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Short communication

A rapid half-cell technique for the pre-screening of polymer fuel cell catalysts

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Abstract

Four platinum-based catalysts with different catalytic activity for the oxygen reduction reaction have been prepared and tested in polymer fuel cells (PFCs) and in half-cells with H₂SO₄ and HF electrolytes. The activity results of PFCs at 0.9 V versus RHE (reversible hydrogen electrode) can be mimicked in parallel by the results obtained in HF electrolyte but not by the results obtained in H₂SO₄ electrolyte. This paper concludes that the pre-screening of a huge number of Pt-based catalysts for the selection of potential catalysts for the PFCs can be carried out by a rapid half-cell technique with a non-adsorbing electrolyte such as HF. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Electrochemical power sources such as advanced batteries and fuel cells are considered as potential candidates for the zero emission vehicle (ZEV). Because of their many attractive features including cold start-up and ruggedness, H₂/O₂ polymer fuel cells (PFC) are being extensively investigated for electric vehicle (EV) applications. The gravimetric and volumetric energy densities (for a long range) of fuel cells are, in general, superior to the advanced batteries whereas the power density (for a higher acceleration) is inferior.

To increase the power density, the kinetic, ohmic and diffusion related polarization losses will have to be reduced. The losses related to poor kinetics, higher resistance and poor mass-transport can be reduced by selecting efficient catalysts, using low resistance polymeric membrane and improving structural formulations

of the electrodes/gas distribution channels, respectively. The current paper deals with the selection of efficient oxygen/air electrode catalysts.

A large number of carbon-supported nanocrystalline Pt-alloys have been evaluated for the oxygen reduction reaction in hot (~180°C) phosphoric acid fuel cells [1,2]. But, only a few Pt-alloys or alloy-mixtures have been investigated in PFCs [3,4]. This situation necessitates that a huge number of Pt-alloy catalysts need to be pre-screened before the final selection of the most efficient catalyst(s) for the PFCs.

The direct evaluation of various Pt-alloy catalysts in a PFC test station is, however, time consuming and expensive: hence, it would be practically useful to devise a rapid half-cell technique which could mimic the complete PFC. The overall objective of this work is, therefore, to demonstrate experimentally that the rapidly obtained liquid based half-cell results can parallelly simulate the oxygen electrode results of a complete polymer fuel cell. In the current work, we have prepared carbon-supported Pt–Cu and Pt–Co alloys and

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tested them in PFC and in a simple half-cell (rotating disk electrode).

2. Experimental

2.1. Preparation of Pt₃Cu/C and Pt₃Co/C alloys

A mixture of 20 w/o Pt/C (E-Tek, Natick, MA) and copper nitrate (Cu(NO₃)₂·5/2 H₂O) was used to prepare a carbon-supported Pt₃Cu alloy. A solution containing 80 ml of water and 1.5 g of Pt/C was ultrasonically blended and the pH was adjusted to 8 using dilute NH₄OH solution. The blending was continued for 30 min and the pH was again adjusted to 6.3 using dilute HNO₃. A powder of copper nitrate (0.1192 g) was added to the solution and the pH was maintained at 6.3. After blending for 30 min more, the solution was filtered and dried in an air oven for 12 h. Finally, the alloying was performed by heat treating the dried mixture at 900°C for 2 h in a flowing argon atmosphere [4].

A mixture of 20 w/o Pt/C and cobalt hydroxide (Co(OH)₂) was used to prepare a carbon supported Pt₃Co alloy using a method described elsewhere [5]. A brief account on the preparation procedure is provided here: The pH of the solution containing 0.016 g of Co(OH)₂ and 50 ml of water + methanol (50/50) mixture was adjusted to 2 using dilute HCl. The solution was ultrasonically blended with 0.5 g of Pt/C for 2 h at about 60°C to achieve a good blending and to reduce the solution volume. After drying the mixture in an air oven for a prolonged period of time, the alloying was carried out by heat treating the dried mixture at 900°C for 2 h in a flowing argon atmosphere.

The as-received Pt/C (hereafter referred as Pt/C (AR)) was heat-treated at 900°C for 2 h in a flowing argon atmosphere (hereafter referred as Pt/C (HT)). These two Pt/C catalysts were used for the purposes of a comparative study.

2.2. Physical characterization of Pt/C and alloys

The alloy and size characteristics of Pt-alloy/C and Pt/C were determined by powder X-ray diffraction (XRD) method. The diffraction patterns of these materials were analysed for the changes in lattice parameters using ASTM (American Standards for Testing Materials) powder diffraction files. The diffractograms were recorded with a copper source. The diffractometer was operated in the step scan mode with a 0.05° step and 12 s fixed time.

The compositional analysis was carried out by both EDAX (energy dispersive analysis of X-rays) and NAA (neutron activation analysis) methods.

2.3. Preparation of PFC electrodes

2.3.1. Anode

A standard 20 w/o Pt/C electrode (0.4 mg cm⁻² Pt loading; E-Tek, Natick, MA) was impregnated with Nafion® (ca. 0.7 mg cm⁻² dry Nafion® loading) and used as an anode (5 cm² geometric area).

2.3.2. Cathode

The Nafion® impregnated Pt/C active layer on an uncatalyzed carbon-cloth backing was prepared as follows: a mixture of 12.9 mg of Pt/C (AR), Pt/C (HT), Pt₃Cu/C or Pt₃Co/C with 0.1 ml of 5 w/o Nafion® solution (Aldrich Chemicals) and 0.7 ml of water was ultrasonically blended in a closed vial for 60 min to obtain a thick catalyst paint. The paint was brushed onto a pre-weighed carbon-cloth backing (5 cm² geometric area; E-Tek). To enhance the drying rate of the catalyst paint, the carbon-cloth backing was placed on a lightly heated hot-plate during the brushing step. The electrode was then vacuum dried at 70°C for 1 h and weighed. The weight of the active layer (Pt/C and dry Nafion®) was obtained from the difference of the weights (before and after brushing the paint). Since the initial weight ratio between Pt/C and Nafion® is known, the platinum loading in the electrode can be calculated. Platinum loadings in these electrodes are: 0.160 mg Pt cm⁻² for Pt/C (AR); 0.213 mg Pt cm⁻² for Pt/C (HT); 0.167 mg Pt cm⁻² for Pt₃Cu/C; and 0.182 mg Pt cm² for Pt₃Co/C.

2.4. Testing of PFC electrodes

The anode|membrane|cathode single cell assembly was fabricated by hot-pressing a (pre-cleaned) Nafion 117 membrane (5 cm × 5 cm) between the electrodes (5 cm²) at 150°C and 3200 psig (1 psig = 6.895 kPa) for 60 s. The cell assembly was mounted in a single cell test fixture and connected to a fuel cell test station purchased from GlobeTech (TX, USA). Polarization measurements were carried out versus RHE (reversible hydrogen electrode) under the following experimental conditions: cell temperature of 80°C, hydrogen pressure of 30 psig and oxygen pressure of 60 psig. The hydrogen and oxygen flow rates were controlled using mass flow meters (MKS instruments, Andover, MA) at 0.15 and 0.25 SLM (standard liter per min), respectively. All the test results are referenced to RHE.

2.5. Preparation of half-cell electrodes

A dried layer of catalyst paint spread on the surface of a rotating disk electrode (RDE) was used as the working electrode in a half-cell. The dried active catalyst layer preparation procedure has already been explained in our previous publications [6,7] and only a

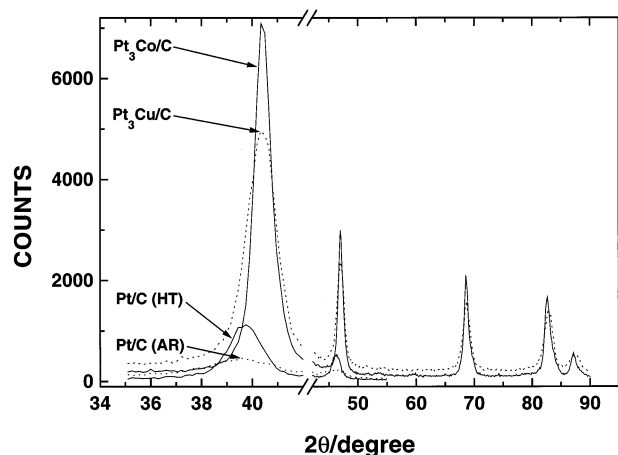


Fig. 1. X-ray diffractograms of the Pt/C and Pt-alloy/C catalysts.

brief process description is provided here: A volume of 10 μl of blended paint containing 12.9 mg of Pt/C (AR), Pt/C (HT), Pt₃Cu/C or Pt₃Co/C with 0.1 ml of 5 w/o Nafion[®] solution (Aldrich Chemicals) and 0.7 ml of water was pipetted and spread as a thin catalyst layer on the surface of a vitreous carbon RDE (0.196 cm² geometric area). This layer was then dried in an air oven at 80°C for about 10 min. The volume of 10 μl paint corresponds to a Pt/C or Pt-alloy/C loading of 0.823 mg cm⁻² which in turn translates to a Pt metal loading of about 0.165 mg cm⁻². In order to insure the reproducibility of the results, three electrodes, as a minimum, were prepared and tested for each catalyst.

2.6. Testing of half-cell electrodes

The RDEs with the catalyst layers were used as working electrodes in oxygen saturated H₂SO₄ (1.17 M) and HF (1.17 M) acids. A platinum foil served as the counter-electrode in both acids. A saturated calomel electrode (SCE) and RHE were used as reference electrodes in H₂SO₄ and HF acids, respectively. All the measurements were carried out at a rotation speed of 1500 rpm and a scan rate of 10 mV s⁻¹ using an RDE setup purchased from Pine Instruments Company. All the test results are referenced to the RHE. It may be

worth mentioning that the testing of a half-cell electrode in liquid electrolyte requires only about 10 min whereas in SPFC it accounts for more than 100 min.

Testing of the RDEs in H₂SO₄ acid was carried out in a standard glass cell whereas in HF acid it was carried out in a specially made two-compartment Teflon cell. The master compartment contained the working electrode (RDE), counter electrode and oxygen saturated HF acid. The minor compartment contained RHE and HF acid, and it was separated from the master compartment by a Nafion 117[®] membrane.

3. Results and discussion

3.1. Physical properties of the catalysts

A shift in the XRD peak positions, in Fig. 1, of the bimetallic Pt–Co/C and Pt–Cu/C catalysts towards higher diffraction angles, as compared to Pt/C peak positions, indicates the effect of alloying and a contraction in the lattice parameters. The sizes of the nano-sized Pt and Pt-alloy crystallites were calculated using FWHM (full width at half-maximum) of the most prominent (111) peak. The specific area S (m² g⁻¹) for the crystallites was calculated using the following equation [8]:

$$S = 6 \times 10^4 \rho^{-1} d^{-1}$$

where d is the diameter of the particle (\AA) and ρ is the density of platinum metal (21.4 g cm⁻³). The characteristic features of XRD studies are summarized in Table 1. Higher crystallite sizes or lower specific areas noted in Table 1 for the Pt-alloy/C and Pt/C (HT) catalysts, as compared to Pt/C (AR), are attributed to higher temperature heat-treatment of the catalysts. The compositions obtained from NAA and EDAX analyses are shown in Table 1.

3.2. Relative activity of Pt-alloy catalysts in PFCs

The polarization curves for all the four catalysts in PFC are shown in Fig. 2. This figure indicates that

Table 1
Elemental composition and XRD data of carbon-supported Pt and Pt-alloy catalysts

Catalyst type	Size/ \AA	Metal area/m ² g ⁻¹	Atomic composition ^a /%		
			Pt	Cu	Co
Pt/C (AR)	27	104	100	—	—
Pt/C (HT)	56	50	100	—	—
Pt ₃ Cu/C	68	41	74.4 (75.4)	25.6 (24.6)	—
Pt ₃ Co/C	114	25	79.7 (80.8)	—	20.3 (19.2)

^a Determined by NAA and EDAX. The values from the latter analysis are shown in parentheses.

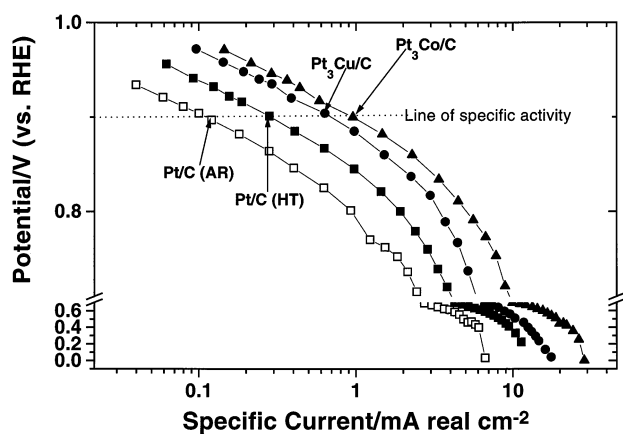


Fig. 2. PFC polarization curves for the Pt/C and Pt-alloy/C catalysts (test conditions: 80°C; H₂/O₂ at 30/60 psig).

there is an improvement in specific activity (calculated by mass activity (in mA mg⁻¹ Pt) ÷ specific area (in real cm² mg⁻¹ Pt)) at 0.9 V, as compared to the Pt/C (AR) catalyst, for the Pt/C (HT) and Pt-alloy/C catalysts. The order of specific activity of the tested catalysts in PFC is: Pt₃Co/C > Pt₃Cu/C > Pt/C (HT) > Pt/C (AR).

3.3. Relative activity of Pt-alloy catalysts in H₂SO₄ acid

The RDE cathodic curves for the oxygen reduction reaction in sulfuric acid are shown in Fig. 3. This figure indicates that the specific activity at 0.9 V is independent of the catalyst type used. This observation is inconsistent with the result obtained in PFC. The unchanging activity of different catalysts in sulfuric acid could be due to the competition of anion adsorption of sulfuric acid with the oxygen adsorption [6]. In order to mimic the PFC result in parallel, it therefore becomes necessary to select a non-adsorbing liquid acid for the half-cell studies.

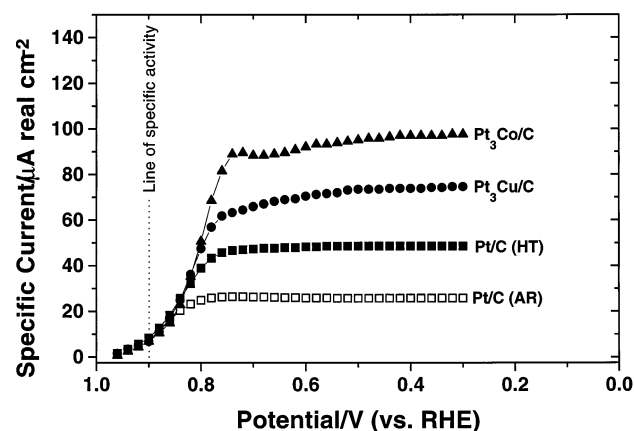


Fig. 3. RDE cathodic curves for the Pt/C and Pt-alloy/C catalysts in oxygen saturated H₂SO₄ at room temperature.

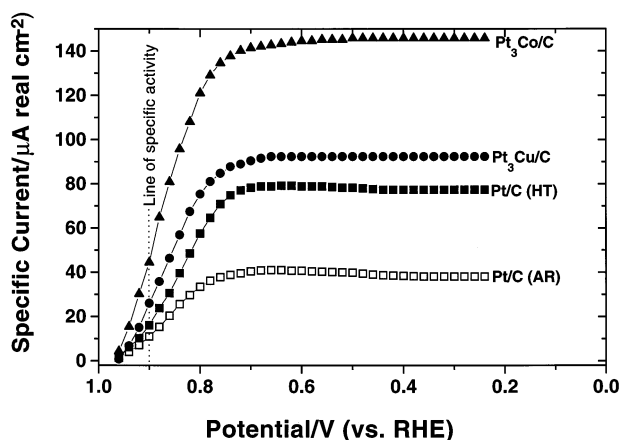


Fig. 4. RDE cathodic curves for the Pt/C and Pt-alloy/C catalysts in oxygen saturated HF at room temperature.

3.4. Relative activity of Pt-alloy catalysts in HF acid

It is well known that HF acid is a non-adsorbing electrolyte and it was confirmed in our previous study [6]. The RDE cathodic curves for the oxygen reduction reaction in HF acid is shown in Fig. 4. The order of specific activity of the tested catalysts in HF at 0.9 V is: Pt₃Co/C > Pt₃Cu/C > Pt/C (HT) > Pt/C (AR) which is exactly the same as that in PFC.

This study thus indicates that the electrode|membrane interface of PFC could be mimicked by the electrode|HF interface, and not by the electrode|H₂SO₄ interface. The parallel simulation of PFC by HF and non-parallel simulation of PFC by H₂SO₄ are shown in Fig. 5. It is recommended that the RDE studies in HF should be restricted only to the pre-screening of the catalysts and should not be extended to the long-term endurance testing of the selected catalysts. The endurance testing of the selected catalysts should be done in the real PFC environments.

The order of specific current in sulfuric acid at less positive potential, for example at 0.5 V, also appears to follow the specific activity order of PFC. This ob-

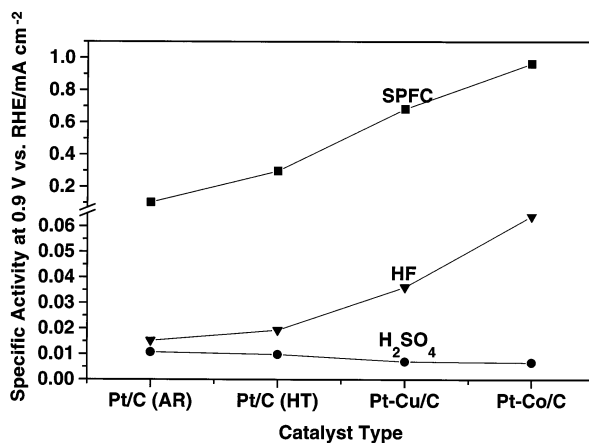


Fig. 5. Parallel and non-parallel simulation of PFC by HF and H₂SO₄, respectively.

ervation tends to suggest that the adsorption of anions from H_2SO_4 is potential dependent and it becomes negligible at less positive potential; hence, the true order of activity is observed at less positive potentials.

4. Conclusions

Four catalysts with different catalytic activity for the oxygen reduction reaction have been tested in PFCs and in half-cells with adsorbing H_2SO_4 electrolyte and non-adsorbing HF electrolyte. It is concluded that the oxygen reduction performance of a Pt-based PFC cathode can be simulated in parallel by a rapid rotating disk electrode with a non-adsorbing electrolyte such as HF. The practical importance of this conclusion is that the pre-screening of a large number of Pt-alloy catalysts, in order to select potential candidates for PFC cathodes, can be carried out by a much less time consuming rotating disk electrode technique.

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