

Lithium batteries utilizing $\text{SOCl}_2\text{--SO}_2\text{Cl}_2$ mixed electrolytes

W. P. Kilroy

Naval Surface Warfare Center, Silver Spring, MD 20903 (U.S.A.)

C. Schlaikjer and R. Yetman

Battery Engineering, Inc., Hyde Park, MA 02136 (U.S.A.)

M. Alamgir and K. M. Abraham

EIC Laboratories, Inc., Norwood, MA 02062 (U.S.A.)

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Abstract

The performance of C-size commercial cells containing mixtures of $\text{SOCl}_2\text{--SO}_2\text{Cl}_2$ mixed depolarizers with 1.0 and 1.8 M LiAlCl_4 has been compared with that of Li/SOCl_2 cells as a function of discharge temperature. Fresh cells as well as those stored at 70 °C were discharged at constant resistive loads equivalent to 1 and 10 mA/cm^2 at 25, 0 and –30 °C. Cell capacity, voltage regulation and start-up characteristics were found to depend on storage, $\text{SOCl}_2/\text{SO}_2\text{Cl}_2$ ratio and LiAlCl_4 concentration. The mixed depolarizer cells had superior performance at the lower discharge temperatures and after storage. The behavior of metal phthalocyanine catalysts was evaluated in 1.8 M LiAlCl_4 60/40 $\text{SO}_2\text{Cl}_2/\text{SOCl}_2$ electrolyte at 10 mA/cm^2 at 25 °C after storage at 70 °C. The NiPc and CuPc catalysts improved overall cell performance.

Introduction

Because of rapidly developing new weapons technologies, there is an increasing demand for greater power and energy densities from portable power supplies. In responding to this demand, we have evaluated the performance of C-size Li cells containing a mixed electrolyte-cum-cathode depolarizer of $\text{SOCl}_2\text{--SO}_2\text{Cl}_2/\text{LiAlCl}_4$. The behavior of these cells has been compared with that of Li/SOCl_2 cells. Studies precedent to this investigation demonstrated that a 50–50 mixture of a $\text{SOCl}_2\text{--SO}_2\text{Cl}_2$ depolarizer (i) improved the low temperature utilization of carbon in carbon-limited laboratory cells [1] and (ii) exhibited much higher AlCl_3 utilization efficiencies in flowing electrolyte cells than cells employing electrolyte based upon either SOCl_2 or SO_2Cl_2 alone [2]. We also investigated the effect of catalysis on the performance of the mixed depolarizer cells. Carbon cathodes containing various metal phthalocyanines sintered at 600 °C were evaluated at ambient temperature and after 70 °C storage. Previous studies in SOCl_2 laboratory cells containing a metal phthalocyanine catalyst indicated that improved cell performance depended on the nature of the metal atom in the phthalocyanine

and/or the sintering temperature of the carbon-metal phthalocyanine mixture [3, 4].

Experimental

Spiral wound C-size carbon-limited cells were used as test vehicles. Two cells were discharged for each evaluation. However two additional cells were discharged if there was any ambiguity in the cell tests. The range of cell capacities are shown by error bars in the Figs.

LiAlCl_4 was prepared *in situ* by combination of LiCl (Foote), dried at 200 °C under vacuum, and AlCl_3 (Fluka). The thionyl chloride (Mobay) was distilled. The electrolyte solution was refluxed over lithium chips for about 15 h or until IR spectroscopy indicated it was dry. An appropriate amount of distilled SO_2Cl_2 (Eastman) was added to prepare the mixed depolarizer electrolyte. The uncatalyzed thionyl chloride and mixed depolarizer cells contained 17.6 g of 1.0 or 1.8 M LiAlCl_4 electrolyte.

The cathodes employed were 0.063 cm thick, each containing 2.9 ± 0.2 g wet-rolled or a fixed 2.85 g dry-pressed, Chevron acetylene black carbon with 10% Teflon binder. The wet-rolled cathodes were prepared by mixing the carbon/Teflon mixture with 50/50 isopropyl alcohol/water followed by spreading on nickel screens with a dough sheeting machine. They were air dried and 'cured' by heating briefly in air to 280 °C. The dry-pressed cathode material was cured first, chopped in a blender and then pressed dry onto nickel screens. The cathodes measured 3.8×25.4 cm with a total geometric area of 193.5 cm² per two sides. The anodes were $3.8 \times 29.2 \times 0.025$ cm containing 5.8 A h Li. Cells with pure SO_2Cl_2 contained 1.9 ± 0.2 g carbon. They were also designed to be carbon limited. Additional wet-rolled cells were made with 0.03 and 0.13 cm thick, 2.85 g cathodes for comparison studies. All the cells containing 0.03, 0.063 and 0.13 cm thick cathodes were designed to have approximately the same amount of Li and electrolyte.

Catalyzed cells were constructed similarly to the uncatalyzed cells. The cells contained 1.8 M LiAlCl_4 and 19.3 g electrolyte. The cathodes were dry-pressed, 0.063 cm thick and contained 2.85 g carbon with 5 wt.% metal phthalocyanine (MPc) that were heat treated at 600 °C under nitrogen. The MPc catalysts were obtained from Strem Chemical Company. New control cells were prepared for this study using the dry-pressed cathodes.

Cells were discharged under constant loads of 1.5 or 17 Ω equivalent to 10 and 1 mA/cm², respectively.

Discussion of results

In order to produce cells with a uniform carbon loading, distribution, porosity and thickness, the dry-pressed process was preferred to the wet-rolled process. The capacity of dry-pressed cathodes cells was not as high

as the best wet-rolled cathodes, but the capacity was adequate, more reproducible and more suited to the study of the effects of the sulfuryl chloride/thionyl chloride ratio on the capacity. The capacity appeared not to be as much affected by the amount of carbon as by the technique used to make the cathode, i.e. the loss of the cohesive binding power of the Teflon after curing.

Ambient temperature performance

The open circuit potential of the mixed electrolyte cells was 3.90 V compared with 3.65 V for the Li/SOCl₂ cells. Thus, the mixed electrolyte cells had a potential very close to the 3.95 V inherent in SO₂Cl₂ cells. Typical performance for the 70% SO₂Cl₂/30% SOCl₂ cells are compared with that of SOCl₂ cells after high temperature storage in Fig. 1. The discharge curves are characterized by a constant voltage profile during most of the discharge followed by an abrupt voltage drop at the end of the useful life of the cells. In contrast to the previous study performed in laboratory cells [1] that showed a mixed electrolyte had the greatest improvement in capacity relative to the SOCl₂ system at ambient temperatures, the C-size cell data show that the greatest benefit of mixed electrolytes occurred with fresh cells at low temperatures and in stored cells at high temperatures. The data in the bar graphs of Fig. 2 indicate only a slight increase in capacity is achieved by use of mixed depolarizers at ambient temperatures compared with SOCl₂. Similar results were observed for cells discharged at 17 Ω (1 mA/cm²). However, the mixed depolarizer cells containing 1.0 M electrolyte responded to activation more rapidly. After 2 weeks storage at 70 °C, the average start-

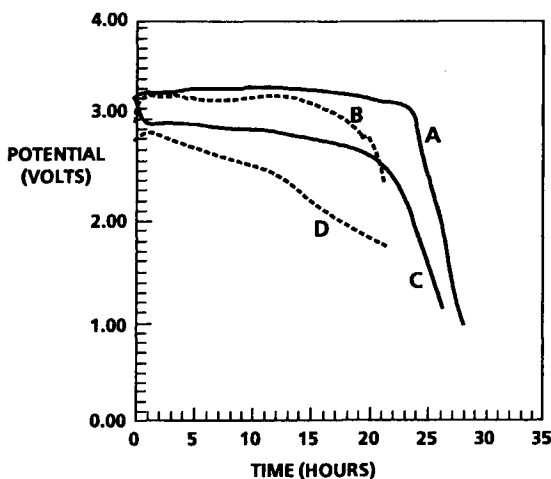


Fig. 1. Performance of C-size cells containing 1.0 M LiAlCl₄ discharged at 17 Ω (1 mA/cm²). Curve A: 70% SO₂Cl₂/30% SOCl₂ cell stored for 2 weeks at 70 °C and discharged at 25 °C. Curve B: SOCl₂ cell stored for 2 weeks at 70 °C and discharged at 25 °C. Curve C: 70% SO₂Cl₂/30% SOCl₂ cell stored for 2 weeks at 70 °C and discharged at -30 °C. Curve D: SOCl₂ cell stored for 2 weeks at 70 °C and discharged at -30 °C.

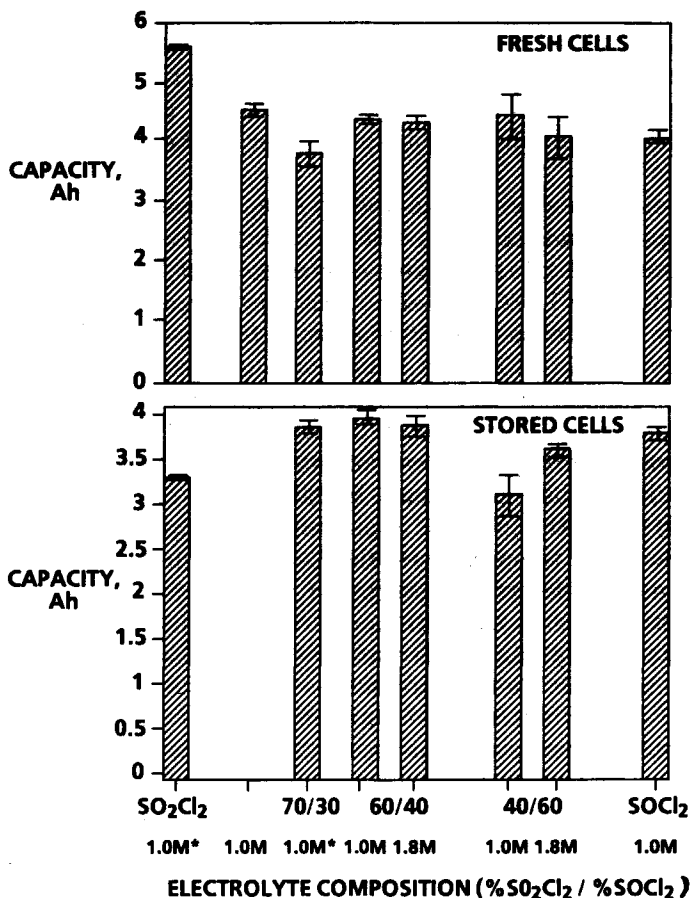


Fig. 2. Comparison of average capacity to 2.0 V for fresh cells and cells stored for 2 weeks at 70 °C. Cells were discharged at 1.5 Ω (10 mA/cm²) at 25 °C. *Dry-pressed cathodes.

up times for cells discharged at 17 Ω to a limit of 3.0 V were 10 and 70 min for SOCl₂ and SO₂Cl₂, respectively, whereas the potential of the mixed depolarizer cells containing 40, 60, 70% SO₂Cl₂ never fell below 3.0 V.

Low temperature performance

The behavior of the mixed 40% SOCl₂-60% SO₂Cl₂ system was compared with that of SOCl₂ and SO₂Cl₂ at 0 °C. The data are shown in Table 1. At the 1.5 Ω load (10 mA/cm²) rate, the mixed electrolyte demonstrated better startup performance and higher capacity especially after high temperature storage. At the lower rate, there was no perceptible improvement in capacity especially after storage because the cells became lithium limited. However, the 1.0 M mixed depolarizer system still offered improved activation times to 3.0 V.

The capacity data for cells discharged at -30 °C at 1.5 Ω is shown in Fig. 3. When the data in Fig. 3 is compared to the ambient temperature

TABLE 1

Comparison of average performance of 40/60% SOCl₂/SO₂Cl₂ vs. SOCl₂ and SO₂Cl₂ C-size cells discharged at 0 °C

Composition	Concentration of LiAlCl ₄ (M)	Storage	Resistive load			
			1.5 Ω		17 Ω	
			Startup time to 2 V (min)	Capacity (A h)	Startup time to 3.0 V (min)	Capacity (A h)
SOCl ₂	1.0	fresh	5.0	1.68	1.0	3.61
40/60	1.0	fresh	^a	2.66	^a	4.10
40/60	1.8	fresh	5.5	3.98	^a	4.66
SOCl ₂	1.0	2 wk, 70 °C	^b	0	10	4.45
SO ₂ Cl ₂	1.0	2 wk, 70 °C	55.0	0.91	336	5.66
40/60	1.0	2 wk, 70 °C	9.0	2.98	^a	4.45
40/60	1.8	2 wk, 70 °C	29.0	3.84	60	4.20

^aDuring discharge, the cells never fell below this voltage.

^bDuring discharge, the cells never reached this voltage.

performance in Fig. 2, the advantage of the mixed electrolyte is evident. At the lower 1 mA/cm² rate, however, no clear pattern was observed. In general, the SOCl₂ cells with 1.0 M electrolyte had better capacity at the 1 mA/cm² rate than the mixed depolarizer systems with either the 1.0 or 1.8 M electrolyte after 2 weeks storage at 70 °C. This was not true at the high rate of discharge. However in fresh cells, although the capacity of the 1.0 M SOCl₂ cells was comparable to cells with 1.0 or 1.8 M 40/60% SOCl₂/SO₂Cl₂, the 30/70% SOCl₂/SO₂Cl₂ cells had 40% better capacity than SOCl₂ cells. This was attributed to the better voltage regulation of the mixed depolarizer. Typical low temperature behavior is shown in Fig. 1C. It is interesting that the mixed depolarizer systems had much quicker activation times than cells containing either individual depolarizer. The comparison data are presented in Table 2.

Effect of carbon thickness

The 40/60% SOCl₂/SO₂Cl₂ 1.0 M LiAlCl₄ mixture was selected to evaluate the influence of carbon thickness on cell capacity. The cathodes were all wet-rolled and had nearly constant weight. Figure 4 illustrates the significant effect that the electrode configuration can have on cell capacity. The carbon electrode surface areas were 350, 194 and 110 cm² with lengths of 45.7, 27.9 and 14 cm for the 0.03, 0.063 and 0.13 cm thick cathodes, respectively. At ambient temperatures and low rate discharge, the capacity increased with increasing cathode thickness. Conversely, the 0.03 cm thick cathodes performed best at -30 °C. The inferior performance of the thicker cathodes is attributed to the poor transport properties of the electrolyte in the porous cathode at the lower temperatures.

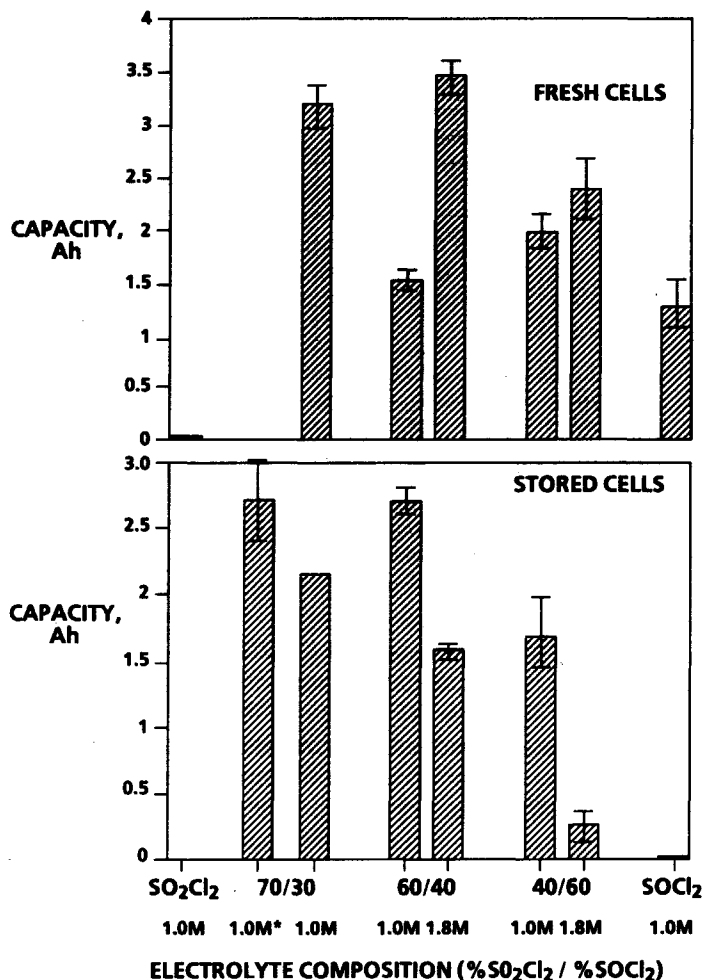


Fig. 3. Comparison of average capacity to 2.0 V for fresh cells and cells stored for 2 weeks at 70 °C. Cells were discharged at 1.5 Ω (10 mA/cm²) at -30 °C. *Dry-pressed cathodes.

Effect of salt concentration

The data in Tables 1 and 2 and Fig. 3 reveal that the mixed depolarizer systems responded to activation more rapidly and had better capacity in both fresh and stored cells. The cells containing the lower 1.0 M electrolyte concentrations had better startup performance, presumably due to reduced anode corrosion. In cells that were stored, those with 1.0 M LiAlCl₄ also provided better voltage regulation and cell voltage, especially at the lower temperatures. Thus in cells with 1.8 M LiAlCl₄, the increased rate of self discharge that occurs during storage reduces the useful capacity to a 2.0 V cutoff. Barring this poor voltage regulation, the stored cells containing 1.8 M salt would have demonstrated better capacity to a 1.8 V cutoff than

TABLE 2

Comparison of average startup times of C-size cells at $-30\text{ }^{\circ}\text{C}$

Cell composition $\text{SOCl}_2/\text{SO}_2\text{Cl}_2$ (%)	Concentration of LiAlCl_4 (M)	Average startup time (min)	
		to 2.0 V (1.5 Ω)	to 3.0 V (17 Ω)
Fresh cells			
100/0	1.0	6.5	b
60/40	1.0	1.2	b
40/60	1.0	a	b
30/70	1.0	a	a
0/100	1.0	45	b
60/40	1.8	a to 2.4	a
40/60	1.8	8.4	b
Cells stored 2 weeks at $70\text{ }^{\circ}\text{C}$			
100/0	1.0	b	b
60/40	1.0	2.0	b
40/60	1.0	7.2	b
30/70	1.0	7.8	b
60/40	1.8	11.5	b
40/60	1.8	7.2	b

*During discharge, the cell potential never fell below this voltage.

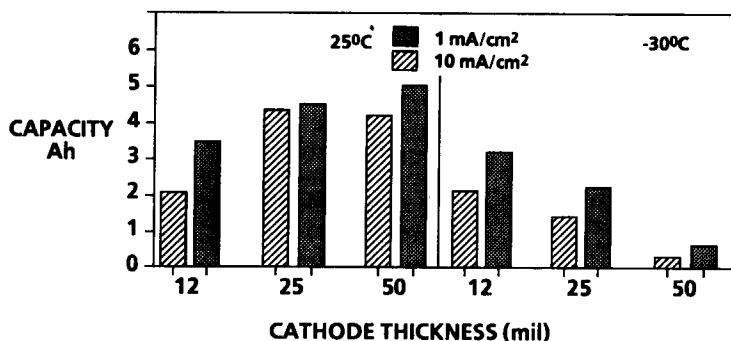
^bDuring discharge, the cell potential never reached this voltage.

Fig. 4. Effect of cathode thickness on the average capacity of 1.0 M LiAlCl_4 60/40%, $\text{SO}_2\text{Cl}_2/\text{SOCl}_2$ mixed depolarizer cells as a function of temperature and current density. Average cathode weight was 2.83 ± 0.08 g.

cells containing a 1.0 M salt concentration, 3.1 versus 2.85 A h. In fresh cells, the improvement in capacity for cells with higher salt concentration is illustrated for the 60% SO_2Cl_2 -40% SOCl_2 mixture in Fig. 5. The increase in cell capacity is attributed to improved Li^+ mass transport at the higher salt concentrations. Figure 5 graphically illustrates the advantage in low temperature performance of the mixed depolarizer systems after storage at

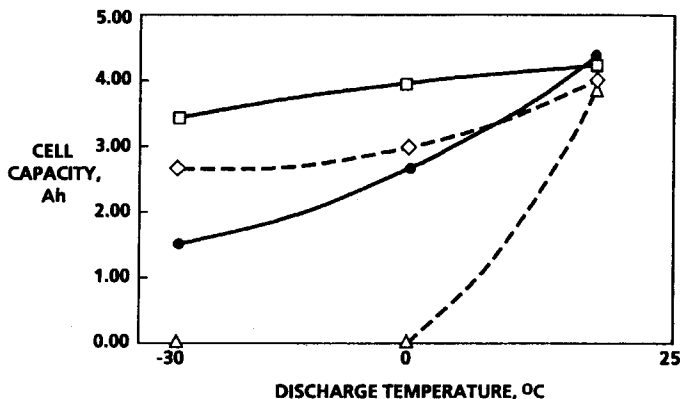


Fig. 5. Comparison of average C-size cell capacity to 2.0 V at 1.5 Ω vs. discharge temperature. (a) 1.0 M LiAlCl₄ cells stored for 2 weeks at 70 °C. \diamond : 60% SO₂Cl₂/40% SOCl₂, \triangle : 100% SOCl₂. (b) Effect of LiAlCl₄ concentration of fresh cells containing 60% SO₂Cl₂/40% SOCl₂. \square : 1.8 M LiAlCl₄, \bullet : 1.0 M LiAlCl₄.

high temperatures. Cells containing SOCl₂ with 1.8 M LiAlCl₄ were not studied. Presumably they would have performed even more poorly under these conditions due to increased anode corrosion.

Effect of metal phthalocyanine (MPc) catalysts – fresh cells

The effect of MPc catalysts on fresh C-size mixed depolarizer cells containing 1.8 M LiAlCl₄ was examined under ambient temperature discharge at 10 mA/cm². Five catalysts were studied; VOPc, MnPc, CoPc, NiPc and CuPc. The effect of FePc as a catalyst in SOCl₂ cells has been reported [5].

Cell voltage was improved by addition of catalyst. Although several of the catalysts had little effect on improving cell capacity of cells containing either the 60% or 70% SO₂Cl₂ depolarizer system, it is interesting to note that the average cell capacity increased with increasing atomic number of the metal. Whereas the VOPc decreased the capacity and load voltage substantially, the cell capacity to 3.0 V averaged for both depolarizer systems was 3.39, 3.70, 3.83 and 4.10 A h for the Mn(25), Co(27), Ni(28) and Cu(29) phthalocyanines, respectively. The average capacity of the control cells was 3.72 A h.

Although both NiPc and CuPc improved the capacity of Li/SOCl₂ cells, far better capacity and voltage improvement was reported in laboratory cells discharged at higher current densities [3].

Effect of MPc catalysts – stored cells

The data in Table 3 show the average cell performance of the five MPc catalysts after 30 days storage at 70 °C. The cells were discharged at 1.5 Ω at ambient temperature. The data indicate that the addition of catalyst appears to increase the startup time in the SOCl₂ electrolyte system but with the exception of VOPc; this is not readily apparent in the mixed depolarizer

TABLE 3

The effect of various MPc catalysts on the average cell performance of C-size cells (A, B, C)* discharged at 1.5 Ω at ambient temperature after 30 days storage at 70 °C

	Startup time to 2.0 V (min)			Mid-discharge voltage (V)			Capacity to 2.0 V (A h)			Capacity to 3.0 V (A h)		
	A	B	C	A	B	C	A	B	C	A	B	C
Control	11	14	34	2.65	2.95	3.00	3.03	3.36	3.29	0	1.08	0.47
VOPc	30	221	268	2.10	2.55	2.45	2.45	2.84	2.93	0	0	0
MnPc	6	17	32	2.75	3.00	3.15	3.19	3.33	3.81	0.22	1.21	2.97
CoPc	48	37	49	2.20	2.75	2.95	2.89	3.33	3.53	0	0	0.2
NiPc	23	14	17	2.60	3.15	3.00	3.75	4.33	3.99	0	2.75	2.05
CuPc	65	34	35	2.57	3.15	3.05	3.61	4.52	3.99	0	3.09	2.49

*A = 100% SOCl₂, B = 60% SO₂Cl₂-40% SOCl₂, C = 70% SO₂Cl₂-30% SOCl₂.

systems. The mid-discharge voltage appears to be improved by the use of the mixed depolarizer rather than by benefit of any catalyst. There was no benefit in cell capacity from the MnPc or CoPc in either the SOCl₂ system or the 60/40 mixture. However, the MnPc enhanced the performance of the 70/30 mixture. The NiPc and CuPc catalysts improved the cell capacity and voltage regulation of both mixed depolarizer systems. It is anticipated that the catalytic benefits on cell performance would be still further enhanced at lower temperatures. Additional studies are warranted at other LiAlCl₄ concentrations, current densities and carbon compositions. Studies at sintering temperatures other than 600 °C need to be investigated since it appears that the MPc catalytic behavior is dependent on the sintering temperature of the cathode [4]. The nature of the actual catalytic species formed as a result of thermal treatment is not well understood [6]. TGA studies indicate some MPcs decompose at higher temperatures [7] and some undergo polymorphic changes [8].

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