SHORT COMMUNICATION

High efficiency cathodes for alkaline air electrodes

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1. Introduction

Carbon electrodes have been used as cathodes in alkaline air fuel cells with some success [1–3]. The material is reasonably durable though forms that yield significant concentrations of hydrogen peroxide are slowly degraded. However, the activity of carbon can be enhanced considerably by impregnation with a suitable catalyst. The most effective of these catalysts to date have proved to be noble metals such as platinum, and 7–15 wt % platinum is commonly used. This is a very costly route, and macrocyclic transition-metal derivatives have also been explored as less expensive alternatives [4, 5], either as films on metallic substrates or impregnated on various forms of carbon.

The carbon derived from coconut-shell charcoal, when suitably pretreated, has been found to be an excellent cathode material in air fuel cells operating in concentrated alkali [1]. It appears to reduce dioxygen to water with no detectable formation of hydrogen peroxide and to be able to sustain load currents of about $200\,\mathrm{mA\,cm^{-2}}$ for long periods without serious degradation. Studies are now being carried out on this material to improve its performance by impregnating it with suitable catalysts. In this communication we describe the performance of the carbon, loaded with transition-metal porphyrins and phthalocyanines, in alkali; attempts to enhance the activity of these metal chelates by thermal pretreatment are also reported. It has been found that the performance of the electrode when loaded with iron phthalocyanine is comparable to that observed for the same wt % loading of platinum.

2. Experimental details

High-surface-area carbon was prepared from coconut-shell charcoal by the procedure described elsewhere [1]. Briefly, the charcoal was 'soxhlet' extracted over at least a week with concentrated HCl, comminuted with CO_2 at 900° C and further treated with NH_3 at the same temperature. The transition-metal chelates were either obtained commercially or synthesized via standard routes. Iron phthalocyanine (Alfa Products) and all the other phthalocyanines (Eastman Kodak) were purified by repeated sublimation at 500° C under a dynamic vacuum of 10^{-2} torr [6]. Cobalt tetraphenylporphyrin (Co-TPP) was synthesized by condensing pyrrole and benzaldehyde with cobalt acetate [7–9]. The condensate was purified by extracting the porphyrin with chloroform, and the purity of all compounds was finally checked chromatographically.

Impregnation of the carbon substrate was carried out from solution. For iron phthalocyanine two techniques were investigated. In the first FePc was dissolved in 'Specpure' pyridine, the required amount of carbon added to make a slurry and the solvent removed by distillation at 80–90° C [6]. In the second method concentrated sulphuric acid was used as the solvent, carbon was again added to form a slurry and precipitation was then effected by dilution with water. In this case separation was by centrifugation, and the impregnated carbon was washed and dried in an oven at approximately 100° C. The other phthalocyanines were also deposited from sulphuric acid as the solvent [6], and Co-TPP was deposited from chloroform [10].

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Attempts were made to enhance the activity of the FePc and Co-TPP impregnated samples by thermal pretreatment. To this end the electrodes were heated at 800° C in dry nitrogen for 30 min. All impregnated samples were then fabricated into porous electrodes by hot-pressing a mixture of the carbon and a polyethylene binder (in the ratio 4:1) at 140° C onto a platinum–metal screen with a compaction pressure of 0.05 tons cm^{-2} as described earlier [1]. The electrochemical cell was identical to that described earlier [1]; the most important feature was that oxygen was admitted at a pressure of approximately 130 mm Hg into a gas chamber in the reverse side of the electrode; the pressure forced the gas into the pores of the electrode where it dissolved in electrolyte premeating through from the front side. The current–potential curves were obtained galvanostatically and were *not I–R* corrected. The temperature of operation lay between 30 and 35° C.

3. Results and discussion

Figs 1 and 2 show the short-term polarization curves obtained for dioxygen reduction in 6 M NaOH solution on carbon electrodes impregnated with FePc, CoPc, NiPc, MnPc and Co-TPP. The order of activity found is FePc > CoPc ~ Co-TPP > NiPc $\gg$ MnPc ~ C.

In a recent Moessbauer experiment, Scherson *et al.* [6] observed some decomposition of FePc in concentrated sulphuric acid. For this reason the different modes of deposition of FePc were investigated as described above. Little difference in activity between the two samples was observed. The effect of thermal pretreatment has also been discussed in the literature [4, 5, 11–13, 17–19]; however, there is no concensus as to the direction of the effect it has or the underlying causes of its influence [6, 20, 21]. In our own study thermal pretreatment enhances the performance both of FePc and Co-TPP as shown in Figs 1

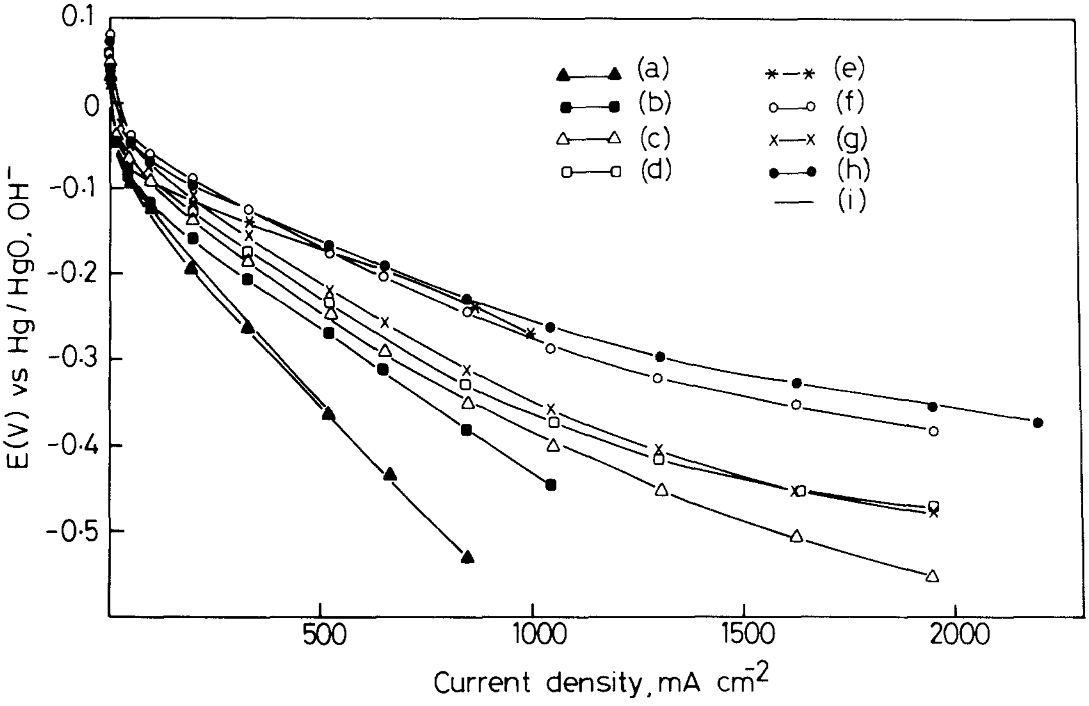

Fig. 1. Current–potential curves for oxygen reduction on: (a) 7 wt % MnPc/C; (b) 7 wt % NiPc/C; (c) 7 wt % CoPc/C; (d) 7 wt % FePc/C (sulphuric acid deposition); (e) 7 wt % FePc/C (pyridine deposition); (f) 7 wt % FePc/C, thermally pretreated; (g) 15 wt % FePc/Vulcan XC-72, thermally pretreated (after [6]); (h) 7 wt % Pt/C, thermally pretreated (after [14]); (i) treated carbon (after [1]).

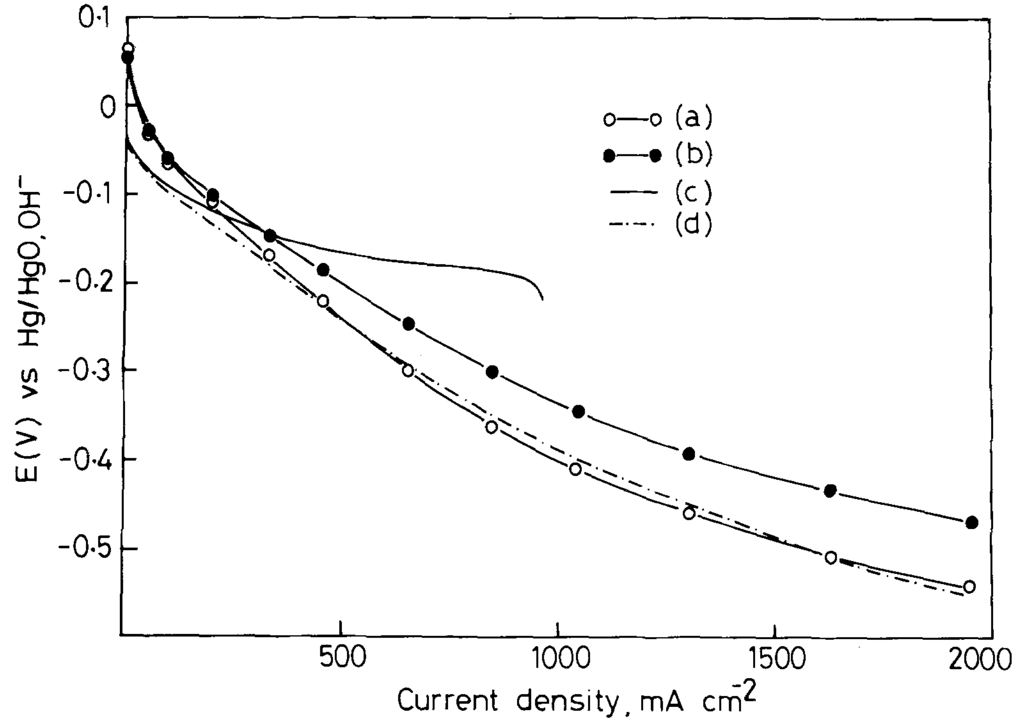

Fig. 2. Current–potential curves for oxygen reduction on: (a) 7 wt % Co-TPP/C; (b) 7 wt % Co-TPP/C, thermally pretreated; (c) 4.8% Co-TMPP/Vulcan XC-72 (after [20]) (d) 7 wt % CoPc/C.

and 2; whether this is due to the formation of cobalt–oxide or metallic–iron particles which can act as promoters (as reported by Scherson *et al.* [6, 20]) or whether reaction of the macrocyclic derivatives with active groups on the carbon can lead to enhanced stability and/or activity is not known [15, 16, 21].

Also shown in Fig. 1 is the polarization curve of 7 wt % platinum-impregnated carbon [14]. It can be seen that the performance is comparable to the thermally pretreated 7 wt % FePc electrode. For comparison, the performance of a recently reported [6] 15 wt % FePc/Vulcan XC-72 electrode is also included in Fig. 1.

Even after thermal pretreatment the performance of our 7 wt % Co-TPP electrode, shown in Fig. 2, did not match that recently reported by Scherson *et al.* [20] for the methoxyphenylporphyrin derivative of cobalt, Co-TMPP, on Vulcan XC-72, save at relatively low (< 300 mA cm^{-2}) and at very high ($\geqslant 1000$ mA cm^{-2}) current densities. This may reflect the higher basicity of the TMPP ligand. The relatively poor activity of MnPc is disappointing, though in line with previous work [4, 5]. Only for MnPc deposited on carbon black has any enhancement of activity been observed [22].

As a final comment it is noteworthy that the activity for the metal chelates deposited onto carbon substrates containing surface –CN groups has been reported to be higher than when the carbon used possesses other surface groups [4, 15]. From the pretreatment process described above it is clear that our carbon possesses such –CN groups [1, 16].

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SHORT COMMUNICATION

A model for correlating mass transfer data in parallel plate gas sparged electrochemical reactors

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Nomenclature

a	cross-sectional area of the cell (cm^2)
c	dimensionless constant
C	concentration of electroactive species ($mol\,cm^{-3}$)
C_b	bulk concentration ($mol\,cm^{-3}$)
C_i	interfacial concentration ($mol\,cm^{-3}$)
D	diffusivity of electroactive species ($cm^2\,s^{-1}$)
E	input of mechanical energy to the cell ($dyn\,s^{-1}$)
e	energy dissipated per unit mass of liquid ($cm^2\,s^{-3}$)
F	Faraday constant
g	acceleration due to gravity ($cm\,s^{-2}$)
h	height of the gas liquid dispersion in the cell (cm)
K	mass transfer coefficient ($cm\,s^{-1}$)
l	active electrode height (cm)
N	rate of mass transfer ($mol\,cm^{-2}\,s^{-1}$)
ΔP	gas pressure drop in the cell ($g\,cm^{-2}$)
Q	volumetric flow rate of gas ($cm^3\,s^{-1}$)
t	time (s)
$\bar{t}$	contact time (s)
u	viscosity of the solution (poise)
V	velocity parameter of small scale eddies ($cm\,s^{-1}$)
V_g	gas superficial velocity ($cm\,s^{-1}$)
x	length parameter of small scale eddies (cm)
y	distance perpendicular to electrode surface (cm)
St	Stanton number (K/V_g)
Sc	Schmidt number (v/D)
Re	Reynolds number ($\varrho V_g l/u$)
Fr	Froude number (V_g^2/lg)
Sh	Sherwood number (Kl/D)
Gr	Grashaf number ($gl^3\varepsilon/v^2(1-\varepsilon)$)
ϱ	density of the solution ($g\,cm^{-3}$)
v	kinematic viscosity ($cm^2\,s^{-1}$)
ε	gas hold up (void fraction)
ε_L	liquid hold up in the cell