

Influence of macrocyclic compounds on the electrochemical reduction of thionyl chloride at glassy carbon cathodes

O. A. Baturina, L. S. Kanevsky, V. S. Bagotzky*, V. V. Volod'ko, A. L. Karasev and A. A. Revina

A. N. Frumkin Institute of Electrochemistry, Academy of Sciences of the USSR, 117071 Moscow (U.S.S.R.)

(Received February 20, 1991)

Abstract

The specific features of electrochemical reduction of thionyl chloride were studied on a smooth glassy carbon electrode in the presence of tetraphenylporphyrins (TPP) or tetra(*p*-methoxyphenyl)porphyrins (TMPP) of copper, manganese, iron, nickel, cobalt and also of metal-free TPP and TMPP. In the presence of metal-free porphyrin and its metallo complexes the potential of the maximum on voltammograms shifts markedly in the positive direction. Introduction into the solution of FeTPP, CoTPP and NiTPP leads to an increase of the maximum current on cyclic voltammograms. The amount of electricity necessary for electrode passivation also changes thereby. This indicates that the role of porphyrins in the SOCl_2 electroreduction is due both to electrocatalytic action and to changing the electrode passivation conditions. With the use of a combination of spectroscopic methods (electron absorption and ESR spectra) it has been found that thionyl chloride interacts chemically with the porphyrins. These chemical interaction products act as catalysts of SOCl_2 electroreduction.

The possibility of using various catalytic additives to improve the performances of lithium/thionyl chloride cells is the subject of ever increasing attention [1]. Methods for improving the discharge voltage and discharge time by introduction of macrocyclic compounds, including phthalocyanines and porphyrins [2, 3], are available, but their mechanism is not well understood as yet. Investigating the cathodic reduction of thionyl chloride SOCl_2 at a glassy carbon cathode Madou *et al.* [4] noted a shift of the electrode steady-state potential upon addition of iron and cobalt phthalocyanines into the electrolyte. According to refs. 5–7, in the presence of iron phthalocyanine the reduction mechanism of SOCl_2 undergoes a change, in particular, a larger number of electrons participates in the reaction, i.e. the degree of cathodic reduction of thionyl chloride increases. It was established in ref. 8 that iron phthalocyanine affects the formation conditions of the reaction products deposits on a carbon black cathode and also their morphology and appearance.

For a detailed investigation of the effect of porphyrins on SOCl_2 reduction, this process was studied in solutions containing tetraphenylporphyrins (TPP)

*Author to whom correspondence should be addressed.

or tetra(*p*-methoxyphenyl)porphyrins (TMPP) of copper(II), manganese(III), iron(III), nickel(II), cobalt(II) and also metal-free TPP and TMPP (H_2TPP and H_2TMPP).

The reduction of $SOCl_2$ was studied on a smooth glassy carbon cathode in a three-electrode cell. The working electrode was the rear end of a glassy carbon rod (SU-20), 2.3 mm in diameter, pressed into a Teflon mandrel. To obtain reproducible results, before plotting each polarization curve the rear end of the glassy carbon rod was ground by coarse ($28\ \mu m$) emery cloth and then carefully polished to mirror finish with fine ($2\ \mu m$) emery cloth, washed with ethanol and dried under vacuum. The reference and the auxiliary electrodes were obtained by pressing metallic lithium into glass tubes (5–6 mm in diameter) followed by cutting off the rear end of the pressed lithium in argon. The preparation of lithium electrodes for operation and assembly of the cell was performed in a glove box in dry argon (moisture content less than 15 ppm). The base electrolyte used was a 1 M $LiAlCl_4$ solution in twice-distilled $SOCl_2$, prepared by successive dissolution of thoroughly dried twice-recrystallized lithium chloride and high purity aluminium chloride, obtained by zone melting. All investigations were performed at room temperature.

Figure 1 shows cyclic voltammograms obtained on glassy carbon without additives and in the presence of different TPP (all potentials are referred to the reversible lithium electrode in the same solution). As can be seen from the Figure, the reduction of $SOCl_2$ in the absence of additives is described by a curve with a clearly defined current maximum i_p at the potential E_p of about 2.75 V. The current drop at less positive potentials seems to be due to passivation of the electrode by lithium chloride [9].

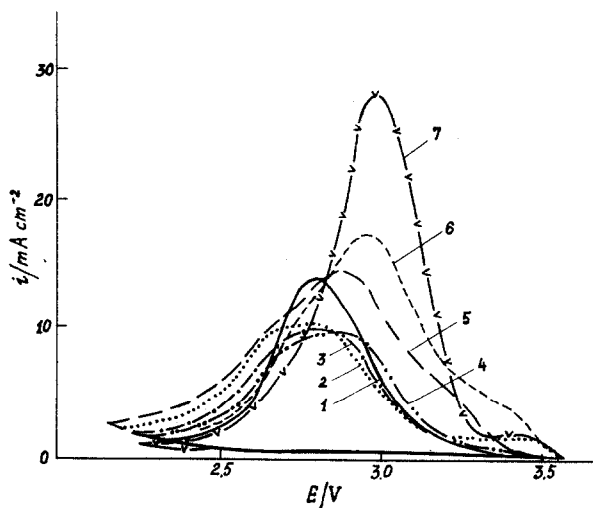


Fig. 1. Cyclic voltammograms plotted in 1 M $LiAlCl_4 + SOCl_2$ without (1) and with additions of 0.5%: 2, MnTPP; 3, CuTPP; 4, H_2TPP ; 5, FeTPP; 6, CoTPP; 7, NiTPP; $v = 0.1$ V/s.

Introduction into the solution of metal-free tetraphenylporphyrin and its metallo complexes leads to an increase of the maximum current i_p . In the presence of FeTPP, CoTPP and NiTPP the potential of the maximum E_p shifts markedly in the positive direction. The amount of electricity Q necessary for electrode passivation also changes thereby (see Table 1). For example, in the presence of NiTPP this amount is almost twice as much as in the solution without additives.

Since there is evidence in the literature that in the presence of electron-donor substituents the electrocatalytic activity of tetraphenylporphyrins increases [10], a study was made of various complexes of tetra(*p*-methoxyphenyl)porphyrins. The results show, against expectation, that introduction of methoxy groups into the benzene rings of porphyrins does not enhance the electrocatalytic effect of macrocyclic complexes.

Further studies were made mainly in solutions with NiTPP since in the presence of this compound SOCl_2 reduction at glassy carbon electrodes is most strongly intensified (see Fig. 1 and Table 1).

Figure 2 shows cyclic voltammograms in the presence of different amounts of NiTPP in the electrolyte. The potential of the maximum E_p of these curves does not depend on the porphyrin concentration (c) and the maximum current i_p increases monotonically with c up to $c=2\%$ (Fig. 3), a tendency being observed thereby for the i_p, c dependence to reach a limit.

The areas under curves 1–4, Fig. 2, correspond to $Q=0.050, 0.088, 0.122, 0.114 \text{ C/cm}^2$. Hence it follows that an increase in the NiTPP concentration over 1% is accompanied by a decrease in efficiency, which can be associated, for example, with the formation of large associates of nickel porphyrins in the electrolyte.

Figure 4 shows voltammograms in the presence of 0.5% NiTPP at different scanning rates v . The shift of E_p towards cathodic potentials with increasing v characterizes the irreversibility of the SOCl_2 reduction process. The dependences of i_p on \sqrt{v} for solutions without and with 0.5% NiTPP addition (Fig. 5) are both linear, but differ in slope. Similar features of these dependences were observed for thionyl chloride reduction at pyrographite cathodes in

TABLE 1

Characteristics of voltammetric curves of SOCl_2 reduction at smooth glassy carbon electrodes in 1 M LiAlCl_4 solution in SOCl_2 with addition of 0.5% macrocyclic compounds (scanning rate 0.1 V/s)

Type of macrocyclic compounds	E_p (V)	i_p (mA/cm ²)	Q (C/cm ²)
NiTPP	2.80	13	0.050
CoTPP	3.00	28	0.088
FeTPP	2.96	17	0.079
FeTPP	2.88	14	0.068
CuTPP	2.85	10	0.048
H ₂ TPP	2.80	10	0.042

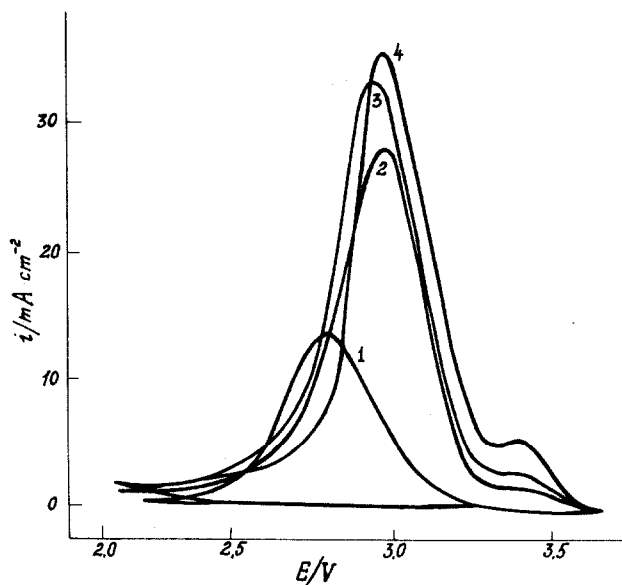


Fig. 2. Cyclic voltammograms plotted in 1 M $\text{LiAlCl}_4 + \text{SOCl}_2$ without (1) and with additions of NiTPP: 2, 0.5%; 3, 1%, 4, 2%; $v = 0.1$ V/s.

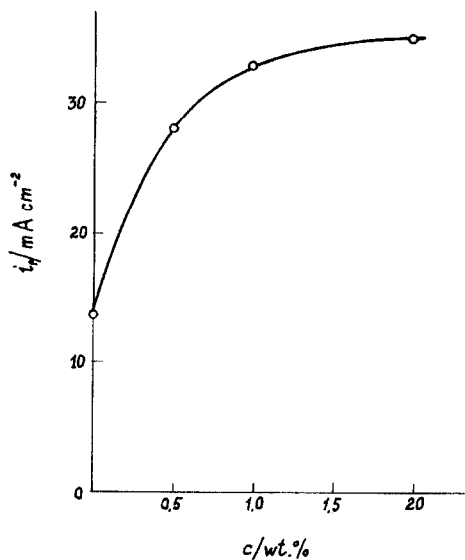


Fig. 3. Dependence of the maximum current i_p on NiTPP concentration in 1 M $\text{LiAlCl}_4 + \text{SOCl}_2$.

solutions without and with iron phthalocyanine (FePc) addition [11]. In interpreting these results the authors suggested that FePc alters the reaction path and it proceeds by a 2.5 electron mechanism — rather than by a 2 electron mechanism. A greater change in the slope of i_p , \sqrt{v} curves in the

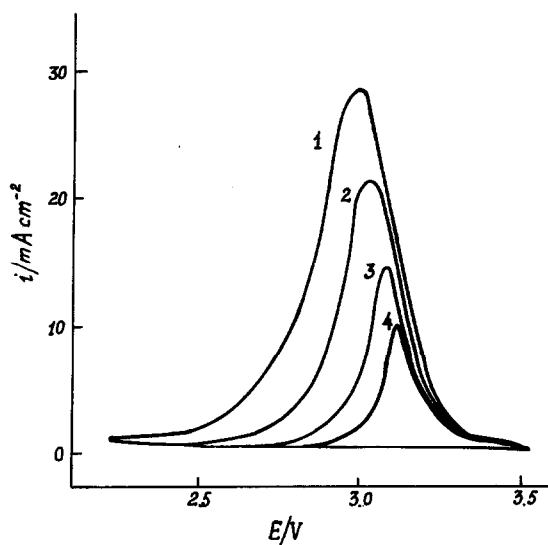


Fig. 4. Cyclic voltammograms plotted in 1 M $\text{LiAlCl}_4 + 0.5\%$ NiTPP + SOCl_2 at scanning rates v (V/s): 1, 0.01; 2, 0.02; 3, 0.05; 4, 0.10.

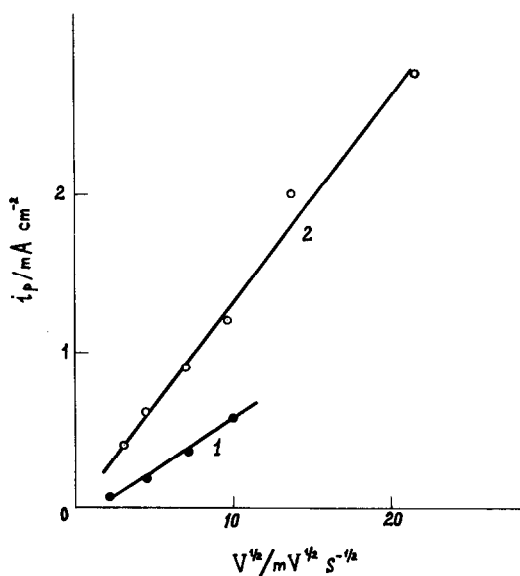


Fig. 5. Dependence of the maximum current i_p on \sqrt{v} in 1 M $\text{LiAlCl}_4 + \text{SOCl}_2$ (1) and 1 M $\text{LiAlCl}_4 + \text{SOCl}_2 + 0.5\%$ NiTPP (2).

case of NiTPP addition points to a different (than for FePc) mechanism and also to a greater efficiency of NiTPP in SOCl_2 electroreductions.

When a passivating film is formed on the electrode the effect of macrocyclic compounds may consist not only in a decrease of overvoltage or a change of the reduction mechanism, but also in a change of the formation conditions

of this film [8]. To separate these effects, steady-state polarization curves were plotted with the solution stirred by a magnetic mixer. Figure 6 shows such curves in solutions without (curve 1) and with 1% NiTPP and CoTPP addition (curves 2 and 3). As can be seen, curve 1 has no linear sections and the slope of the $E, \log i$ curve increases monotonically. Such a shape of the polarization curve can be associated with both the formation of a semiconducting film caused by interaction of SOCl_2 with glassy carbon [12] and the deposition of a lithium chloride film.

The presence of cobalt and nickel porphyrins in the solution results in a significant change in the shape of the polarization curve. Of particular interest is the fact that in the current density range above $0.06\text{--}0.10 \text{ mA/cm}^2$ linear sections with a slope of 120 mV can be found. This permits the following conclusions to be made: in the presence of porphyrins, the interaction of SOCl_2 with glassy carbon to form a semiconducting film is hindered; during measurements (2–3 min) with the solution being stirred, there is not enough time for the glassy carbon electrode surface to become passivated with reduction products; the slow step of the SOCl_2 reduction reaction in the presence of porphyrins can be considered to be the transfer of the first electron.

The mechanism of the effect of porphyrins on the passivation of glassy carbon electrodes needs special investigation. It may be assumed, in particular, that the functional groups on the glassy carbon surface act as axial ligands of macrocyclic complexes, which hinders both the formation of a deposit from SOCl_2 reduction products on the electrode and the interaction of SOCl_2 with glassy carbon to form a semiconducting film.

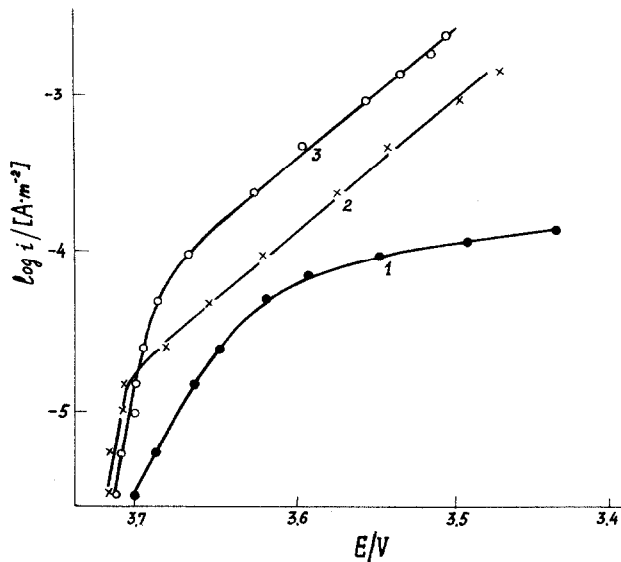


Fig. 6. Steady-state polarization curves obtained in solutions: 1 M $\text{LiAlCl}_4 + \text{SOCl}_2$ (1), 1 M $\text{LiAlCl}_4 + 1\% \text{ NiTPP} + \text{SOCl}_2$ (2) and 1 M $\text{LiAlCl}_4 + 1\% \text{ CoTPP} + \text{SOCl}_2$ (3).

The presence of linear polarization curve sections with a slope of 120 mV can lead to the suggestion that with the solution being stirred electrode passivation during SOCl_2 reduction by small currents might not occur until the whole electrolyte becomes saturated with lithium chloride. Direct verification of this presumption showed however that passing the current for a longer time leads to passivation and this occurs long before the solubility product of lithium chloride in the electrolyte bulk is reached. But the amount of electricity Q necessary for passivation at a given current density differs significantly in solutions without porphyrin and in the presence of 1% CoTPP and NiTPP. As seen from Fig. 7 the most significant increase of Q is observed in the solution containing NiTPP. The slowing down of passivation in the presence of CoTPP is much less significant.

Thus, when investigating the influence of macrocyclic complexes on SOCl_2 electroreduction, one should take into account two factors: the catalytic activity of the complex proper and its influence on electrode passivation. According to the data obtained in the present study, among the compounds studied, nickel tetraphenylporphyrin has the greatest effect on the reaction rate.

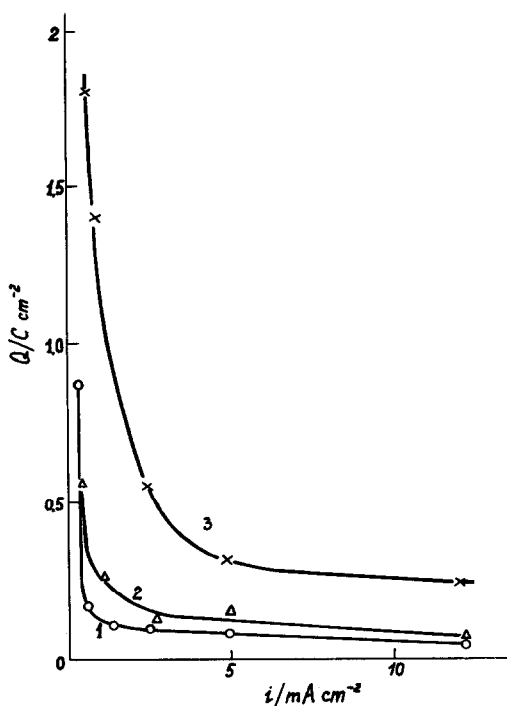


Fig. 7. Dependence of the amount of electricity Q necessary for electrode passivation on current density in solutions: 1 M $\text{LiAlCl}_4 + \text{SOCl}_2$ (1), 1 M $\text{LiAlCl}_4 + 1\%$ CoTPP + SOCl_2 (2) and 1 M $\text{LiAlCl}_4 + 1\%$ NiTPP + SOCl_2 (3).

The voltammograms 2–7 shown in Fig. 1 are characterized by the presence in the potential range 3.4–3.6 V of a wave preceding the reduction peak of SOCl_2 proper. This prewave appears only when the solution contains macrocyclic complexes. Figure 8 shows a cyclic voltammogram for this region in the presence of 1.2×10^{-2} M CuTPP. The potentials of the maxima on the cathodic and anodic branches of the curve differ by no more than 0.1 V. Analyses of the cathodic voltammograms plotted at different scanning rates v exhibit a linear dependence of the maximum current i_p on \sqrt{v} and the lack of dependence of the peak potential E_p on v . According to ref. 13, such features are characteristic for processes whose limiting step is the diffusion of reacting particles to the electrode surface. The proportionality between the value of i_p and the porphyrin concentration in solution suggests that the particle being reduced is either porphyrin itself or a product of its interaction with SOCl_2 .

Metal-free porphyrins and metallo complexes can both be electrochemically reduced [14], but are, probably, less strong oxidants than SOCl_2 , as evidenced by the fact that during the first day after the introduction of porphyrins into the thionyl chloride electrolyte the open-circuit potential shifts to more negative values. It is known [15] that cobalt, iron, chromium and manganese phthalocyanines react with SOCl_2 to form cation radicals, the metal and the π -electron system of the ligand can both undergo oxidation thereby. Tetraphenylporphyrins are also chemically oxidized to form cation radicals [16], but no evidence is available for the oxidation of tetraphenylporphyrin by thionyl chloride. To investigate the chemical interaction of these substances we measured the electron absorption and ESR spectra of these solutions.

The optical spectra of a 10^{-4} M NiTPP solution in SOCl_2 show a change with time of the electronic structure of NiTPP caused by its interaction with SOCl_2 . In the initial period after dissolution the NiTPP spectrum contains two characteristic absorption bands corresponding to NiTPP: the Soret band ($\lambda_{\text{max}} = 437$ nm) and a wide Q band ($\lambda_{\text{max}} = 547$ nm). In the course of time,

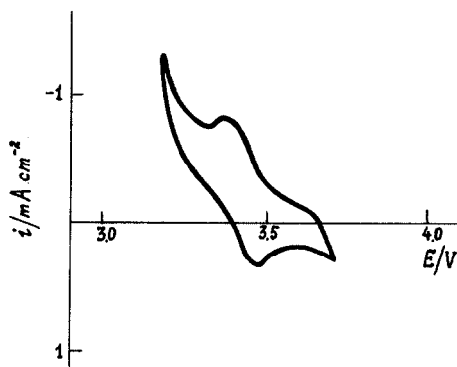


Fig. 8. Cyclic voltammograms plotted in 1 M $\text{LiAlCl}_4 + 1.2 \times 10^{-2}$ M CuTPP + SOCl_2 ; $v = 0.1$ V/s.

due to interaction with SOCl_2 , the initial NiTPP changes to the product P_1 which has a Soret band with $\lambda_{\text{max}} = 449$ nm. This product is relatively unstable and gradually is transformed into another product P_2 for which the Soret band has a maximum already at 481 nm, and the Q band is ill-defined. The half-transformation time of the initial NiTPP to product P_2 under given conditions was about 100 h and the process reached completion in about 220–250 h from the moment of porphyrin dissolution in SOCl_2 . An increase of the NiTPP concentration in the solution led to an increased time of its transformation to products P_1 and P_2 . Thus, for a 10^{-2} M NiTPP solution, the time of its complete transformation to product P_2 is about 500 h.

The shape of the ESR spectrum of the 10^{-2} M NiTPP solution in SOCl_2 varies with time from the moment of its preparation. In 1–3 h after dissolution the solution spectrum consists of two singlet lines ($g_1 = 2.00604$, $g_2 = 2.0108$), after 24 h only one singlet (g_1) remains; thereby the value of its g factor increases to 2.00670 and its intensity passes through a maximum. Thus, the structure of the ESR spectrum of an NiTPP solution in SOCl_2 and the concentration of paramagnetic centers vary with time. This indicates that the dissolution process involves irreversible chemical changes in the system. Due to absence of a superfine structure, it is not possible to identify unambiguously the obtained signals, but their g factors differ considerably from those of oxidized NiTPP forms known from the literature [17]. It is highly probable that the singlet with $g = 2.00670$ belongs to the SOCl_2 reduction product – the free radical SOCl^\cdot .

The cyclic voltammetric curves plotted in fresh solutions and in those stored for a long time showed that in the latter the effect of NiTPP on the cathodic SOCl_2 reduction increases considerably; in particular, the amount of electricity on the cathodic branch of the curve is much greater. This indicates that as the system undergoes 'ageing', the content of chemical interaction products of tetraphenylporphyrin and thionyl chloride, which act as catalysts of SOCl_2 electroreduction, increases. It can be assumed that the catalytic activity of these products is based on their acting as mediators.

References

- 1 A. J. Hills and N. A. Hampson, *J. Power Sources*, 24 (1988) 253–272.
- 2 N. Doddapaneni, *J. Electrochem. Soc.*, 132 (1984) 344c.
- 3 N. Doddapaneni, *US Patent 4 613 551* (1986).
- 4 M. I. Madou, I. I. Smith and S. Szpak, *J. Electrochem. Soc.*, 134 (1987) 2794–2798.
- 5 N. Doddapaneni, *Proc. 30th Power Sources Symp., Atlantic City*, The Electrochem. Soc. Inc., Pennington, NJ, 1982, pp. 169–171.
- 6 H. Janke, M. Shanborn and G. Zimmermann, *Top Current Chem.*, 61 (1976) 135–137.
- 7 F. Walsh and M. Yaniv, in J. P. Gabano (ed.), *Proc. Symp. Lithium Batteries*, Publ. 84-1, The Electrochem. Soc. Inc., Pennington, NJ, 1984, pp. 103–110.
- 8 I. I. Smith, S. Szpak and W. A. West, in L. J. Pearce (ed.), *Power Sources 11*, Taylor and Francis, Basingstoke, U.K., 1987, pp. 243–254.
- 9 K. Behl, *Proc. 27th Power Sources Symp., Atlantic City*, The Electrochem. Soc. Inc., Pennington, NJ, 1976, pp. 30–33.

- 10 S. A. Pobedinskii, A. A. Trofimenko and S. I. Koifman, *Izv. VUZov, Khimia i khim. tehnologija*, 31 (1988) 67–69.
- 11 N. Doddapaneni, *Proc. Symp. Chemistry and Physics Electrocatalysis*, Publ. 84-12, The Electrochem. Soc. Inc., Pennington, NJ, 1984, pp. 630–634.
- 12 N. I. Chakhov, Yu. M. Povarov and Yu. V. Pleskov, *Electrokhimiya*, 16 (1980) 1445–1449.
- 13 Z. Galus, *Fundamental Principles of Electrochemical Analysis*, Pol. Sci. Publ., Warsaw, 1976, p. 520.
- 14 M. R. Tarasevich and K. A. Radyushkina, *Catalysis and Electrocatalysis by Metalloporphyrins*, Nauka, Moscow, 1981, pp. 167 (in Russian).
- 15 I. F. Muers, G. W. R. Ganham and A. B. P. Lever, *Inorg. Chem.*, 14 (1975) 461–468.
- 16 A. P. Bobrovskii, N. P. Eletsii and V. I. Titov, *Theoret. i exp. khimija*, 12 (1976) 826–829.
- 17 A. Wollerg and J. Manassen, *J. Am. Chem. Soc.*, 92 (1970) 2982–2993.