

## Short Communication

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### Oxygen-reducing Electrodes for Acid Fuel Cells

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Electrochemical data are reported for oxygen reduction on platinized coconut-shell charcoal electrodes in 2.5M H<sub>2</sub>SO<sub>4</sub> and 7M H<sub>3</sub>PO<sub>4</sub>. In both these media the electrodes exhibit good activity and can sustain currents up to 600 mA cm<sup>-2</sup> at a polarization of about 400 mV from their rest potentials. The overall performance is comparable with the best type of carbon-supported platinum electrodes reported in the literature.

Various types of active carbon have been examined [1 - 4] as supports for platinum metal catalysts used for the reduction of oxygen in acid solutions. Both the activity as well as the corrosion resistance of such electrodes have been found to depend markedly on the nature of the carbon substrate. When suitably pretreated, carbon derived from coconut-shell charcoal has been shown [5 - 9] to be nearly ashless and to be an excellent substrate for oxygen-reducing electrodes in alkaline fuel cells. In particular, it appears that oxygen is reduced to water without detectable formation of hydrogen peroxide [8, 9] as an intermediate species. A study of the feasibility of coconut-shell charcoal as a support for platinum metal catalysts in acid-based fuel cells is reported here.

A high surface-area carbon substrate was prepared from coconut shells using the method described previously [5]. The desired quantity of platinum was dispersed on to the carbon substrate by reducing chloroplatinic acid with sodium formate solution using the following procedure. A solution of chloroplatinic acid containing 8 mg of platinum/ml was mixed with half its volume of isopropanol and then neutralized with a dilute solution of sodium carbonate. An appropriate quantity of treated carbon was added to this solution and the resulting mixture was then dried in an air oven. The residue was added, with vigorous stirring, to an excess of boiling 5 wt.% sodium formate in order to reduce the chloroplatinic acid to platinum. After filtration, the prepared material was washed repeatedly with hot, distilled water and finally dried in an air oven. The optimum deposit of platinum on to the carbon substrate was determined by conducting electroactivity tests on

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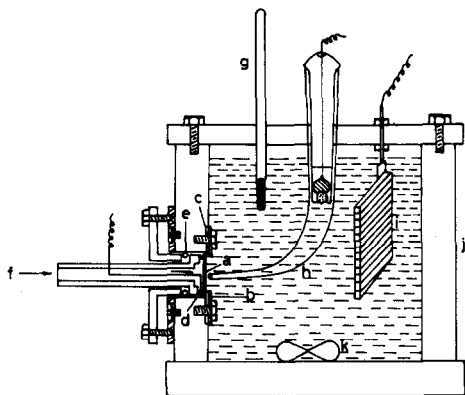


Fig. 1. Electrochemical cell assembly: (a) working electrode; (b) 316-stainless steel plate; (c) Viton rubber spacer; (d) platinum ring; (e) O-ring; (f) gas inlet; (g) thermometer; (h) Luggin capillary; (i) counter electrode; (j) plexiglas container; (k) magnetic stirrer.

electrodes with different platinum loadings. From these measurements, 10 wt.% of platinum was found to be optimum. The details of electrode fabrication have been described previously [5].

A schematic diagram of the cell used for the measurement of electrochemical performance parameters is shown in Fig. 1. The design consists of a rectangular, plexiglas container with a lid that has provision for a reference electrode, a Luggin capillary, a high surface area, flat-bed counter electrode made from platinized platinum, a heating element, and a thermometer. The electrolyte was either 2.5M  $\text{H}_2\text{SO}_4$  or 7M  $\text{H}_3\text{PO}_4$  which, in both cases, was stirred mechanically. Reference electrodes of  $\text{Hg}/\text{Hg}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{Hg}/\text{Hg}_2\text{HPO}_4$ ,  $\text{H}_3\text{PO}_4$  were employed in 2.5M  $\text{H}_2\text{SO}_4$  and 7M  $\text{H}_3\text{PO}_4$  electrolytes, respectively. All potentials are reported with respect to these reference electrodes. The working electrode was pressed against a Teflon-coated, 316-stainless-steel plate. The latter was held tightly against one of the inner walls of the plexiglas container by Teflon-coated, 316-stainless-steel screws. Gas sealing and electrical insulation of the electrode from the stainless-steel plate was achieved by inclusion of a Viton rubber spacer. A plexiglass plunger with a gas inlet provided a gas chamber at the rear of the working electrode. A platinum wire (dia. 0.5 mm), spot welded to a platinum ring (dia. 1 mm) that was pressed tightly against the reverse side of the working electrode, served as a current collector. The other end of the plexiglas plunger was connected to a medical-grade oxygen cylinder equipped with a gas pressure control valve and a mercury manometer. For temperature control, the electrochemical cell was fitted with a bimetal, power-regulated heater. Galvanostatic-polarization studies were carried out with a regulated d.c. power supply and a high power-rated rheostat in series with the electrochemical cell.

### Results and discussion

Current-potential curves for the cathodic reduction of oxygen in 2.5M  $\text{H}_2\text{SO}_4$  and 7M  $\text{H}_3\text{PO}_4$  electrolytes between 30 and 60 °C, and at an optimal gas pressure of  $5 \times 10^3 \text{ N m}^{-2}$  are shown in Figs. 2 and 3, respectively. In Fig. 2, the polarization curve for a bare (*i.e.*, catalyst-free) carbon electrode in 2.5M  $\text{H}_2\text{SO}_4$  at 30 °C is also included (curve (a)). The performance of this electrode is rather poor as it shows considerable polarization at load currents of  $30 \text{ mA cm}^{-2}$ . The observed rest-potentials of the electrodes in each of

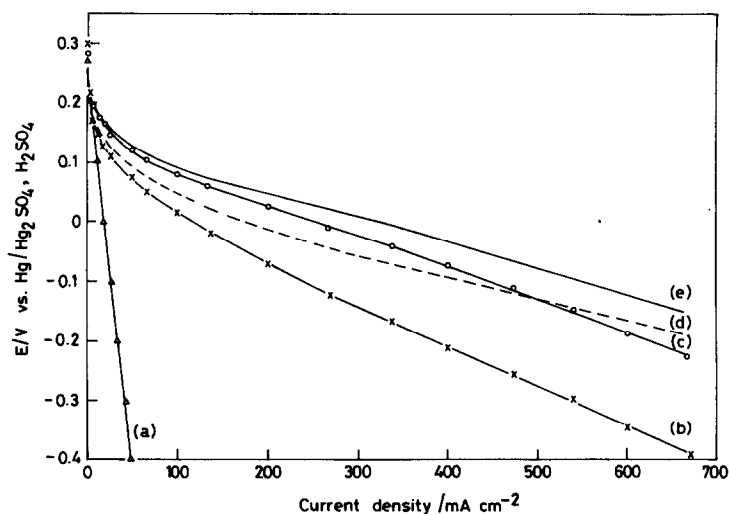


Fig. 2. Current-potential curves for oxygen reduction in 2.5M  $\text{H}_2\text{SO}_4$ : (a) bare-carbon electrode at 30 °C; and platinized-carbon electrodes at: (b) 30 °C; (c) 60 °C; (d) 30 °C with  $iR$  correction; and (e) 60 °C with  $iR$  correction.

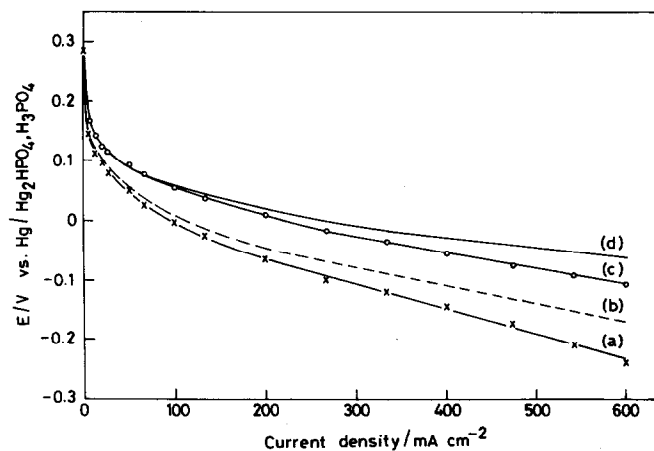


Fig. 3. Current-potential curves for oxygen reduction on platinized-carbon electrodes in 7M  $\text{H}_3\text{PO}_4$  at: (a) 30 °C; (b) 30 °C with  $iR$  correction; (c) 60 °C; and (d) 60 °C with  $iR$  correction.

the acid electrolytes are nearly 200 - 250 mV below the corresponding reversible potentials. This deviation from the reversible potential is due to the establishment of a mixed potential that results because the electrochemical splitting of the oxygen molecule is strongly impeded by the high stability of O=O as an intermediate product. Such an effect is an inherent feature of air electrodes.

The polarization curves, shown in Figs. 2 and 3, are practically rectilinear in the current ranges used in the study. This suggests that the rate of the electrode reaction is not controlled at any of these currents by mass-transfer processes. In such a situation, the observed polarization at the electrode can be attributed to charge transfer and ohmic polarization processes. It appears that temperature has little effect on electrode performance. This behaviour is probably due to a decrease in either the hydrophobicity of the electrode or the oxygen solubility of the electrolyte with increasing temperature [10].

Kinetic data (*i.e.*, Tafel slope, exchange current) for the electrodes in 2.5M H<sub>2</sub>SO<sub>4</sub> and 7M H<sub>3</sub>PO<sub>4</sub> electrolytes are given in Table 1. These kinetic parameters were obtained after correcting the current potential data for both the ohmic as well as the mass-transfer polarization components. The values lie in the range reported in the literature [2]. The observed increase in the exchange current with increasing temperature suggests that the activation polarization at the electrode becomes suppressed at increased temperatures. The Tafel slopes in 2.5M H<sub>2</sub>SO<sub>4</sub> electrolyte are found to increase with increasing temperature; a reverse trend, though not considerable, is seen in 7M H<sub>3</sub>PO<sub>4</sub> electrolyte. An almost invariant value of the Tafel slope with increasing temperature in H<sub>3</sub>PO<sub>4</sub> is also reported by McBreen [4]. However, a decrease in Tafel slope with increasing temperature has also been reported by McBreen *et al.* [3].

The electrodes used in the present study were optimized for the mass-transfer polarization component. Hence, the decrease in the Tafel slope observed at 60 °C in 7M H<sub>3</sub>PO<sub>4</sub> electrolyte is most likely due to a reduction in the ohmic and charge-transfer components of the electrode polarization. The reverse Tafel-slope/temperature behaviour observed for electrodes in 2.5M H<sub>2</sub>SO<sub>4</sub> electrolyte is probably due to the fact that the reduction in

TABLE 1

Kinetic parameters for oxygen reduction on platinized carbon electrodes in 2.5M H<sub>2</sub>SO<sub>4</sub> and 7M H<sub>3</sub>PO<sub>4</sub> electrolytes

Electrolyte	Tafel slope (V)		Exchange current density (A cm <sup>-2</sup> )	
	30 °C	60 °C	30 °C	60 °C
	2.5M H <sub>2</sub> SO <sub>4</sub>	0.085	0.15	1 × 10 <sup>-8</sup>
7M H <sub>3</sub> PO <sub>4</sub>	0.09	0.085	9 × 10 <sup>-8</sup>	2 × 10 <sup>-7</sup>

the ohmic and charge-transfer polarization components is compensated by the corrosion currents of the electrode. In an earlier communication [6], we reported an enhancement in the activity of platinized-carbon electrodes in alkaline medium by heat treatment under vacuum. However, no such effect was observed in acid electrolytes. Nevertheless, the overall electrochemical features of these electrodes are comparable with those of other electrodes reported in the literature [3, 4, 11].

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