

CARBON-BASED ELECTRODES CARRYING PLATINUM-GROUP BIMETAL CATALYSTS FOR OXYGEN REDUCTION IN FUEL CELLS WITH ACIDIC OR ALKALINE ELECTROLYTES

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Summary

The electrochemical activity for oxygen reduction in acid and alkali electrolytes of carbon electrodes with platinum-group bimetal catalysts, *viz.*, Pt-Ru and Pt-Pd, has been measured as a function of electrode composition. Electrodes containing 4 wt.% Pt + 6 wt.% Pd have been found to exhibit the maximum catalytic activity, and this is also higher than that of the individual metal catalysts.

Introduction

In an earlier communication [1], we reported the use of activated coconut-shell charcoal as a substrate for oxygen-reducing electrodes in alkaline fuel cells. The performance of these electrodes was found to be competitive with other carbon-based, oxygen-reducing electrodes [2 - 7]. The electrodes fabricated from coconut-shell charcoal appear to reduce oxygen directly to water without detectable formation of hydrogen peroxide [8]. On coating a suitable amount of platinum catalyst on to these electrodes, a substantial enhancement in their catalytic activity for reducing oxygen in alkaline media has been observed [9]. These platinized-carbon electrodes require heat pre-treatment under vacuum in order to reduce the level of platinum oxide impurities, but this causes sintering of platinum crystallites and consequently a loss in the active surface area [10]. It is therefore necessary to find a chemical pathway whereby such losses in catalytic activity can be averted. Some platinum-group bimetallics are known to exert a synergistic effect on the kinetics of fuel cells [11 - 13] and other heterogeneous catalytic reactions [14]. In a recent study [15] we have demonstrated that the deposition of Pt-Ru bimetal on carbon prevents the formation of platinum oxidation impurities, with the result that the electrocatalytic activity for hydrogen

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oxidation is higher than that on platinized-carbon electrodes. In this communication, carbon-based electrodes containing platinum-group bimetal catalysts (*viz.*, Pt-Ru and Pt-Pd) are investigated for their activity towards oxygen reduction in fuel cell systems with either acidic or alkaline electrolytes.

Experimental

Active carbon was prepared from coconut-shell charcoal using the method described previously [1]. This carbon was impregnated either with Pt (4 wt.%)^{*} and Ru (6 wt.%) or with Pt (4 wt.%) and Pd (6 wt.%), by immersion in solutions of the metals' respective salts, followed by reduction with 5 wt.% sodium formate solution. Electrodes were fabricated by hot pressing the catalyzed-carbon substrate with 20 wt.% polyethylene binder on expanded platinum metal screens at a pressure of $5 \times 10^5 \text{ kg m}^{-2}$ [1]. Electrochemical measurements on the electrodes so formed were carried out in both alkali (6 M KOH) and acid (2.5 M H₂SO₄ or 7 M H₃PO₄) electrolytes employing a cell similar to that described in an earlier communication [16]. In alkaline media, the counter electrode was made from sintered nickel, while the reference electrode was Hg/HgO, OH⁻ (6 M KOH). In acid media, the counter electrode was a platinized platinum foil, and the reference electrode either Hg/Hg₂HPO₄, PO₄³⁻ (7 M H₃PO₄) or Hg/Hg₂SO₄, SO₄²⁻ (2.5 M H₂SO₄). The steady-state galvanostatic polarization curves for the cathodic reduction of oxygen were obtained at an optimal gas pressure of 4000 N m⁻² in the temperature range 30 - 60 °C. Each experimental run was repeated to confirm the reproducibility of the data. In some cases, the current-potential curves were *iR*-corrected by the interrupter method.

Results and discussion

Current-potential curves for the reduction of oxygen on 4 wt.% Pt + 6 wt.% Ru active carbon (4Pt + 6Ru/C_t) electrodes, and on 4 wt.% Pt + 6 wt.% Pd active carbon (4Pt + 6Pd/C_t) electrodes, in 6 M KOH at 30 °C are shown in Fig. 1. For purposes of comparison, data for bare and platinized-carbon electrodes are also included. The observed rest potentials for these electrodes are about 250 mV below the reversible value owing to the establishment of a mixed potential [2]. It is evident that the bare carbon electrodes as such have reasonably high catalytic activity. The impregnation of these carbon electrodes with platinum catalyst has been reported to result in significant improvement in performance [9]. The enhanced activity has been attributed to a reduction in both the charge transfer and the ohmic components of the overall polarization at the electrodes.

^{*}These are the optimized amounts of the catalysts. Pd-Ru bimetal do not possess any catalytic activity towards oxygen reduction.

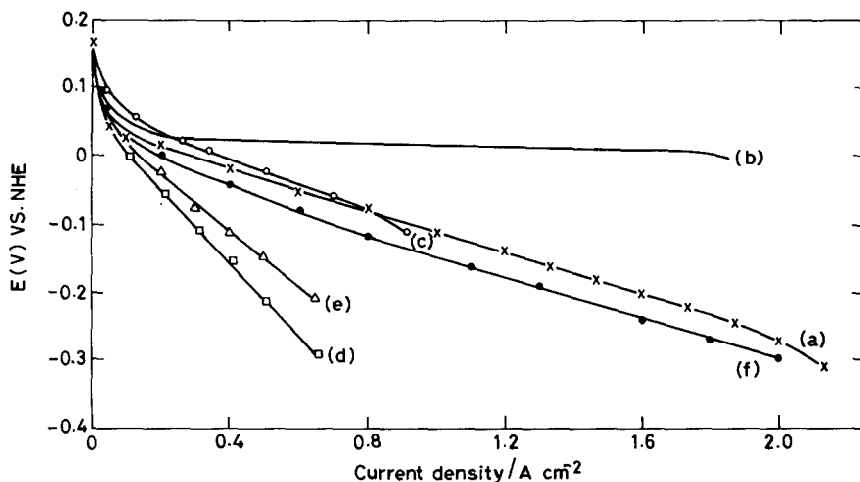


Fig. 1. Current-potential curves for oxygen reduction in 6 M KOH at 30 °C on: (a) 4Pt + 6Pd/C_t; (b) 4Pt + 6Pd/C_t with *iR*-correction; (c) 4Pt + 6Ru/C_t, (d) bare carbon; (e) 7Pt/C_t; and (f) 7Pt/C_{v_t} electrodes.

The better performance for electrodes of vacuum heat-treated, platinized carbon substrate (7Pt/C_{v_t}) compared with their platinized-carbon counterparts (7Pt/C_t) has been attributed [10] to the elimination of oxidic impurities of platinum during the vacuum heat-treatment. Carbon electrodes containing platinum-group bimetal catalysts, in particular 4Pt + 6Pd/C_t electrodes, exhibit greater electrocatalytic activity than 7Pt/C_{v_t} electrodes. This is mainly because the platinum crystallites in the latter electrodes undergo a loss in active surface area due to sintering of platinum crystallites during heat treatment [10, 15]. In addition, both the charge-transfer and ohmic polarization components for the 4Pt + 6Pd/C_t electrodes are smaller than those for 7Pt/C_{v_t} electrodes. Finally, the formation of platinum oxidation impurities is greatly reduced on platinum-group bimetals. The combination of these factors results in 4Pt + 6Ru/C_t and 4Pt + 6Pd/C_t electrodes having higher activities than 7Pt/C_t and 7Pt/C_{v_t} electrodes. It is observed that the 4Pt + 6Pd/C_t electrode can withstand load currents as high as 2 A cm⁻² at an overall polarization of about 450 mV. The *iR*-compensated curve for these electrodes is practically linear between 0.2 and 1.8 A cm⁻², thus indicating that in this current range the electrode reaction is not governed by mass-transfer processes. Therefore, the observed polarization can be mainly attributed to the ohmic component; however, below 200 mA cm⁻², the polarization is largely activation controlled. Studies also show that elevation in temperature up to 60 °C has no effect on the performance of these electrodes. This is possibly due to a decrease in both the hydrophobicity of the electrodes and in the oxygen solubility at elevated temperatures.

Exchange-current densities and Tafel slopes obtained for 4Pt + 6Ru/C_t and 4Pt + 6Pd/C_t electrodes are summarized in Table 1, along with the values reported for 7Pt/C_t and 7Pt/C_{v_t} electrodes [17]. These values have

TABLE 1

Kinetic parameters for oxygen reduction on different catalyzed carbon electrodes in 6 M KOH at 30 °C

Electrode	Tafel slope (V/decade)	Exchange-current density ($\times 10^8$ A cm $^{-2}$)
4Pt + 6Ru/C _t	0.050	0.5
4Pt + 6Pd/C _t	0.055	3.0
7Pt/C _t *	0.045	0.2
7Pt/C _{vt} *	0.057	2.7

*From ref. 17.

been obtained after correcting for both the ohmic and the mass-transfer polarization components in the current range 0.2 - 1.2 A cm $^{-2}$. It can be seen that the values of both the Tafel slope and the exchange-current density for the 4Pt + 6Pd/C_t electrode are higher than those for 4Pt + 6Ru/C_t and 7Pt/C_t electrodes, but are similar to those for the 7Pt/C_{vt} electrode.

Current-potential curves for the reduction of oxygen on 4Pt + 6Ru/C_t and 4Pt + 6Pd/C_t electrodes in 2.5 M H₂SO₄ and in 7 M H₃PO₄ between 30 and 60 °C are shown in Figs. 2 and 3, respectively. The performance curve for a 10 Pt/C_{vt} electrode has also been included for comparison. In 2.5 M H₂SO₄, it is evident that of all the electrodes tested, the 4Pt + 6Pd/C_t electrode exhibits the best performance (at 30 °C). This electrode can sustain

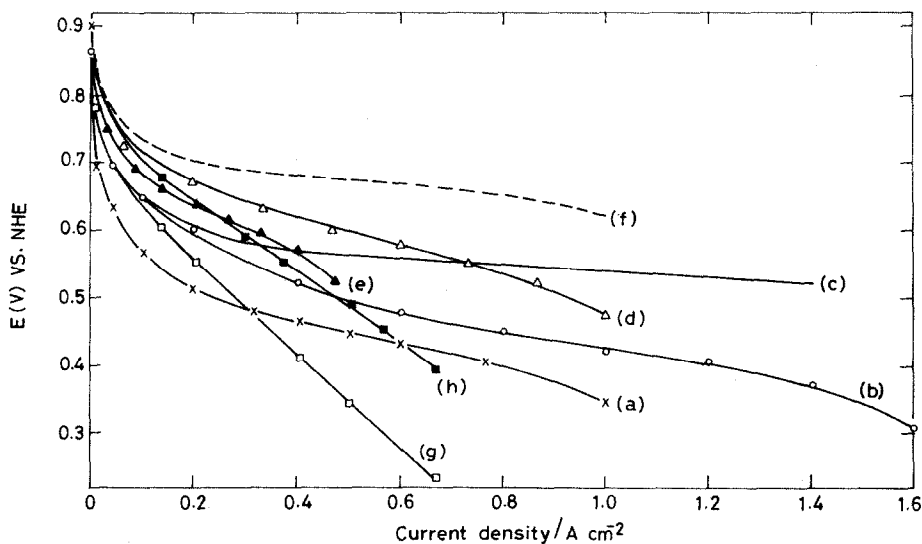


Fig. 2. Current-potential curves for oxygen reduction in 2.5 M H₂SO₄ on: (a) 4Pt + 6Ru/C_t at 30 °C; (b) 4Pt + 6Ru/C_t at 60 °C; (c) 4Pt + 6Ru/C_t at 60 °C with *iR*-correction; (d) 4Pt + 6Pd/C_t at 30 °C; (e) 4Pt + 6Pd/C_t at 60 °C; (f) 4Pt + 6Pd/C_t at 30 °C with *iR*-correction; (g) 10Pt/C_t at 30 °C; (h) 10Pt/C_t at 60 °C.

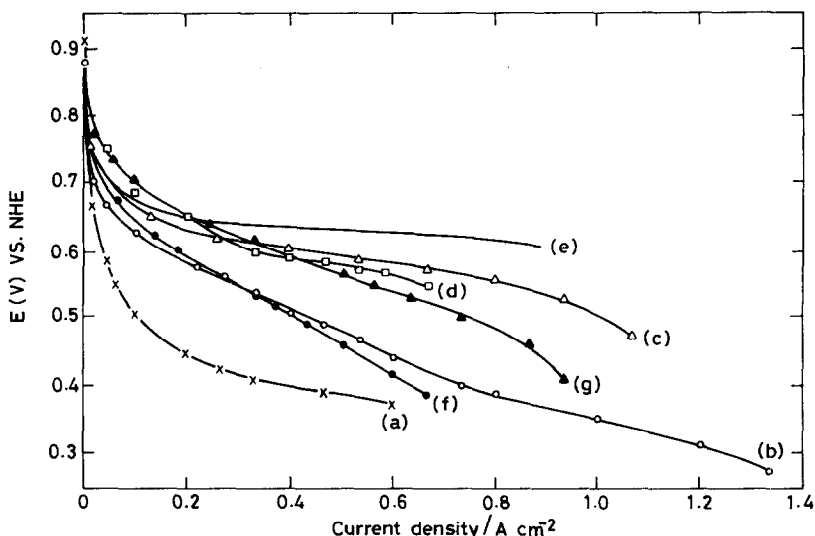


Fig. 3. Current-potential curves for oxygen reduction in 7 M H_3PO_4 on: (a) 4Pt + 6Ru/ C_t at 30 °C; (b) 4Pt + 6Ru/ C_t at 60 °C; (c) 4Pt + 6Pd/ C_t at 30 °C; (d) 4Pt + 6Pd/ C_t at 60 °C; (e) 4Pt + 6Pd/ C_t at 30 °C with iR -correction; (f) 10 Pt/ C_t at 30 °C; and (g) 10Pt/ C_t at 60 °C.

load currents as high as 1 A cm^{-2} at a polarization of about 450 mV, but shows reduced activity at 60 °C. Conversely, the performance of the 4Pt + 6Ru/ C_t electrode improves with rise in temperature. At 60 °C, this electrode delivers a current of 1.6 A cm^{-2} at a polarization of 600 mV. This performance is superior to that of a 10Pt/ C_t electrode. In 7 M H_3PO_4 electrolyte at 60 °C, the 4Pt + 6Ru/ C_t electrode can sustain load currents of 1.3 A cm^{-2} at a polarization of 600 mV. A comparison of current-potential curves obtained, both with and without iR -compensation for the 4Pt + 6Ru/ C_t electrode indicates the presence of a substantial ohmic component. Kinetic parameters obtained for the various catalyzed-carbon electrodes in the acid electrolytes are summarized in Table 2. In 2.5 M H_2SO_4 at 60 °C, the kinetic parameters of 4Pt + 6Ru/ C_t and 4Pt + 6Pd/ C_t electrodes cannot be compared with those of 10Pt/ C_t electrodes as the corresponding Tafel regions are quite different. Comparison is possible, however, at 30 °C, and it can be seen that the 4Pt + 6Pd/ C_t electrode has higher exchange current density and Tafel slope than the 4Pt + 6Ru/ C_t electrode. This is in agreement with the higher activity of the 4Pt + 6Pd/ C_t electrode at 30 °C.

The electronic resistivities of the various electrodes have been obtained by the interrupter method and are given in Table 3. In this method, when the current is interrupted, a rapid drop in the electrode potential, followed by an exponential decline, is observed; this is attributed to the iR -drop of the electrode [18]. The ratio of potential drop to load current is the resistance of the electrode, which is found to be almost constant over the entire current range. In acid electrolytes, the resistivities (Table 3) of electrodes decrease with temperature. Of the three electrolytes studied here, the resis-

TABLE 2
Kinetic parameters for oxygen reduction on different catalyzed electrodes in acidic electrolytes at 30 °C and 60 °C

Electrode	2.5 M H ₂ SO ₄ (30 °C)		2.5 M H ₂ SO ₄ (60 °C)		7 M H ₃ PO ₄ (30 °C)		7 M H ₃ PO ₄ (60 °C)	
	Tafel slope (V/decade)	Exchange-current density (A cm ⁻²)	Tafel slope (V/decade)	Exchange-current density (A cm ⁻²)	Tafel slope (V/decade)	Exchange-current density (A cm ⁻²)	Tafel slope (V/decade)	Exchange-current density (A cm ⁻²)
10Pt/C _t	0.085	1 × 10 ⁻⁸	0.150	6 × 10 ⁻⁵	0.09	9 × 10 ⁻⁸	0.085	2 × 10 ⁻⁷
4Pt + 6Ru/C _t	0.035	4 × 10 ⁻¹⁵	0.080	5 × 10 ⁻⁹	0.05	2.5 × 10 ⁻¹⁵	0.100	1.7 × 10 ⁻⁷
4Pt + 6Pd/C _t	0.040	4 × 10 ⁻¹⁴	0.055	2 × 10 ⁻¹²	0.05	2 × 10 ⁻¹⁵	0.060	3 × 10 ⁻¹⁴

TABLE 3

Electronic resistivities (ohm cm) of different catalyzed electrodes

Electrode	Electrolyte					
	6 M KOH		2.5 M H ₂ SO ₄		7 M H ₃ PO ₄	
	30 °C	60 °C	30 °C	60 °C	30 °C	60 °C
10 Pt/C _t	3.08	—	—	—	—	—
4Pt + 6Ru/C _t	4.37	—	3.70	2.57	2.42	1.63
4Pt + 6Pd/C _t	2.52	—	3.17	3.07	1.73	1.54

tivities of all the electrodes are least in 7 M H₃PO₄, both at 30 °C and at 60 °C. At 30 °C, the 4Pt + 6Pd/C_t electrode exhibits the lowest resistivity, which is also reflected by its higher catalytic activity in relation to the other electrodes.

Conclusion

This study clearly demonstrates that carbon-based fuel-cell electrodes with platinum-group bimetal catalysts exhibit higher catalytic activities than those observed for pure platinum, both in acidic and in alkaline electrolytes.

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