

Short Communication

Nafion[®]-bound carbon electrodes containing transition-metal phthalocyanines for oxygen reduction in solid-polymer-electrolyte fuel cells

Neelam Phougat, P. Vasudevan* and Santosh

Centre for Rural Development and Appropriate Technology, Indian Institute of Technology, New Delhi-110016 (India)

A.K. Shukla

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012 (India)

(Received February 15, 1993; accepted April 21, 1993)

Abstract

Catalytic activities of some transition metal-phthalocyanine complexes towards electroreduction of molecular oxygen are examined on Nafion[®]-bound and bare porous carbon electrodes in 2.5 M H₂SO₄ electrolyte. It is found that these metal complexes exhibit better catalytic activities towards oxygen reduction with the Nafion[®]-bound electrodes.

Introduction

Fuel cells with solid-polymer electrolytes have practical advantages over those with immobilized liquid electrolytes as they provide essentially total nonvolatility of electrolyte material, drastic reduction of corrosion and materials problems, production of pure water only and hence negligible electrolyte leaching, integrity of the thin electrolyte layer, and ease in edge sealing of cells. Solid-polymer-electrolyte fuel cells are, however, still in the developmental stage and one of the many research priorities is to find effective, low-cost alternative catalysts to platinum, viz., nonprecious metals, oxides and transition-metal complexes including macrocycles. Some of these, while lacking adequate stability in concentrated acids or alkalis, may become stable with the polymer electrolytes.

In this study, some transition-metal complexes of macrocycles have been deposited on activated charcoal and have been integrated with a Nafion[®]-solid-polymer-electrolyte membrane. The porous structure of the electrode is governed mainly by the amount of the polytetrafluoroethylene (PTFE) binder, and by the load and time of compaction. The statistical analysis by Shukla *et al.* [1, 2] carried out in 2.5 M H₂SO₄ on Nafion[®]-bound electrodes (or area 2.4 cm²) identified the following optimum conditions: a compaction load of 400 kg; a compaction time of 5 min; a proportion of dehydrated

*Author to whom correspondence should be addressed.

Nafion[®] gel of 14 wt.%; a PTFE-binder loading of 27 wt.%. The usage of Nafion[®] gel helps to bind the Nafion[®] to the catalyzed carbon and enables porous carbon to be integrated with the electrolyte. The electrodes fabricated under these conditions gave excellent results in 2.5 M H₂SO₄ over the whole temperature range explored (40–90 °C). Further optimization for each operating temperature was found to be unnecessary. The electrodes were tested for electroreduction of oxygen at 60 °C. It was found that the catalysts performed better than when exposed directly to a strongly acidic medium.

Experimental

Cobalt phthalocyanine polymers with imido (A) and carboxylic (B) end-groups were prepared according to the procedure given in ref. 3. Cobalt [bis(3,4-phthalimido-carbonyl)] 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 in a similar fashion [4, 5]. Cobalt phthalocyanine (G) and iron phthalocyanine (FePc) were obtained from Polysciences, Inc., Warrington and Alfa Products, USA, respectively. Copper phthalocyanine polymer (pCuPc) was prepared according to the procedure reported in ref. 6. All these complexes were found to be substantially stable in 2.5 M H₂SO₄.

Activated, coconut shell carbon was prepared and subjected to gravity separation with saturated calcium chloride solution. It was then repeatedly extracted with azeotropic HCl followed by distilled water. The carbon was subsequently comminuted by treatment with carbon dioxide gas at 900 °C for a specified period [1].

The Nafion[®]-bound electrode was made by depositing 10 wt.% of a complex on 49 wt.% active carbon by adding active carbon to a solution of the complex in sulfuric acid, mixing, and then adding distilled water to the resulting slurry to precipitate the finely-divided catalyst on to the carbon. The resulting mass was repeatedly washed with either distilled water (for complexes A and F) or sodium chloride solution (for other catalysts) until no traces of acid were detected. The carbon and complex mixture was mixed thoroughly with 14 wt.% Nafion[®] gel and 27 wt.% PTFE. The electrodes (area 2.4 cm²) were prepared by hot pressing the mixture for 5 min at 95 °C and 400 kg between platinum mesh on one side and Nafion[®]-117 membrane on the other.

Bare-carbon electrodes were prepared by depositing 10 wt.% of a complex on 63 wt.% active carbon. The carbon-complex mixture was mixed thoroughly with 27 wt.% PTFE. The electrodes were prepared by hot pressing the above mixture for 5 min at 95 °C and 400 kg on platinum mesh.

The electrodes thus prepared were subjected to galvanostatic polarization in 2.5 M H₂SO₄ electrolyte at 60 °C in a Plexiglas cell using a platinized platinum counter electrode and a Hg/Hg₂SO₄, SO₄²⁻ (2.5 M H₂SO₄) reference electrode [7]. Oxygen was admitted to the rear of the electrodes at a pressure of 10 mm Hg. The data were not IR corrected.

Results and discussion

The polarization data for the oxygen reduction reaction on Nafion[®]-bound and bare-carbon electrodes in 2.5 M H₂SO₄ containing various complexes are shown in Figs. 1 and 2, respectively. Although the performance of these catalysts is inferior to

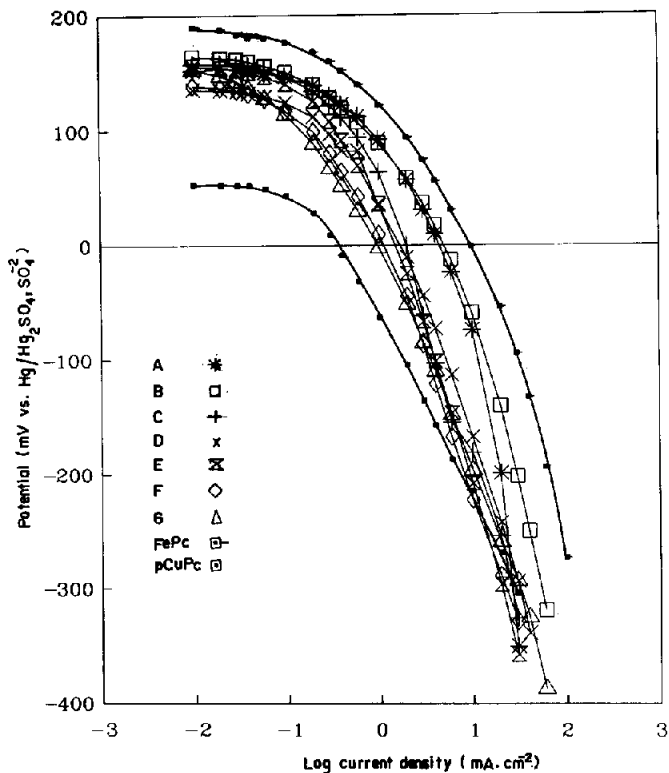


Fig. 1. Oxygen reduction polarization curves in 2.5 M H_2SO_4 for Nafion[®]-bound electrodes containing complexes.

platinum [2] at low current loads, the overpotentials are found to be fairly low. The catalytic activity of the complexes at higher current loads is superior for the Nafion[®]-bound electrodes. The order of activity is $\text{FePc} > \text{B} > \text{A} > \text{C} > \text{E} > \text{D} > \text{F} > \text{G} > \text{pCuPc}$ for the Nafion[®]-bound electrode, and $\text{B} > \text{A} > \text{C} > \text{E} > \text{F} \approx \text{D} \approx \text{G} > \text{pCuPc} > \text{FePc}$ for the bare-carbon electrode.

It is noteworthy that A, B, C, D, E, F and G contain cobalt as the central metal ion and that this dictates the electrocatalytic activity. Surprisingly, FePc showed poor catalytic activity for bare-carbon electrodes but the highest activity with Nafion[®]-bound electrodes. On the other hand, cobalt phthalocyanine complexes performed reasonably well with both types of electrodes. Interestingly, catalysts A and B, which are polymeric cobalt phthalocyanine derivatives, were found to be better than the monomeric cobalt phthalocyanine derivatives C, D, E, F and G. This suggests that the polymerization of the catalyst improves the catalyst performance, both in bare and in Nafion[®]-bound electrode configurations. Although the effect of functional groups is insignificant, these may influence the stability of the complexes. Furthermore, unlike pyrolyzed phthalocyanines, which are known to yield better catalytic activities towards the oxygen reduction reaction [8], complex B on heat treatment ($600\text{ }^\circ\text{C}$ in 10^{-4} mm vacuum for 30 min) showed poor activity towards oxygen reduction compared with the untreated catalyst.

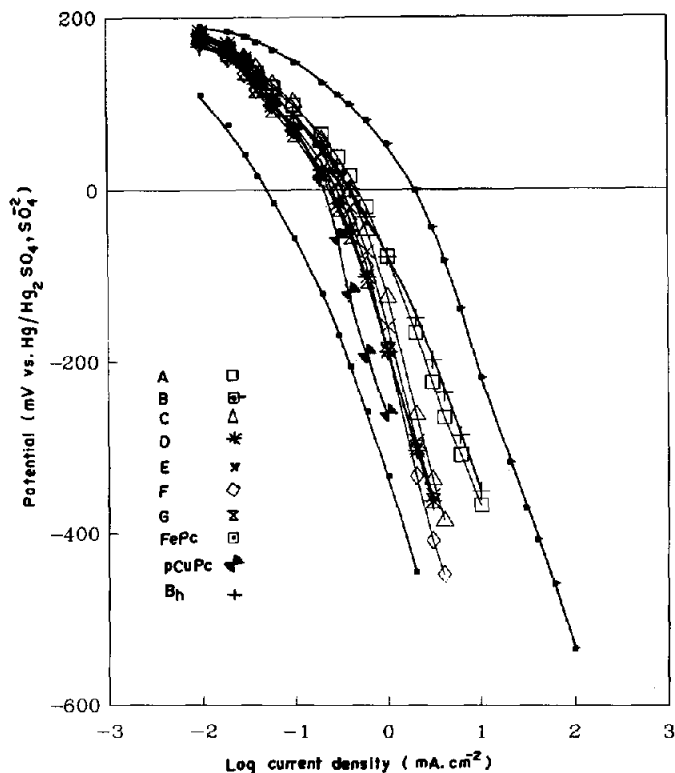


Fig. 2. Oxygen reduction polarization curves in 2.5 M H₂SO₄ for bare-carbon electrodes containing complexes.

The present study indicates that suitably modified polymeric iron and cobalt phthalocyanines act as feasible electrocatalysts for the electroreduction of oxygen with Nafion[®]-bound carbon electrodes.

Acknowledgement

The authors are grateful to the Department of Non-Conventional Energy Sources, Government of India, New Delhi for financial support.

References

- 1 A.M. Kannan, A.K. Shukla and A. Hamnett, *J. Appl. Electrochem.*, **18** (1988) 149.
- 2 A.K. Shukla, P. Stevens, A. Hamnett and J.B. Goodenough, *J. Appl. Electrochem.*, **19** (1989) 383.
- 3 D. Wobrl and E. Preubner, *Macromol. Chem.*, **186** (1985) 2189.
- 4 H. Shirai, S. Yagi, A. Suzuki and N. Hozo, *Macromol. Chem.*, **178** (1977) 1889.
- 5 H. Shirai, K. Kobayashi, Y. Takemae and N. Hozo, *J. Polym. Sci., Polym. Lett. Ed.*, **17** (1979) 343.
- 6 D.R. Boston and J.C. Bailar Jr., *Inorg. Chem.*, **11** (1972) 1578.
- 7 K.V. Ramesh and A.K. Shukla, *J. Power Sources*, **15** (1985) 201.
- 8 J.A.R. Van Veen and J.F. Van Veer, *Rev. Inorg. Chem.*, **4** (1982) 293.