JOURNAL OF APPLIED ELECTROCHEMISTRY 13 (1983) 337–340

Transition metal catalysts for porous carbon air-electrodes in neutral chloride electrolytes

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Received 3 February 1982

Porous carbon air-electrodes activated by CoPC, FePHP, PdPC, PtPC and metal-free PC were studied in 2 mol dm^{-3} NaCl electrolyte. The activity of heat-treated carbon activated by CoPC was compared to carbon activated by *in situ* formed Co oxide. All the results show that the main catalytic activity of the catalyst used comes from the central metal atom used, while the chelate or oxide structures serve predominantly to keep the metal in the stable form at the carbon surface. Metal-free phthalocyanine does not show any catalytic activity for oxygen reduction.

1. Introduction

Transition metal chelates of various kinds have been studied extensively as oxygen reduction catalysts in porous carbon electrodes after Jasinski demonstrated the catalytic activity of Co phthalocyanine on a carbon support in alkaline solutions [1–19].

Bagotzky *et al.* [6] showed recently that a considerable increase in the catalytic stability can be achieved by heat treatment at 800–900° C in an inert atmosphere. We have shown [9] that Co and Fe phthalocyanines (PC) and tetraphenylporphyrines (TPHP) also catalyse oxygen reduction at the porous carbon electrode in neutral chloride (2 mol dm^{-3} NaCl) solution in a similar way to alkaline media. In fact, the slow diffusion out of the porous structure of OH$^-$ ions generated by the electrochemical reaction makes the pH inside the pores above 14, i.e., the electrolyte in which the catalyst operates is a very alkaline chloride solution. In the experiments presented here an attempt was made to correlate the catalytic effects of the central metal ion and the surrounding structure in real operating conditions inside the porous carbon-air-electrode.

2. Experimental

The porous carbon air-electrodes used in these experiments were made in our laboratory using Yugoslavian active carbon (Miloje Zakić Factory, Kruševac, Type G-52) and our own manufacturing technique. The electrodes were of the two layer type, the solution side was made of the partially hydrophobized (20% Teflon emulsion) catalytically activated active carbon, 60–71 μm fraction, and a hydrophobic porous polyethylene layer made of the 100–120 μm fraction, on the gas side. More details of the electrode manufacture can be found elsewhere [20, 21]. However, the manufacturing technology has not been optimized yet and the electrochemical characteristics of these electrodes as presented here are not the best possible. It has been used merely as a standard procedure in order to be able to compare the activities of the catalysts added.

Catalysts were introduced into the pores of active carbon prior to the final electrode pressing by the impregnation of carbon powder with an adequate amount of chelate dissolved in pyridine (for PC) or chloroform (for TPHP), or with an aqueous solution of the cobalt sulphate, followed by vacuum drying to remove the solvent. Some of the carbon impregnated with CoPC, or with sulphate were heated at 950° C, either in N_2 or air. For comparison some of the elctrodes were made of non-catalysed active carbon with and without heat treatment at 950° C in N_2 or air. Other chemicals used were the same as in ref. [9].

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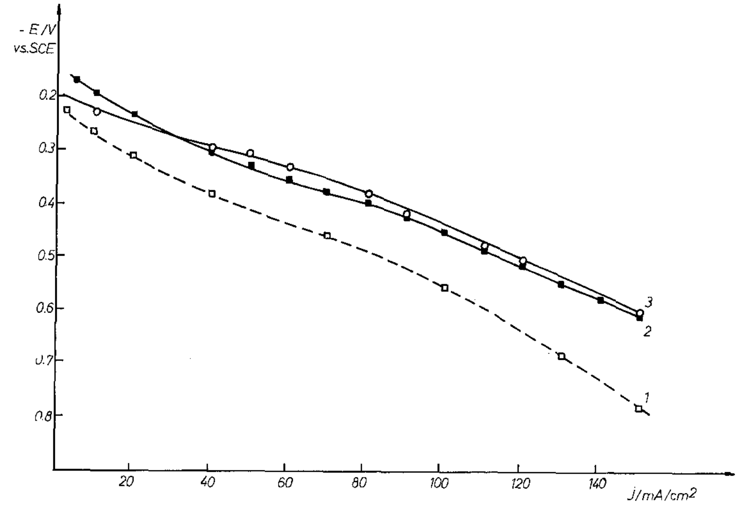

Fig. 1. Steady-state cathodic polarization curves for carbon air-electrodes in 2 mol dm^{-3} NaCl: 1, non-catalysed carbon; 2, 1 mg cm^{-2} Co(II) PC; 3, 1 mg cm^{-2} Fe(II) TPHP.

The polarization curves presented here were measured as steady state values at constant currents in 2 mol dm^{-3} NaCl solution at room temperature. A saturated calomel electrode was used as the reference electrode.

3. Results and discussion

The results obtained in the first set of experiments are shown in Fig. 1. The catalytic effects are practically the same for CoPC and FeTPHP. As shown before [9] increasing the amount of chelate catalyst over 1 mg cm^{-2} (approximately 1% by weight) does not improve the electrode performance when it is added by impregnation. Hence, there is no real difference between the curves of CoPC and FeTPHP.

In the second set of experiments the effects of the heat treatment of the carbon activated by CoPC was examined, following the results of Bagotzky *et al.* [6]. Since heat treatment might affect the structure and area of the real surface of active carbon (which is of importance for the performance of the gas diffusion electrode) separate tests with electrodes made of non-activated carbon heated in N_2 or air were carried out. As expected, the heat treatment of pure carbon somewhat improves the electrode performance (Fig. 2 curves 2 and 3). As shown elsewhere [20] this is due to an increase of the active carbon real surface area by slow oxidation of carbon, and the improvement of gas transport through the more developed submicroporous system, while more severe oxidation (in air) leads to an opposite effect. Heating the carbon activated with CoPC in N_2 at 950° C (curve 4) seems to have a very small

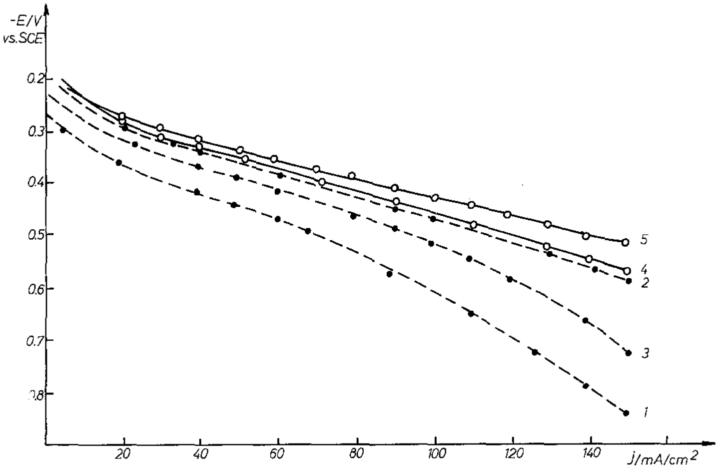

Fig. 2. Steady-state cathodic polarization curves for carbon air-electrodes in 2 mol dm^{-3} NaCl: 1, non-treated carbon; 2, carbon without catalyst heated at 950° C in N_2; 3, carbon without catalyst heated at 950° C in air; 4, with 1 mg cm^{-2} Co(II) PC heated in N_2; 5, with 1 mg cm^{-2} Co(II) PC heated in air.

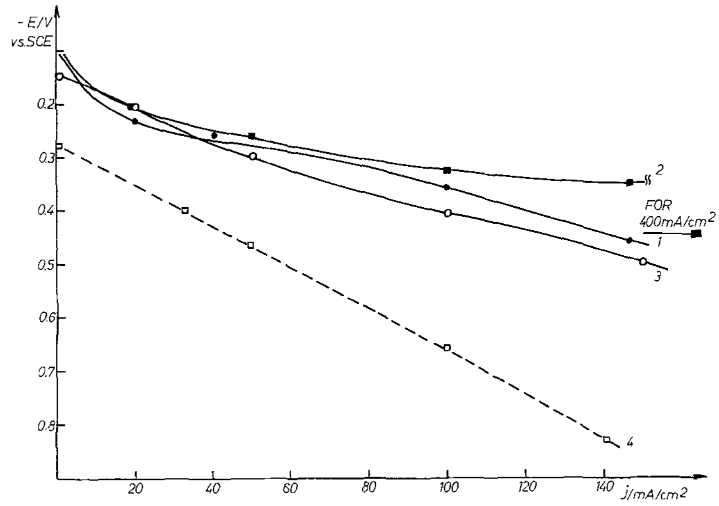

Fig. 3. Steady-state cathodic polarization curves for carbon air-electrodes in 2 mol dm^{-3} NaCl: 1, 0.2 mg cm^{-2} Pt; 2, 0.7 mg cm^{-2} Pt; 3, 3 mg cm^{-2} Co_3O_4; 4, metal free.

effect compared to non-activated carbon heated in the same way (curve 2). However, heating in air is more effective (curve 5) showing a decrease of polarization of around 100 mV at 100 mA cm^{-2}, compared to non-catalysed carbon (curve 3). This is approximately the same catalytic effect as shown in Fig. 1, for non-heated CoPC, and FeTPHP.

The effect of the central atom of the phthalocyanine complex was tested (as well as FePC and CoPC, which have been previously compared, show approximately the same activities) with PdPC and PtPC. At 100 mA cm^{-2} the porous carbon electrode catalysed with 1 mg PtPC cm^{-2} or 1 mg PdPC cm^{-2} had lower polarization of about 80 mV, than those catalysed with the same amount of CoPC.

The polarization curves presented in Fig. 3 could be separated into two groups. Curves 1 and 2 represent electrodes made of carbon activated with metallic Pt (obtained by the reduction of $PtCl_2$ with hydrazine) with 0.2 and 0.7 mg cm^{-2}. The first figure corresponds approximately to the amount of metal of 1 mg PtPC cm^{-2}. Curve 1 is practically the same as for the electrodes activated with PtPC or PdPC mentioned previously. The larger weight of Pt is used to show the performance of those electrodes when activated in the usual way and often cited in literature. The second group is represented by curves 3 and 4.

Curve 3 was obtained for electrodes made of carbon impregnated with $CoSO_4$ solution and activated by heating in air at 950° C. They are highly reproducible and in accord with the similar results obtained for alkaline electrolytes by the Bulgarian group [22].

The same activities obtained for CoPC activated electrodes (cf. Fig. 1a) and electrode impregnated with $CoSO_4$ and heated in air (cf. Fig. 1, curve 3) suggest that it is Co in the chelate which has nearly the same activity as in the oxide form, while the role of ligands in the chelate complex is of secondary importance.

Finally, curve 4 in Fig. 3 represents the polarization curve for the electrode made of active carbon impregnated with 1 mg cm^{-2} of the metal-free phthalocyanine. As shown, the electrode performance is somewhat lower than for non-catalysed carbon (cf. Fig. 1). Hence, it could be concluded that the phthalocyanine structure without the central metal atom has no catalytic activity for oxygen reduction at a porous carbon air-electrode.

From the experimental results presented one can conclude: (a) the catalytic activities of CoPC and FeTPHP are approximately the same, while those of PdPC and PtPC are larger, (b) heat treatment at 950° C increases the activity due to an increase in the surface area of the carbon itself and probably due to the partial or total oxidation of CoPC; (c) activities of electrodes activated with PtPC or metallic Pt in the same amount are approximately the same; and (d) introducing metal-free PC does not activate the electrodes.

Acknowledgements

The authors wish to express their thanks to Dr B. Nikolić for helpful discussions and to the Research Fund of Serbia for financial support.

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