# STUDIES OF ADVANCED CATALYSTS FOR Li/SOCl$_2$ CELLS

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## Summary

The mechanism of electrocatalytic reduction of SOCl$_2$ by transition metal complexes was examined by investigating the role of the metal atom in two of the most promising macrocyclic complexes, namely, cobalt dibenzo-tetraazaannulene (CoTAA) and cobalt phthalocyanine (CoPc). Several new metal phthalocyanines have been found to increase both capacity and voltage in Li/SOCl$_2$ cells.

## Introduction

Despite the fact that a variety of catalytic materials, including platinum [1] and copper [2] metals, and a number of metal macrocyclic complexes [3 - 5] have improved cell performance [1 - 4] or cell safety [5], the present understanding of the fundamental mechanism of electrocatalysis in the Li/SOCl$_2$ cell is rather poor. The disparate data [3 - 5] on the discharge products found in catalyzed Li/SOCl$_2$ cells indicate the need for additional investigations in order to systematically design new and improved catalysts. Advanced catalysts are desirable to improve rate capability and overall safety of the Li/SOCl$_2$ cell. There are indications that the actual catalytic species in a transition metal macrocyclic complex may be the related metal oxide [6] or finely-divided metal that forms from the decomposition of the metal macrocyclic compound during heat treatment of the doped cathode [6 - 8].

In this paper we report the results of our studies examining the role that cobalt metal, its oxide, and oxidation state play on the discharge reaction of CoTAA and CoPc catalyzed Li/SOCl$_2$ cells. We have also begun an investigation of a series of phthalocyanine complexes in order to assess the role of the metal atom in metal phthalocyanine catalysis of Li/SOCl$_2$ cells.

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## Experimental

Acetylene black carbon cathodes were doped with the precursors $Co(NO_3)_2$, $CoCO_3$, $Co_2(CO)_8$, and $Co_4(CO)_{12}$. The $Co(NO_3)_2$ and $CoCO_3$ were deposited from slurries of carbon in aqueous and ethanol/water media, respectively. These mixtures were dried at 100 °C. $Co_2(CO)_8$ and $Co_4(CO)_{12}$ were deposited from THF and diethyl ether, respectively. The solvents were removed by pumping under vacuum. The doped carbons were then sintered at appropriate temperatures (see Table 1) under argon prior to fabricating the Teflon-bonded electrodes.

Cathodes were also fabricated using acetylene black carbon mixed with various weights percent. (wt.%) of commercially available transition metal phthalocyanines. In a typical preparation, 2.25 g of the catalyst were dissolved in 150 ml of conc. $H_2SO_4$ at room temperature. This solution was added to 37.75 g of acetylene black carbon and mixed well at room temperature by stirring with a spatula for approximately 30 min. All of the catalyst

TABLE 1

Discharge data at 20 °C and 10 mA cm$^{-2}$ for Li/SOCl$_2$ cells containing cathodes doped with various precursors

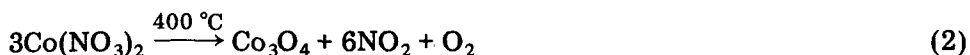| Cell no. | Precursor | Precursor (wt.%) | Temp. (°C) | Mid-discharge voltage (V) | Capacity (A h g$^{-1}$ carbon) |
|---|---|---|---|---|---|
| 1 | $Co(NO_3)_2$ | * | 130* | 3.13 | 0.90 |
| 2 | $Co(NO_3)_2$ | 5 | 400 | 3.04 | 1.59 |
| 3 | $Co(NO_3)_2$ | 10 | 400 | 2.99 | 1.35 |
| 4 | $Co(NO_3)_2$ | 20 | 400 | 2.98 | 1.23 |
| 5 | $Co(NO_3)_2$ | 5 | 900 | 3.09 | 1.18 |
| 6 | $Co(NO_3)_2$ | 10 | 900 | 3.09 | 0.95 |
| 7 | $CoCO_3$ | 5 | 500 | 2.91 | 1.25 |
| 8 | $CoCO_3$ | 10 | 500 | 3.01 | 0.98 |
| 9 | $CoCO_3$ | 5 | 900 | 3.12 | 1.37 |
| 10 | $CoCO_3$ | 10 | 900 | 3.15 | 1.28 |
| 11 | $CoCO_3$ | 20 | 900 | 3.11 | 0.81 |
| 12 | $Co_2(CO)_8$ | 5 | 200 | 3.10 | 1.29 |
| 13 | $Co_2(CO)_8$ | 5 | 300 | 3.10 | 1.24 |
| 14 | $Co_2(CO)_8$ | 10 | 300 | 3.08 | 0.96 |
| 15 | $Co_2(CO)_8$ | 5 | 600 | 3.12 | 1.12 |
| 16 | $Co_4(CO)_{12}$ | 10 | 200 | 3.08 | 1.17 |
| 17 | $Co_4(CO)_{12}$ | 10 | 200 | 3.10 | 1.07 |
| 18 | $Co_4(CO)_{12}$ | 5 | 600 | 3.10 | 0.93 |
| 19 | $Co_4(CO)_{12}$ | 10 | 600 | 3.10 | 0.66 |
| 20 | No catalyst | — | — | 2.98 | 1.36 |

*Finished cathodes dipped in 7 wt.% solution followed by drying at 130 °C.

was absorbed into the carbon during this period. The carbon was washed with distilled water several times, until the washings indicated neutral pH. The carbon was dried overnight in an oven at 110 °C. The doped carbons were then sintered at 600 °C in an argon atmosphere, and Teflon-bonded carbon electrodes were prepared.

In order to construct laboratory test cells, the $3.5 \times 3.0 \times 0.1$ cm cathodes with glass separators were sandwiched between two 15 mil thick Li anodes pressed into Ni screens. The electrode package was inserted into rectangular glass vials, the top of which was sealed by a polypropylene plate with electrical feedthroughs. Each cell contained about 4 ml of 1.8 M $LiAlCl_4/SOCl_2$ so that it had a carbon-limited configuration. The cells also contained a Li reference electrode.

## Discussion of results

The chemical reactions which are believed to take place in the deposition of cobalt oxides and finely divided Co into the carbon electrodes are depicted in eqns. (1) - (4). The temperature shown in each equation is the lowest decomposition temperature for the corresponding precursor.

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

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

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

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

The discharge data for the cathodes containing various precursors are shown in Table 1. The electrochemical performance of doped cathodes appears to be sensitive to heat treatment. As the sintering temperature increased, small increases in cell voltage were generally observed. Conversely, with the exception of the cathodes containing $CoCO_3$ precursor, the cell capacities decreased with sintering at higher temperatures. None of the precursor-doped cathodes improved cell performance over uncatalyzed Li/$SOCl_2$ cells. Also, increasing concentrations of oxides or metal did not increase the cell capacity, expressed as A h $g^{-1}$ carbon. In fact, at the higher concentrations of the dopants, the cell capacities were significantly lower. This behavior perhaps reflects an overall decrease in the available electrode active sites as the dopants begin to occupy significant fractions of the cathode pore volume. Thus, capacities of cells 3 and 4 are approximately 85 and 77 percent. of the capacity of cell 2. The decrease in capacity in these two cells corresponds approximately to the amount of catalyst added beyond 5 wt.%.

The general lack of catalytic activity of the precursor-doped cathodes indicates that either the products from any thermal degradation of CoTAA

TABLE 2

Discharge results for Li/SOCl$_2$ cells containing transition metal complex-doped cathodes sintered at 600 °C and discharged at 10 mA cm$^{-2}$ at 20 °C

| Complex | Complex (wt.%) | Mid-discharge voltage (V) | Capacity (A h g$^{-1}$) |
|---|---|---|---|
| No catalyst | — | 2.98 | 1.36 |
| VOPc | 5 | 3.34 | 1.98 |
| VOPc | 10 | 3.26 | 1.94 |
| MnPc | 5 | 3.29 | 2.21 |
| MnPc | 10 | 3.09 | 1.43 |
| CoPc | 5 | 3.32 | 1.94 |
| NiPc | 5 | 3.09 | 2.17 |
| NiPc | 10 | 3.13 | 2.23 |
| CuPc | 5 | 3.16 | 2.29 |
| CuPc | 10 | 3.16 | 2.15 |

or CoPc are different from the materials derived from these precursors or that the organic moieties in the complexes play a significant role in the catalysis of the Li/SOCl$_2$ cell discharge reaction.

The role of the metal atom in transition metal macrocyclic, complex-catalyzed cathodes was evaluated by studying the catalytic activity of V, Mn, Co, Ni, and Cu phthalocyanines. The results are summarized in Table 2. As the data indicate, we have found several transition metal phthalocyanines, impregnated in acetylene black carbon followed by sintering at 600 °C under argon, to be highly active catalysts for the reduction of SOCl$_2$. It appears that the catalytic activity of Mn, V and Ni phthalocyanines in Li/SOCl$_2$ cells has been reported for the first time here. Typical discharge performances of MnPc- and VOPc-catalyzed Li/SOCl$_2$ cells are compared with an uncatalyzed cell in Fig. 1. CoPc was previously investigated as a catalyst in Li/SOCl$_2$ cells [4]. Our results agree with the prior data.
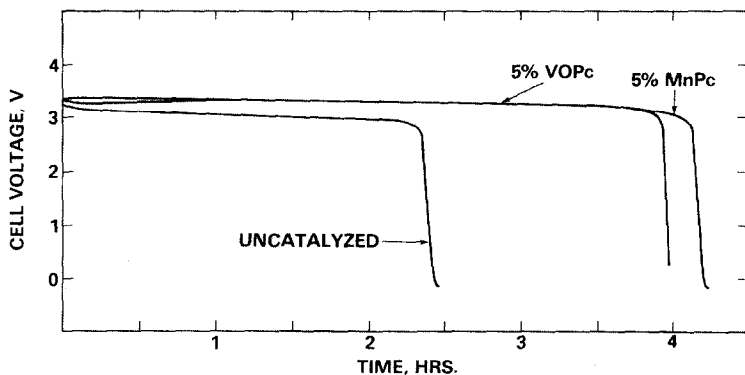


Fig. 1. A comparison of the discharge performance of uncatalyzed and VOPc and MnPc catalyzed cells at 10 mA cm$^{-2}$ at 20 °C.

TABLE 3

Discharge performance of Li/SOCl$_2$ cells containing 5 wt.% transition metal complex-doped cathodes at $-30$ °C at 10 mA cm$^{-2}$

| Complex | Mid-discharge voltage (V) | Capacity to 2.0 V (A h g$^{-1}$ carbon) |
|---|---|---|
| VOPc | 2.74 | 0.91 |
| MnPc | 2.71 | 0.58 |
| CoPc | 2.81 | 0.51 |
| NiPc | 2.44 | 0.95 |
| CuPc | 2.63 | 1.54 |
| Uncatalyzed | 2.54 | 0.77 |

In their role as catalysts in acid fuel cells, the activity of the phthalocyanines decreased in the order Fe > Co > Ni > Cu [8]. The activity of NiPc and CuPc was, in fact, very small. Furthermore, MnPc was completely inactive [8]. The catalytic activity trend observed in the Li/SOCl$_2$ cell is certainly different from that found in acid fuel cells. Unlike its behavior in the fuel cells, MnPc seems to be one of the best catalysts for Li/SOCl$_2$ cells.

The data in Table 2 indicate that with the exception of MnPc, the utilization of the cathode is not critically affected by the amount of complex added. Cells with MnPc are presently being evaluated to clarify its abnormal behavior at 10 wt.% loading. Cells containing MnPc, CuPc and NiPc exhibited similar behavior at room temperature, increasing capacity by an average of 65% when discharged at 10 mA cm$^{-2}$ at 20 °C. Their performances were superior to that of CoPc and VOPc. However, VOPc produced the greatest improvement in cell voltage.

The effect of the metal complexes on Li/SOCl$_2$ cells discharged at $-30$ °C at 10 mA cm$^{-2}$ is summarized in Table 3. Of the five materials investigated, CuPc showed the greatest capacity improvement. A comparison of these preliminary CuPc data with our prior CoTAA results seems to indicate that the latter is the preferred material for applications involving both room and low temperatures. We have found that C-cells with CoTAA had a mid-discharge voltage of $\sim 2.85$ V and a capacity of 1.8 A h g$^{-1}$ carbon at $-30$ °C and 10 mA cm$^{-2}$ [3]. However, work on the new metal phthalocyanine complexes is continuing and it is possible that mixtures of materials might offer even superior performances to that of CoTAA. Certainly, the full potential of these new catalysts, and others under investigation, remains to be ascertained, especially as the mechanism of electrocatalysis in Li/SOCl$_2$ cells is being elucidated. Our present data seem to suggest that the criteria for the selection of catalysts for the reduction of SOCl$_2$ might be different from those for O$_2$ in fuel cells.

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