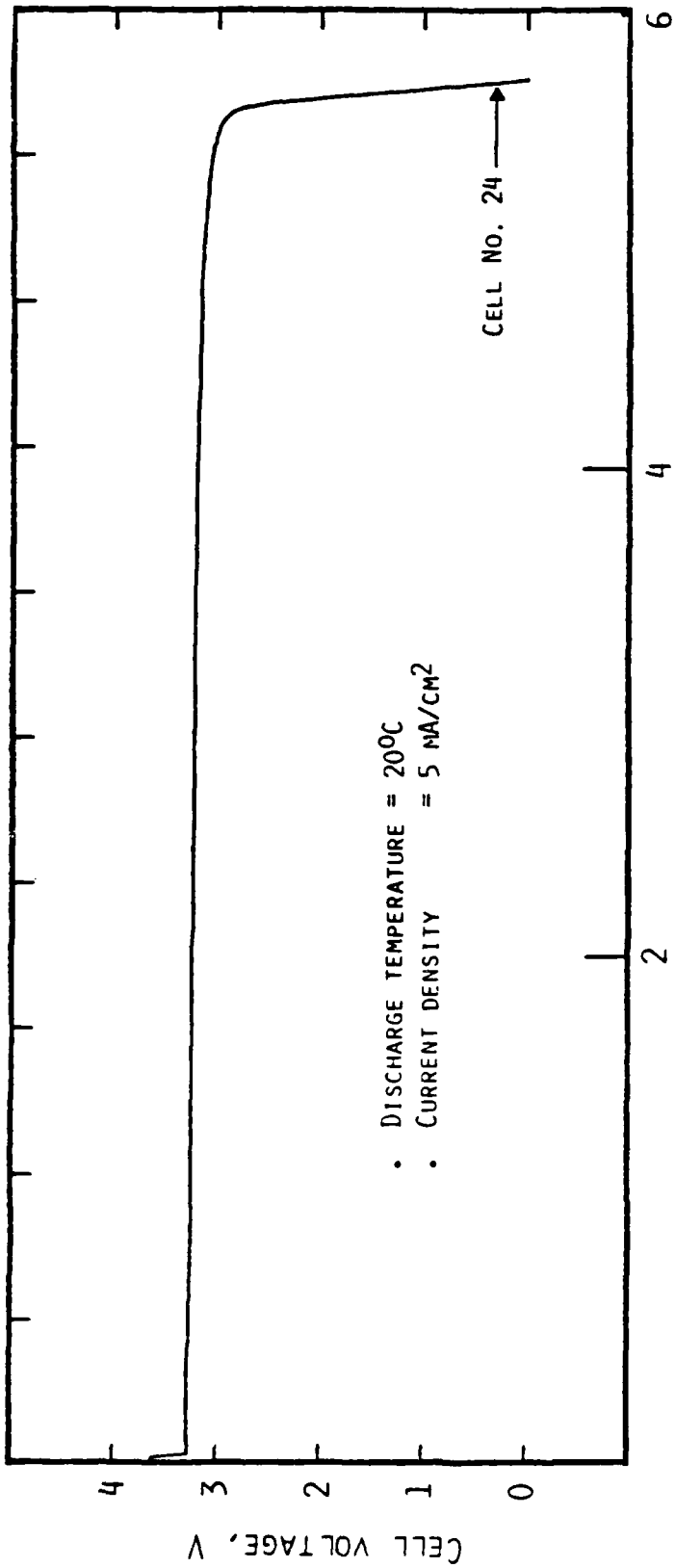


FIGURE 9. DISCHARGE PLOT OF A LABORATORY Li/$SOCl_2$ CELL CONTAINING 5 w/o $Co_2(CO)_8$, SINTERED AT 200°C, AS CATHODE DOPANT

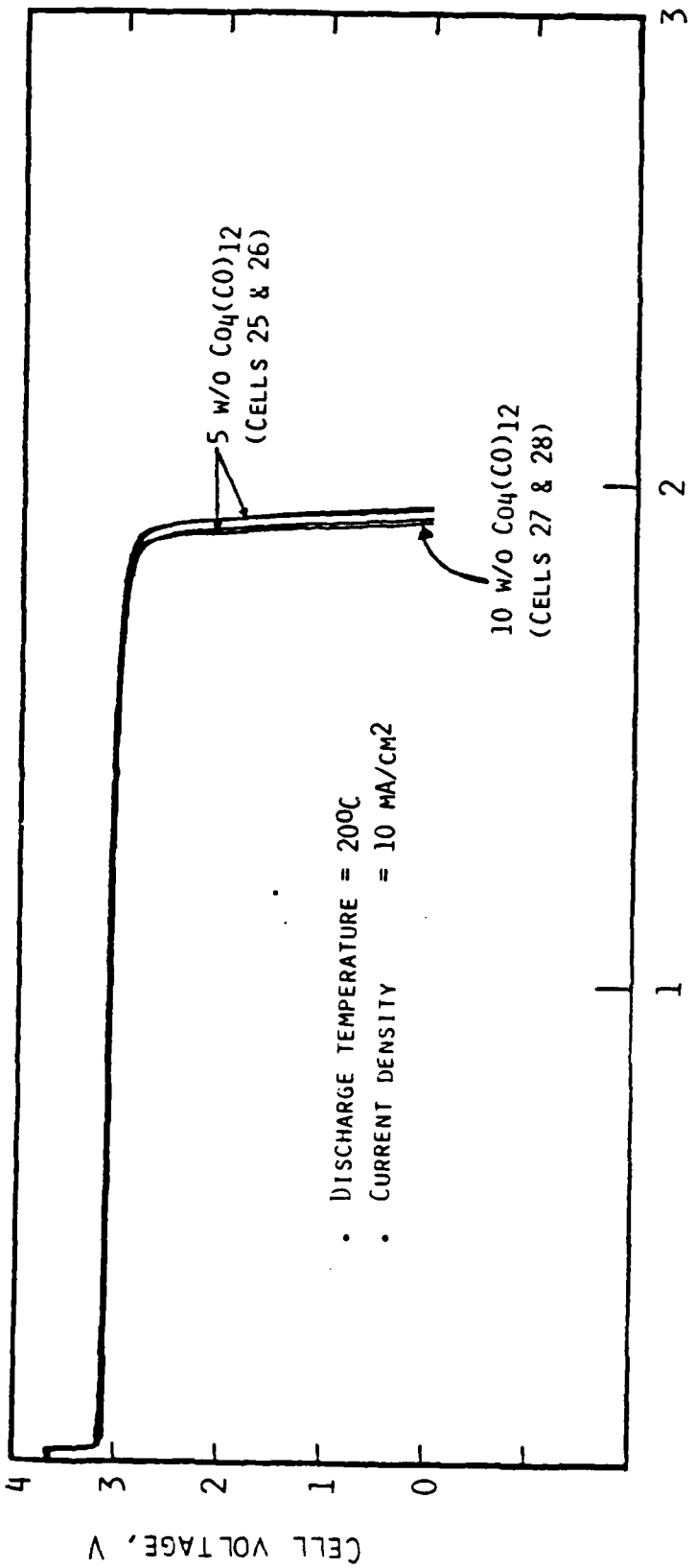


FIGURE 10. DISCHARGE PLOTS OF LABORATORY $Li/SOCl_2$ CELLS CONTAINING $Co_4(CO)_{12}$, SINTERED AT 200°C, AS CATHODE DOPANT

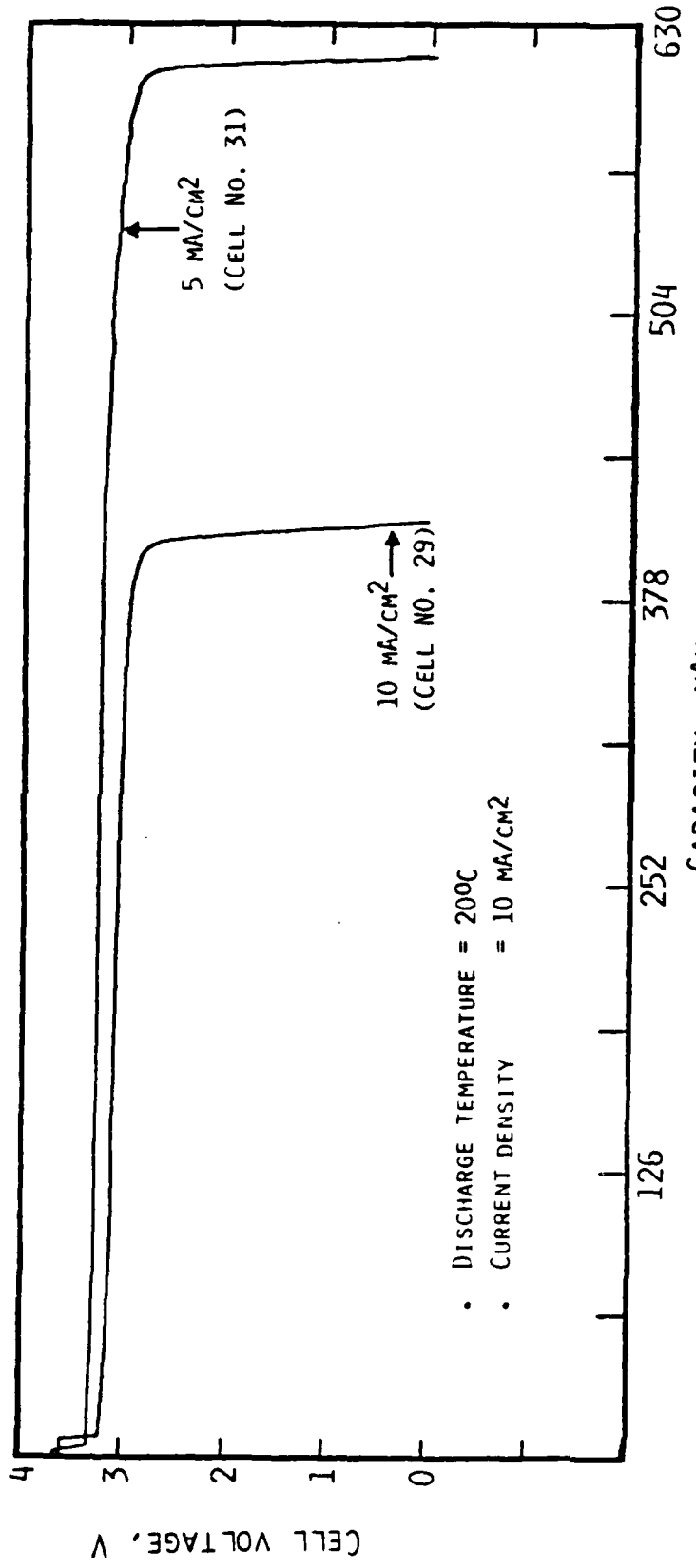


FIGURE 11. DISCHARGE PLOTS OF LABORATORY $Li/SOCl_2$ CELLS CONTAINING 5 w/o $Co_4(CO)_{12}$, SINTERED AT 600°C, AS CATHODE DOPANT AT DIFFERENT CURRENT DENSITIES

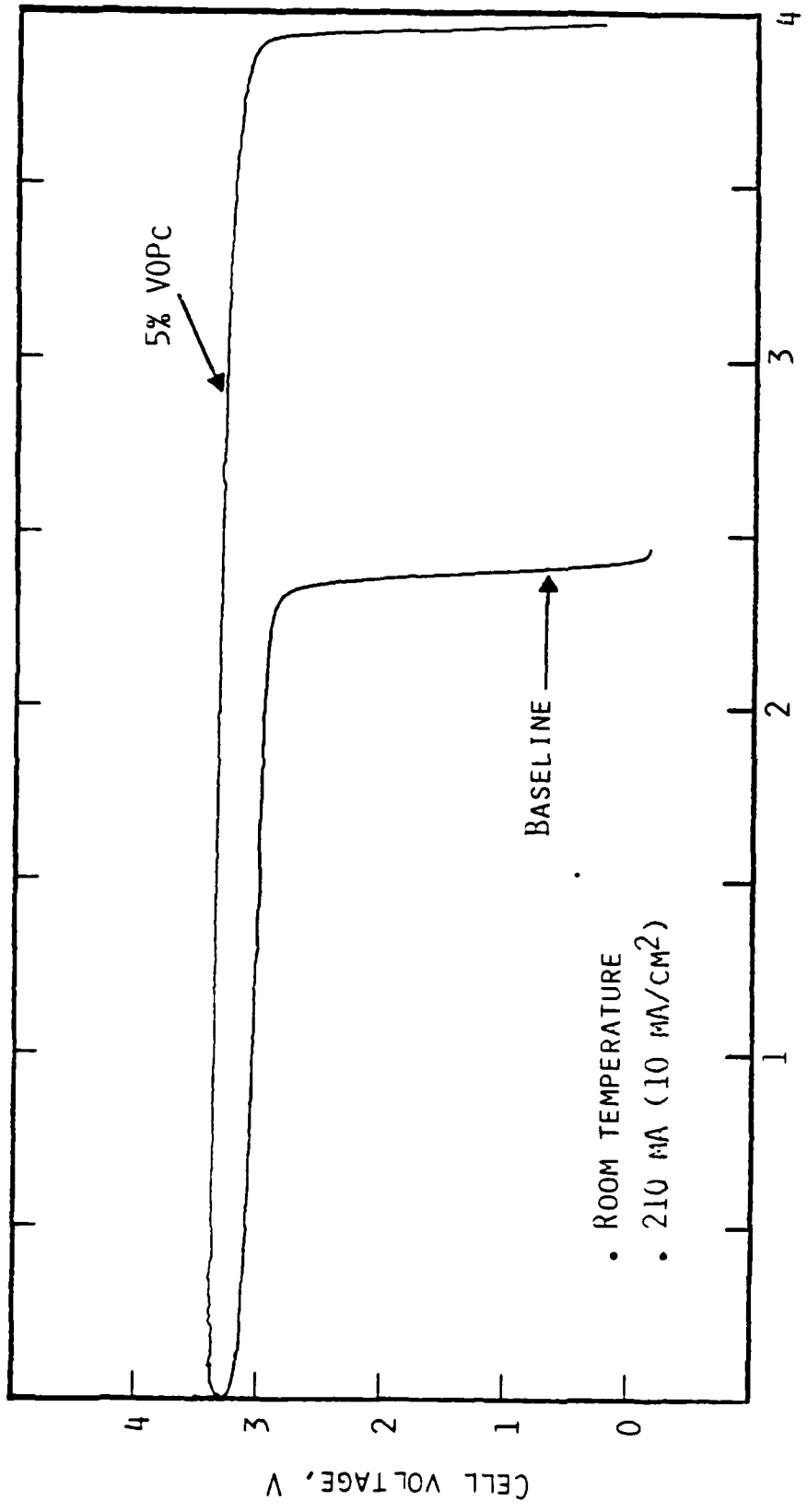


FIGURE 12. DISCHARGE PLOT OF LABORATORY Li/$SOCl_2$ CELLS CONTAINING 5% VOPc-DOPED, AND BASELINE CATHODES

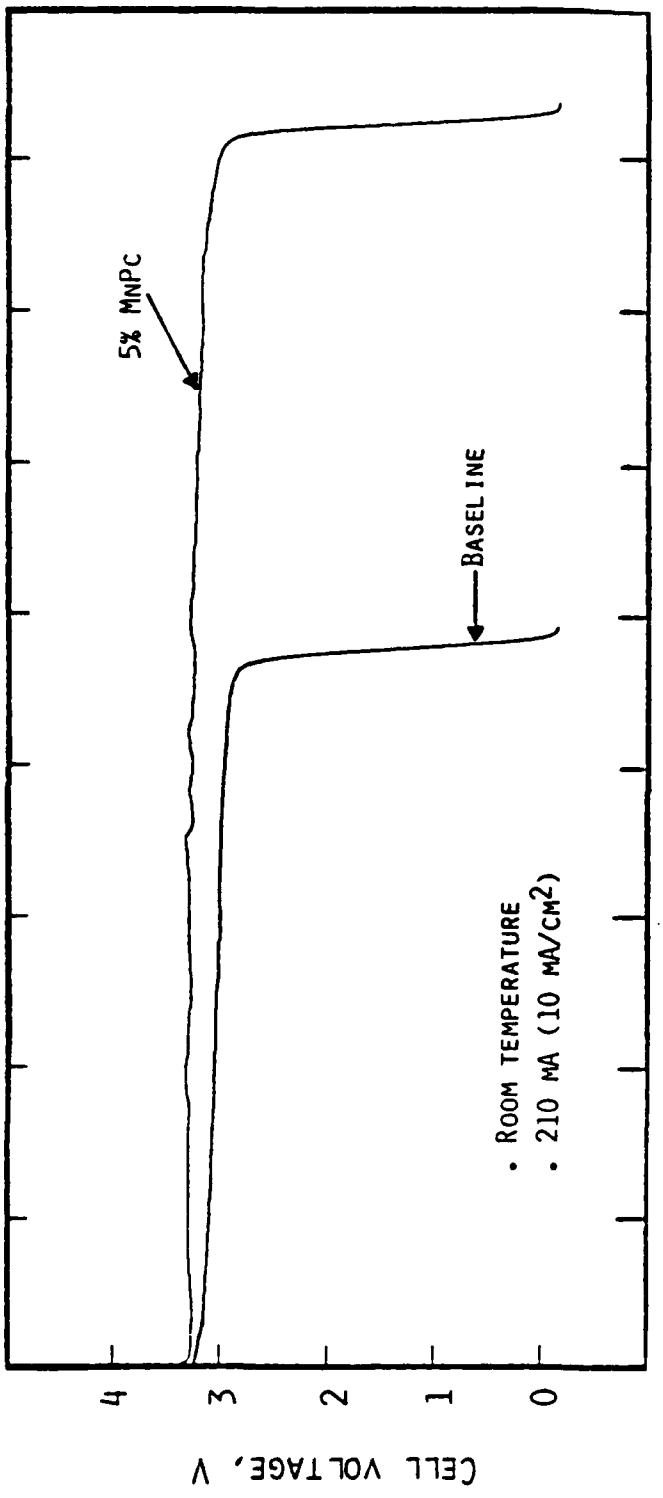


FIGURE 13. DISCHARGE PLOTS OF LABORATORY Li/$SOCl_2$ CELLS CONTAINING 5% MnPc-DOPED, AND BASELINE CATHODES

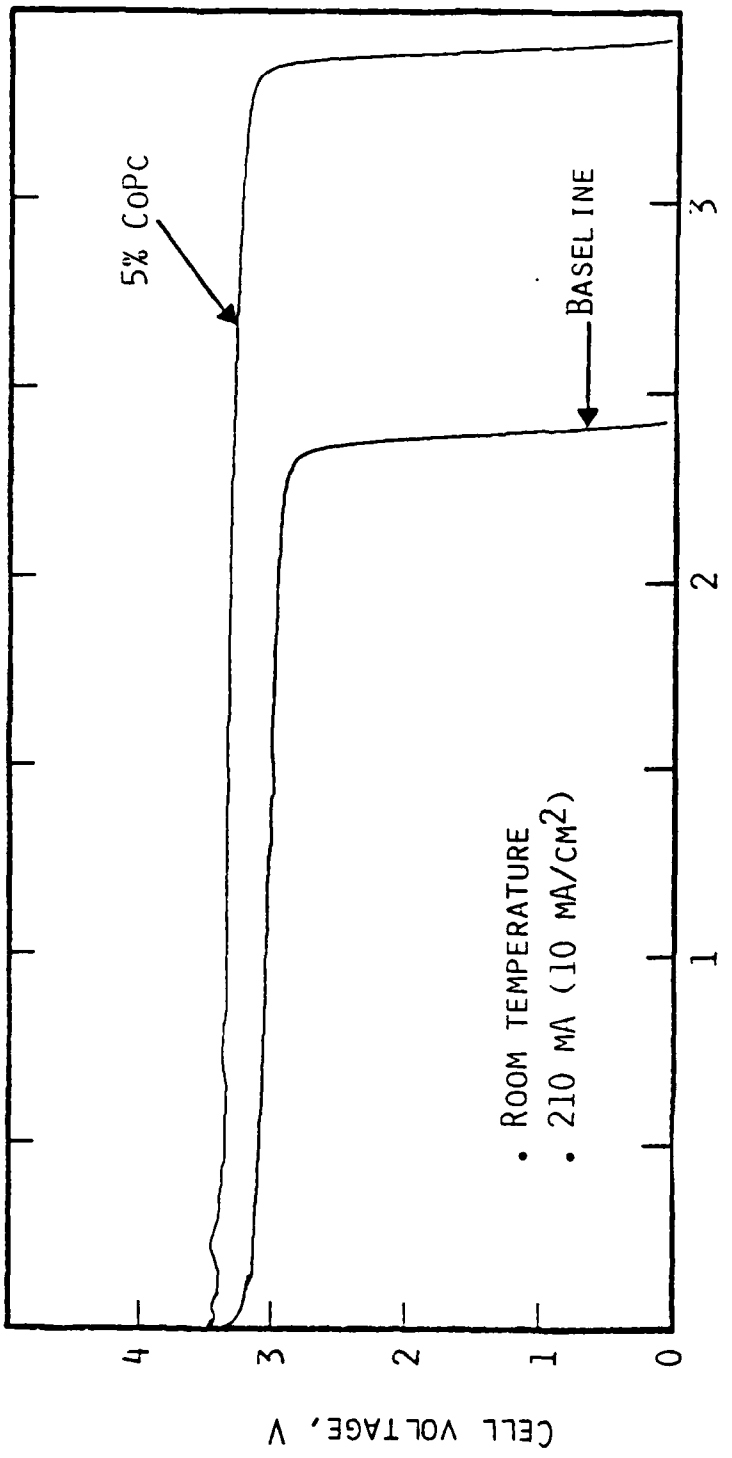


FIGURE 14. DISCHARGE PLOTS OF LABORATORY Li/$SOCl_2$ CELLS CONTAINING 5% CoPc-DOPED, AND BASELINE CATHODES

TABLE 2. DISCHARGE RESULTS FOR Li/$SOCl_2$ CELLS CONTAINING $CoCO_3$-DOPED CATHODES
[CURRENT = 210 mA (10 mA/cm^2)]

Cell No.	Weight Percent of $CoCO_3$	Carbon Sintering Temperature, °C	Discharge Temperature, °C	Mid-Discharge Voltage, V	Capacity* mAh	Capacity* Ah/g
12	5	500	20	2.91	475	1.25
13	10	500	20	3.01	439	0.98
14	5	900	20	3.12	561	1.37
15	10	900	20	3.15	526	1.28
16	10	900	-30	2.6	274	0.62
17	20	900	20	3.11	340	0.81

*Capacity in cells without catalyst = 1.36 Ah/g at 20°C.

TABLE 3. DISCHARGE RESULTS FOR $Li/SOCl_2$ CELLS CONTAINING $Co_2(CO)_8$-DOPED CATHODES
[CURRENT = 210 mA (10 mA/cm^2) EXCEPT WHERE NOTED]

Cell No.	Weight Percent of $Co_2(CO)_8$	Carbon Sintering Temperature, °C	Discharge Temperature, °C	Mid-Discharge Voltage, V	Capacity*	
					mAh	Ah/g
18	5	300	20	3.10	460	1.24
19	10	300	20	3.05	358	0.83
20	10	300	20	3.1	594	1.09
21	5	600	20	3.12	506	1.12
22	5	200	20	3.10	498	1.23
23	5	200	20	3.09	489	1.34
24	5**	200	20	3.24	599	1.39

*Capacity in cells without catalysts = 1.36 Ah/g.
**Discharge current was 105 mA (5 mA/cm^2).

TABLE 4. DISCHARGE RESULTS FOR $Li/SOCl_2$ CELLS CONTAINING $Co_4(CO)_{12}$-DOPED CATHODES
[CURRENT = 210 mA (10 mA/cm^2) EXCEPT WHERE NOTED]

Cell No.	Weight Percent of $Co_4(CO)_{12}$	Carbon Sintering Temperature, °C	Discharge Temperature, °C	Mid-Discharge Voltage, V	Capacity*	
					mAh	Ah/g
25	5	200	20	3.11	410	1.20
26	5	200	20	3.05	413	1.14
27	10	200	20	3.10	415	1.08
28	10	200	20	3.11	408	1.06
29	5	600	20	3.10	410	0.93
30	10	600	20	3.10	473	0.66
31	5**	600	20	3.26	613	1.40

*Capacity in cells without catalysts = 1.36 Ah/g.
**Discharge current was 105 mA (5 mA/cm^2).

TABLE 5. DISCHARGE RESULTS FOR Li/$SOCl_2$ CELLS CONTAINING TRANSITION METAL COMPLEX-DOPED CATHODES DISCHARGED AT ROOM TEMPERATURE

Cell No.	Complex	Weight Percent of Complex	Carbon Sintering Temperature, °C	Discharge Temperature, °C	Mid-Discharge Voltage, V	Capacity*	
						mAh	Ah/g
32	VOPc	5	600	20	3.34	830	1.98
33	VOPc	10	600	20	3.26	969	1.94
34	MnPc	5	600	20	3.29	866	2.21
35	MnPc	10	600	20	3.09	599	1.43
36	CoPc	5	600	20	3.32	718	1.94

*Capacity in cells without catalyst = 1.36 Ah/g.

TABLE 6. DISCHARGE RESULTS OF $Li/SOCl_2$ CELLS CONTAINING (5%) TRANSITION METAL COMPLEX-DOPED CATHODES AT -30°C AT 10 mA/cm^2

Cell No.	Complex	Mid-Discharge Voltage, V	Capacity, Ah/g (2.0V)	(0.0V)
37	VOPc	2.74	0.91	0.97
38	CoPc	2.81	0.51	0.57
39	MnPc	2.71	0.58	0.64
	Baseline cathode without catalyst	2.60	0.70	1.0

The discharge results obtained by using $CoCO_3$ as the catalyst precursors are summarized in Table 2. Relevant discharge curves are presented in Figures 5 and 6. The discharge capacities are similar to or less than that obtained in the baseline cell. $CoCO_3$ doping seems to decrease the capacity of the baseline electrode in proportion to the amount of the added dopant. X-ray analysis of $CoCO_3$-doped carbon after heat treatment showed the presence of cobalt carbides and Co_3O_4 (discussed later). It appears that cobalt carbides have little or no catalytic activity on the reduction of $SOCl_2$.

DISCHARGE BEHAVIOR OF Li/$SOCl_2$ CELLS USING CATHODES DOPED WITH COBALT CARBONYLS

As mentioned earlier, the reasoning behind the use of cobalt carbonyls as catalyst precursors has been the incorporation of finely divided metallic cobalt in the carbon cathode.[14] It is possible that such electrodes may also contain cobalt carbides or oxides, the former being formed during heat treatment of the carbonyl and the latter during reactions following the heat treatment with atmospheric oxygen.

Discharge data for cells using cobalt carbonyl-doped cathodes, heat treated at various temperatures, are summarized in Tables 3 and 4. $Co_2(CO)_8$ was deposited on the carbon from a THF solution and $Co_4(CO)_{12}$ from a diethyl ether medium. After the carbon was mixed with the respective solutions, the solvent was removed by pumping under a vacuum. The carbon deposited with the cobalt carbonyl was heat treated in Ar at the various temperatures indicated in Tables 3 and 4. Typical discharge curves obtained with these carbon electrodes are given in Figures 7 through 11. Carbon utilization data are presented in Tables 3 and 4. Neither the $Co_2(CO)_8$-doped nor the $Co_4(CO)_{12}$-doped electrodes showed any evidence for catalytic activity.

DISCHARGE BEHAVIOR OF Li/$SOCl_2$ CELLS CONTAINING TRANSITION METAL COMPLEX-CATALYZED CATHODES

Transition metal complexes that have so far shown the highest activity in Li/$SOCl_2$ cells are the phthalocyanine (Pc) complexes of Co and Fe, and Co-TAA. FePc was found to be soluble in $SOCl_2/LiAlCl_4$ and, therefore, its use is limited to reserve cells. The cobalt and iron phthalocyanines have apparently been chosen previously for use as catalysts in Li/$SOCl_2$ cells because of their ability to catalyze the reduction of oxygen in fuel cells. Based on that criterion MnPc and VOPc should not function as active catalysts for $SOCl_2$ reduction, since they do not catalyze the reduction of oxygen well. Thus the use of MnPc and VOPc provided a test for the selection criteria of catalysts for use in the Li/$SOCl_2$ cell on the basis of their catalytic activity in fuel cells.

The phthalocyanines were dissolved in concentrated H_2SO_4. Acetylene black carbon was mixed intimately with this solution and later washed with distilled water until the pH of the washings became neutral. The mixture was heat treated at 600°C under flowing Ar. Cathodes were fabricated in the usual way by mixing with Teflon binder followed by drying and sintering at 300°C in Ar atmosphere. The discharge results obtained at 10 mA/cm^2 at room temperature are summarized in Table 5.

Figure 12 depicts the discharge plot of a cell containing 5 percent VOPc. The load voltage is 3.35V. The capacity to 0.0V amounted to 1.98 Ah/g. The load voltage of the cell containing 10 percent VOPc was slightly lower but the cathode utilization was similar. VOPc shows a 45 percent improvement in capacity and a 10 percent improvement in cell voltage, both at 10 mA/cm^2.

The discharge behavior of a laboratory cell containing 5 percent MnPc-doped cathode is illustrated in Figure 13. The load voltage of this cell is about 50 mV lower than that of the VOPc containing cell; however, the capacity is higher. The cell containing a 10 percent load of MnPc performed worse than that containing 5 percent MnPc. It appears that the amount of catalyst is more critical with MnPc than with VOPc. The performance improvement attained with MnPc is a 60 percent increase in capacity and ~10 percent increase in cell voltage. The performance of MnPc at room temperature surpasses that of CoPc which we have evaluated to check the validity of our procedure. The discharge curve for the $Li/SOCl_2$ cell containing CoPc catalyzed cathodes is given in Figure 14. The performance we have achieved with CoPc is similar to what has been reported in the literature.[4]

Cells using cathodes which contained 5 percent loads of CoPc, VOPc, and MnPc were also discharged at -30°C, at a current density of 10 mA/cm^2. The results are summarized in Table 6. Discharge curves are presented in Figures 15 through 18. All the catalyzed cells showed higher mid-discharge voltages than the baseline cell. The VOPc catalyzed cell exhibited the best performance. The voltage regulation, compared with the baseline cell, was excellent, yielding practically all the capacity at a constant potential. This is extremely significant, since uncatalyzed cells usually exhibit a downward sloping potential profile at low temperatures, yielding a significant fraction of the capacity at potentials below 2.0V; Figure 18.

Cells containing CoPc and MnPc catalyzed cathodes also showed better voltage regulation at -30°C (Figures 16 and 17). However, their capacities were somewhat lower than that of the baseline cathode.

The preliminary results obtained so far with transition metal complex catalyzed cathodes indicate that MnPc is the preferred catalyst from the standpoint of performance at room temperature, while VOPc is the preferred material for applications involving both room and low temperatures. On the other hand, it is possible that a mixture of VOPc and MnPc might be the best catalyst composition for superior cell performance at both room and low temperatures.

We have also carried out discharges of $Li/SOCl_2$ cells containing cathodes doped with 5 w/o Co-TAA. This Co-TAA was synthesized by a different procedure[12] than the material previously reported.[1,2] It showed a slightly different IR spectrum than the previous material (discussed later). Co-TAA was dissolved in dimethyl formamide (DMF) (1 ml DMF/1.5 mg Co-TAA) and mixed with Shawinigan acetylene black carbon. DMF was removed by heating the mixture at 70°C under vacuum. Cathodes were made by blending the dried carbon-Co-TAA mix with 10 w/o Teflon binder and spreading it onto Ni screens. After drying overnight at 100°C to remove water, the cathodes were sintered at 300°C for 20 minutes under flowing Ar.

The discharge performance of Co-TAA catalyzed laboratory $Li/SOCl_2$ cells at room temperature and at two different rates is illustrated in Figure 19. At 5 and 10 mA/cm^2 discharge rates, the cathode utilizations were 2.02 and 1.75 Ah/g,

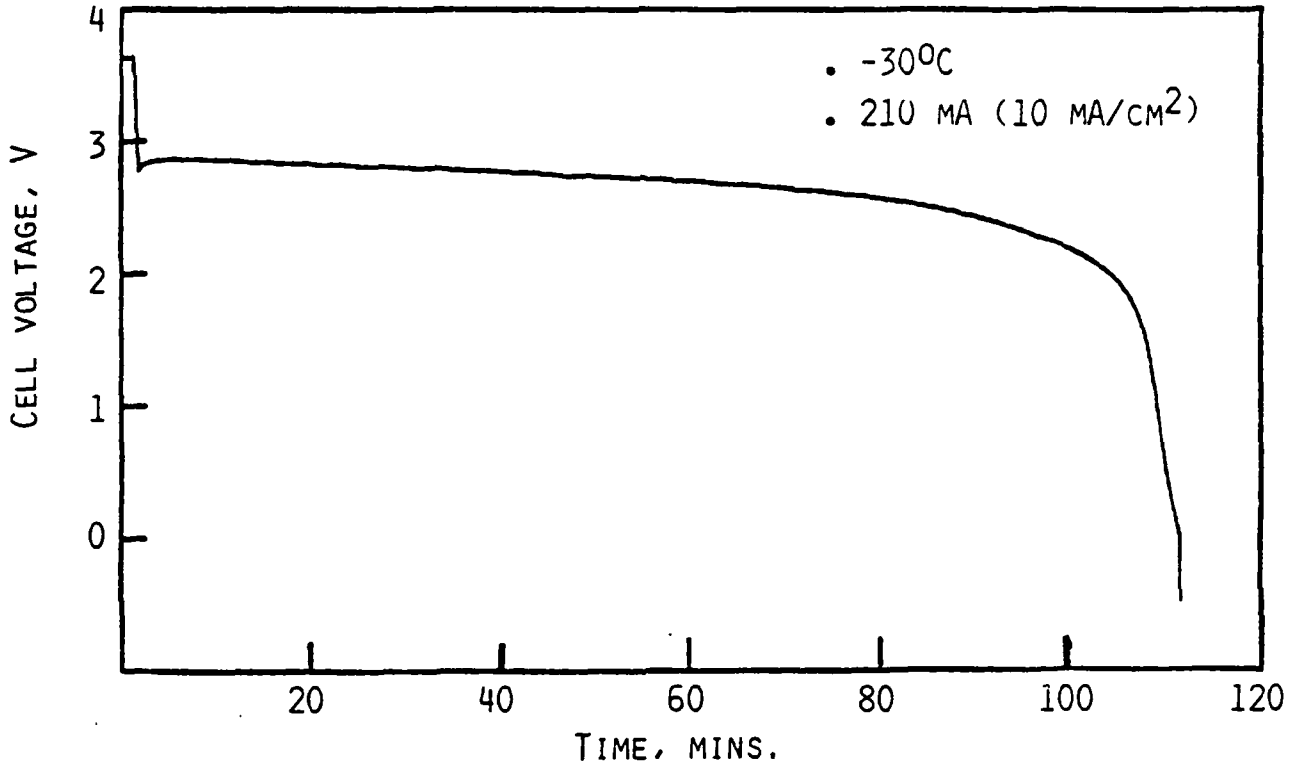


FIGURE 15. DISCHARGE PLOT OF A CELL CONTAINING 5% VOPc-DOPED CATHODE

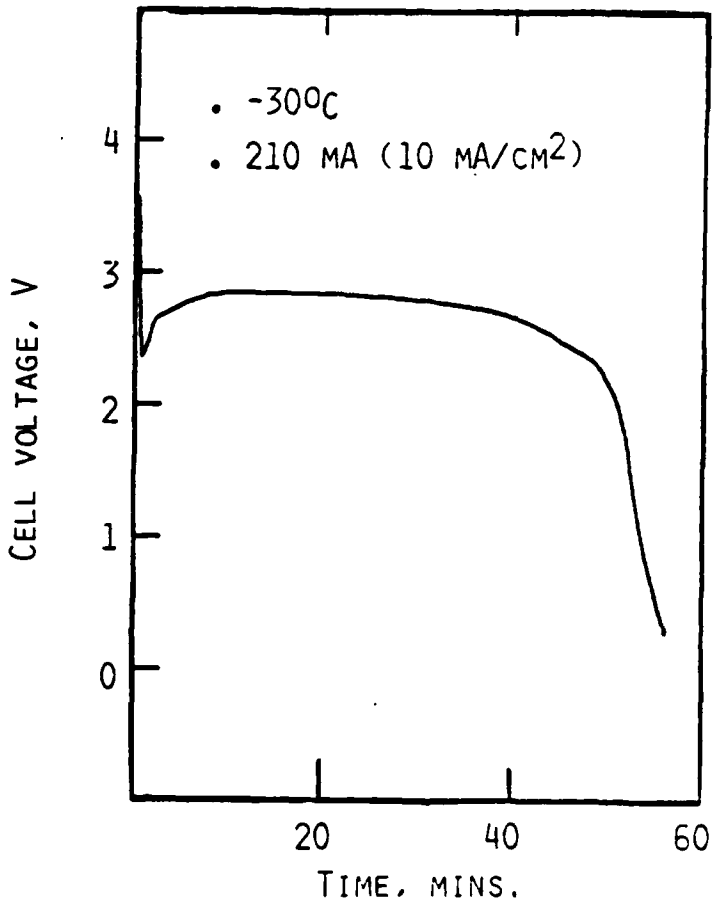


FIGURE 16. DISCHARGE PLOT OF A CELL CONTAINING 5% MnPc-DOPED CATHODE

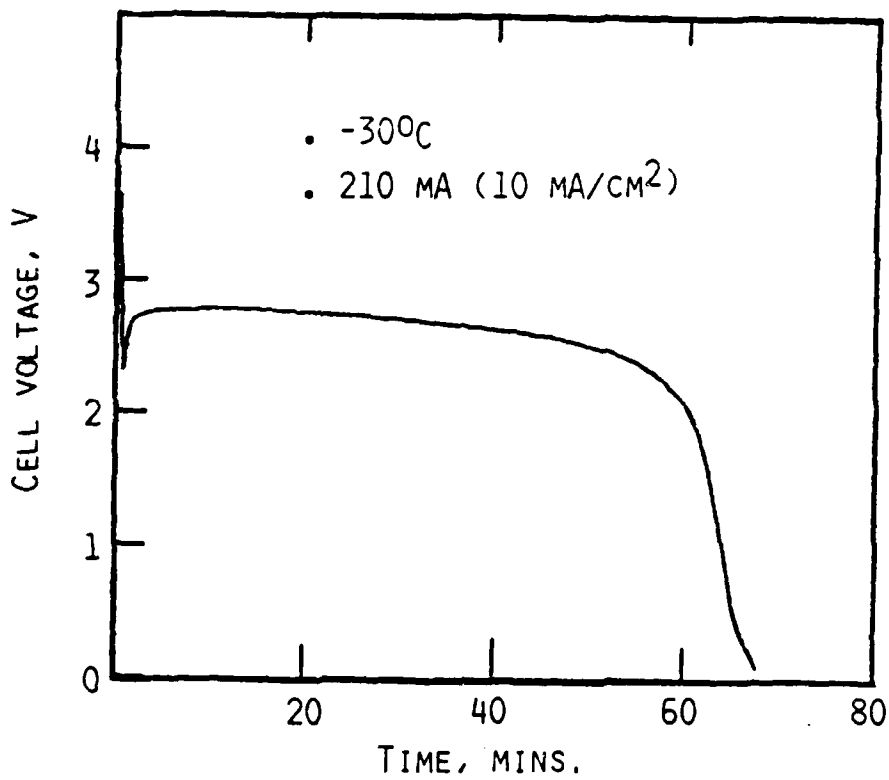


FIGURE 17. DISCHARGE PLOT OF A CELL CONTAINING 5% CoPc-DOPED CATHODE

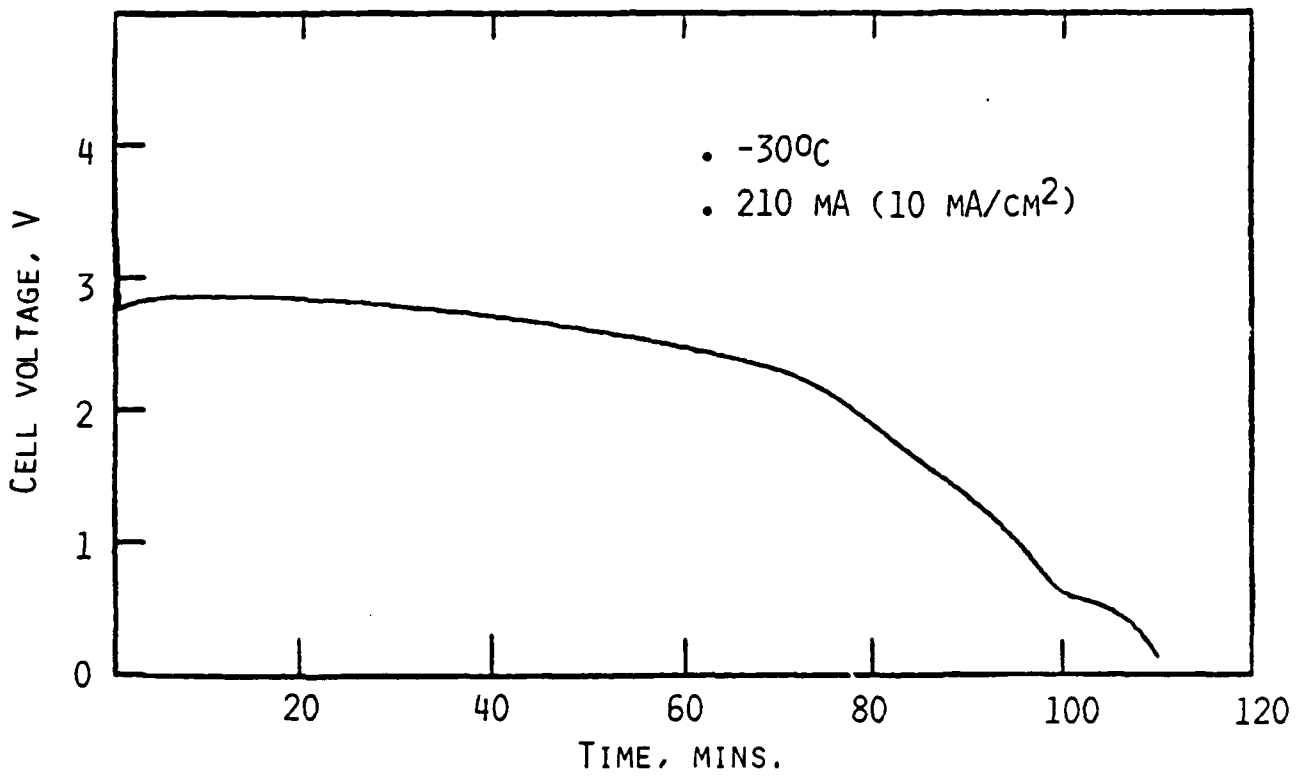


FIGURE 18. DISCHARGE PLOT OF AN UNCATALYZED CELL

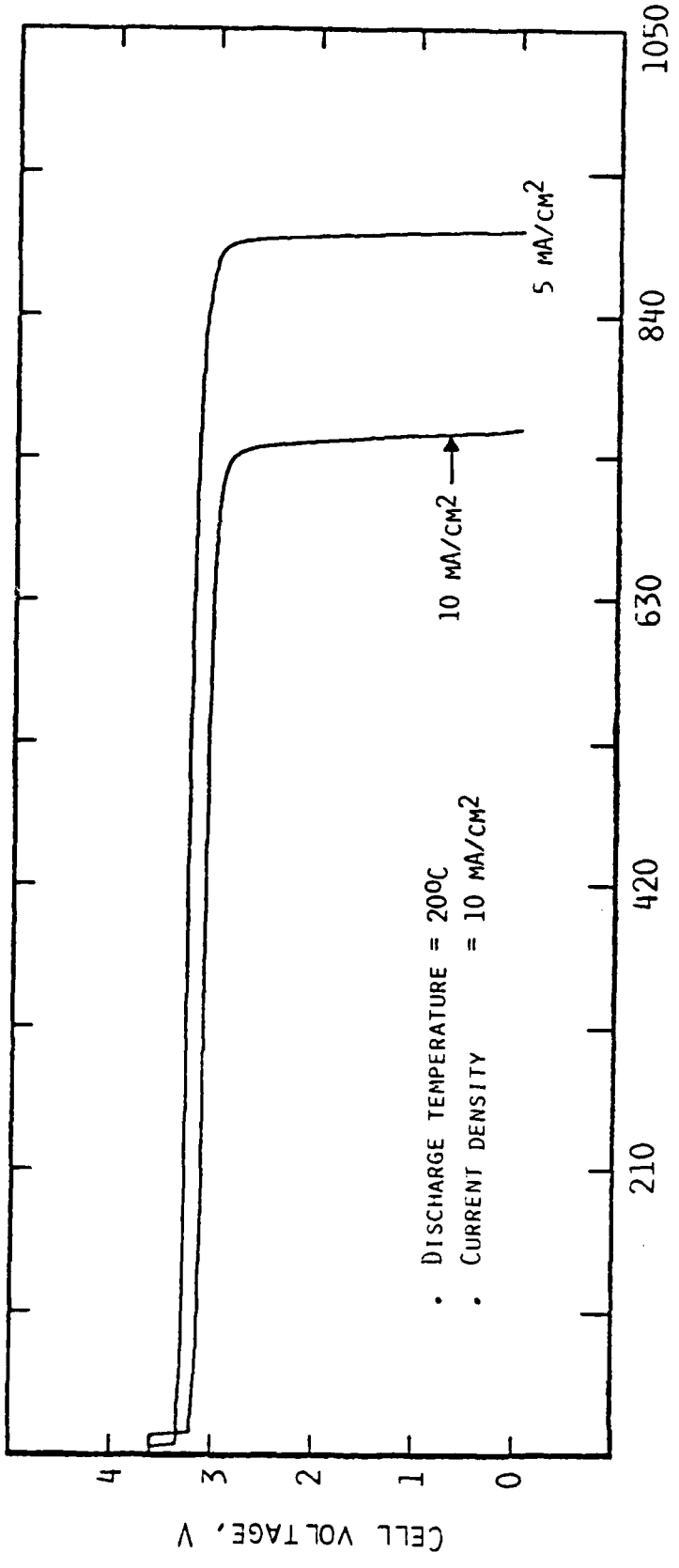
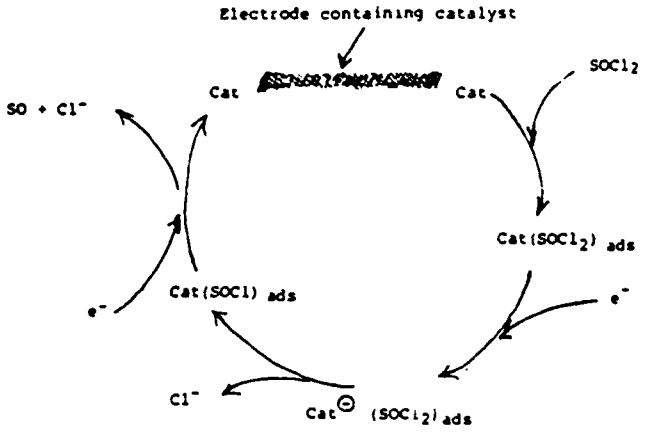


FIGURE 19. AMBIENT TEMPERATURE DISCHARGE PERFORMANCE OF LABORATORY $Li/SOCl_2$ CELLS CONTAINING 5 w/o OF THE Co-TAA-DOPED CATHODES PREPARED BY THE TEMPLATE SYNTHESIS

respectively. The average load potential of these cells at 5 mA/cm^2 was 3.37V, while that at 10 mA/cm^2 was 3.2V.

MECHANISM OF ELECTROCATALYSIS IN $Li/SOCl_2$ CELLS

Our tentative model for electrocatalysis in $Li/SOCl_2$ cells is schematically illustrated below. This scheme suggests the formation of an adsorption complex between $SOCl_2$ and the catalyst, followed by reduction of the complex, and desorption of the reduction products. The actual mechanism might be more complex than the one illustrated. Considerable experimental data are required to fully elucidate the mechanism of electrocatalysis in $Li/SOCl_2$. It also remains to be established whether the same mechanism can explain catalysis by all catalysts that have so far been identified.



X-ray analysis of the catalyzed cathodes was performed before and after their use in $Li/SOCl_2$ cells. The results are presented in Tables 7 to 9.

The X-ray data for the various catalyst-doped cathodes given in Table 7 show that only with $CoCO_3$ precursors could any assignment of the catalyst species be made. The X-ray data seem to indicate that several cobalt carbides and Co_3O_4 are formed in the thermal treatment of the $CoCO_3$ impregnated carbon. The transition metal macrocyclic complex catalyzed cathodes only show the carbon lines. However, the X-ray data strongly suggest that these cathodes do not contain any oxides or carbides as the peaks for those species are absent. These analyses were performed with 10 percent doped electrodes. At such low levels of catalyst, poorly crystalline materials will escape detection. X-ray analysis on carbon doped with higher levels of catalyst will be performed in the near future.

The data in Tables 8 and 9 indicate that in the case of VOPc and MnPc catalysis, LiCl is a discharge product. Because these cells are flooded, most of the S would go into solution, thereby escaping detection by X-ray. The strongest S line is present in the X-ray patterns of the MnPc catalyzed cathode. Clearly, these data are insufficient to draw a picture of the mechanism of electrocatalysis. However, the absence of Li_2O suggest that no significantly different products from those formed in baseline cells are probably formed. Further analysis, including quantitative analysis of Cl^-, S, and SO_2 will be performed in future studies.

TABLE 7. X-RAY DATA FOR THE UNDISCHARGED CATHODES CONTAINING THE VARIOUS DOPANTS

Dopant Level (wt %)	Sintering Temperature (°C)	d, A	I/I_o	Assignment
20% $CoCO_3$	500	7.34	100	Carbon
		4.85	50	Carbon
		2.45	45	Co_2C, Co_3C, Co_3O_4
		2.12	68	Co_2C, Co_3C
		1.48	30	
20% $Co(NO_3)_2$	900	7.41	100	Carbon
		4.91	35	$Co(NO_3)_2$, Carbon
10% VOPc	600	7.34	100	Carbon
		4.88	17	Carbon
		3.46	Trace	Carbon
10% MnPc	600	7.34	100	Carbon
		4.85	23	Carbon
		3.17	13	
5% CoPc	600	7.34	100	Carbon
		4.86	30	Carbon
10% $Co_4(CO)_{12}$	200	7.34	100	Carbon
		3.59	60	
		1.95	30	

TABLE 8. X-RAY DATA FOR THE CATHODE OF A $Li/SOCl_2$ LABORATORY CELL CONTAINING 5 w/o VOPc AS CATHODE DOPANT AND DISCHARGED AT 10 mA/cm^2

d, Å	I/I_o	Assignment
3.85	Trace	S
2.97	100	LiCl
2.58	90	LiCl
1.83	60	LiCl
1.56	30	LiCl
1.48	10	LiCl
1.29	Trace	LiCl
1.18	10	LiCl
1.15	10	LiCl
1.05	10	LiCl
0.99	10	LiCl
0.91	Trace	LiCl
0.87	Trace	LiCl
0.86	Trace	LiCl
0.82	Trace	LiCl

TABLE 9. X-RAY DATA FOR THE CATHODE OF A Li/$SOCl_2$ LABORATORY CELL CONTAINING 5 w/o MnPc AS CATHODE DOPANT AND DISCHARGED AT 10 mA/cm^2

d, Å	I/I_o	Assignment
4.81	Trace	C
3.85	20	S
3.47	Trace	
3.20	Trace	$LiAlCl_4$
3.08	Trace	
2.97	100	LiCl
2.84	Trace	$LiAlCl_4$
2.73	90	
2.57	90	LiCl
2.42	Trace	
2.29	10	
1.93	10	
1.87	Trace	$LiAlCl_4$
1.82	50	LiCl
1.73	Trace	$LiAlCl_4$
1.57	20	
1.55	30	LiCl
1.46	20	LiCl
1.36	Trace	
1.29	Trace	LiCl
1.22	Trace	
1.18	10	LiCl
1.15	20	LiCl
1.05	20	LiCl
1.03	Trace	
0.99	20	LiCl
0.87	20	LiCl
0.86	20	LiCl
0.81	10	LiCl

The IR spectrum of Co-TAA prepared by two different methods is illustrated in Figures 20 and 21. Comparison of these spectra reveal that Co-TAA as prepared by Reference 2, and previously discussed in Reference 1, is possibly somewhat different from that prepared by the template synthesis described in Reference 12. Studies to evaluate these differences are in progress.

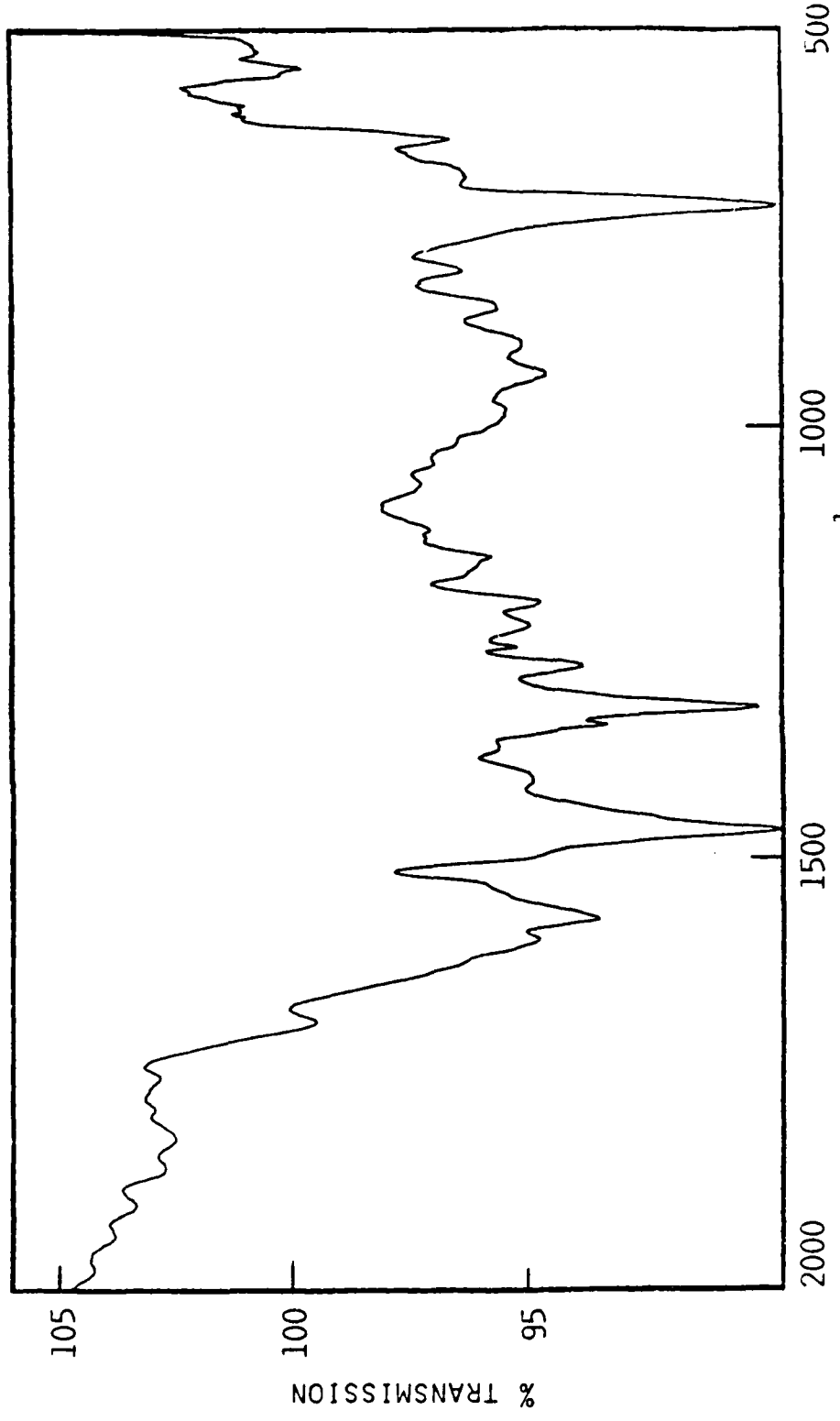


FIGURE 20. IR SPECTRUM OF Co-TAA SYNTHESIZED BY THE CONVENTIONAL METHOD (1,2)

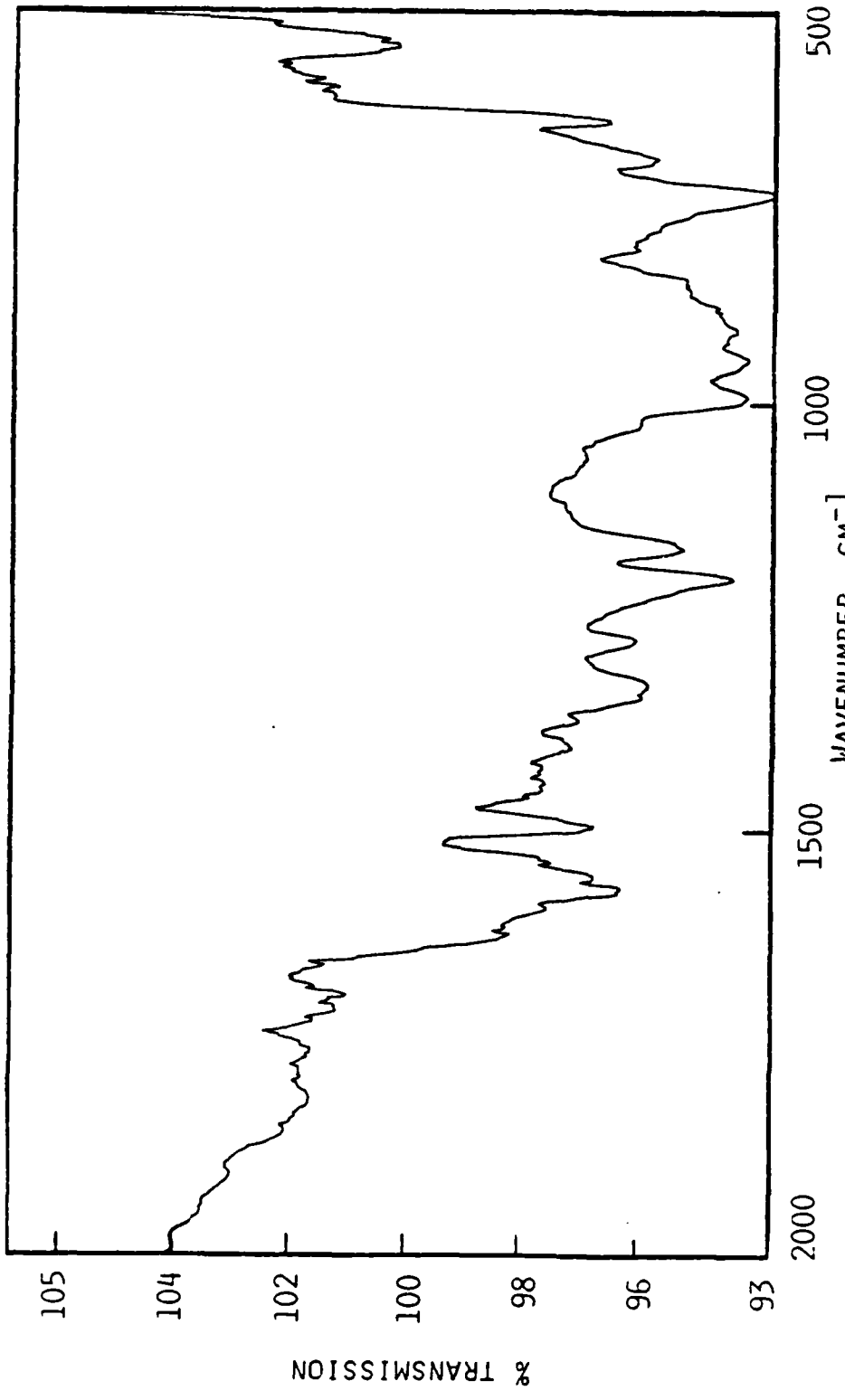


FIGURE 21. IR SPECTRUM OF Co-TAA PREPARED BY THE TEMPLATE SYNTHESIS (12)

CHAPTER 4

CONCLUSIONS

Doping acetylene black carbon with cobalt species generated by the thermal decomposition of $CoCO_3$, $Co_2(CO)_8$, and $Co_4(CO)_{12}$ did not result in cathodes suitable for catalyzing the discharge reaction of the $Li/SOCl_2$ cell. X-ray analysis revealed that $CoCO_3$ impregnated carbon generates cobalt carbides and Co_3O_4 upon thermal treatment at 500°C. The dopant species derived from $Co_2(CO)_8$ and $Co_4(CO)_{12}$ could not be identified by X-ray.

Mixing acetylene black with $Co(NO_3)_2$ followed by thermal treatment resulted in increased capacity for the electrode. The cell voltage remained the same as in baseline $Li/SOCl_2$ cells. Further studies, especially with regard to the amount of $Co(NO_3)_2$ and optimum temperature for thermal treatment, are needed.

Acetylene black carbon impregnated with transition metal phthalocyanines, followed by sintering at 600°C, resulted in highly enhanced capacity and higher cell voltage for the high rate discharge (viz., 10 mA/cm^2) of $Li/SOCl_2$ cells. Two new catalysts, VOPc and MnPc, have been discovered. These catalysts appear to be superior to many of the catalysts presently available. MnPc-containing cathodes showed a 60 percent increase in capacity and a 10 percent increase in cell voltage at 10 mA/cm^2 at room temperature. VOPc-containing cathodes increased the cell capacity by 45 percent and cell voltage by 10 percent at 10 mA/cm^2 at room temperature. VOPc also improved cell performance significantly at -30°C.

Currently available data indicate that transition metal macrocyclic complexes have special features that allow catalytic activity for the discharge of $Li/SOCl_2$ cells. The fact that VOPc and MnPc are highly active for $SOCl_2$ reduction, while inactive in fuel cells for O_2 reduction, suggests that the criteria for selection of catalysts for the reduction of $SOCl_2$ are different from those in fuel cells.

MnPc, VOPc, an CoPc were incorporated into the carbon by heating at 600°C. At these temperatures, these complexes are known to decompose. Questions remain about the nature of the active catalyst species when phthalocyanines are used. X-ray analysis did not provide the necessary answers because of the low concentrations of the catalyst species. Further work is planned.

Limited analyses of discharged cathodes seem to suggest that the discharge products are most probably LiCl, SO_2, and S, as in uncatalyzed cells. Quantitative analysis remains to be performed.

The new catalysts VOPc and MnPc appear to be of considerable potential for practical use. Therefore, further studies exploring the full extent of the usefulness of these new catalysts in practical batteries should be performed.

Additional studies are required to explain any differences in the catalysis process arising from samples reported to be Co-TAA but, as indicated by IR data, possibly differ in structure.

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