233

ELECTROCATALYSIS OF THE OXYGEN REDUCTION PROCESS ON METAL CHELATES IN ACID ELECTROLYTE

V. S. BAGOTZKY, M. R. TARASEVICH, K. A. RADYUSHKINA, O. A. LEVINA and S. I. ANDRUSYOVA

Institute of Electrochemistry, Academy of Sciences of the U.S.S.R., 117071 Moscow (U.S.S.R.)

Summary

The electrochemical performances of carbon gas–diffusion oxygen electrodes in acid solution were investigated. Active carbon AG-3 was promoted with 5 - 10 wt.% organic complexes of cobalt (phthalocyanine, tetraphenyl-porphin, tetrabenzoporphin, tetra(*p*-metoxyphenyl)porphin); Teflon was used as binder. It was shown that a heat treatment of the mixture of carbon with the organic complexes of cobalt in an inert gas atmosphere at 800 - 900 °C significantly improves the stability of the catalyst. Oxygen electrodes with this catalyst operated in sulphuric acid solution for several thousand hours without any deterioration.

Introduction

In recent years much attention has been given to fundamental and technological studies of the electrocatalysis of the oxygen reduction reaction. This reaction is used as a cathodic process in various kinds of electrochemical power sources (*e.g.* fuel cells, metal–air cells and batteries). In acid solutions only platinum metals have been used so far as catalysts for this reaction. Organic complexes of metals are very promising in this respect. Of particular interest are metal derivatives of porphin (phthalocyanines, tetraarylporphins, *etc.*) owing to their semiconducting properties and chemical stability.

It was shown [1 - 3] that an active oxygen electrode for alkaline solutions can be obtained using cobalt phthalocyanine monomer (CoPc) or polymer (CoPc$_i$) on a carbon carrier (*e.g.* carbon black) as catalyst. In 12 N KOH, carbon electrodes containing 20 - 30 wt.% CoPc$_i$ were found to yield a current density of 0.3 A cm^{-2} at a potential (ϕ) of 0.80 V (potentials are referred to the reversible hydrogen electrode in the same solution).

The electrochemical characteristics of carbon–oxygen electrodes, promoted by organic complexes of metals, are compared in Table 1 for sulphuric acid solutions. Carbon black [4] or activated carbons [5 - 7] were

TABLE 1

Electrochemical characteristics of carbon oxygen electrodes promoted by organic complexes of metals in H_2SO_4 solutions (3 - 4,5 N), t = 25 - 30 °C

Composition of active layer	ϕ (V) at a current density, mA cm^{-2}				Life	Source
	10	20	40	50	(h)	
1. Carbon black + CoPc$_i$ + polyethylene	0.70	0.60	0.50	0.43	no data	[4]
2. Carbon black + FePc$_i$ + polyethylene	0.85	0.78	0.72	0.70	no data	[4]
3. Norit FNX + 30% CoPc$_i$ + 10% Teflon	0.72	0.69	0.64		150	[5]
4. Norit BRX + 5% CoTMPhP + polyethylene	0.75	0.70	0.60	0.63	300	[7]

used as carriers. The catalyst was introduced into the carrier by impregnation with a solution of the organic complex in either concentrated sulphuric acid or an appropriate organic solvent (dimethylformamide, dioxane, *etc.*). In order to maintain a stable interface between gas and electrolyte, electrodes were made hydrophobic by introducing a waterproofing agent (Teflon, polyethylene) into the active mass. This agent also acted as a binder.

Carbon electrodes promoted by FePc$_i$ were found to be unstable in acid solutions, though they have a high activity [4]. Electrodes promoted by CoPc$_i$ retain their activity for about 150 h, whereupon their performance deteriorates [5]. The instability of the oxygen–carbon electrodes containing phthalocyanines is probably due to partial dissociation of tetrabenzo-tetraazaporphin complexes [7] with formation of Fe^{2+} ions and protonized forms of phthalocyanine without metals (H_2PcH^+). Hydrogen peroxide, formed in acid solutions as an intermediate product of oxygen reduction, [8] can also affect stability. Hydrogen peroxide oxidises phthalocyanines, this process being accompanied by the splitting of the macro-ring [9]. Tetrabenzoporphin complexes are less readily oxidized by hydrogen peroxide: electrodes of active carbon Norit BRX, containing 5 wt.% tetra(p-metoxyphenyl)porphin (CoTMPhP) and a binder showed stable operation in 3 N H_2SO_4 for 300 h [7].

In this communication we present details of an activation process for carbon electrodes containing organic complexes of cobalt [(CoPc, CoPc$_i$, Co-tetrabenzoporphin (CoTBP), CoTMPhP, Co-tetraphenylporphin (CoTPhP)] which ensures stable operation of oxygen electrodes in 4.5 N H_2SO_4 at room temperature for long periods of time (> 10,000 h).

Experimental

Electrodes consist of a mixture of commercial activated carbon AG-3 with 5 - 10 wt.% organic catalyst and 15 wt.% Teflon. Electrodes were

prepared by the following procedure. The carbon carrier was impregnated with a solution of the organic catalyst in an appropriate solvent, carefully mixed, and the solvent removed by dilution with water or evaporation on a water bath. The mixture was heated in an inert gas atmosphere at 800 - 900 °C for 20 - 30 minutes. After addition of the waterproofing agent the electrode (surface area 13 cm^2) was moulded from the heat-treated active mass (70 mg cm^{-2}) using a pressure of 700 kg cm^{-2}. The electrode was pressed together with a thin porous Teflon layer (8 mg cm^{-2}). The experiments were carried out in a Teflon cell with separate anode and cathode compartments. A 4.5 N H$_2$SO$_4$ solution ("extra pure") was used as electrolyte; the oxygen pressure Δp was 0.1 atmos. Analogous electrodes with a non heat-treated active mass were tested for comparison.

Results and discussion

Electrode stability

Figure 1 shows the polarization curves of oxygen reduction on carbon electrodes (heat-treated and not heat-treated) promoted by cobalt chelates. The heat treatment does not affect the initial activity of the catalysts studied, but influences significantly their stability of operation (Fig. 2). At the current density of 10 mA cm^{-2} (ϕ = 0.77 V) the electrodes worked for 10,000 h;
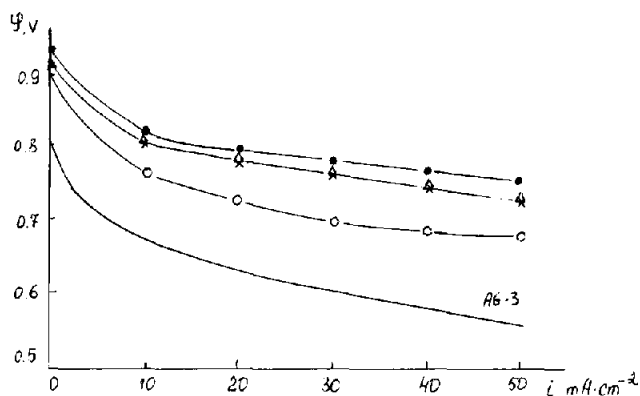

Fig. 1. Electrochemical characteristics of porous carbon electrodes, promoted by organic complexes of cobalt in 4.5 N H$_2$SO$_4$ at 20 °C. $\triangle$ CoTMPhP, not heat-treated; $\circ$, $\times$, $\bullet$, heat-treated CoTBPh, CoTPhP, CoTMPhP, respectively.

another group of electrodes worked at 30 mA cm^{-2} (ϕ = 0.75 V) for over 2500 h. In both groups no change in the characteristics was observed. Heating the mixture of carbon with CoTMPhP [10] and CoPc [11] in an inert gas atmosphere at 300 - 500 °C leads to increased activity of the carbon–oxygen electrodes. The studies of the influence of the heat treatment temperature on the life of the electrodes showed that from this point of view 800 - 900 °C is the optimum temperature (Table 2).
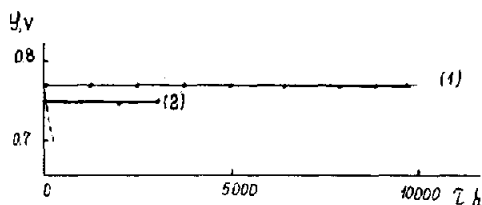
Fig. 2. Life of carbon oxygen electrodes, promoted by 5% CoTMPhP heat-treated at 800 °C, in 4.5 N H$_2$SO$_4$ (20 °C) at i = 10 mA cm^{-2} (1) and 30 mA cm^{-2} (2). — — — Norit BRX + 5 wt.% CoTMPhP, 3 N H$_2$SO$_4$, 30 °C, from the data of ref. [7].

TABLE 2

Influence of heat treatment temperature on the life of carbon—oxygen electrodes with 5 wt.% CoTMPhP in 4.5 N H$_2$SO$_4$ at i = 10 mA cm^{-2}

Heat treatment temperature (°C)	Time of operation without loss of activity, (h)
400	150
600	350
700	500
800	> 10,000
900	> 10,000
1000	1,000

In order to elucidate the mechanism of the effect of heat treatment on the active mixtures, a study was made of their macro- and micro-kinetic characteristics. It is known [12] that the activity and stability of electrodes is markedly influenced by the porosity of the active layer. However, as can be seen from Table 3, the heat treatment does not lead to any significant changes in the main structure and composition of the porous layer. On the other hand, the reaction rate of the heterogeneous decomposition of H$_2$O$_2$ is much higher on heat-treated powder catalysts than on untreated ones (Table 4). This seems to point to the determining role of the surface properties of the catalyst in the stabilization of the electrochemical characteristics of porous gas electrodes. Organic complexes may undergo degradation [13] as a result of high temperature heat-treatment. This may be accompanied by formation of radicals which promote polymerization and formation of a stable polyconjugated structure. It follows from the X-ray diffraction patterns (Fig. 3) that the heat treatment of cobalt chelates leads to the formation of compounds containing at least three phases: β-Co, carbon and a phase at $\theta \sim 14°$ which shows marked line-broadening. According to the data of an elemental analysis, the amount of carbon decreases by 10% and that of hydrogen by 50%. For example, the empirical formula of initial CoTMPhP is Co$_{51}$H$_{42}$O$_4$N$_4$Cl$_2$Co$_1$ and of the compound heat-treated at 800 °C is C$_{47}$H$_{25}$O$_4$N$_4$Co$_1$. It is suggested that during heat treatment polymeric compounds including Co are formed. These compounds are extremely stable in sulphuric acid. Detailed studies are in progress on the chemical structure of these compounds.
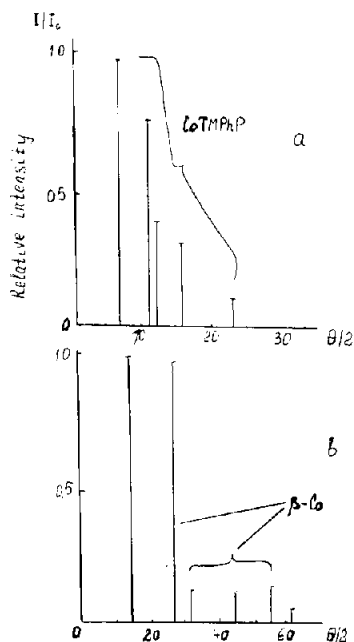
Fig. 3. X-ray diffraction patterns of initial (a) and heat-treated (b) CoTMPhP, radiation CoK_α.

TABLE 3

Structural characteristics of the electrodes in 4.5 N H_2SO_4

Composition of active layer	Total porosity (%)	Hydrophobic pores (%)
1. AG-3 + 15% Teflon	61	11
	58	9
	59	9
2. AG-3 + 15% Teflon + 5% CoTMPhP non heat-treated	56	11
	55	12
	57	11
3. AG-3 + 15% Teflon + 5% CoTMPhP, heat-treated, 800 °C	57	10
	59	7
	56	9

Electrode activity

The studies of the mechanism of oxygen electroreduction on different electrode materials, carried out so far, show that oxygen can be reduced directly to water (rate constant k_1) or via intermediate formation of hydrogen peroxide (k_2), which is cathodically reduced to water (k_3), or undergoes chemical decomposition (k_4) [12].

TABLE 4

Heterogeneous decomposition of hydrogen peroxide on heat-treated
and untreated organic complexes of cobalt.

Composition of active mass	Half-life of H_2O_2 (min)
1. AG-3	35
2. AG-3 + 10% CoPc	37
3. AG-3 + 5% CoTMPhP	7
4. AG-3 + 5% CoTPhP	21
5. AG-3 + 10% CoPc, 800 °C	7
6. AG-3 + 5% CoTMPhP, 800 °C	1
7. AG-3 + 5% CoTPhP, 800 °C	1

$$O_2 \xrightarrow[k_2]{+\,2e} H_2O_2 \xrightarrow[k_3]{+\,2e} H_2O \qquad\qquad (1)$$
$$k_1 \downarrow {+\,4e} \qquad k_4 \downarrow$$
$$H_2O \qquad\qquad O_2$$

Thus the molecular oxygen reduction is a complex multistage process. The
catalysis of this reaction can take place at any stage. In order to investigate
the characteristics of oxygen reduction, the reaction has been studied using
the rotating ring–disc electrode technique proposed by Frumkin and
Nekrasov [14]. Intermediate products formed during oxygen reduction on a
disc of the test material were detected by oxidation on a platinized platinum
ring. With these data and the analysis given previously [15], it is possible to
calculate the rate constants and determine the partial currents of individual
reactions of the total process as given by the reaction scheme (1). In studying
the oxygen reduction reaction on disperse mixtures of carbon and organic
complexes of metals, it is necessary to fix them to the disc surface (pyro-
graphite) as an extremely thin layer [16].

Figure 4 compares the polarization curves of oxygen reduction on discs
covered by a thin layer of AG-3 (1) and a mixture of AG-3 and not heat-
treated (2) and heat-treated (3) CoTMPhP, and the corresponding depen-
dences of the limiting currents of hydrogen peroxide oxidation on the ring
(1'–3'). It can be seen that the oxygen reduction reaction in the presence of
both forms of the catalyst proceeds at a much greater rate. For heat-treated
catalysts, the curves for the process on the ring pass through a maximum.
The current increase with decrease in potential is associated with an increase
of the oxygen reduction current and with a corresponding increase of the
amount of hydrogen peroxide formed. The subsequent decrease in current at
potentials below 0.4 V is due to the increase in the rate of reduction of
hydrogen peroxide at the disc.

Calculations have shown that in all cases oxygen reduction involves
intermediate hydrogen peroxide formation ($k_1 = 0$). The increase of the value
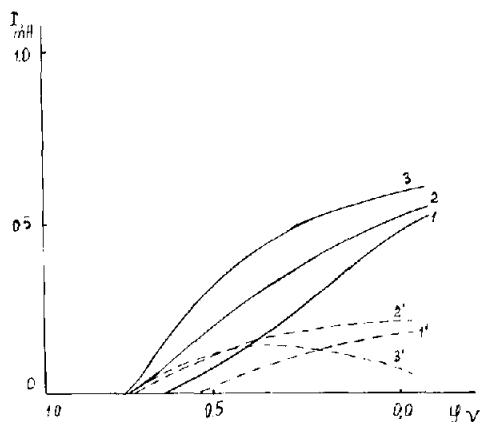of the rate constant of oxygen reduction to hydrogen peroxide (k_2) for

Fig. 4. Polarization curves of O_2 reduction on a rotating disc electrode covered by a thin layer of AG-3 (1) and AG-3 + 5% CoTMPhP not heated (2) and heated at 800 °C in He (3) and corresponding dependences of the limiting currents of H_2O_2 oxidation on the ring (1' - 3'); 0.1 N H_2SO_4, m = 960 rev/min.

different catalysts is shown in Table 5. On the other hand, the rate of further transformation of hydrogen peroxide (k_3) also rises. A high rate of H_2O_2 decomposition on such catalysts leads to a decrease of its concentration in the pores of the active layer. This also may contribute to the stabilization of the oxygen electrodes in acid solutions.

TABLE 5

Rate constant of O_2 reduction to H_2O_2 (k_2) in 0.1 N H_2SO_4

Composition of active mass	$k_2 \times 10^{-3}$ cm/s at		
	0.60 V	0.50 V	0.40 V
AG-3	< 0.1	< 0.1	6
AG-3 + 5% CoTMPhP non heat-treated	< 0.1	6.5	20
AG-3 + 5% CoTMPhP heat-treated	13	37	60

References

1 R. Jasinski, J. Electrochem. Soc., 112 (1965) 526.
2 K. A. Radyushkina, R. H. Burshtein, B. D. Berezin, M. R. Tarasevich and S. D. Levina, Elektrokhimiya, 9 (1973) 410.
3 K. A. Radyushkina, O. A. Levina, M. R. Tarasevich, R. H. Burshtein, B. D. Berezin, L. P. Shormanova and O. I. Koifman, Elektrokhimiya, 11 (1975) 989.
4 H. Jahnke and M. Schonborn, SERAI Troisièmes Journées Int. d'Etude des Piles à Combustible, Presses Acad. Européennes, Brussels, 1969, p. 60.

5   M. Musilova, J. Mrha and J. Jindra, J. Appl. Electrochem., 3 (1973) 213.
6   F. Beck, Ber. Bunsen Ges. Phys. Chem., 77 (1973) 353.
7   H. Alt, H. Binder and G. Sandstede, J. Catal., 28 (1973) 8.
8   M. R. Tarasevich, K. A. Radyushkina and S. I. Andruseva, Bioelectrochem. Bioenerg., 4 (1977) 18.
9   B. D. Berezin, Zh. Fiz. Khim., 36 (1962) 494.
10 G. Richter and H. J. Henkel, Germ. Pat. 775834 (1968).
11 R. Bosch, Fr. Pat. 1582905 (1969).
12 Yu. A. Chizmadjev, V. S. Markin, M. R. Tarasevich and Yu. G. Chirkov, Macrokinetics of Processes in Porous Media, Nauka, Moscow, 1971.
13 A. A. Berlin, Usp. Khim., 44 (1975) 502.
14 A. N. Frumkin and L. N. Nekrasov, Dokl. Akad. Nauk U.S.S.R., 126 (1959) 115.
15 V. S. Bagotzky, M. R. Tarasevich and V. Yu. Filinovsky, Elektrokhimiya, 5 (1969) 1218.
16 K. A. Radyushkina, M. R. Tarasevich and S. I. Andruseva, Elektrokhimiya, 11 (1975) 1079.