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The electrochemical properties of imidazol-linked iron phthalocyanine – carbon electrodes

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Electrodes for the electrochemical reduction of oxygen have been studied galvanostatically. The electrodes were of the activated carbon–polymeric iron phthalocyanine (FePc) type, made hydrophobic with a Teflon treatment. A link between the FePc and the carbon was achieved by covalently binding imidazol to the carbon surface and then letting the FePc co-ordinate to the free nitrogen of the imidazol molecule. In this way an initial improvement of the stability of the electrode potential and the polarization data was achieved. It has furthermore been established that the potential responds more rapidly to changes, i.e. it is more reversible, than an analogous electrode based on carbon that has not been treated with imidazol.

1. Introduction

Phthalocyanines, especially condensed or polymeric ones, and other MN_4 cyclic chelates of the transition elements have been shown to be good catalysts for the electrochemical reduction of oxygen [1–3]. Most important are the iron and cobalt compounds and these have been studied intensively during the last ten years, e.g. [4–9]. The possibility of finding a good catalyst for the oxygen electrode in fuel cells which does not contain any precious metal has been the challenge of these investigations. Several obstacles are met, however, on the route towards this goal. One of these is the rather limited lifetime of electrodes prepared by using these compounds as catalysts. In most cases the polymeric phthalocyanines (or similar substances) are precipitated on to the surface of a carbonaceous material, e.g. activated carbon. The potential that electrodes prepared from such materials attain, at not too high a load, is several hundred millivolts higher than that of the pure carbon electrode. It decreases, however, rather rapidly [4, 10, 11].

This decline is probably caused by several factors [4]. One is the oxidative degradation of the carbon surface [12], which affects the three-phase balance necessary for a porous gas electrode [13]. Another factor, which is specifically related to the catalysts discussed here, is the displacement of the metal ion from the cyclic N_4 structure [14, 15]. It should be noted, however, that a release of metal ions does not directly lead to a decrease of electrode potential [16].

In order to avoid such a deterioration of the complexes one could try to fix the central metal to the carbon support by a molecular link, in a similar fashion that Nature uses for bridging the haem iron atom to the protein structure in haemoglobin. In this latter case the linking molecule is imidazol, as is now well known [17]. It therefore occurred to us that if imidazol was covalently bonded to the carbon surface and the phthalocyanine was then absorbed on to the imidazol one would achieve a considerable stabilization of the system. Possibly the imidazol link would also confer an increase in charge transfer ability to the catalytic system.

Chemical modifications of electrodes have been studied intensely during the last five years. A collection of relevant literature citations can be found, e.g., in the review by Snell and Keeman

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[18] and in the recent papers by Oyama *et al.* [19] and by Laviron [20]. In several cases the modifying agent is 'just' irreversibly adsorbed on the surface of the electrode, in other cases covalent links are established with techniques developed primarily for applications in the field of enzyme technology [21] and the heterogenization of catalytically active co-ordination compounds [22].

In most of these electrochemical investigations the authors have confined themselves to fixing the active complex at a peripheral point, e.g., by forming a C–N link to the nitrogen of tetra(p-NH_2-phenyl) porphyrin [23]. In this way the redox potential of the complex is established in close proximity to the electrode surface. A loss of metal from the porphyrin–metal complex is, however, still possible. If such a process is to be avoided, it seems necessary to establish a bond directly to the central metal atom of the complex.

2. Experimental procedure

The starting material was activated carbon (Norit FNX). In order to increase the number of oxygen-containing functional groups (mainly COOH) on the carbon surface, the activated carbon was treated with a sodium hypochlorite solution at room temperature for a week. After filtration the carbon was washed with water and ethanol. It was difficult to separate the treated carbon from the reaction medium because the carbon was less hydrophobic due to the many hydrophilic carboxyl groups which gave the product colloidal properties.

The carboxyl groups were then transformed to acid chloride groups by reacting with thionyl chloride ($SOCl_2$) in benzene solution for about 24 h [18]. The carbon was washed with dichloromethane and dried. It was then reacted in a dessicator with imidazol in dichloromethane at room temperature for 24 h. In order to remove physically adsorbed imidazol the carbon was carefully washed with dichloromethane and water acidified with acetic acid. Thereafter it was extracted in a Soxhlet apparatus with dichloromethane for 12 h. The resulting material was investigated using the X-ray photo-electron analysis (ESCA) technique (using an AEI ES 200 instrument). A strong N_{1s} signal was clearly observed indicating the presence of nitrogen on the carbon surface. This is taken as evidence for the successful bonding of imidazol to the carbon surface.

The polymeric iron(II)phthalocyanine (FePc) was prepared from urea and pyromellitic acid dianhydride in a melt at 300° C for five hours. The product was recrystallized from concentrated sulphuric acid and further purified by extraction with water in a Soxhlet apparatus [24, 25]. The method of preparing electrode masses by dissolving the polymer phthalocyanine in concentrated sulphuric acid, adding the carbon and precipitating the phthalocyanine by adding water [4] was avoided here since it could result in an acid hydrolysis of the carbon–nitrogen bond. An alternative method was therefore chosen. The polymer phthalocyanines were dissolved in water-free dimethylsulphoxide (DMSO), the surface-modified activated carbon was added under agitation and the phthalocyanines were precipitated by adding slightly acidified water (pH = 4). The electrode mass was dried in vacuum at 100° C. The electrodes were prepared as before [5] by adding a Teflon suspension to the mass and pressing the resulting mixture on to a gold grid.

The electrodes were tested for their ability to electrochemically reduce molecular oxygen in acid medium. The same half-cell arrangement as in earlier work was used [4, 5], The electrolyte was 2.3 M H_2SO_4 and the electrode potentials were measured against an Hg/Hg_2SO_4 reference electrode (+ 640 mV against a hydrogen reference electrode immersed in the same electrolyte) via a Luggin capillary ending at the surface of the electrode under investigation. The electrodes were tested galvanostatically with a constant load of 10 mA cm^{-2} interrupted after 7 h by a polarization measurement.

3. Results

Some representative results are recorded in Figs. 1 and 2. Fig. 1 shows the electrode potentials during the first 6 h at constant load (10 mA cm^{-2}). It is seen that the electrode containing the imidazol-treated activated carbon without any polymer phthalocyanine completely loses its ability to reduce oxygen. This is probably caused by an adverse effect on the carbon surface from the heavy oxidation during the preparation. The fact that the hydrophobicity of the carbon is decreased

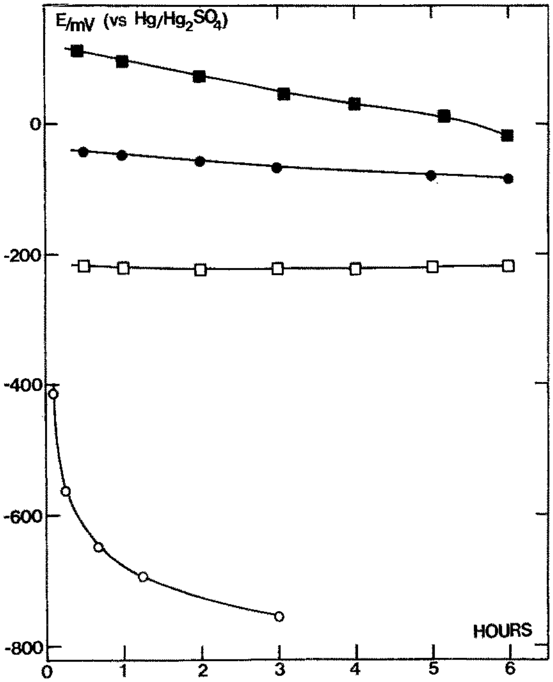

Fig. 1. Potential versus time at 10 mA cm^{-2} load, 1 atm O_2 pressure and in 2.3 M H_2SO_4. ●, 90% [25% FePc + 75% FNX (imidazol)] + 10% PTFE; ○, 90% FNX (imidazol) + 10% PTFE; ■, 90% [25% FePc + 75% FNX] + 10% PTFE; □, 90% FNX + 10% PTFE.

may reduce the possibility of establishing a good three-phase contact in the electrode. The corresponding potential of an electrode containing untreated activated carbon is about −200 mV.

When the FePc polymer is attached to the chemically modified carbon a considerable improvement of the electrode potential is obtained (Fig. 1). Despite this the potential is somewhat lower than the one obtained with a conventional FePc/carbon electrode (e.g., after 30 min the difference is 130 mV). It is interesting to note that the decrease of the potential of the electrode containing the imidazol-treated carbon is lower than that of the electrode containing untreated activated carbon. The potential decrease is about 8 mV h^{-1} compared with 20 mV h^{-1} during the first 5 h at constant load. These results indicate that the presence of groups or molecules on the surface of the activated carbon has a pronounced influence on the electrochemical properties of electrodes of the type described here. Specifically the imidazol seems to form a strong link between the polymer phthalocyanine and the surface of the activated carbon in such a way that a stabilization of the electrode potential is obtained. This effect is further born out by Fig. 2 where the potentials of the two electrodes have been measured over a period of 150 h under the same load of 10 mA cm^{-2}. Because of the low rate of decline, the potential of the imidazol-treated FePc electrode becomes more positive than that of the untreated FePc electrode after about 15 h and stays so for about 150 h. Thereafter a further decline seems to set in that might possibly be caused by the acid hydrolysis of the imidazol–carbon link.

In passing, one can note that the potentials as well as the rates of potential decrease are less favourable for the electrodes studied here than for those studied in an earlier work [5]. The actual catalytic efficiency of the phthalocyanines is, however, strongly dependent on the method of preparation. Therefore only the relative differences are of concern here.

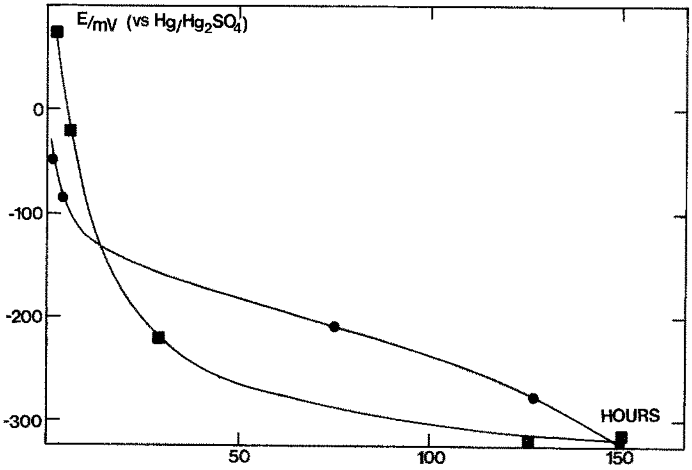

Fig. 2. Extended test for the two FePc-containing electrodes. The same symbols are used as in Fig. 1.

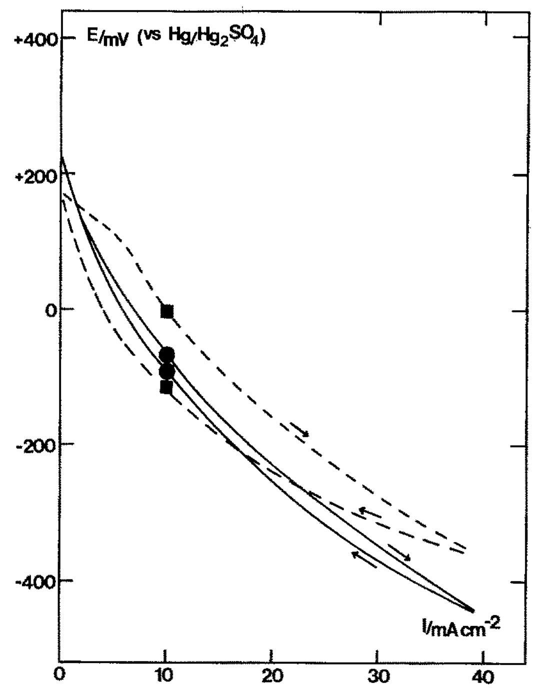

Fig. 3. Hysteresis effect of the polarization curves for the electrodes containing FePc. The same symbols as in Fig. 1. The arrow indicates the direction of change of the current density. This measurement was made after the electrodes had gone through the first seven hours of the test.

A most pronounced difference between the imidazol-treated and the conventional FePc electrodes can be seen in Fig. 3. The polarization curves have been recorded galvanostatically with a stepwise increasing current density up to 40 mA cm^{-2}, followed by a stepwise decrease back to zero. One can see that the potential adjustment is more rapid for the imidazol electrode than for the other one. This effect indicates a better reversibility of the electrode system, possibly caused by an increase of the electron transfer from the electrode carbon to the active centres of the oxygen reduction.

4. Conclusion

The results gained so far seem to indicate that an improvement of the effect and lifetime of the phthalocyanine-catalysed oxygen electrodes can be achieved by introducing an electron-conducting bridge between the carbon support and the central atom of the phthalocyanine. In order to avoid hydrolysis the linking bond should be made stronger than the C–N used here. Alternatively, the electrodes should be used in buffered electrolytes.

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