

Development of porous carbon electrodes for direct methanol fuel cells

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Abstract

Porous carbon electrodes containing platinum and platinum–ruthenium catalysts are prepared by a rolling technique with polytetrafluoroethylene as a binder. The 5 and 10 wt.% of the catalyst is deposited on a carbon substrate (Vulcan XC-72) by a colloidal dispersion technique. Half-cell polarization studies in 2.50 M H₂SO₄ electrolyte containing CH₃OH (1.0–3.0 M) have been carried out. The polarization values of electrodes containing platinum–ruthenium are lower than that of catalysts containing platinum only. Porous electrodes containing 2–5.0 mg cm⁻² of catalyst exhibit a polarization value of less than 300 mV at 100 mA cm⁻² at 60 °C in 2.50 M H₂SO₄. © 1997 Elsevier Science S.A.

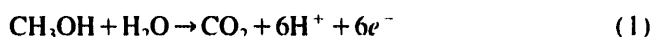
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1. Introduction

The direct methanol fuel cell (DMFC) is a promising power source for applications that require small-scale power units [1,2] in view of its favourable specific energy. Due to its ease of handling, availability, non-toxic nature and high solubility in acidic or alkaline solutions, methanol is considered to be a candidate fuel for these cells [3].

The DMFC converts methanol into CO₂ and H₂O and is therefore pollution free and environmentally favourable. The selection of the proper electrocatalyst is important in ensuring that the anodes and the cathodes have good life. Since 1960, much attention has been paid towards the development of suitable electrocatalyst materials for the direct electrochemical oxidation of methanol [4,5]. It is now widely accepted that the most promising catalyst materials used for the methanol oxidation reaction (MOR) are all platinum-based bimetallics. The use of bimetallic Pt–Sn [6–8] or Pt–Ru [9–12] catalysts has been reported to decrease the poisoning effect of the intermediate product and to increase the long-term stability of the electrocatalysts. The catalyst plays a bifunctional role in that it absorbs methanol and oxygen species from the electrolyte at the same potential and the adsorbed intermediate is oxidized easily. Recent studies have shown that Pt–Ru catalysts can be prepared in a highly dispersed form to achieve high activity per unit mass [13–15].

Gas-diffusion electrodes are promising as practical anodes for DMFCs [16–20]. It is reported that high loadings of catalyst (5–20 mg cm⁻²) are required since the activity for methanol oxidation is relatively lower. The oxidation reaction



is accompanied by the evolution of CO₂ on the electrode and results in the catalyst clusters being covered with CO₂ bubbles. As a result, the anodes generally exhibit high overpotentials at low current densities. Moreover, problems relating to methanol diffusion towards the cathode, that cause depolarization, are also identified. The development of catalysts, other than Pt that are not affected by the presence of methanol in the electrolyte have also been reported [21,22].

To overcome the above problems, proton-exchange membranes (PEM) are used as the electrolyte in cells that can deliver significant power outputs in the 60–90 °C range [23–25]. This requires fabrication of electrodes containing Pt catalysts bonded to SPE membranes using carbon cloth/felt as a current-collector material [26].

A schematic of a DMFC is shown in Fig. 1. The electrode structure consists of a three-phase zone, where the electrode is partially wetted, and filled with the electrolyte. The catalysts near the wetted portion contribute to the electrochemical reaction. The CO₂ that is evolved fills the macropore region of the porous electrode. The capillary force tends to fill the micropores with the electrolyte solution, while the gas pressure tends to push out the solution [27]. Hence, it is prefer-

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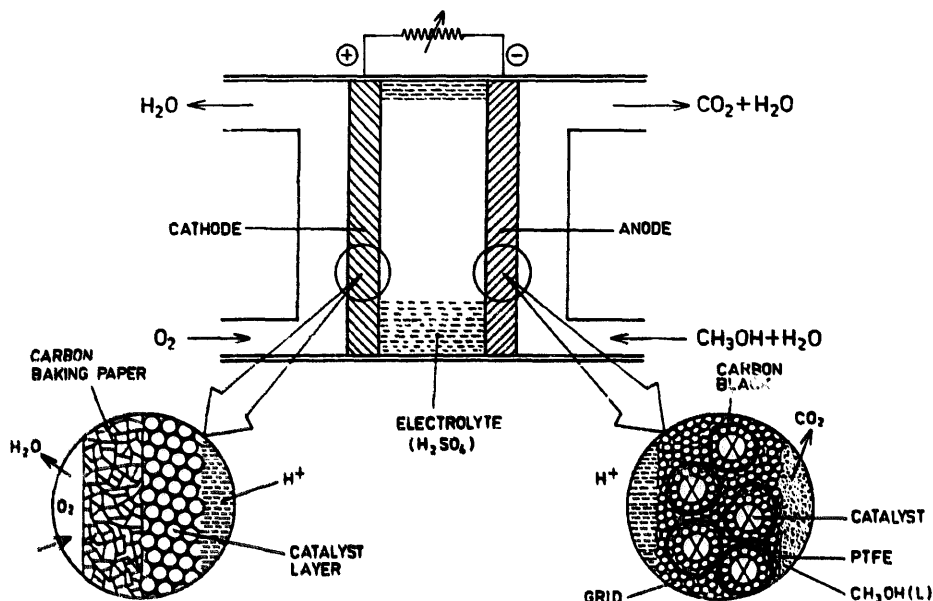


Fig. 1. Schematic model of a direct methanol fuel cell.

able to control the pore-size distribution of the electrodes. This has encouraged attempts to prepare porous electrodes by a rolling technique, in addition to the preparation of active catalysts (Pt, Pt–Ru) in the highly dispersed form on the carbon support. The performance of electrodes that contain $2\text{--}5\text{ mg cm}^{-2}$ catalysts evaluated by constructing half-cells in acid medium.

2. Experimental

Fuel-cell grade, carbon black, Vulcan XC-72 from Cabot, USA, was chosen as the catalyst support. This carbon was subjected to high-temperature heat treatment in a CO_2 atmosphere according to the method reported by Manoharan and Shukla [28]. The resulting carbon black had the following characteristics:

1. BET surface area: $245\text{ m}^2\text{ g}^{-1}$;
2. average particle size: $9.4\text{ }\mu\text{m}$;
3. resistivity: $2.75 \times 10^3\text{ }\Omega\text{ cm}$;
4. pH: 6.7, and
5. percentage weight loss: 20.5%.

2.1. Preparation of electrocatalysts

Pt and Ru salts obtained from Arora Mathey, India, were used to prepare solutions in double-distilled water. The carbon was digested with Pt and Pt–Ru solutions. This was achieved by using a modification of the colloidal reduction method, i.e. treatment with H_2O_2 and sodium dithionite, as described by Watanabe et al. [9]. The entire operation is indicated in the schematic (Fig. 2). The catalyst samples were dried and heat-treated in hydrogen at 673 K for 1 h. The catalyst loadings were kept at 5 and 10 wt.%.

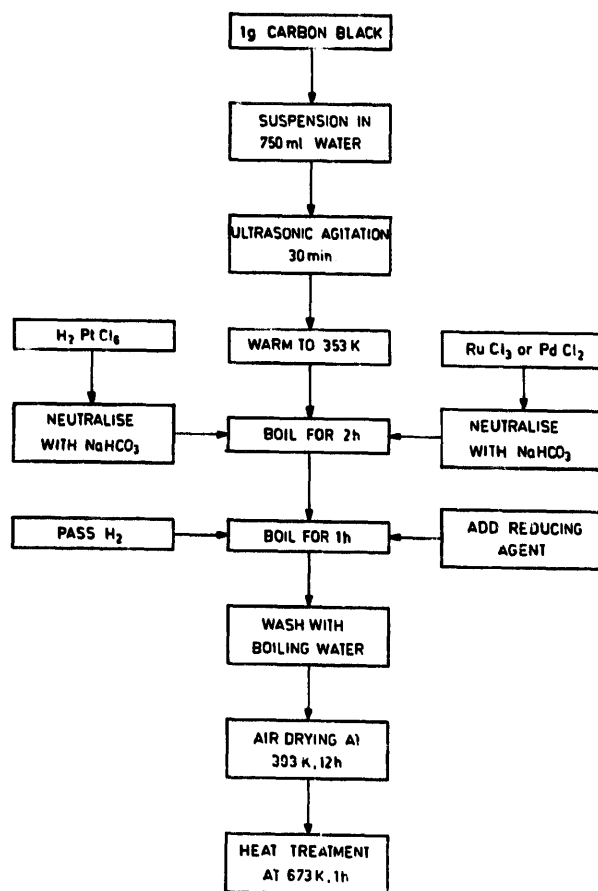


Fig. 2. Schematic for the preparation of Pt and Pt–Ru catalysts on carbon supports.

2.2. Preparation of porous carbon electrodes

Porous carbon electrodes were prepared by mixing the catalyzed carbon with 30 wt.% polytetrafluoroethylene (PTFE) powder or emulsion (Hindustan Fluorocarbon, Hyderabad, India) into a paste using rectified spirit and

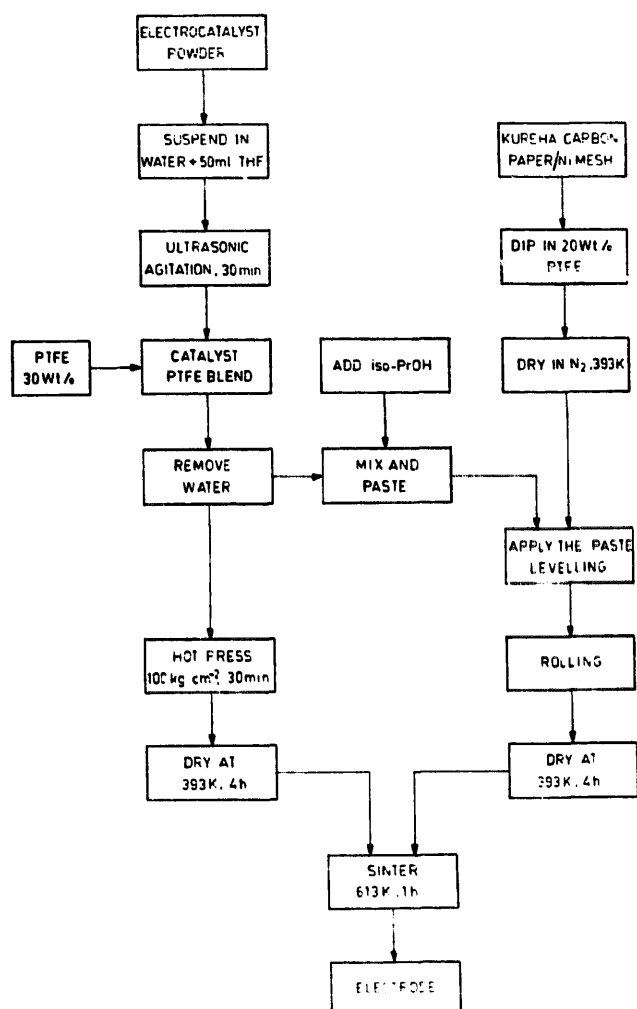


Fig. 3. Schematic for the preparation of porous carbon electrodes.

tetrahydrofuran (THF). The details have been reported in Ref. [29]. The paste was made into the form of an electrode by rolling (using a lightweight roller) over Kureha carbon paper and further compaction at 100 kg cm^{-2} . The Kureha carbon paper served as a current collector. Then, the electrodes were baked at 473 K for 1 h . A schematic of the entire operation is given in Fig. 3.

2.3. Electrochemical polarization studies

Electrochemical measurements were made with electrodes mounted in a conventional glass assembly. The electrolyte was sulfuric acid and methanol. The concentrations were varied from 1.0 to 3.0 M . A Pt foil was used as the counter electrode and a standard calomel electrode as the reference electrode. Steady-state galvanostatic polarization curves were obtained for the anodic oxidation of methanol on the above catalysed electrodes at 35°C .

3. Results and discussions

3.1. Characteristics of dispersed catalysts

The characteristics of Pt and Pt–Ru bimetallic catalysts employed in this investigation are summarized in Table 1.

Table 1
Physical characteristics of various catalysts

Catalyst	Support	Amount (wt.%)	Metal surface area ($\text{m}^2 \text{g}^{-1}$)
Pt	XC-72	1	101
Pt	XC-72	2	94.2
Pt	XC-72	5	89.4
Pt	XC-72	10	77.6
Pt	Commercial	2	89.5
Pt	Commercial	5	72.0
Pt	Commercial	10	70.6
Pt–Ru	XC-72	5	68.3
Pt–Ru	XC-72	10	70.8

X-ray diffraction (XRD), chemisorption and electrochemical techniques were employed in evaluating the crystallite size and metal surface (MSA) of the catalysts as reported in Refs. [30,31]. For comparison, 5 and 10 wt.% Pt/C samples from Arora Mathey were also used for preparing the electrodes. The crystallite size of the catalysts increased with the amount of catalyst and with a decrease in metal surface area.

3.2. Characteristics of porous carbon electrodes

Initially, attempts were made to prepare platinized carbon electrodes with different catalyst loadings. Different electrode-making procedures were adopted, e.g., hot/cold pressing and sintering at 400°C , rolling, etc., as indicated in Fig. 3. The electrodes made by the pressing technique had a diameter of either 4.4 or 6.2 cm , and those made by rolling were cut into $2 \text{ cm} \times 5 \text{ cm}$ size.

Surface examination of the porous electrodes was carried out using a JEOL JSF 35 Model scanning electron microscope (SEM). SEM graphs of the electrodes are shown in Fig. 4. Visual surface examination of the electrodes revealed that the hot-pressed and rolled electrodes were rubber or leather like, and that the surface of the cold-pressed electrode was not smooth. The SEM graphs indicate a uniform distribution of pores for the hot-pressed and rolled electrodes, and large holes for the cold compacted and sintered electrodes. Proper curing was applied to remove the Teflon binder from the electrode. An electron probe image analysis for the Pt distribution in the electrode is shown in Fig. 4(d). A uniform distribution of catalyst particles is observed.

3.3. Polarization characteristics of anodes with Pt catalysts in acid medium

Polarization curves for platinized carbon electrodes with different amounts of catalyst (wt.%) and obtained in $1.0 \text{ M H}_2\text{SO}_4 + 1.0 \text{ M CH}_3\text{OH}$ at 308 K are presented in Fig. 5. The polarization is found to be lower at high catalyst contents per unit area. Current densities of the order of 50 and 80 mA cm^{-2} are obtained at an overpotential of 500 mV for catalyst loadings of 2 and $5 \text{ wt.}\%$, respectively. At the lowest catalyst loading of 1 mg cm^{-2} with $1 \text{ wt.}\%$ Pt, a specific activity value

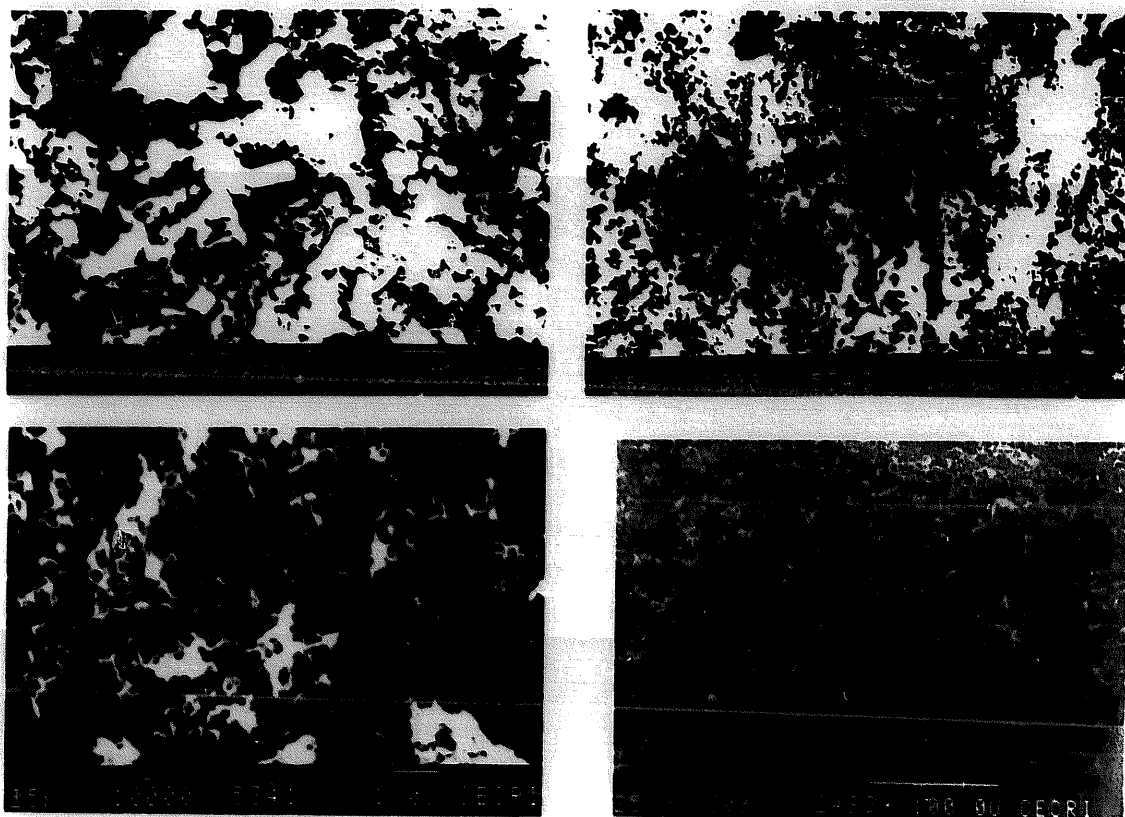


Fig. 4. SEM graphs of the electrodes: (a) rolled electrode on carbon paper; (b) rolled electrode on nickel mesh; (c) cold compacted and sintered electrode, and (d) electron probe microanalysis image of Pt distribution.

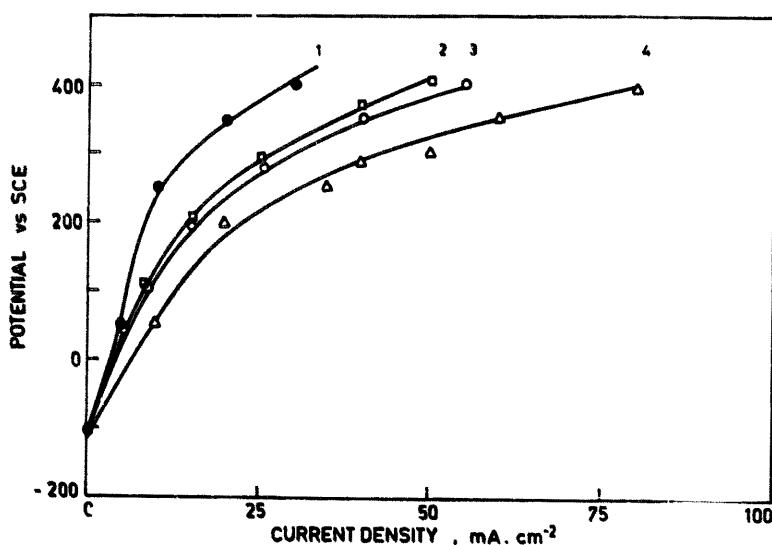


Fig. 5. Steady-state polarization of porous electrodes with different catalysts loadings: (1) 1 wt.%; (2) 2 wt.%; (3) 3 wt.%, and (4) 5 wt.%,

of 30 A g^{-1} is obtained. The low polarization values at high catalyst loadings is an indication of the availability of catalyst, per unit geometric area of the electrode surface, for the electrochemical reaction and leads to a higher utilization of the catalyst surface. An optimum value of 2.0 mg cm^{-2} was chosen for comparison of the different types of electrode.

The specific activities (A g^{-1}) of the different catalysts are given in Table 2. It is found that the specific activity for the oxidation of CH_3OH in $1.0 \text{ M H}_2\text{SO}_4$ decreases with increase in catalyst loading. It is reported that the overpoten-

tial versus $\log(\text{activity})$ curves are parallel and give a Tafel slope of 110 to 130 mV in the current density $10\text{--}100 \text{ mA cm}^{-2}$ range [7,14].

In Fig. 6, a comparison is given of the electrocatalytic activity for methanol oxidation of Pt catalysts prepared in our laboratory by colloidal route and of a commercially available sample. Overpotential versus $\log(\text{specific activity})$ are given for 2, 5 and 10 wt.% Pt on carbon (commercial sample) and 10 wt.% Pt on carbon in prepared samples. The last-mentioned sample exhibits a better activity of 40 A g^{-1} than the

Table 2
Comparison of specific activity of Pt and Pt-Ru catalysts for CH₃OH (1.0 M) oxidation in acid medium (1.0 M H₂SO₄) at 300 mV

Catalyst amount	Loading (mg cm ⁻²)	Current density (mA cm ⁻²)	Specific activity per real area (A g ⁻¹)	Specific activity per real area (A m ⁻²)
<i>Commercial sample</i>				
2	2	50	25	0.28
5	2	60	30	0.42
10	2	80	40	0.56
<i>Prepared samples with Pt catalyst</i>				
1	1	20	20	0.19
2	2	50	25	0.26
5	2	80	40	0.45
5	5	100	20	0.35
10	2	90	45	0.58
10	3	120	40	0.51
<i>Pt-Ru catalyst</i>				
5	2	200	100	1.46
10	2	240	120	1.70

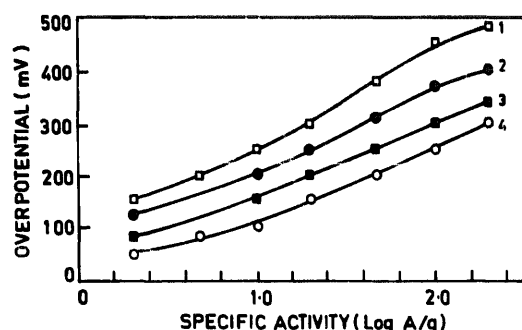


Fig. 6. Tafel plots for Pt/C electrodes: (1) 2 wt.%; (2) 5 wt.%; (3) 10 wt.% (commercial), and (4) 10 wt.% (prepared).

commercial sample (30 A g⁻¹) at the same catalyst loading (10 wt.%) and 2 mg cm⁻² per electrode. The 10 wt.% Pt on carbon catalysts always led to higher activities, namely, 50 and 40 A g⁻¹ for the prepared and commercial samples, respectively.

3.4. Influence of concentration of methanol and sulfuric acid

The polarization characteristics of porous carbon electrodes (5 wt.% Pt) in 1.0 and 3.0 M CH₃OH in 1.0 and 2.5 M H₂SO₄ solutions show that the polarization is lower at higher concentrations. This can be attributed mainly to the higher conductivity of the electrolyte and the mass transport of CH₃OH molecules to the reaction site on the porous electrodes. A similar phenomenon has been reported recently [32].

3.5. Polarization characteristics with electrodes containing Pt-Ru catalyst

It has been reported earlier [14] that the bimetallic Pt-Ru (60:40 wt.%) catalysts exhibit a maximum in activity [14]. The polarization behaviour of these electrodes in 1.0 and 3.0 M H₂SO₄, is shown in Fig. 7. Compared with Pt catalysts,

the bimetallic catalyst always exhibits a superior activity. The specific activity values are also compared in Table 2.

It is clear that porous carbon electrodes containing Pt-Ru catalysts exhibit a polarization difference of 100 mV at current densities greater than 100 mA cm⁻². The long-term stability of these electrodes have been tested. It is found that these electrodes suffer a loss of 0.2 mV h⁻¹ at 100 mA cm⁻². The electrodes have been also tested for 100 h intermittently at 333 K.

3.6. Comparison of activity of various anodes with cathodes

Carbon electrodes containing Pt catalysts have been tested for oxygen reduction in acid and alkaline fuel cells [29]. The polarization loss is about 150 to 200 mV at 100 mA cm⁻² in 3.0 M H₂SO₄. The polarization values obtained in solutions of 3.0 M CH₃OH and 3.0 M H₂SO₄ (Fig. 7) indicate a shift of the polarization curve in a similar manner to its behaviour in 3.0 M H₂SO₄, due to the fact that the equilibrium potential

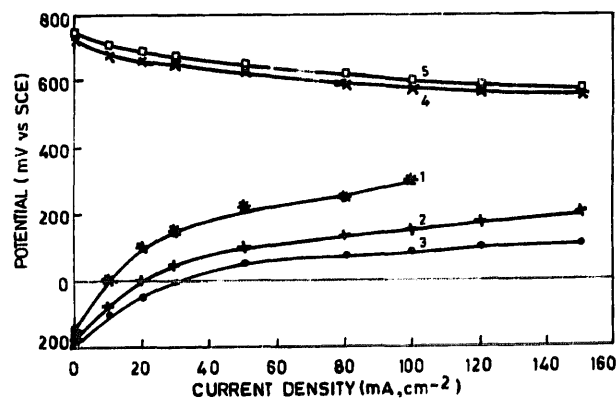


Fig. 7. Comparison of polarization curves: (1) Pt/C in 1.0 M CH₃OH + 1.0 M H₂SO₄ at 303 K; (2) Pt-Ru/C in 1.0 M CH₃OH + 2.5 M H₂SO₄ at 303 K; (3) Pt-Ru/C in 1.0 M CH₃OH + 2.5 M H₂SO₄ at 333 K; (4) oxygen cathodes (Pt/C) in 1.0 M CH₃OH + 1.0 M H₂SO₄ at 303 K, and (5) at 333 K.

of the oxygen electrode is shifted by 100 mV in the presence of methanol. This behaviour represents the performance of the anodes and cathodes in the same electrolyte composition, but does not represent the behaviour of an actual cell.

From the above results, it is clear that a methanol fuel cell will have the following characteristics. The open-circuit voltage will be around 0.85 V at 303 and 333 K. At a current density of 50 mA cm⁻² at 303 K, a cell voltage of 0.45 and 0.55 V could be realized with Pt and Pt–Ru catalysts, respectively, for a 2 mg cm⁻² catalyst loading on both the electrodes. At 333 K, the cell voltage will be increased to 0.6 V with Pt–Ru catalysed electrodes. High current densities of 100 mA cm⁻² can be realized at 0.45 V at 333 K. The performance is comparatively better than the value reported in literature, i.e. at an overpotential of 300 mV, the current density is 120 mA cm⁻² at a catalyst loading of 2 mg cm⁻². The best values reported are 150 mA cm⁻² at 5 mg cm⁻² [16], and 100 mA cm⁻² at 2 mg cm⁻² [17].

4. Summary

Porous carbon electrodes containing Pt–Ru catalysts (5 wt.%) and at a catalyst loading of 2 mg cm⁻² exhibit a polarization of less than 300 mV at 100 mA cm⁻². It is possible to develop practical fuel cells operating at this current density. The cells deliver a voltage higher than 0.6 V/cell at 60 °C. Improvements in the cathode performance to overcome the initial shift of the equilibrium potential will be communicated in a subsequent paper.

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