

Short Communication

Electroreduction of Oxygen on some Novel Cobalt Phthalocyanine Complexes

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Summary

The catalytic activity of cobalt phthalocyanine monomer and some of its polymeric derivatives towards the electroreduction of molecular oxygen in salt and alkaline solutions is examined. It is found that most of these complexes exhibit a higher catalytic activity than the cobalt phthalocyanine monomer.

Introduction

Gas-diffusion electrodes employed in fuel cells and primary metal/air cells require a catalytic coating on their surface for efficient reduction of oxygen. The traditional catalysts are usually the noble metals, such as platinum, that have limited resources and are expensive. In order to make these power systems commercially feasible, it is desirable to prepare catalytic materials to serve as viable alternatives to noble metals. To this end, a class of chemical compounds that have been studied extensively are macrocyclic- N_4 -chelates. Investigations on the electrocatalytic properties of transition-metal chelates started with Jasinski's [1] discovery of cobalt phthalocyanine as a catalyst for reducing oxygen. Since then, several other transition-metal chelates have been examined as oxygen-reducing catalysts. In general, metal chelates are poor electrical conductors and, hence, their utilization as catalysts in electrodes for fuel cells and metal/air cells requires them to be deposited onto an electrically conducting support of high surface area, such as active carbon.

This communication reports a study on the catalytic performance of a novel class of transition-metal phthalocyanines, deposited on active coconut-shell charcoal, with respect to the oxygen reduction reaction (ORR)

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in alkali and salt solutions. The performance of these electrodes is found to be superior to that of carbon electrodes catalyzed with cobalt phthalocyanine.

Experimental

Cobalt phthalocyanine polymers with imido (A) and carboxylic end-groups (B) were prepared according to the procedure given in ref. 2. Cobalt [bis(3,4)phthalimidocarbonyl] phthalocyanine (C), cobalt [bis(3,4)dicarboxybenzoyl] phthalocyanine (D), cobalt [bis(3,4)dicarboxybenzoyl] phthalocyanine dianhydride (E), and *N,N'*-diphenyl-cobalt [bis(3,4)dicarboxybenzoyl] phthalocyanine diimide (F) were prepared according to the procedure given in refs. 3 and 4. Cobalt phthalocyanine (CoPC) was obtained from Polysciences Inc., Warrington. It was found that, among these catalysts, only complexes A and F are stable in alkali. Activated coconut-shell charcoal was prepared as described in ref. 5. In brief, it was subjected to gravity separation with saturated calcium chloride solution and then repeatedly extracted with azeotropic HCl, followed by distilled water. It was subsequently comminuted by treatment with carbon dioxide gas at 900 °C for a specified period. 10 wt.% of the catalyst was deposited onto the active carbon substrate as follows. To the solution of the catalyst in concentrated sulphuric acid, the required amount of active carbon (68% weight loss during gas activation) was added and mixed thoroughly. Distilled water was added to the resulting slurry to precipitate finely-divided catalyst onto the carbon. The mass was repeatedly washed with distilled water (for complexes A and F) or sodium chloride solution (for other catalysts) until no trace of acid was detected. The dried mass was mixed with 21 wt.% polyethylene of sub-micron size. The electrodes were prepared under an optimum compaction pressure of 60 kg cm⁻² for a period of ~4 min at 120 °C.

The electrodes thus prepared were electrochemically characterized in 1 M NaCl or 6 M KOH solutions in a plexiglas cell [6]. The steady-state current-potential (without *IR* correction) curves were obtained galvanostatically using a sintered-nickel counter electrode.

Results and discussion

The polarization data for the ORR on carbon electrodes containing various catalysts in 1 M NaCl and 6 M KOH solutions at 30 °C are shown in Figs. 1 and 2, respectively. It is evident that the performance of complex C (in NaCl) and complex F (in KOH) is superior to the CoPC catalyst in the corresponding electrolyte. Polarization curves in Fig. 1 indicate that the carbon electrode containing the complex C catalyst in salt solution (1 M NaCl) can sustain a load current-density of 100 mA cm⁻² with a polarization of about 300 mV. Similarly, a polarization of about 500 mV (Fig. 2) at 100 mA cm⁻² is observed for the carbon electrode containing the complex F catalyst in 6 M KOH solution. By contrast, higher polarization values are observed for carbon electrodes containing CoPC catalyst at similar load-currents. The e.s.r. spectra of these complexes, recorded after deposition on-

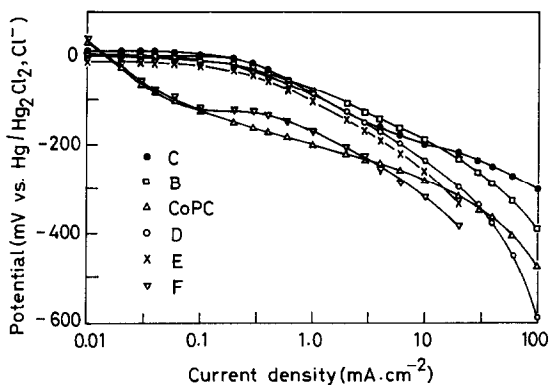


Fig. 1. Polarization curves for oxygen reduction reaction on carbon electrodes containing cobalt phthalocyanine (CoPC) or its complexes (B \rightarrow F) in 1 M NaCl at 30 °C.

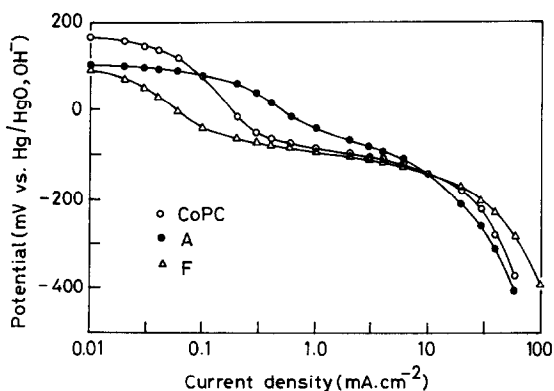


Fig. 2. Polarization curves for oxygen reduction reaction on carbon electrodes containing cobalt phthalocyanine or its complexes (A, F) in 6 M KOH at 30 °C.

to the active carbon showed substantial shifts in the spectroscopic splitting factor (*i.e.*, the *g* value) compared with those for the pure complexes. This observation could be attributed to structural deformation of the catalyst molecules.

From this study, it is concluded that the structural modification of metal phthalocyanines may enhance their catalytic activity.

Acknowledgement

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