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Carbon electrodes with phthalocyanine catalyst in acid medium

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The catalytic properties of polymeric phthalocyanines with Fe and Co as central atoms for the electroreduction of oxygen in 0·5–2·3 M H_2SO_4 were studied. No noticeable dependence of the electrode potential on the concentration of H_2SO_4 was found. The electroactivity of the catalyst with a central Fe atom undergoes considerable deterioration under the given conditions, whereas the stability of the catalyst with a central Co atom is very good and the potential of an electrode containing 30% catalyst in the active mass is 100 mV more positive than that of an electrode with 13% platinum, both at 40 mA cm^{-2}. The electrode performance depends markedly on the sort of carbon substrate, showing a parallelism with respect to oxygen electrodes in alkaline medium. The gold mesh current collector can be replaced by the addition of carbon black to the active layer.

1. Introduction

The use of phthalocyanine derivatives and similar organic N_4 macrocycles in the electrocatalysis of oxygen reduction, especially in acid media, was no doubt motivated by biochemical analogies arising from the necessity to completely eliminate hydrogen peroxide whose presence is noxious both in living organisms and in the pores of oxygen electrodes. Hydrogen peroxide, a cellular toxin for living organisms, is decomposed by the enzyme catalase [1]. Tobler [2], in his study of active carbon electrodes for oxygen in acid and alkaline media, used (intentionally) catalysts of a catalase-like structure. Brdička [3, 4] found a catalytic effect of haemin and haemoglobin on the polarographic reduction of hydrogen peroxide, and a catalytic effect of haemin on the reduction of peroxide and oxygen on carbon electrodes.

In addition to an efficient decomposition of hydrogen peroxide, a four-electron reduction of oxygen is also desirable for good performance of the oxygen electrode. Catalase has a favourable influence on the polarographic reduction of oxygen [5–7], where (in contrast to haemin, in which case the peroxide reduction wave remains separated) the limiting current due to reduction of oxygen to peroxide increases at the expense of the limiting current due to reduction of peroxide to water. The same effect was reported [8] with phthalocyanine in the medium of methyl alcohol and lithium hydroxide.

Organic N_4 macrocycles have been used in the reduction of oxygen on porous electrodes at current densities of several tens of mA cm^{-2} since 1964, when Jasinski [9, 10] introduced phthalocyanine with a central Co atom in the electroreduction of oxygen in alkaline medium. It is remarkable that in the same medium an increased catalytic activity of active carbon heated in a stream of ammonia [11, 12] or activated with salmiac [11] had already been observed and later substantiated in both alkaline [13–15] and acid [16–18] media. This effect can be attributed, in our opinion, to the catalytic activity of nitrogen macrocycles formed on the active carbon surface, which always contains traces of iron functioning as a central atom in the organic complexes. Later, the catalytic effect of phthalocyanine has been further studied [18–27] and other analogous complexes have been proposed for the same purpose [28–30].

The present work deals with a study of polymeric phthalocyanine complexes, especially with regard to their stability in acid medium, since low stability has been reported [33] for certain N_4 chelates.

2. Experimental

Polymeric phthalocyanines of Fe(II) and Co(II) (which for convenience will be designated as FePc and CoPc) were prepared by melting a mixture of pyromellitic acid di-anhydride, urea, the corresponding metal sulphate, and ammonium molybdate as catalyst according to the modified method of Drinkard and Baillard [31]. The product was purified by extraction with water, pyridine and acetone in a Soxhlet apparatus and recrystallized twice by diluting its solution in concentrated sulphuric acid with water and washing the precipitate with water until it reacted only weakly acidic. The polymerization degree was determined on analogously prepared samples by the method of gel chromatography [32] to be 14–16.

The catalyst was supported on Norit FNX type active carbon, on which the phthalocyanine was precipitated from concentrated H_2SO_4. The suspension was washed with water to attain a weakly acidic reaction and dried. The content of catalyst in percent given in this work is referred to the dry active carbon-catalyst mixture. In some cases, a -60 μm fraction of G-1000 type active carbon (Hrušov Chemical Works) and a -60 μm fraction of spectral carbon (prepared by grinding rods of spectral graphite manufactured by Elektrokarbon, Topolčany) were used. The active mass for the electrodes consisted of the active carbon with the deposited catalyst and 10% Teflon. The conductivity of some electrodes was improved by the addition of Philburgin acetylene black. Disk-shaped electrodes, 31 mm in diameter and about 1 mm in thickness (70 mg of active mass per cm^2) were made by pressing the active mass supported on a gold gauze (0·3 mm in thickness, mesh size 2 × 2 mm), which served as a current collector. The electrode was kept in a Plexiglass holder provided with a gas compartment and was fed with oxygen at 15 cm H_2O overpressure. The free geometric surface area of the electrode in the holder (exposed to current) was 5 cm^2.

Electrochemical measurements were made in a half-cell arrangement. The electrode with the holder and a Pt counter electrode were placed in an electrolytic vessel filled with 2·3 M H_2SO_4. Potentials were measured against a $Hg|Hg_2SO_4$ reference electrode in the same electrolyte. The test electrodes were subjected to a constant current of 10 mA cm^{-2} for 150 h; polarization curves were recorded after 6 and 150 h in a stepwise manner so that the potential was read 2 min after every change of the current by 5 mA cm^{-2}. An average was taken from the readings obtained whilst the current was increased from 0 to 40 mA cm^{-2} and back again.

3. Results and discussion

In preliminary experiments, the role of the Teflon concentration, pressing pressure and amount of active material per 1 cm^2 was studied. The role of the Teflon concentration is not too critical; from the point of view of the electrical conductivity and technology of the electrode, 10% Teflon content was chosen as optimum. With increasing pressing pressure the mechanical strength and electrical conductivity of the electrode improves but the mass transport in the gas pores becomes more hindered. Consequently, an optimum pressing pressure of 430 kp cm^{-2} was chosen. With regard to the electrode performance the smallest amount of active mass was 70 mg cm^{-2} at the given pressing pressure, Teflon content and gold mesh collector.

Changes of sulphuric acid concentration from 0·5 to 2·3 M cause only small changes of the electrode potential due apparently to changing electrolyte conductivity so that the form of *E-t* curves remains the same. The stability of the CoPc catalyst is apparently not affected by changing the acid concentration in the given range. To obtain a higher conductivity, 2·3 M H_2SO_4 was used throughout.

Since the activity of the phthalocyanine catalyst is determined by the central atom, the properties of the oxygen cathode with FePc and CoPc polymers were studied. The catalytic activity of the former is higher but decreases rapidly with time since this complex is not

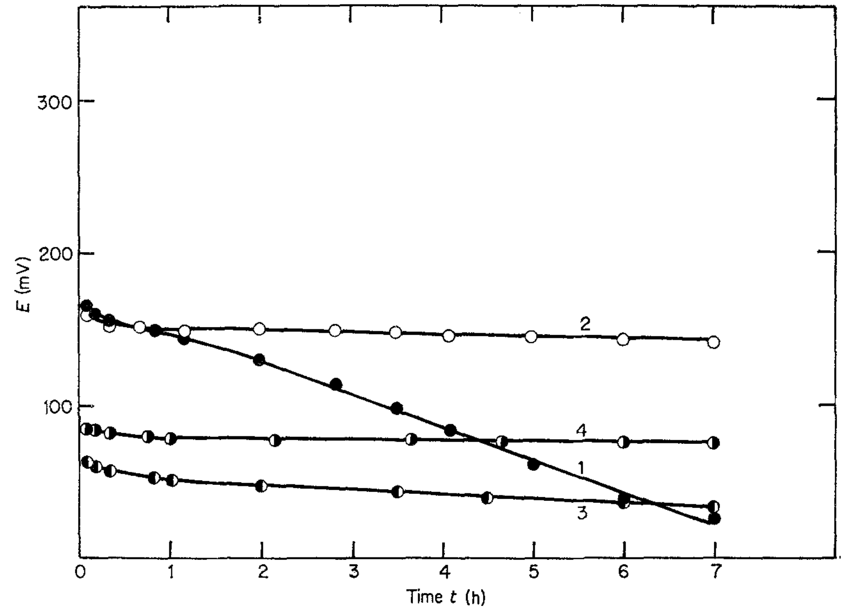

Fig. 1. *E-t* Curves from 0 to 7 h. 1, 10% FePc; 2, 50% FePc; 3, 10% CoPc; 4, 50% CoPc.

stable; in acid media the central Fe(II) is dissolved and replaced by protons [21]. The resulting phthalocyanine without the central metal atom undergoes hydrolysis [32]. The activity of the CoPc polymer is smaller but its stability in acid media is very good. *E-t* curves for electrodes with 10% and 50% FePc and CoPc charged at 10 mA cm^{-2} are shown in Fig. 1. With 10% catalyst, the higher activity of FePc was observed only during 6 h, then the decrease of activity prevails and the electrodes with CoPc are distinctly better. This difference is even more apparent from Fig. 2. In spite of the pronounced decrease of activity, especially

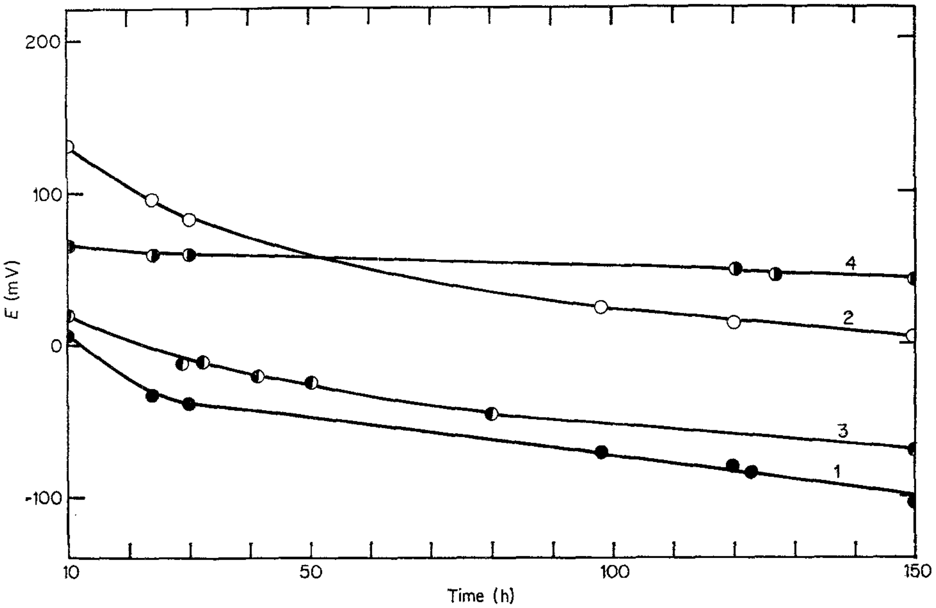

Fig. 2. *E-t* Curves from 10 to 150 h. 1, 10% FePc; 2, 50% FePc; 3, 10% CoPc; 4, 50% CoPc

with electrodes containing 10% FePc, the activity of electrodes with the catalyst is higher than without the catalyst (Fig. 3, curve 1). With electrodes containing 50% catalyst, the higher activity of FePc was observed during 50 h.

Because of the better stability of CoPc, this catalyst was used exclusively in further experiments. Polarization curves for electrodes containing increasing amounts of CoPc as well as for those with a Pt catalyst and with pure substrate are shown in Fig. 3. Best results were obtained with electrodes containing 30% CoPc; their potential was, at 40 mA cm^{-2}, more than 100 mV higher than for electrodes with platinized carbon. These electrodes represent an optimum compromise between the contents of the substrate and catalyst; increasing content of the catalyst results in an increase of activity but at the same time a drop in conductivity and porosity since the porous active carbon particles enabling transport of electrolyte are replaced by nonporous particles of the catalyst. Thus, with 50% CoPc the negative influence of the smaller conductivity and porosity prevails. On the contrary, with 10% CoPc a shortage of the catalyst is noticeable. The specific load of the catalyst is in this case too high. With the Pt catalyst, a moderate shift of potential to more positive values was observed, due apparently to progressive wetting of the electrode, the activity of the Pt catalyst being unchanged. These results are illustrated in Fig. 4.

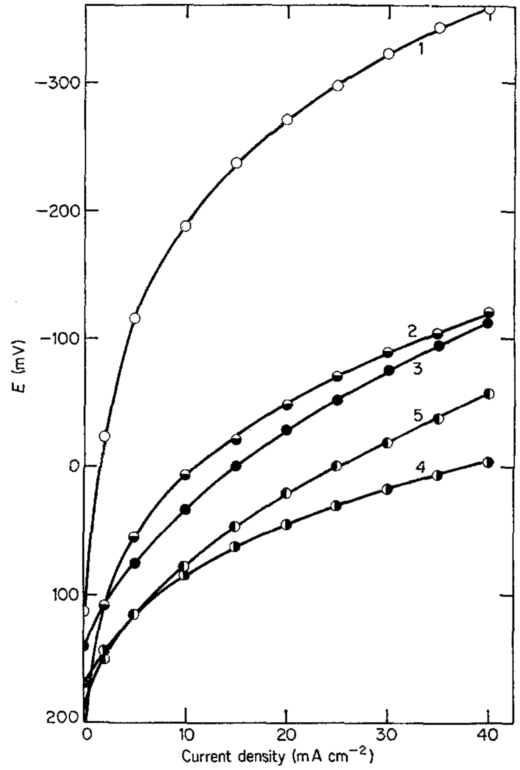

Fig. 3. Influence of type and amount of catalyst on polarization curves of carbon cathode. 1, Norit FNX; 2, 14% Pt; 3, 10% CoPc; 4, 30% CoPc; 5, 50% CoPc.

The effect of the catalyst substrate is apparent from Figs. 5 and 6 which show polarization curves for pure substrates and with 10% CoPc. A parallelism between the electrochemical activity of the substrate in acid and alkaline media was observed. It is obvious that the activity of the electrode is determined not only by the catalyst proper but also by the chemical character of the surface of the substrate (surface oxides).

For economic reasons, the gold mesh as current collector is undesirable. Therefore, electrodes without any metallic collector were prepared and their conductivity was adjusted by addition of carbon black. To increase their mechanical strength, the electrodes were provided on both sides with pressed-in plastic meshes, the specific content of the active mass was increased to 110 mg cm^{-2} and the pressing pressure was raised to 710 kp cm^{-2}. The polarization curves for electrodes containing varying ratios of carbon black to active mass (the latter containing 30% CoPc) are shown in Fig. 7. It can be seen that at a ratio of 4:1 a sufficiently continuous network of carbon black particles was formed resulting in a good electrode conductivity. At a greater content of carbon black, however, the content of the catalyst, which should be at least 10%, as well as that of the Teflon, decrease and thus the mechanical strength of the electrode becomes less.

It can be concluded that the catalytic activity of CoPc for electroreduction of oxygen in acid medium is very good and time-independent. This was confirmed by a long-term test of an electrode with 30% CoPc in the active mass under a current load of 10 mA cm^{-2} showing a constant potential shift of 70 μV h^{-1}. Evidence for a participation of the substrate of the catalyst in the catalytic

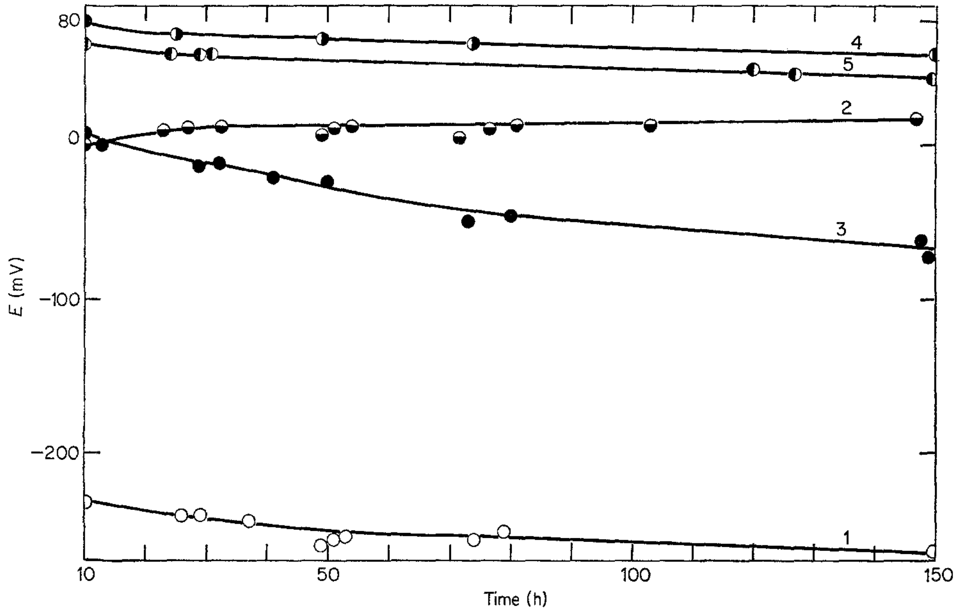

Fig. 4. *E-t* Curves from 0 to 150 h. 1, Norit FNX; 2, 14% Pt; 3, 10% CoPc; 4, 30% CoPc; 5, 50% CoPc.

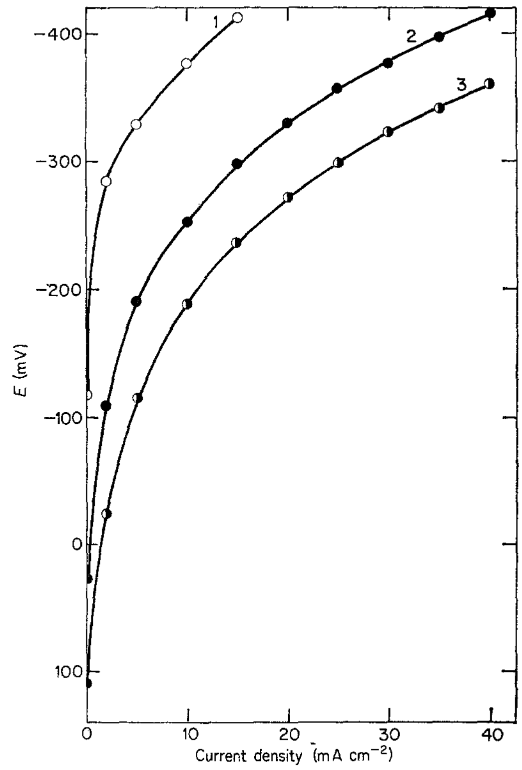

Fig. 5. Polarization curves for different carbon cathodes without catalyst. 1, Spectral carbon; 2, G-1000; 3, Norit FNX.

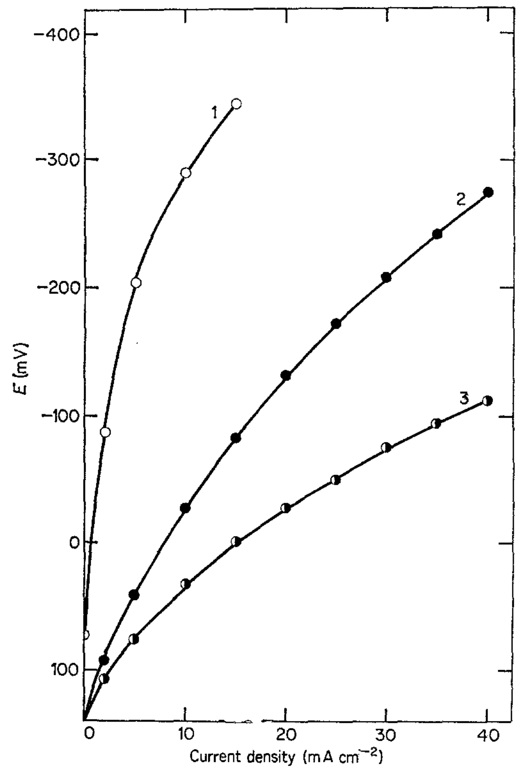

Fig. 6. Polarization curves for different carbon cathodes with 10% CoPc. 1, Spectral carbon; 2, G-1000; 3, Norit FNX.

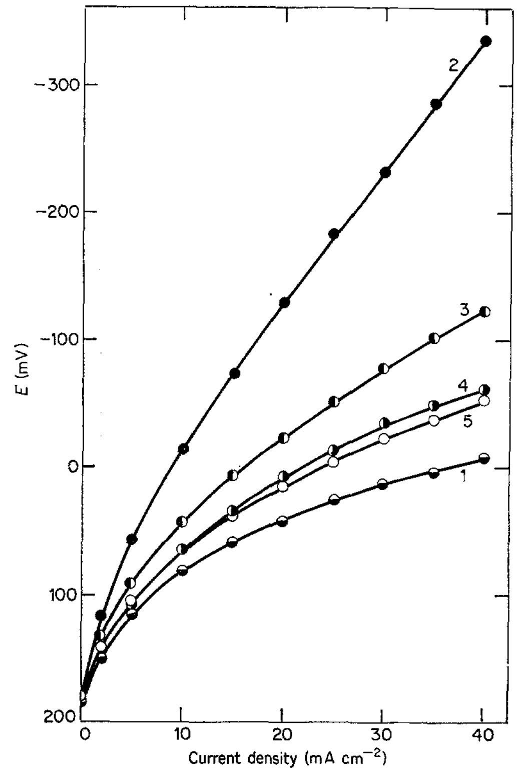

Fig. 7. Influence of replacement of Au current collector by carbon black on polarization curves. Active mass with 30% CoPc; 1, with current collector; 2, without current collector; 3, carbon black+active mass 1:6; 4, carbon black+active mass 1:4; 5, carbon black+active mass 1:3.

process was obtained. The character of the activation effect of the substrate on the catalyst (e.g. possible formation of a bond between them) cannot be elucidated as yet.

References

[1] R. Lemberg and J. W. Legge, in *Haematin Compounds and Pigments*, Interscience, New York, 1949.
[2] J. Tobler, *Z. Elektrochem.*, **39** (1933) 148.
[3] R. Brdička and P. K. Tropp, *Biochem. Z.*, **289** (1937) 301
[4] R. Brdička and K. Wiesner, *Naturwissensch.*, **31** (1943) 247.
[5] R. Brdička, K. Wiesner and K. Schäferna, *Naturwissensch.*, **31** (1943) 390.
[6] M. Březina, *Z. anal. Chem.*, **224** (1967) 74.
[7] J. Koutecký, R. Brdička and V. Hanuš, *Chem. Listy*, **47** (1953) 793; *Collection Czech. Chem. Commun.*, **18** (1953) 611.
[8] W. Beyer and F. von Sturm, *Angew. Chem.*, **84** (1972) 154.
[9] R. Jasinski, *Nature*, **201** (1964) 1212, 4925.
[10] R. Jasinski, *J. Electrochem. Soc.*, **112** (1965) 526.
[11] J. Mrha, *Collection Czech. Chem. Commun.*, **31** (1966) 715; **32** (1967) 708.
[12] Y. Maki, *J. Electrochem. Soc. Japan*, **27** E (1959) 115.
[13] K. Schwabe, R. Köpsel, K. Wiesener and E. Winkler, *Electrochim. Acta*, **9** (1964) 413.
[14] D. M. Dražič and R. R. Adžič, *Bull. Soc. Chim. Beograd*, **34** (1969) 203.
[15] M. Marinesco, *C. R. 3émes Journées Int. d'Etude des Piles à Combustible*, Presses Acad. Europ. Bruxelles, p. 66 (1969).
[16] H. Böhm, *Wiss. Ber. AEG-Telefunken*, **43** (1970) 241.
[17] G. Louis and H. Böhm, presented on 4th Int. Symp. on Fuel Cells, RU.C.A., Antwerp, October 2–3, 1972.
[18] G. Richter and G. Luft, presented on 4th Int. Symp. on Fuel Cells, R.U.C.A., Antwerp, October 2–3, 1972.
[19] H. Jahnke, *Ber. Bunsenges. Physik. Chem.*, **72** (1968) 1053.
[20] H. Jahnke and M. Schönborn, *C. R. 3émes Journées Int. d'Etude des Piles a Combustible*, p. 60. Presses Acad. Europ. Bruxelles (1969).
[21] M. Schönborn, H. Jahnke and G. Zimmermann, presented on 4th Int. Symp. on Fuel Cells, R.U.C.A., Antwerp, October 2–3, 1972.
[22] M. Savy, *Ext. Abstr. 21st CITCE Meeting*, p. 193, Prague (1970)
[23] P. Andro, C. Bernard and M. Savy, *Compt. rend.*, **272** (1971) 366.
[24] M. Savy, P. Andro, C. Bernard and G. Magner, *Electrochim. Acta*, **18** (1973) 191.
[25] A. Kozawa, V. E. Zilionis and R. J. Brodd, *J. Electrochem. Soc.*, **117** (1970) 1470 and 1474; **118** (1971) 1705.
[26] R. Larsson and J. Mrha, *Electrochim. Acta*, in press.
[27] L. Y. Johansson, J. Mrha and R. Larsson, *Electrochim. Acta*, **18** (1973) 255.
[28] H. Hiller, R. Polster, F. Beck and H. Guthke, *Ger. pat. appl.*, p. 2046 354.1 (Sept. 19, 1970).
[29] H. Alt, H. Binder, G. Klempert, A. Köhling, W. Lindner and G. Sandstede, *Battelle Information*, **11** (1971) 64.
[30] H. Alt, H. Binder, W. Lindner and G. Sandstede, *J. Electroanal. Chem.*, **31** App. 19 (1971).
[31] W. C. Drinkard and I. C. Baillard, *J. Am. Chem. Soc.*, **81** (1959) 4795.
[32] H. Jahnke, private communication.
[33] B. D. Berezin, *Zhur. Fiz. Khim.*, **36** (1962) 494.