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Efficient oxygen reduction in alkaline solution with platinum phthalocyanine on porous carbon

A. K. SHUKLA*, C. PALITEIRO‡, R. MANOHARAN§, A. HAMNETT, J. B. GOODENOUGH‡

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

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Porous carbon electrodes coated with platinum phthalocyanine are found to be stable at 35° C towards electroreduction of oxygen in concentrated alkali. Moreover, the concentration of Pt is substantially reduced relative to an electrode carrying dispersed Pt.

1. Introduction

Pretreated coconut-shell charcoal has been documented to be an excellent cathode material for alkaline fuel cells [1]. It appears to reduce oxygen directly to water without detectable formation of hydrogen peroxide and is able to sustain currents of 200 mA cm^{-2} for reasonably long periods [2]. A further enhancement in its activity should be achieved if it can be coated with an appropriate catalyst.

At present, carbon electrodes in conventional fuel cells invariably use a catalytic coating or dispersion of noble metals such as platinum, which are expensive, and there is a real need to find cheap alternative catalysts to develop fuel cells for terrestrial applications. To this end, various metal phthalocyanines and porphyrins have been tested as possible catalysts for oxygen reduction [3].

In an earlier study, it was found that, in concentrated alkali, platinum phthalocyanine (PtPc) can reduce oxygen primarily to water with very little production of hydrogen peroxide [4]. In this communication, we report the performance towards oxygen reduction of a porous carbon electrode fabricated with pretreated coconut-shell charcoal and coated with various amounts of PtPc. Electrodes coated with 5 wt % PtPc could sustain load currents as high as 2 A cm^{-2} at an overvoltage of only 300 mV from its rest potential in 6 M KOH at 35° C.

2. Experimental details

2.1. *Pretreatment of coconut-shell charcoal*

The preparation of pretreated coconut-shell charcoal has been described in detail elsewhere [5]. Soxhlet extraction of the charcoal with concentrated HCl over approximately 1 week is followed by comminution of carbon particles to about 30 μm by heating in flowing CO_2 at 900° C.

2.2. *Preparation of PtPc samples*

The PtPc samples were prepared following the method of Barrett *et al.* [6]. Typically, 0.5 g of $PtCl_2$ and 5.6 g of 1,2-dicyanobenzene were ground in a mortar placed inside a plastic box purged with nitrogen. The resulting mixture was then put in a three-necked flask. After purging with N_2, it was heated at 280° C in the presence of a fusion mixture consisting of 40% $NaNO_2$, 7% $NaNO_3$ and 53% KNO_3. The reagent mixture was initially dark cream; it melted quickly and turned blue. After about 10 min it began to solidify; the solidification process was completed in 5 min. Heating was stopped after 20 min of the reaction. The dark blue cake thus obtained was cooled, crushed finely and washed with AnalaR ethanol. About 1.12 g of air-dried product was collected at this stage. The washed reaction product was then placed in a ceramic boat inside a quartz tube mounted in a horizontal furnace; the quartz tube was closed on both ends and connected to a vacuum pump. At 10^{-1} Torr, sublimation started at about 450° C, and PtPc deposited inside the quartz tubing near the mouth of the furnace as blue crystals with a bronze lustre. Sublimation was repeated four times. Very pure PtPc was obtained by this procedure. A typical chemical analysis of the PtPc sample along with theoretical estimates is: chemical analysis: C = 55%, N = 16.1%, H = 2.26%; calculated for PtPc: C = 54.3%, N = 15.85%, H = 2.28%.

2.3. *Preparation of PtPc-coated porous carbon electrodes and their electrochemical characterization*

Samples of PtPc, prepared in the manner described above, were coated onto the pretreated carbon by the following method. PtPc was first dissolved in a small amount of conc. H_2SO_4 and an appropriate amount of pretreated carbon was then added to it. Distilled water was then added to the slurry thus formed, to precipitate finely divided PtPc onto the carbon. The PtPc-

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[*] *Present address*: Solid-State & Structural Chemistry Unit, Indian Institute of Science, Bangalore, India.

[‡] *Present address*: Department of Chemistry, University of Coimbra, Coimbra, Portugal.

[§] *Present address*: Department of Materials Science & Engineering, University of Texas at Austin, Texas, USA.

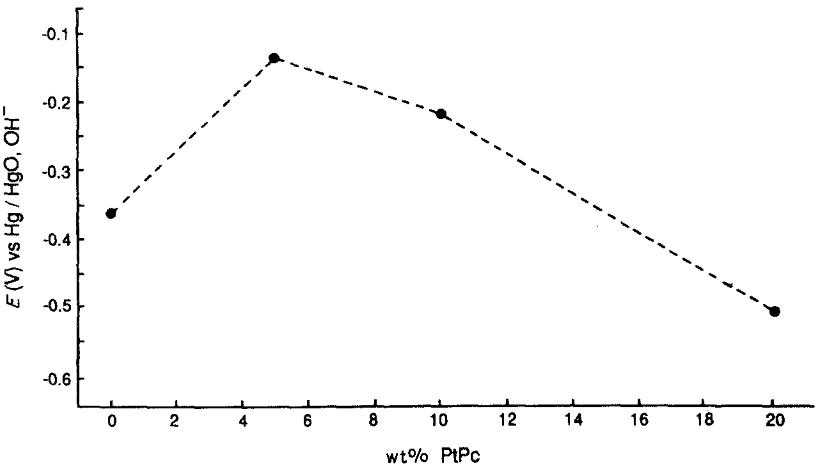

Fig. 1. Steady-state potentials at a load current density of 520 mA cm^{-2} for carbon electrodes coated with various amounts of PtPc.

coated carbon was repeatedly washed with distilled water in a centrifuge until no acid was detected. It was then dried overnight in an oven at 100° C before mixing with polyethylene (medium particle diameter: 20 μm) binder in the weight ratio 4 : 1. Circular porous carbon electrodes of about 0.5 mm in thickness and 1.5 cm^2 in area were fabricated by hot pressing the PtPc/carbon/binder mixture at 140° C onto platinum metal screens under a compaction pressure of 50 kg cm^{-2}, in a hydraulic press having its upper plunger connected to a load cell.

The electrodes were mounted in a working electrode assembly described elsewhere [7]. The essential feature of this assembly is that oxygen gas at 100 mmHg is admitted into a gas chamber on the rear side of the porous electrode and forced into the pores of the electrodes where it dissolves in the electrolyte that permeates through from the front side. Galvanostatic polarization studies for oxygen reduction with these PtPc electrodes were performed in 6 M KOH at 35° C. A high-surface-area nickel counter electrode was used and the polarization potentials of the various PtPc-coated carbon electrodes were recorded against a Hg/HgO,OH$^-$ reference electrode; the polarization data presented here have not been *iR* compensated.

3. Results and discussion

Figure 1 shows the observed steady-state potential for oxygen reduction, at a current density of 520 mA cm^{-2}, on carbon electrodes coated with various amounts of PtPc. The observed electrode polarization is least for the carbon electrode containing 5 wt % PtPc.

Figure 2 compares the polarization curve of such an electrode with carbon electrodes coated with the other metal phthalocyanines [8]. The superiority of carbon electrodes coated with 5 wt % PtPc is evident. The order of activity as found from this comparison is: PtPc $>$ thermally treated FePc $>$ untreated FePc $>$ CoPc $>$ NiPc $\gg$ MnPc $\approx$ C. This order is in accordance with a previous study conducted with metal phthalocyanines deposited onto carbon black [9]. However, a relatively high value for MnPc has been reported in this latter study.

Figure 3 compares the performance of a carbon electrode coated with 5 wt % PtPc with three other electrodes: a carbon electrode loaded with 15 wt % Pt, an optimized electrode prepared by dispersing platinum on an active carbon substrate and an active carbon electrode coated wiith about 5 wt % cobalt tetramethyl porphyrin (CoTMPP) [10–12].

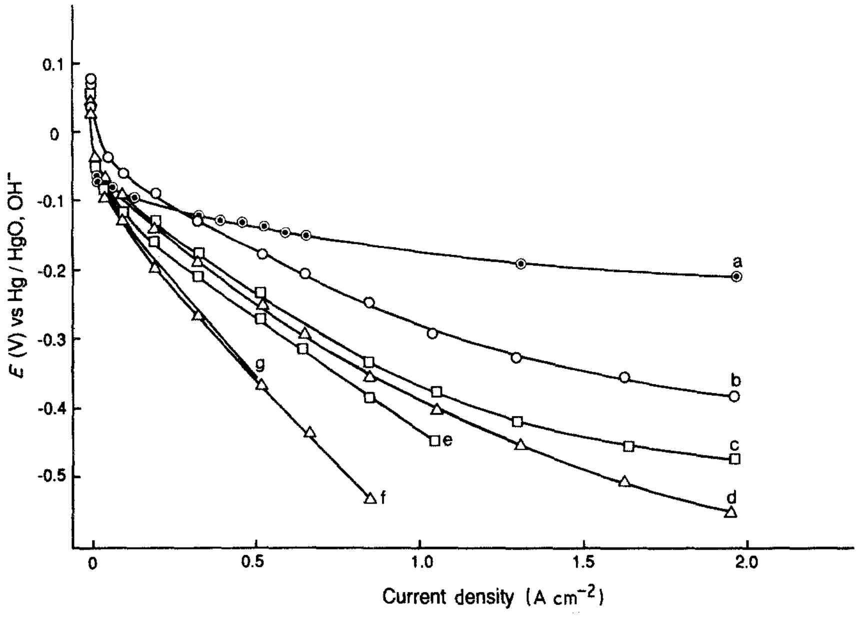

Fig. 2. Polarization of carbon electrodes coated with: (a) 5 wt % PtPc; (b) 7 wt % FePc with thermal pretreatment; (c) 7 wt % FePc without thermal pretreatment; (d) 7 wt % CoPc; (e) 7 wt % NiPc; (f) 7 wt % MnPc; (g) carbon (pretreated coconut-shell charcoal) electrode. Curves (b)–(g) are taken from Ref. [8].

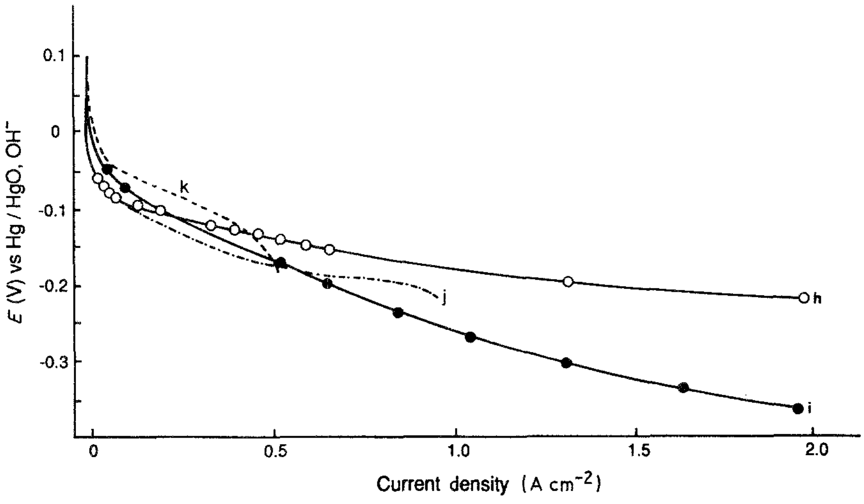

Fig. 3. Polarization data for carbon electrodes coated with: (h) 5 wt % PtPc; (i) 7 wt % Pt with thermal pretreatment (after Ref. [12]); (j) about 5 wt % CoTMPP (after Ref. [10]); (k) 15 wt % Pt (after Ref. [11]).

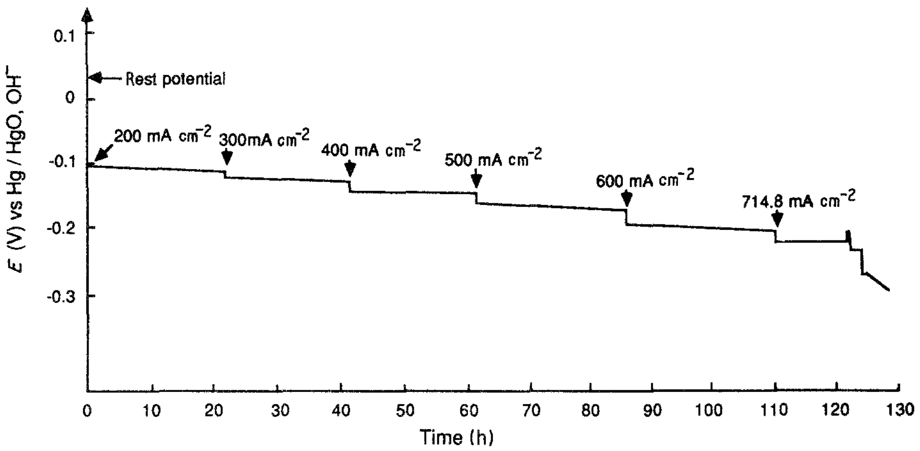

Fig. 4. Stability test for a carbon electrode coated with 5 wt % PtPc.

Figure 4 shows the data from a stability test conducted on a carbon electrode coated with 5 wt % PtPc. The applied current was gradually increased from the initial value of 200 mA cm^{-2} until electrode breakdown was observed. As is evident from Fig. 4, the electrode potential at any load current density up to 600 mA cm^{-2} changes very little with time from its initial value at that current density, and the slopes of the potential/time curves for all current densities up to 600 mA cm^{-2} are very similar. This suggests that for load currents below this figure, it should be possible to run these electrodes for much longer times without deterioration. At load currents above 600 mA cm^{-2}, a deterioration in performance with time is seen, possibly due to local heating within the electrode.

This study corroborates our earlier report [4], based on studies with rotating disc electrodes, that PtPc films deposited on pyrolytic graphite with a gold base show high catalytic activity towards oxygen reduction in concentrated alkali; it also demonstrates that PtPc films may be used with porous carbon electrodes. It is noteworthy that PtPc samples can be prepared with almost 100% yield [6], and 5 wt % PtPc corresponds to an electrode content of only about 1 wt % Pt. We conclude that both the catalytic activity and stability of PtPc are suitable for its utilization as an oxygen-reducing catalyst with porous carbon electrodes in alkaline fuel cells.

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