Organometallic compounds in lithium anode power sources*

O. A. Mashkin**, E. V. Kuzminsky** and **A. S. Ivanov**
Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR, 32/34 Prospect Palladina, 252680 Kiev 142 (U.S.S.R.)

Abstract

Methodical errors which may be made when evaluating inner resistance of the lithium power sources are analyzed. A correlation is suggested which permits determining sufficiently accurately the inner resistance at different stages of the discharge of power sources for electron equipment. The applicability of the correlation is shown in the example of the lithium elements CR-2325.

Introduction

Studies into the use of organometallic compounds in new generation power sources have been generalized.

Over the last few years the practical use of organometallic compounds (OMCs) has embraced a further field of applied chemistry, i.e., the most important aspect of electrochemical studies — lithium anode power sources (LAPS). Use of the organometallic compounds and, in particular, complexes of transition metals with macrocyclic ligands has allowed new, promising electrochemical systems to be considered and has considerably improved operational characteristics for a number of traditional systems. While for inorganic compounds a number of reviews comprehensively discuss the fundamental properties of cathode materials [1–3], data concerning the use of OMCs are, as a rule, only mentioned in passing in the corresponding sections of the reviews. Therefore, a review of the available data on the above-mentioned problem is timely and should prove to be useful.

---

*Paper presented at the 5th International Meeting on Lithium Batteries, Beijing, China, May 28–June 2, 1990.
**Author to whom correspondence should be addressed.

The study of OMCs for use in LAPS proceeds mainly in two directions: (1) the development of new cathode-active substances (CASs); (2) the improvement of traditional lithium systems.

Cathode-active substances based on organometallic compounds

The use of organometallic compounds as depolarizers of LAPS has only recently commenced. The possibility of using these substances as electrode materials in LAPS is due mainly to the availability of several functional groups in their structure that can facilitate electrochemical reactions. These functional groups are the central ion of the transition metal and the different groups of the ligand macro-ring (multiple azomethine, aromatic bonds, etc.). In the former case the reactions proceed in a manner analogous to electroreduction of metal ions in traditional inorganic cathode materials (oxides, phospho-trisulphides of transition metals, etc.). In this latter case the current-producing reaction is connected with electroreduction of the macro-ring multiple bonds (similar to the electroreduction of polyacetylene) and analogous to the reaction of electrochemical hydration. Such reactions for metal complexes were first described by Bush and co-workers on the tetraazamacrocyclic complexes of transition metals [4]. They have shown that electrochemical hydration of multiple azomethine bonds, with the formation of a saturated compound, occur in the proton environment. The presence of several functional groups in metal complexes that are reduced under different potentials defines the stage character of the electroreduction process; the first stage, as a rule, is reversible.

It has been shown by Jamaki and Jamaji, using X-ray structural analysis [5] that in the reaction on the macro-ring a break in the π-bonds does not occur, rather is there the formation of anion-radicals with an accumulation of lithium in the intermolecular spaces. The same authors have also described the use of OMCs as electrode materials in LAPs [6]. They determined the energy characteristics of phthalocyanine complex (MePc)-based cathodes (Table 1, Figs. 1, 2) and proposed the reaction mechanisms leading to their electroreduction. As is evident from the data presented in Table 1 and Fig. 2, such cathode materials possess a high specific capacity (up to 18 electrons per molecule, which is equivalent to 1500 A h kg^{-1} or 2300 W h kg^{-1}. The experimental data obtained support the supposition of not only the central metal ion electroreduction but also participation in the process of electro-reduction by the macro-ring.

This work has been further developed [7, 8] by the study of the electrochemical behaviour of a number of tetraazamacrocyclic complexes of copper and nickel as cathode-active substances (CASs) in LAPS. The specific energy characteristics of such cathode materials have been determined (Table 2). The interrelation of the realized specific capacity values with structural peculiarities of the complexes are shown in Tables 3 and 4. Complexes with a high degree of unsaturation, and with a minimum quantity of substituents,

TABLE 1

Discharge characteristics of cathodes based on phthalocyanine complexes
Final discharge voltage: 1 V

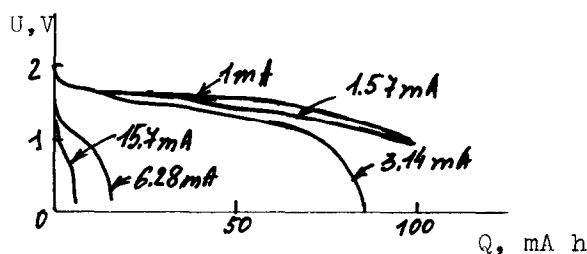| Cathode active substance	Discharge current, 0.3 mA cm^{-2}					
	Initial discharge voltage (V)	Average discharge voltage (V)	Specific capacity (A h kg^{-1})	Specific energy (W h kg^{-1})	Open circuit voltage (OCV) (V)	Specific energy (W h kg^{-1})
β-H$_2$Pc	1.7	1.4	870	1190	3.00	990
Li$_2$Pc	1.8	1.5	450	680	3.02	330
MgPc	1.8	1.5	800	1200	2.90	450
AlClPc	2.0	1.5	500	750	3.07	290
AlCl$_2$Pc	2.0	1.6	450	720	3.05	350
VOPc	1.8	1.5	700	1050	3.10	220
FCrPC	1.5	1.4	950	1330	3.10	530
MnPc	1.7	1.6	1400	2240	3.20	430
FePc	1.9	1.6	1440	2300	3.26	730
CoPc	1.9	1.8	850	1530	3.10	410
NiPc	1.6	1.3	1710	2220	3.12	370
α-CuPc	1.6	1.4	660	920	3.10	310
β-CuPc	1.6	1.4	700	980	3.15	340
γ-CuPc	1.7	1.5	600	900	3.10	530
ZnPc	1.5	1.3	800	1040	3.00	410
GaClPc	1.9	1.5	570	890	3.04	86
AgPc	2.0	1.5	450	680	3.07	240
CdPc	1.8	1.4	450	680	2.90	240
SnCl$_2$Pc	2.4	1.6	700	1120	3.05	600

Fig. 1. Discharge characteristics of the model of element Li/β-H$_2$Pc. Electrolyte: 1 mol dm^{-3} LiClO$_4$ in propylene carbonate.

in the macro-ring possess the highest energy characteristics. A mechanism for the electroreduction of such compounds has been studied using a number of spectrographic methods: a plan of the progression has been suggested (Fig. 3) [8]. The electroreduction of tetraazamacrocyclic complexes is also reversible at the first stage. Under these conditions the redox reactions proceed due to the change in the degree of oxidation of the central ion.

It has also been established that the processes of chemical and electrochemical reduction of the complexes proceed according to different mech-
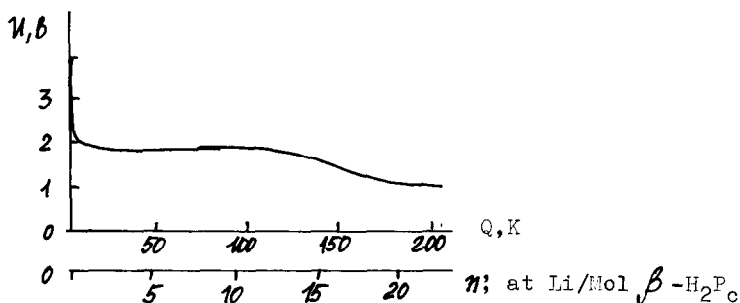
u, b

Fig. 2. Dependence of quasi-equilibrium potential of a β-H$_2$Pc-based cathode relative to lithium comparison electrode on the amount of interstitial lithium (Li atoms per molecule of complex).

TABLE 2

Discharge characteristics of cathodes based on tetraaza-macrocyclic complexes (References 7 and 8)

Cathode-active substance	Average voltage of a discharge (V)	Specific capacity (A h kg^{-1})	Specific energy (W h kg^{-1})
CuMe$_2$-14-diene^{2+}	1.60	330	527
CuMe-14-diene^{2+}	1.30	309	410
CuTd^{2+}	1.85	240	446
CuEt$_4$td^{2+}	1.34	170	228
CuMe$_4$-14-tetraene	1.44	420	604
CuTMTA	1.40	470	
CuTMTNf	1.83	220	402
Cu(en)$^{2+}$	1.70	130	220
CuPh^{2}da^{2+}	1.60	580	929
CuNfda^{2+}	1.65	370	610
CuMe$_4$-14-anN$_4$$^{2+}$	1.55	96	149
CuH$_8$TAAB^{2+}	1.35	238	307
CuH$_4$TAAB^{2+}	1.87	310	580
CuTAAB^{2+}	1.57	390	614
CoTAAB^{2+}	1.42	238	339
NiTAAB^{2+}	1.42	498	709

[a]ClO$_4$$^-$ was used as the anion in all cases other than for the complexes with a charge on the macro-ring.
[b]Concerning lithium electrode. Final comparison discharge voltage U_k 1.0 V. Discharge current, 0.1 mA cm^{-2}. Electrolyte: 1 M LiClO$_4$ in propylene carbonate.

anisms. This difference in the sequence of the electroreduction of tetraazamacrocyclic and phthalocyanine complexes is explained by their structural peculiarities. In the latter case, as a result of steric difficulties, the process of electroreduction begins from the ligand macro-ring. It has been proved that under deep electroreduction the process does not stop at the anion

TABLE 3

Dependence of specific energy characteristics of cathodes based on the complexes Cu TAAB^{2+} on the anion type
Discharge current 0.1 mA cm^{-2}

	Q calc. (A h kg^{-1})	Q exp.		A h kg^{-1}	
		to 0 V^a		to 1.0 V^a	
		Q exp. (A h kg^{-1})	%	Q exp. (A h kg^{-1})	%
Cu TAAB(ClO$_4$)$_2$	1349	1295	96	390	26
Cu TAAB(BF$_4$)$_2$	1402	1331	95	247	18
Cu TAAB Br$_2$	1433	1347	94	347	24
Cu TAAB(NO$_3$)$_2$	1518	1457	96	1235	81

^{a}Relative to lithium comparison electrode.

radical formation stage but can proceed, with the subsequent reduction of the π-bonds of a macro-ring, to compound destruction.

The possibility of using LAPS complexes of transition metals with basic organic ligands, e.g., with the Schiff bases as CAS, has also been discussed [9].

The mechanism of the electroreduction of these compounds by lithium has not been sufficiently studied. It is supposed that electrochemical reactions in such systems proceed by participation of the metal central ion and the C=N short bond.

2. Organometallic compounds as catalysts of electrochemical processes in LAPS

The use of OMCs in traditional lithium systems of LAPS is of comparatively recent origin, and has mainly involved the complexes of transition metals with phthalocyanine ligands. The initial consideration for such a study was that the complexes with phthalocyanine ligands would intensify the process of electroreduction of the depolarizer as a result of their catalytic activity.

Cathode polarisation by the reaction products restricts the current density, especially at high discharge rates. This is actually a function of reactant deposition within the pore structure and the subsequent increased diffusion resistance/active reaction site accessibility. The introduction of phthalocyanine complexes into current collector compositions increases the power density and useful output capacity at these power densities [12, 13]. In the first instance these studies were mainly concentrated on the empirical selection of impurities. It was established that tetra-[14]-azulene-based complexes [14], as well as phthalocyanine complexes of iron [15] and cobalt, possess the best catalytic activity, the former being preferentially used in the systems with thionyl chloride [16, 17] and the latter in the systems with sulfuryl

TABLE 4

Interrelation of structural parameters of MOC with energy characteristics of CM on their base

Affecting factor	Qualitative effect		Quantitative effect	
	Direct	Lateral	Change W (%)	Decrease (%)
Increase in the degree of oxidation	−	Appearance of the ballast mass of the anion	+(10–20) (depends on the anion type)	−
Increase in the number of multiple bonds:				
double (azomethine)	+	No	+54 per 1 bond	4–6
aromatic	+	No	+150 per 1 bond	15–20
Increase in the number of substituents in the side-chains				
aliphatic	−	Hampered restoration of macro-ring	−(20–60)	0–30
aromatic	−	No	−(10–60)	0–20
Appearance of a charge on a macro-ring	+	Hampered electro reduction of a macro-ring −	+(60–80)	0–35
Increase in the degree of chelation (macrocylic effect)	No	Appearance of the ballast mass −	−(20–40)	−

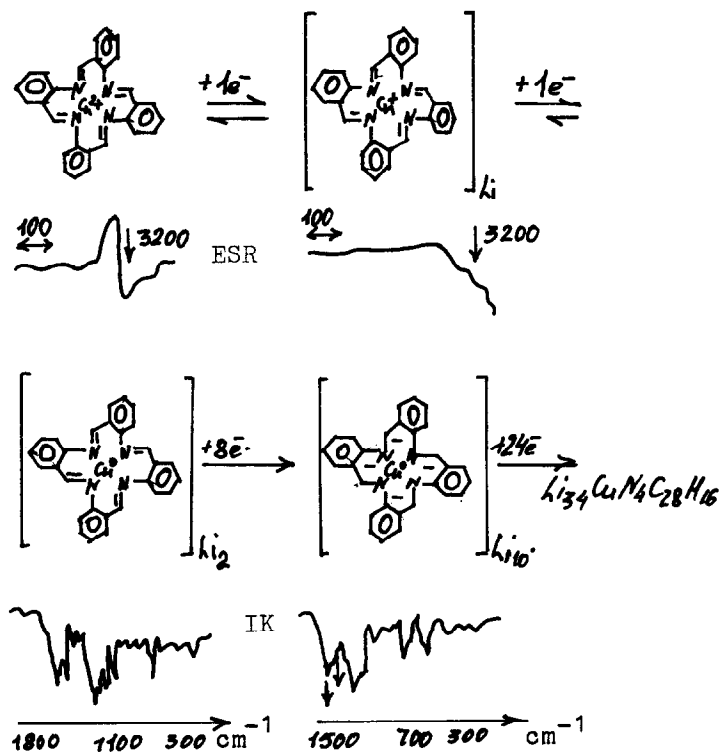Note: +, increase; −, decrease W.

Fig. 3. Scheme of the process of electrochemical reduction of a macrocyclic complex in a solid phase.

chloride [18]. Polymeric cobalt phthalocyanine offers further catalytic activity [19].

After adding the catalyst, the discharge duration increased by 20–50%, with a simultaneous increase in the discharge voltage by 100–450 mV, and at discharge currents increased by more than 3 times. It was established in further investigations that tetracarboxylated cobalt porphyrines [20, 21], complexes of cobalt, copper, and iron with tetracyanoethylene [22, 23], possess catalytic activity. At the same time vanadyl phthalocyanine (VOPc) does not possess catalytic activity [24].

It has been shown [25] that not only mono- but also binuclear complexes possess catalytic activity.

Comparative discharge characteristics of LAPs models with different concentrations of organometallic catalysts [15, 17, 21–23] are presented in Tables 5–8 and in Figs. 4–6. It follows from their analysis that at low current densities there is no significant difference in the behaviour of promoted and control solutions. When current densities are increased, especially in acid solutions, the cathode capacity and specific characteristics of LAPS rise considerably. There is no increase in voltage delay and capacity loss in consequence of storage of a LAPS with catalysed cathode.

TABLE 5

Volt–ampere characteristics of Li/SOCl$_2$ with different catalysts

Density of discharge current (mA cm^{-2})	Cell operating voltage (V)			
	Without catalyst	FePc	CoPc	(CoPc)$_n$
5	3.55	3.52	3.55	3.58
10	3.17	3.25	3.48	3.50
20	3.05	3.15	3.37	3.45
30	3.00	3.10	3.30	3.28
40	2.95	3.06	3.25	3.33

Electrolyte: 1.5 mol dm^{-3} LiAlCl$_4$ in SOCl$_2$. $t = 22.2$ °C.

TABLE 6

Volt–ampere characteristics of Li/SOCl$_2$ with different catalysts

Density of discharge current (mA cm^{-2})	Cell operating voltage (V)			
	Without catalyst	FePc	CoPc	(CoPc)$_n$
10	3.21	3.76	3.81	3.85
20	3.02	3.30	3.45	3.55
30	2.94	3.21	3.37	3.34
40	2.88	3.15	3.32	3.28
60	2.75	3.05	3.20	3.13
80	2.54	2.90	3.11	3.04

Electrolyte: 2.3 M AlCl$_3$ in SOCl$_2$. $t = 22.2$ °C.

TABLE 7

Energy characteristics of a model of Li/SOCl$_2$ containing a dopant of a polymeric complex of iron with ligand TCNE

No.	Polymer (%)	$U_{aver.}$ (V)	$I_{aver.}$ (mA cm^{-2})	Discharge capacity (A h cm^{-2})
1	0	3.01	30.1	27.0
2	0.92	3.22	32.2	62.7
3	3.66	3.25	32.5	71.0
4	3.89	3.18	31.8	56.3
5	3.89	3.24	32.4	89.4
6	17.4	3.28	32.8	61.8
7	25.1	3.27	32.7	85.4
8	26.7	3.25	32.5	57.8

Electrolyte: 1.8 mol dm^{-3} LiAlCl$_4$ in SOCl$_2$. $t = 25$ °C, $U_k = 2.0$ V, $R_{intr.} = 100$ Ω.

TABLE 8

Energy characteristics of the model of the element containing polymeric complex with ligand TCNE dopants

No.	Polymer (%)	$U_{aver.}$ (V)	$I_{aver.}$ (A cm^{-2})	Discharge capacity (A h cm^{-3})
1	0	3.01	30.1	27
2	1.14	3.15	31.5	64
3	2.60	3.22	32.2	69
4	4.31	3.19	31.9	70.6
5	5.28	3.24	32.4	76.6
6	6.47	3.18	31.8	62.2
7	15.4	3.24	32.4	53.3
8	37.1	3.23	32.3	65.3

Electrolyte: 1.8 M LiAlCl$_4$ + SOCl$_2$. $t_p = 25$ °C, $U_k = 2.0$ V, $R_{intr.} = 100$ Ω
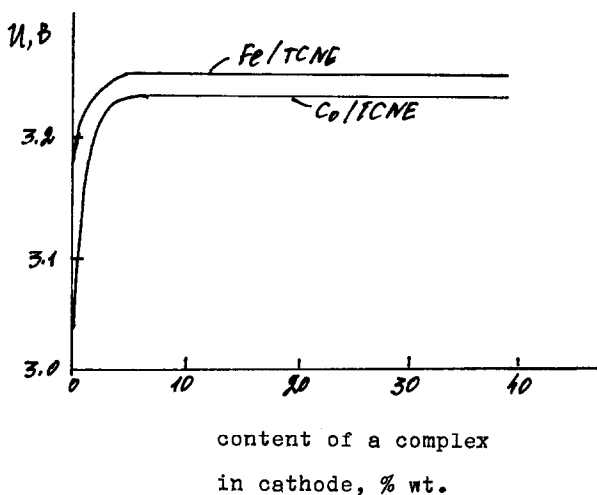
Fig. 4. Voltage dependence of the element Li/SOCl$_2$ model on the content in the cathode of cobalt and iron complexes with ligand TCNE. Electrolyte: 1.8 mol dm^{-3} LiAlCl$_4$ in SOCl$_2$; R_{intr}, 100 Ω; t, 25 °C.

It was then proposed to use phthalocyanine complexes to improve the discharge characteristics of LAPS, based on sulphur dioxide, and to dope the electrolyte solution using tetracarboxylated porphyrin or cobalt phthalocyanine in a thionyl chloride power source. The object was to decrease the passivation of the lithium electrode. The introduction of this doped electrolyte simultaneously with sulphur dioxide solution with a lithium tetrachloraluminate concentration of 1.4 mol cm^{-3} [26] appeared to be especially effective.

Under these conditions, the optimum concentration of the doping agent was approximately 0.05 mg l^{-1}. It is of interest to note that recent studies
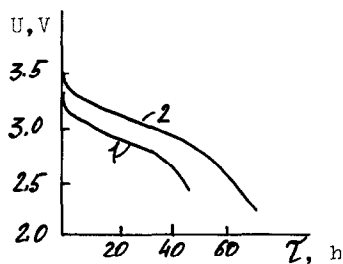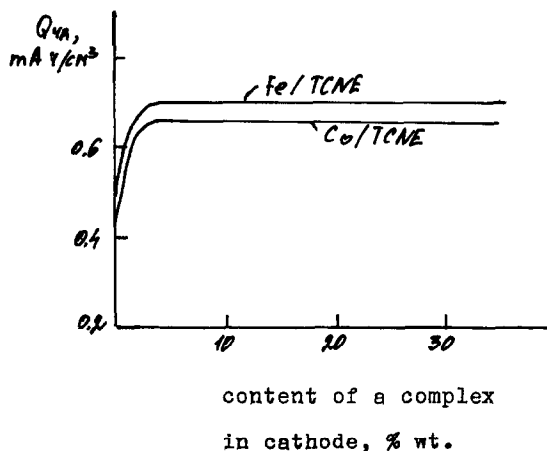
Fig. 5. Specific capacity dependence of the element Li/SOCl$_2$ model on the content in the cathode of cobalt and iron complexes with ligands TCNE. Electrolyte: 1.8 M LiAlCl$_4$ in SOCl$_2$; R_{intr}, 100 Ω; t, 25 °C; U_k, 2.0 V.

Fig. 6. Discharge characteristics of the elements Li/SOCl$_2$ models. 1, a model based on the base system; 2, the cathode of the model is promoted by the complex with dibenzotetraaza-[14]-anulene. Electrolyte: 1.8 M LiAlCl$_4$ in SOCl$_2$; R_{intr}, 300 Ω; $i_{av.}$, 10 mA; U_k, 2.5 V; $t=25$ °C.

involving MePc to decrease polarization further has demonstrated greater success in the electrolyte than when introduced to the cathode (respectively, 200 and 80 mV for FePc and 190 and 130 mV for CoPc) [27].
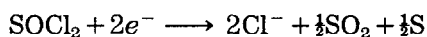
Mechanism of catalytic effect of phthalocyanines

The mechanism resultant from the catalytic effect of the phthalocyanine complex is not completely understood. In their first suppositions the authors drew from the fact that the analysis of the phthalocyanine-catalysed discharged cathode resulted in only 41% of the theoretically calculated lithium chloride being deposited, while the control cathodes produced values close to the theoretical. This fact, combined with the knowledge that the LAPS voltage decline under higher rate discharge in the systems studied is related to cathode polarisation by the lithium chloride film formed as a function of the reaction, allowed the authors to conclude that the introduction of phthalocyanine complexes changes the reaction mechanism of the thionyl chloride electroreduction, resulting in the formation of soluble or partially soluble products. Further study of these reactions, and comparison with the results obtained from copper or copper chloride-catalysed cathodes from the sulphuryl chloride system, suggested an attractive mechanism.
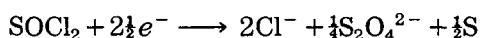
The discharge curve of sulphuryl chloride has two discharge plateaux, whereas only one plateau is observed for the system with catalysed cathodes [17]. Thus the authors deduced that not only sulphuryl chloride, but radicals such as SO$_2$Cl˙ formed during the discharge, were reduced on the active centres of the cobalt phthalocyanine complexes [17]. Electroreduction of

the $SO_2Cl^.$ radicals to sulphur dioxide and Cl^- ions occurs due to the overlapping of dz^2 electrons of cobalt and sp^3-orbitals of sulphur in SO_2Cl^- radicals.

To explain the effect of phthalocyanines catalysts on the electroreduction of thionyl chloride the authors [28] have developed Eager's concept, based on reduction by phthalocyanine–oxygen complexes. The authors argue that the thionyl chloride molecule interacts with cobalt phthalocyanine on the surface of the cathode, with partial charge transfer. Since electron pairs in thionyl chloride are arranged tetrahedrally, it can interact through sulphur p,π-orbitals with nonfilled d-orbitals of cobalt and other transition metals, and this results in the formation of adducts of the phthalocyanines of transition metals and thionyl chloride, and in weakening the sulphur–chlorine bond in the molecule. Such an interaction simplifies the electron transfer from cathode to adduct and the two-electron reduction of thionyl chloride. However, according to the authors [12], in the presence of cobalt phthalocyanine the total number of reacting electrons increases to 2.5, and it would be more correct to describe the process of electroreduction not by a traditional equation:

$$SOCl_2 + 2e^- \longrightarrow 2Cl^- + \tfrac{1}{2}SO_2 + \tfrac{1}{2}S$$

but by:

$$SOCl_2 + 2\tfrac{1}{2}e^- \longrightarrow 2Cl^- + \tfrac{1}{4}S_2O_4{}^{2-} + \tfrac{1}{2}S$$

We consider such a supposition doubtful. It is considered more probable that in a given case, an immediate electroreduction of cobalt phthalocyanine by lithium occurs. This is in agreement with the data of Jamaki and Yamaji [6] that indicate an increase in the lithium atoms participating in the reaction (OCV pairs CoPc lithium-3.1 V). The concentration distribution of the chloride formed with cathode thickness in the process of element discharge proves informative. Figure 7 shows the dependence of the ratio Cl/Al on the electrode thickness at different states of discharge ($1/4C$. $1/2C$, $3/4C$ and a complete discharge). The results unambiguously show that thionyl chloride reduction occurs at the commencement of discharge. The reaction profile changes with time as the reaction zone penetrates the cathode. This can be connected either with de-activation of catalytically active areas or with increase in matrix resistance because of swelling (action by both factors is possible). The observed minima on the curves $C(1/2)$ and $C(3/4)$ are associated with the different relations between the matrix and the electrolyte. At the end of discharge, the reaction limitation is again localized near the electrode/electrolyte interface as a result of swelling of the electron matrix, impairing mass transfer processes.

It is of interest to note that the passivating film formed on the cathode apparently has a higher electron conductivity than that in the system without the catalyst.

Synthesis of metal complexes used in CCS

Since OMCs, as used in LAPS, are a relatively new class of substances and, in addition to their energy characteristics, depend on their method of
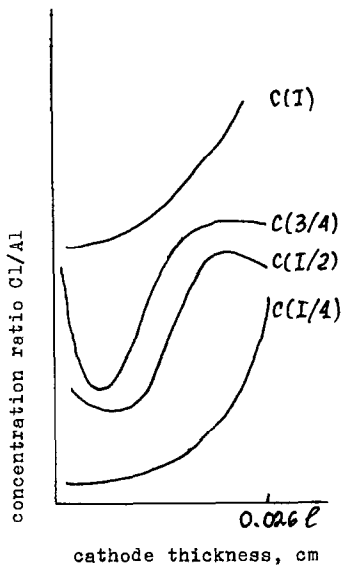
Fig. 7. Diagram of distribution of chloride concentrations with cathode thickness at different stages of the element discharge.

synthesis, we have considered it expedient to pay some attention to the problems of synthesis of the most widely used complexes.

The complexes with polytetracyanethylene are synthesized in cyclohexane solutions, adding the corresponding amounts of acetylacetonate of the corresponding metal to tetraethylene. Water micro-impurities serve as catalysts to the reaction of complex formation [21].

Mononuclear complexes of phthalocyanines are synthesized from salicylaldehyde and phenylenediamine. Binuclear complexes are obtained from methyl isophthalaldehyde and 1,3-diaminopropane in alcohol solutions in the presence of salts of the corresponding metals [25].

The synthesis of the polymer phthalocyanine complex is usually performed by pyrolysis at temperatures of 500–850 °C [29]. It was suggested that this process could not take place on pure phthalocyanine but that the cathode should be manufactured in the presence of soot and a binder. The complex content in a cathode may change within the limits of 0.5–20 mass% soot content. The optimal amount of dopant is 5–10 mass% [29].

The experimental material from many authors concerning both the specific energy characteristics of OMCs and the influence on the electroreduction mechanism shows the practical value of this class of compounds as electroactive substances of primary and secondary LAPS. Their use would be of value in the creation of new cathode materials and for the improvement of traditional lithium systems.

Reference

1 W. Fischer, in *Handbook of Thermodynamics and Transport Properties of Alkali Metals*, *Oxford*, *1985*, p. 181.
2 M. Hughes, N. Hampson and L. Karunathilaka, *J. Power Sources*, *12* (1984) 83.
3 T. Krompton, *Primary Current Sources*, M. Mir, Moscow, 1986, p. 328.
4 N. Takvoryan and K. Farmary, *J. Am. Chem. Soc.*, *96* (1974) 731–742.
5 J. Yamaki and A. Yamaji, *J. Electrochem. Soc.*, *129* (1982) 5–9.
6 J. Jamaki, *U.S. Patent 4 251 607* (Jan. 2, 1980).
7 A. Gorodyskii, Y. Kuzminskii and O. Mashkin, In: *Proc. 11th Coordination Chemistry Conf. Smolenice, CSSR, June 2–5, 1978*, p. 83.
8 O. A. Mashkin, E. V. Kuzminsky and A. V. Gorodysky, *Dokl. Akad. Nauk SSSR, Ser. B, N II* (1987) 48.
9 H. Fizger, *F.R.G. Patent 3 247 309* (June 30, 1983).
10 E. Yeager, *J. Electrochem. Soc.*, *128* (1981) 160.
11 I. A. Kedrinsky, V. E. Dmitrenko, Yu. M. Povarov and I. I. Grudyanov, Khimicheskie istochniki toka s litievym elektrodom (Chemical current sources with lithium electrode), *Krasnoyarsk: Izdatelstvo Krasnoyarskogo universiteta*, 1984, p. 248.
12 V. Hanumanthiya, *Br. Patent 2 073 940* (Oct. 21, 1981).
13 F. Walsh and M. Yaniv, *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9–14, 1983.*
14 R. Scott, *Europ. Patent 14 1209* (June 15, 1985).
15 G. Eichinger and G. Semran, in *3rd Int. Meet. Lithium Batteries, Kyoto, Japan, May 27–30, 1986*, p. 61.
16 J. Hesaywell, *U.S. Patent 4 252 875* (Feb. 24, 1981).
17 N. Doddapaneli, in *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9–14, 1983.*
18 C. Schlaikjer, *J. Power Sources*, *14* (1985) 111.
19 N. Doddapaneni, *U.S. Patent 4 405 693* (Sept. 20, 1983).
20 T. Nippon, *U.S. Patent 4 251 607* (Feb. 17, 1984).
21 R. Gary, *EPV 0 143 937* (June 12, 1985).
22 H. Kadzuya, *Japan Patent 60-49567* (Mar. 18, 1985).
23 A. Keith, *U.S. Patent 4 452 872* (June 5, 1984).
24 V. P. Pankratov and V. A. Mozalevskaya, *Theses of Reports of VII All-Union Conf. on Electrochemistry, Chernovtsy, 1989*, Vol. 1, p. 167.
25 N. Doddapaneni, *U.S. Patent 4 710 437* (Dec. 1, 1987).
26 N. Doddapaneni, *U.S. Patent 4 698 283* (Oct. 6, 1987).
27 A. G. Sergeev and O. V. Volyansky, in *Theses of Reports of VII All-Union Conf. on Electrochemistry, Chernovtsy, 1988*, Vol. 1, p. 107.
28 S. Szpak and H. Venketasetty, in *Proc. 13th Int. Power Sources Symp., Brighton, U.K., 1982*, Vol. 9. p. 403.
29 N. Doddapaneni, *Europ. Patent 0057986* (Aug. 18, 1982).