

# Bifunctional electrodes with a thin catalyst layer for ‘unitized’ proton exchange membrane regenerative fuel cell

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## Abstract

A bifunctional electrode structure for a unitized proton exchange membrane regenerative fuel cell has been developed. The electrode has only a thin catalyst layer; it reduces the loading of the catalyst to  $0.4 \text{ mg cm}^{-2}$ , and minimizes mass transport and ohmic limitations. A satisfactory performance of a unitized proton exchange membrane fuel cell is achieved with this electrode structure. 50 wt.% Pt + 50 wt.%  $\text{IrO}_2$  is a good bifunctional catalyst for the oxygen electrode. Examination of this catalyst by transmission electron microscopy and of the electrode by scanning electron microscopy is reported. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Regenerative fuel cell; Bifunctional electrode; Proton-exchange membrane; Catalyst layer

## 1. Introduction

The conversion and storage of energy with a high efficiency, especially a high specific energy, will be an important factor in future space activities as well as in terrestrial applications. The relatively simple possibility to store hydrogen and oxygen with high specific energy combined with high energy-conversion efficiency in fuel cells and electrolyzers presents a great opportunity for the use of regenerative fuel cell systems (RFCS) as energy storage devices [1,2].

In the design of a regenerative fuel cell, two approaches may be taken: (i) the fuel cell and electrolysis units may be kept separate; (ii) only one unit functions as a fuel cell and an electrolyser, in other words as a ‘unitized’ regenerative fuel cell. The key technology in the development of the unitized regenerative fuel cell is a bifunctional catalyst and electrode. Such an electrode can perform in both the fuel-cell mode and the electrolyser mode. Swette et al. [3] used an integrated dual-character electrode in a unitized proton exchange membrane fuel cell (PEMRF) [3], but the two-layer structure electrode increased the thickness of the catalyst layer of the electrode and inhibited the diffu-

sion of reactant and product. Thin-film catalyst electrodes have been used in proton exchange membrane fuel cells [4,5], but not in unitized PEMRFs. Thus, in this work, we developed a bifunctional electrode with a catalyst layer structure based on the thin-film catalyst electrode.

## 2. Experimental

### 2.1. Catalyst materials

Platinum black was used as bifunctional hydrogen catalyst, and platinum black and iridium oxide was used as a bifunctional oxygen catalyst. Platinum black was made by using HCHO to reduce  $\text{H}_2\text{PtCl}_6$  [6]. Iridium oxide was made by proprietary modification of Adams-type fusion of the iridium salt in a nitrate flux [7].

### 2.2. Preparation of membrane / bifunctional electrode assembly

The bifunctional electrode was composed of a catalyst layer and a support layer that were prepared in separate ways. For the electrode support layer, a sheet of carbon paper was soaked in a Teflon emulsion. The PTFE comprised about 30 wt.% of support layer. For the catalyst layer, a thin film catalyst layer method was used. A

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Nafion/catalyst/glycerol slurry was prepared by thoroughly mixing the components together in an ultrasonic bath; the ratio of catalyst to Nafion (5 wt.% solution in iso-propanol) was 3:1 (in weight of solids) [5]. The protonated form of Nafion in the slurry was converted to the  $\text{Na}^+$  form by the addition of 0.5 M NaOH. Since the addition of alkaline solution directly to the solubilized Nafion results in some coagulation, the NaOH solution was not added until the catalyst and Nafion solution were extremely well mixed.

The transfer printing technique was used to make the catalyst layer [4], the slurry was sprayed on a PTFE film, and then the coated layer was dried for 2 h at 135°C in a vacuum oven. The coated blank, membrane and counter electrode were hot-press together for 1.5 min at 180°C at a pressure of 70 atm. The membrane/catalyst assembly was removed from the press and allowed to cool, then the PTFE film was peeled away from the membrane to leave the thin-film catalyst layer adhering to the membrane. Nafion 115 membrane was used. Finally, the catalyzed membrane was rehydrated and ion-exchanged to produce the  $\text{H}^+$  form by immersion in a lightly boiling 0.5 M sulfuric acid for 30 min, followed by rinsing in deionized water.

50 wt.% Pt + 50 wt.%  $\text{IrO}_2$  was used as the catalyst for the bifunctional oxygen electrode. The loading of each catalyst was  $0.2 \text{ mg cm}^{-2}$ . Platinum black was used as the catalyst of the bifunctional hydrogen electrode with a loading of  $0.4 \text{ mg cm}^{-2}$ .

The support layer was pressed against the catalyst layer by mechanical compression of the cell assembly.

### 2.3. Design and assembly of single cell

A single cell was constructed and comprised the membrane/electrode assembly, two stainless steel plates with bib-channel patterns on the side for gas and water supply, and two Teflon gaskets. The cell assembly is shown in Fig. 1.

In the fuel-cell mode, the gases were supplied at 0.3 MPa and the  $\text{H}_2$  stream was humidified at 90°C. In

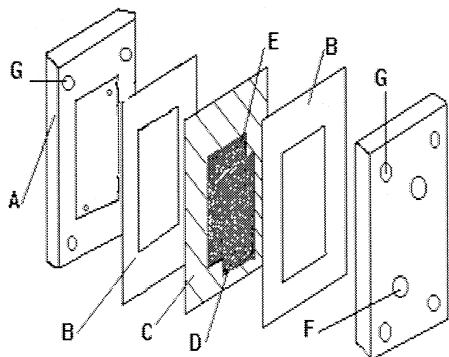


Fig. 1. Cell parts for single cell assembly: (A) stainless-steel plate; (B) Teflon gasket; (C) membrane; (D) hydrogen electrode; (E) oxygen electrode; (F) gas ports; (G) alignment hole.

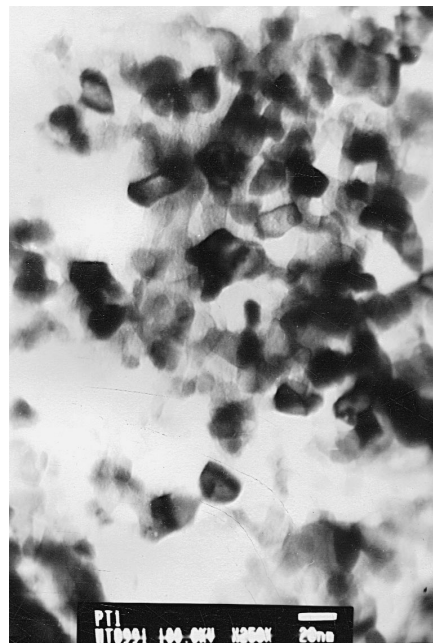


Fig. 2. TEM micrograph of platinum black.

electrolysis, the cell was run at ambient pressure with heated water pumped into the positive electrode chamber. The active area of electrodes was  $5 \text{ cm}^2$ .

Data for fuel-cell operation mode were first collected. The fuel cell was conditioned for 12 h at 50°C before the data were collected. The cell was then run as an electrolyser, in which mode hydrogen was produced at hydrogen electrode and oxygen at the oxygen electrode. After data collection in the electrolysis mode, the cell was immedi-

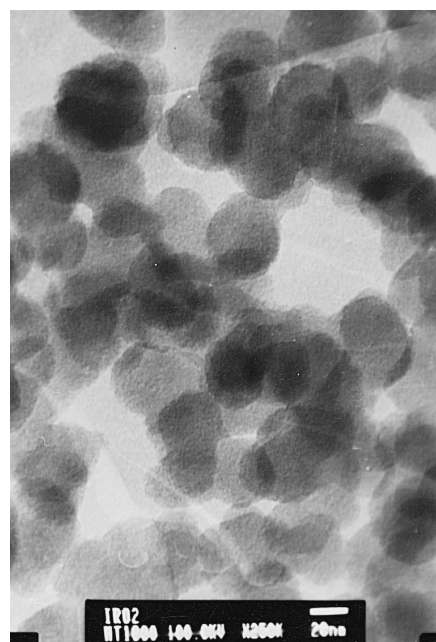


Fig. 3. TEM micrograph of iridium oxide.

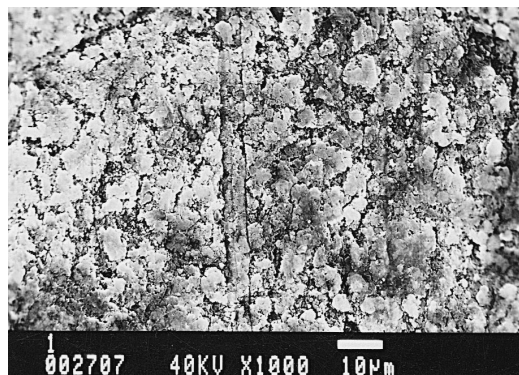


Fig. 4. Scanning electron micrograph of the catalyst layer of a bifunctional oxygen electrode.

ately connected as a fuel cell by passing the reactant gases through the cell. A current ( $100 \text{ mA cm}^{-2}$ ) could be immediately drawn from the cell. A period of 1 h was again allowed for cell conditioning at  $80^\circ\text{C}$ . This was followed by data collection as a fuel cell. The cycle of fuel cell-electrolyser was then repeated.

#### 2.4. Analysis by transmission electron microscopy

Analysis by transmission electron microscopy (TEM) was conducted on the platinum black powders and the iridium oxide catalyst powders. The powders were dispersed in ethanol, using an ultrasonic bath, and then mounted on standard copper TEM grids. A JEM-1200EX microscope was used.

#### 2.5. Analysis by scanning electron microscopy

The catalyst layer surface of the electrode and the cross-section of the membrane/electrode assembly were observed by means of a scanning electron microscope (SEM, JEM-1200EX). For such analyses, samples of the membrane and electrode assemblies were broken, with two

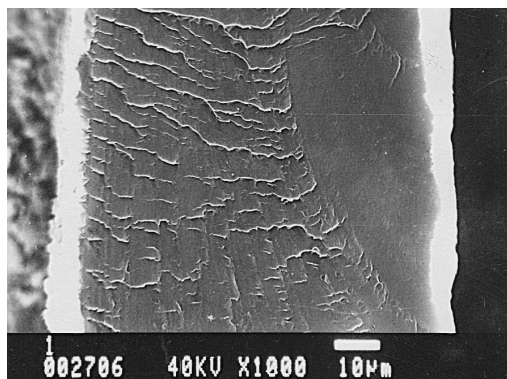


Fig. 5. Scanning electron micrograph of the cross-section of membrane with two catalyst layers.

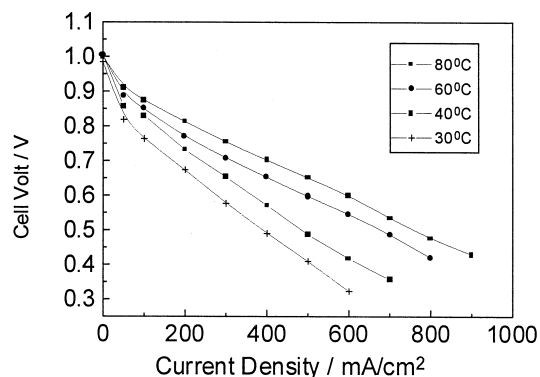


Fig. 6. Fuel cell performance of PEMRFC ( $P_{O_2} = 0.3 \text{ MPa}$ ,  $P_{H_2} = 0.3 \text{ MPa}$ , Nafion 115).

small nippers, from a large piece previously cooled in liquid nitrogen (77 K).

### 3. Results and discussion

#### 3.1. TEM analysis

TEM photographs of the platinum crystallites and iridium oxides used in the preparation of the electrode are given in Figs. 2 and 3, respectively. The particles of platinum crystallites have diameters between 15 and 20 nm. by contrast, the particle size of iridium oxide is about 40 nm.

#### 3.2. SEM analysis

A SEM photograph of the top catalyst layer of the oxygen electrode is shown in Fig. 4. The porous structures of the platinum and iridium oxide agglomerates are uniformly distributed in the electrocatalyst layer and are in close contact. When iridium oxide mixed with platinum is used in the catalyst layer, the platinum particles can be more uniformly distributed in the electrocatalyst layer, and thus the loading of the platinum catalyst can be reduced. It is well known that iridium oxide is not a good electrical

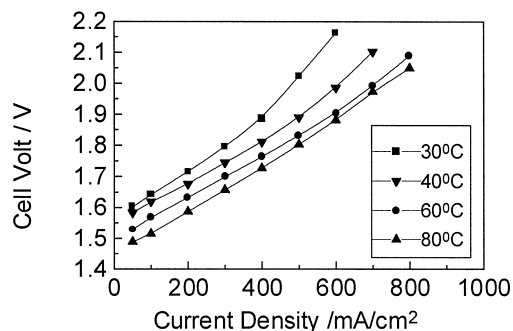


Fig. 7. Electrolysis performance of PEMRFC (ambient pressure, Nafion 115).

conductor, but addition of platinum can increase the conductivity of catalyst layer.

The general features of the cross-section of the membrane and electrode assemblies without diffusion layers are illustrated in Fig. 5. The membrane with two catalyst layers is easily distinguishable. It is important to note the very good adhesion of the electrodes to the membrane. The thicknesses as of the catalyst layer and membrane are about 5 and 85  $\mu\text{m}$ , respectively.

### 3.3. Electrochemical experiments

A unitized fuel cell requires: (i) a hydrogen electrode that is active for both  $\text{H}_2$  oxidation and  $\text{H}_2$  evolution; (ii) an oxygen electrode that is active for both  $\text{O}_2$  reduction and  $\text{O}_2$  evolution. The general approach to achieve bifunctional electrode structures is to partially distribute the charge and discharge functions to the separate catalyst layers of a composite electrode, each catalyst layer is optimized primarily for one function.

When the electrolyser and fuel cell operate at high current densities, most of the current tends to be generated near the front surface of the electrocatalyst layer of the electrode. Thus, the thickness of the electrocatalyst layer of the electrode should be reduced and the electrocatalyst layer of the electrode must be bound tightly to the membrane. A two-layer catalyst structure electrode enlarges the thickness of the catalyst layer of the electrode and inhibits the mass transport. In order to minimize the mass transport and ohmic limitations within the active layer, it is desirable to have a thin electrocatalyst layer in the electrode. In this work, a thin-film catalyst layer electrode structure has been designed in which the membrane and the electrode were compressed tightly by hot pressing at high temperature. The electrode provides satisfactory performance in the fuel cell and the electrolyser modes.

The fuel-cell performance of the unitized PEMRFC is shown in Fig. 6. When the current density is 400  $\text{mA cm}^{-2}$ , the cell voltage is 0.7 V, at 80°C and  $\text{H}_2/\text{O}_2$  pressures of 0.3 MPa. The electrolysis performance of the unitized PEMRFC is presented in Fig. 7. When the current density is 400  $\text{mA cm}^{-2}$ , the cell voltage is 1.71 V, at 80°C and ambient pressure.

### 3.4. Cycle performance

The cycle performance of the PEMRFC is given in Fig. 8. Both the fuel-cell and the electrolysis performance decreases on the second cycle, however improve slightly after three cycles. This may be because the carbon backing was wetted, leading to an increase in the gas transport limitation after the cell was run in electrolysis mode on the first cycle. The reason for the improvement in the performance may be that the gas and water transport paths in the electrode are rebuilt after two cycles. The data in Fig. 8

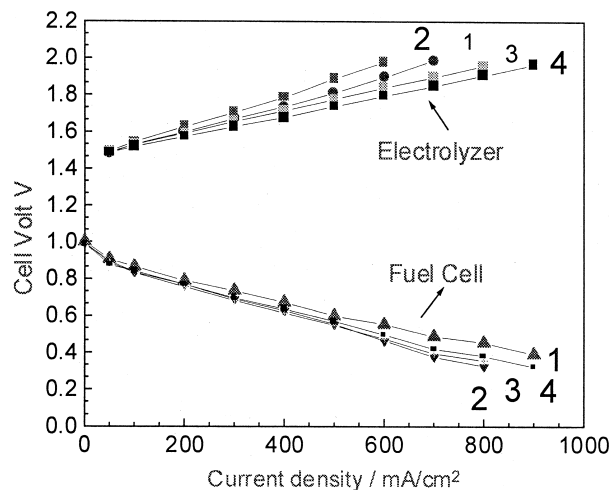


Fig. 8. Performance of PEMRFC after four cycles (numbered in diagram). Fuel cell mode:  $P_{\text{O}_2} = 0.3$  MPa,  $P_{\text{H}_2} = 0.3$  MPa, 80°C, Nafion 115. Electrolysis mode: ambient pressure, 80°C, Nafion 115.

indicate that the unitized PEMRFC with a thin film catalyst layer electrode shows a promising stability.

## 4. Conclusions

From the results obtained in the present work, the following conclusions can be drawn.

(1) Used in the unitized PEMRFC, platinum is a good bifunctional catalyst for the hydrogen electrode, while 50 wt.% Pt + 50 wt.%  $\text{IrO}_2$  is a good bifunctional catalyst for the oxygen electrode.

(2) A bifunctional electrode with a thin catalytic layer can reduce the loading of the catalyst and minimize mass transport and ohmic limitations. This structure may not use a catalyst support and simplifies the electrode structure.

(3) SEM analysis demonstrates extremely a good adhesion of the electrode to the membrane. The thickness of the catalyst layer in the bifunctional electrode about 3 to 5  $\mu\text{m}$ .

(4) Satisfactory fuel-cell and electrolysis performance of the unitized PEMRFC is achieved with a thin-film catalyst structure electrode. The unitized PEMRFC with a bifunctional electrode can achieve reproducible performance and has a promising stability.

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