

Short Communication

Electrocatalytic activity of some metal phthalocyanine compounds for oxygen reduction in phosphoric acid

Neelam Phougat, P. Vasudevan *

Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

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Abstract

The oxygen reduction activity of carbon electrodes containing some copper- and cobalt-phthalocyanine monomer and polymer derivatives in phosphoric acid electrolyte is determined. It is found that the electrocatalytic activity of cobalt[bis(dicarboxybenzoyl)]phthalocyanine derivatives towards oxygen reduction is higher than that of a unsubstituted cobalt phthalocyanine monomer. © 1997 Published by Elsevier Science S.A.

Keywords: Fuel cells; Phosphoric acid; Electrocatalysts; Phthalocyanine; Oxygen reduction

1. Introduction

Fuel cells using phosphoric acid as the electrolyte have very promising prospects because phosphoric acid is stable at temperatures of 200 °C with a very low vapour pressure in the fuel cell environment; it has also good electrical conductivity. Between 150 and 220 °C, the anode performance is good even if the fuel contains up to 5% carbon monoxide.

Use of platinum as the electrocatalyst increases the cost of fuel cells. Thus, attempts are being made to reduce the cost by replacing platinum with cheaper compounds such as metal oxides, metal alloys, and transition metal macrocycles. Because of their highly conjugated structure and high chemical stability, metal phthalocyanines and metal porphyrins have encouraging electrocatalytic activity for oxygen reduction. A review on the electrocatalytic activity of these compounds for oxygen reduction has been published by the authors [1].

The study reported here examines the electrocatalytic activity of some copper- and cobalt-phthalocyanine monomer and polymer derivatives for the oxygen reduction reaction in 6 M H₃PO₄ at room temperature.

2. Experimental

Cobalt phthalocyanine polymers with imido (A) and carboxylic end-groups (B) were prepared according to the

procedure reported previously [2]. Diimides of cobalt [bis(3,4-dicarboxybenzoyl)]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 using the method of Shirai and co-workers [3,4]. The synthetic routes and structures of polymer A and polymer B are shown in Scheme 1, and those of compounds C–F in Scheme 2. Cobalt phthalocyanine monomer (G) was obtained from Polysciences, Warrington. Copper phthalocyanine polymer (pCuPc) was prepared according to the procedure of Borton and Bailar [5].

The electrode composition was as follows: 10 wt.% metal phthalocyanine compound, 21 wt.% polyethylene powder, 69 wt.% active carbon substrate (Regal 660 R). Electrodes were prepared by adding a weighed amount of active carbon to a solution of the compound in concentrated sulfuric acid and then mixing thoroughly. Distilled water was added to the resulting slurry to precipitate finely-divided catalysts on to the carbon. The mass was repeatedly washed with distilled water until no trace of acid was detected. The dried mass was mixed with a weighed amount of polyethylene powder (sub-micron size, spectrophotometric grade, Aldrich). The electrodes (pellets of area 2.4 cm²) were prepared under an optimum compaction pressure of 60 kg cm⁻² for 4 min at 120 °C.

The electrodes thus prepared were electrochemically characterized using 6 M phosphoric acid as the electrolyte, with

* Corresponding author. Centre for Rural Development and Technology, Indian Institute of Technology, Hauz Khas, New Delhi-110016, India.

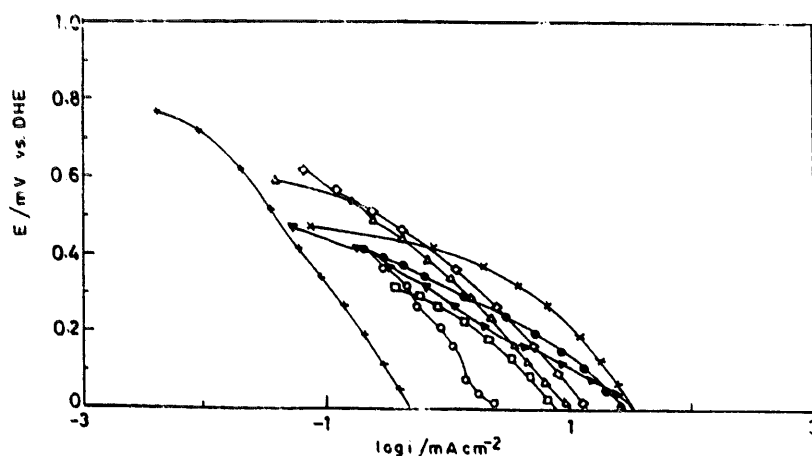
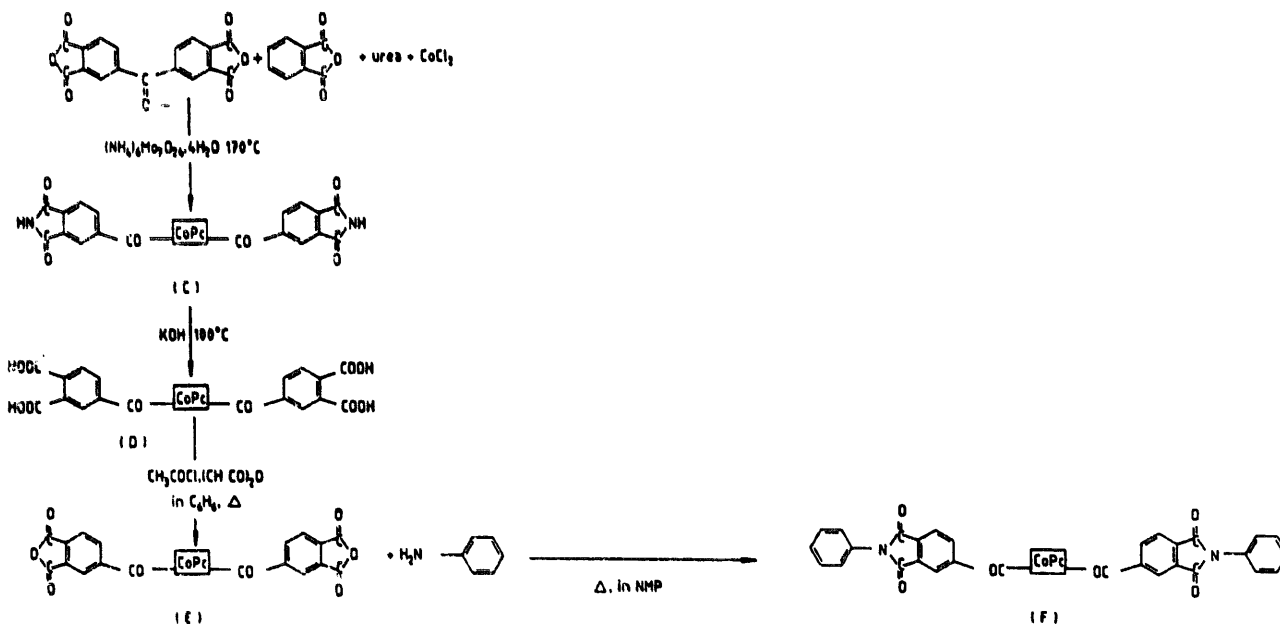
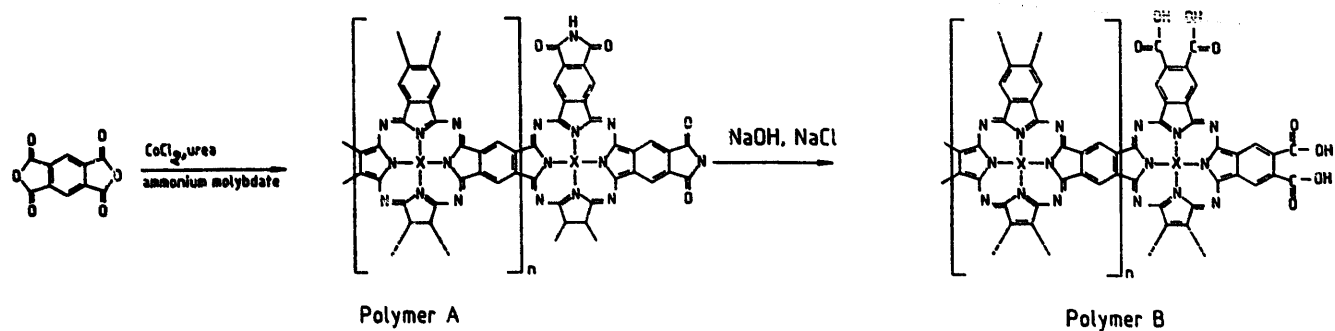


Fig. 1. Polarization curves for oxygen reduction reaction on carbon electrodes containing compounds: (+) A, (○) B, (●) C, (◇) D, (△) E, (X) F, (▼) G and (□) pCuPc in 6 M H_3PO_4 .

oxygen being admitted from the rear of the electrode at a pressure of 10 mmHg. The steady-state current–potential curves (without *IR* correction) at room temperature (30 °C) were obtained potentiostatically using a platinum foil as a counter electrode and a dynamic hydrogen electrode as a reference electrode.

It has been reported [6] that method of preparation of a compound also affects the electrocatalytic activity for oxygen reduction. In addition, the atmosphere during the preparation may influence the oxidation state of the metal which, in turn, will affect the electrocatalytic activity of the compound for oxygen reduction. To examine the effect of the atmosphere

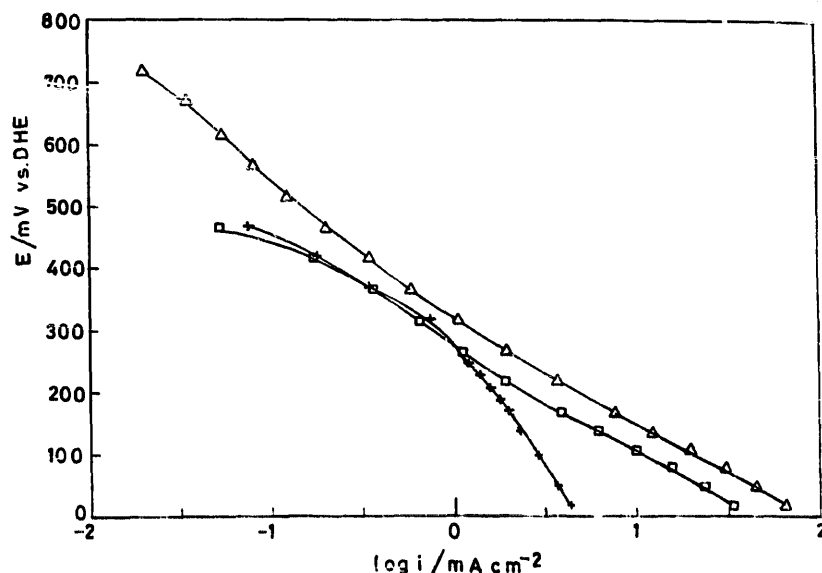


Fig. 2. Polarization curves for oxygen reduction reaction on carbon electrodes containing three samples of cobalt phthalocyanine monomer (CoPc): (□) commercial sample G; (△) sample 1; (+) sample 2 in 6 M H_3PO_4 .

during the preparation of a compound on oxygen reduction activity, two batches of cobalt phthalocyanine compound were prepared in either an oxygen or a nitrogen atmosphere (samples 1 and 2, respectively) according to a given procedure [7]. The samples were then purified.

3. Results and discussion

Polarization curves for various compounds at room temperature in 6 M H_3PO_4 are shown in Fig. 1. The activity of all the three polymeric samples (i.e. cobalt- and copper-phthalocyanine polymers) is found to be less than that of the monomeric samples. The activity of substituted cobalt phthalocyanine monomers are higher than that of commercial cobalt phthalocyanine monomer. The same behaviour has been observed [8] in 6 M KOH and 1 M NaCl electrolytes.

The polarization curves of three samples of cobalt phthalocyanine monomer, (namely, commercial sample G), sample 1 and sample 2 are presented in Fig. 2. Samples G and 2 display similar activity. Sample 1 exhibits slightly better activity and this suggests that the oxygen atmosphere during preparation of the cobalt phthalocyanine may exert a beneficial effect on the electrocatalytic activity.

Acknowledgements

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References

- [1] P. Vasudevan, N. Mann, Santosh and S. Tyagi, *Trans. Met. Chem.*, **15** (1990) 81.
- [2] D. Wohrle and E. Preupner, *Makromol. Chem.*, **186** (1985) 2189.
- [3] H. Shirai, S. Yagi, A. Suzuki and N. Hozo, *Makromol. Chem.*, **178** (1977) 1889.
- [4] H. Shirai, K. Kobayashi, Y. Takemae and N. Hozo, *J. Polym. Sci., Polym. Lett. Ed.*, **17** (1979) 343.
- [5] D.R. Borton and J.C. Bailar, Jr., *Inorg. Chem.*, **11** (1972) 1578.
- [6] T. Hirai, J. Yamaki and A. Yamaji, *J. Appl. Electrochem.*, **15** (1985) 77.
- [7] H.S. Nalwa and P. Vasudevan, *J. Mater. Sci. Lett.*, **2** (1983) 22.
- [8] P. Vasudevan, Neelam Mann, Santosh, A.M. Kannan and A.K. Shukla, *J. Power Sources*, **28** (1989) 317.