

AC Impedance Study of the Electrochemical Behavior of Hydrogen/Oxygen Gas Mixture at Nafion/Catalyst Electrode Interface

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Abstract

The anodic reaction of hydrogen/oxygen gas mixture at platinum or palladium electrode interfacing with a solid polymer electrolyte was investigated using AC impedance method. The impedance spectrum of the electrode reactions of the mixture depends on the gas composition, electrode roughness, the mode of electrochemical operation and the cell potential. For electrolysis mode of operation, the spectrum taken for the reaction on a rough platinum electrode for the gas mixture revealed clearly that the local anodic reduction of oxygen gas takes place concurrently with the anodic oxidation of hydrogen gas.

1. INTRODUCTION

If the gas mixture of hydrogen and oxygen is applied to the anode of a proton exchange membrane fuel cell (PEMFC), the oxygen not only increases the overpotential of hydrogen oxidation reaction, but actually undergoes a local reduction by reacting with the proton generated. The investigation regarding the electrode reaction of the gas mixture was exercised for the following reason. Prompted by cogeneration of hydrogen and oxygen from radiolysis and the necessity of utilizing the gas mixture its electrical behavior in contact with liquid electrolytes was well studied in 1940s¹⁾ and the electrochemical system that utilizes such mixture was invented²⁾. Our group studied the behavior of the gas mixture contacting a solid polymer electrolyte³⁾. The study revealed that oxygen is indeed reduced at the anode where hydrogen is oxidized. The study also showed that the degree of the local oxygen reduction at the anode depends on whether the electrochemical cell is arranged in electrolytic (enrichment) or galvanic (fuel cell) mode.

In this study we investigated the anodic behavior of the gas mixture in more details using AC impedance method, with particular attention to unveil the nature of the local oxygen reduction. We measured the impedance as a function of the surface roughness, the cell arrangement and the anodic potential while the mole fraction of hydrogen gas

is fixed at 0.6. The aim of the study was to find the means to suppress the local oxygen reduction so that the fuel gas and electrical energy are not wasted. But it was also hoped that through the study more insight would be gained into the fundamental mechanism of oxygen reduction, particularly at the catalyst/polymer interface.

2. EXPERIMENTAL

Membrane treatment - Nafion® 115 used in this study as the proton exchange membrane was prepared by the following procedures. The membrane was boiled in 3 wt% H₂O₂ solution for 1 hour and then rinsed in boiling deionized water for 2 hours to remove any organic compounds. It was then boiled in 0.5M H₂SO₄ for 1 hour to remove metal compound and to exchange Na⁺ for H⁺ in the membrane and finally rinsed in boiling deionized water for 2 hours.

Electrode Platinum (Pt) or palladium (Pd) electrodes of high surface area were prepared by loading carbon supported Pt on gas diffusion backing or evaporating Pd on carbon sheet. The loading level was approximately 0.4 mg cm⁻². Perforated Pt foil was used as the low surface area electrode. To increase the three-dimensional contacting areas between the solid electrolyte and the catalytic layer, the catalytic surface was impregnated with 0.8 mgcm⁻² Nafion® (Aldrich Chemical Company).

Pd/H₂ reference - Diameter of the

palladium wire used to make the reference electrode was $100\ \mu\text{m}$ (99.9%, Aldrich Chem. Co.). The electrical contact of the palladium reference electrode was made using silver paste. The palladium wire was covered with PVdF (Poly Vinylidene Fluoride, Kynar 741, elf Atochem).

Cell configuration - The pretreated membrane and electrodes were bonded together by heating and pressing the components under $120\ \text{°C}$ and $70\ \text{atm}$ for $90\ \text{sec}$. The gas mixture prepared in a variety of mixing ratios with the help of mass flow controllers (SAM SFC280E) was analyzed by gas chromatography (Hewlett-Packard 5890), then fed into the anode for the hydrogen enrichment or the PEMFCs through a humidifier. The temperature of the electrochemical cell and humidifiers was set at $60\ \text{°C}$ and $65\ \text{°C}$, respectively.

Analyses - A scheme of experimental setup for the electrochemical operation is shown in Fig. 1. The electrochemical impedance spectrum was recorded in the $1\ \text{mHz}$ f $10\ \text{kHz}$ frequency range using a personal computer with EG&G M398 software, the frequency response detector (EG&G Model 1025) and potentiostat/galvanostat (EG&G Model 263A). For the enrichment mode, the cathode was used as the reference electrode (RHE)⁴). When oxygen/hydrogen gas mixture was applied to the anode of proton exchange membrane fuel cell (PEMFC), the palladium/hydrogen electrode⁵) was used as the reference electrode for measuring the impedance spectrum of the anode.

3. RESULTS AND DISCUSSIONS

Electrochemical behavior of a hydrogen/oxygen gas mixture - The electrochemical behavior of hydrogen/oxygen gas mixture was examined first by comparing the V_{appl}/i curves with those of hydrogen/nitrogen gas mixture. Figure 2(a) and (b) show the applied voltage versus the current density (V_{appl}/i) of the enrichment cell whose Pt anode of high surface area utilizes hydrogen/nitrogen and hydrogen/oxygen gas mixture, respectively.

A monotonous reduction of current density at a given voltage with the increase of nitrogen mole fraction shown in Fig 2(a) implies that the hydrogen partial pressure is the only factor to determine the current density. In this case, the reduction of current with the decrease of the mole fraction of hydrogen is solely attributed to the change in e.m.f. of the hydrogen oxidation. The current at a given applied voltage drops sharply as the mole fraction of hydrogen drops below 0.6 for the H_2/O_2 mixture. Judging from the characteristic values of the voltage and current shown in Fig. 2, we found that the oxygen reduction at the anode was the prime cause for the current reduction when the hydrogen/ oxygen gas mixture was used. Similar plots were made for the behavior of hydrogen/nitrogen and hydrogen/oxygen gas mixture on the Pd anode as shown in Fig. 2(C) and (d), respectively. It is seen

that the current drop at Pd anode for hydrogen/oxygen mixture is not as severe as that shown in Pt anode, implying that the oxygen reduction at Pd anode is not active, at least as long as the hydrogen mole fraction is high.

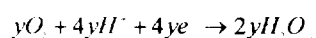
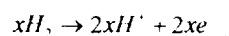
It is interesting to note that the potential of Pt anode (vs. hydrogen cathode) contacting hydrogen/oxygen mixture depends on the hydrogen mole fraction and also on the roughness of the anode as shown in Fig. 3. It shows that the Pt anode of high surface area acts as hydrogen or oxygen electrode depending on whether the hydrogen mole fraction is above or below 0.6, respectively. But the smooth Pt electrode shows a continuous change as the hydrogen mole fraction increases. This trend reflects the fact that the limiting process in overall reaction on a smooth electrode is the charge transfer process, not the diffusion that becomes the limiting one for a rough electrode when the overpotential is high. Therefore, the nature of the electrochemical behavior of such electrodes, as shown in *i*-*V* curves or in the electrode potential, should be clearly revealed in the impedance measurements.

Hydrogen oxidation at the enrichment cell anode - The impedance spectrum of the oxidation of pure hydrogen at the Pt electrode of high surface area is shown in Fig. 4(a). When hydrogen was mixed with nitrogen, the impedance spectrum shown in Fig. 4(b) remained basically the same as the one for pure hydrogen, implying that nitrogen is not involved in any faradaic process. The small arc

developed in the low frequency region of Fig. 4 is due to diffusion-related process across the gas diffusion-backings and the catalyst layer.

Hydrogen oxidation and oxygen reduction reaction - When the hydrogen/oxygen gas mixture was supplied to the Pt anode of enrichment cell, the local reduction reaction of oxygen (ORR) was proved experimentally. The compositions of the hydrogen/oxygen gas mixtures were checked at inlet and outlet of the anode using gas chromatography. The purifying cell was operated over 800 mAcm⁻¹ and the hydrogen mole fraction of the feeding gas was 0.9. The results of the analysis showed that the oxygen mole fraction of the outlet gas mixture was indeed lower than that of the inlet gas mixture.

The impedance spectra of H₂/O₂ gas mixture (the hydrogen mole fraction being 0.6) are shown in Fig. 5 (a),(b),(c) for Pt electrode of high and low surface area and for Pd electrode, respectively. Only the spectrum for Pt electrode of high surface area shows a large low frequency arc which grows as the applied potential increases. When these spectra are compared to those of pure hydrogen or the H₂/N₂ mixture, it is obvious that the second arc is related to the electrodic reaction of the oxygen gas. The overall anodic reactions of the mixture gas can be conceived as the following two reactions:



But we do not know for sure whether the reactions take place independently or not.

The earlier work³⁾ showed that the two processes occur to some extent independently when a rotating platinum gaze electrode contacts liquid electrolyte saturated with the gas mixture. The characteristics of the gas mixture, according to the study, depend on the applied potential and the chemical nature of the electrolyte.

As χ_{H_2} , the diameter of the second arc increases, indicating the increase of R_{ct} for the oxygen reduction. As pointed out before, the increase of the applied potential also results in a decrease in the overpotential for the oxygen reduction and this to some extent contributes to the increasing R_{ct} for the oxygen reduction. The increase of the applied potential of the enrichment cell anode results in an increase in the overpotential for the hydrogen oxidation and a decrease in that for the oxygen reduction. But the hydrogen overpotential increase beyond 0.2 V (vs. NHE) should bring in the diffusion limited overpotential⁶⁾ and thus, the charge transfer resistance R_{ct} should grow too. The surface concentrations of the species involved in hydrogen oxidation decrease as the overpotential increases. For the oxygen to be reduced independently at the anode it is crucial that some anodic surface be exposed to the approaching oxygen molecules. With high R_{ct} value at which the surface concentration is low, the oxygen molecules can be involved in the electrodic reaction that is manifested in the lower frequency arc shown in Fig. 5(a). As the applied potential increases at

a given

For the smooth Pt electrode, its impedance spectrum shows only one arc regardless of the cell potential. As the surface area gets smaller, the charge transfer rate becomes the limiting factor, thus making the hydrogen oxidation not separable from the oxygen reduction⁷⁾. For the Pd electrode its impedance spectrum also shows only one arc. This is attributed to its poor catalytic function for oxygen reduction.

The $\text{im}\chi_{H_2} = 0.6$) is 350 mV vs. NHE.) It implies that the anodic overpotential is still far below the region of the diffusion limited overpotential, making the hydrogen oxidation not subject to the diffusion control. From the results presented thus far it can be said that an efficient way to purify hydrogen/oxygen gas mixture electrochemically using a solid polymer membrane is to select a proper electrode (anode) on which the local oxygen reduction is suppressed even at a high over potential region. Pd electrode seems to partly meet that requirement. Impedance spectrum for the pure hydrogen oxidation at the fuel cell anode (Fig. 6) shows the opposite trend of R_{ct} dependency on the overpotential. As the terminal voltage decreases (same as the increase in the hydrogen overpotential) the diameter of the high frequency arc decreases. It is attributed to the small increase of the anodic overpotential. As the terminal voltage decreases from OCV (over 1 V) to 0.5 V, the net increase of the anodic overpotential is less than 80 mV vs. NHE.

(It was measured against Pd/H₂ reference electrode.) (On the other hand, as the applied voltage to the enrichment cell increases from 0.1 to 0.5 V, the net increase of the anodic overpotential of pure hydrogen gas is near 200 mV vs. NHE. Moreover, the net increase of the anodic overpotential of the H₂/O₂ gas mixture)

4. Conclusions

The electrochemical behavior of hydrogen/oxygen gas mixture at Pt or Pd electrode interfacing with a solid polymer electrolyte was studied using AC impedance method. The behavior turned out to be dependent on the electrochemical cell arrangement and electrode roughness. It was found that the anodic oxygen reduction is clearly manifested in electrolytic arrangement at Pt electrode of high surface area. This is attributed to both the catalytic nature of Pt for oxygen reduction and a large departure of the anodic cell potential from the thermodynamic value which brings the electrode reactions to the diffusion-controlled region. Such behavior is not found for Pd electrode due to its poor catalytic activity for oxygen

reduction and also for a smooth Pt electrode at which the hydrogen oxidation and the oxygen reduction are coupled to each other, establishing a mixed-potential like cell potential.

ACKNOWLEDGEMENT

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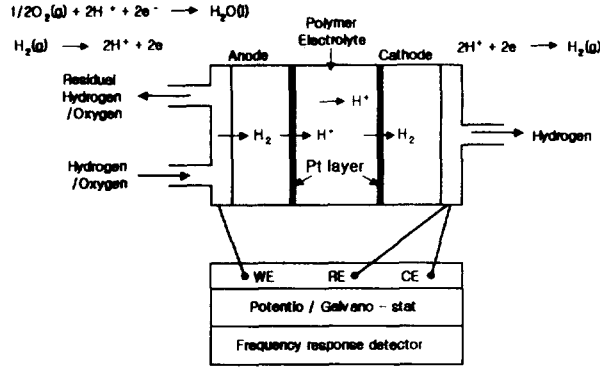


Fig. 1. Schematic experimental setup and instrumentation system

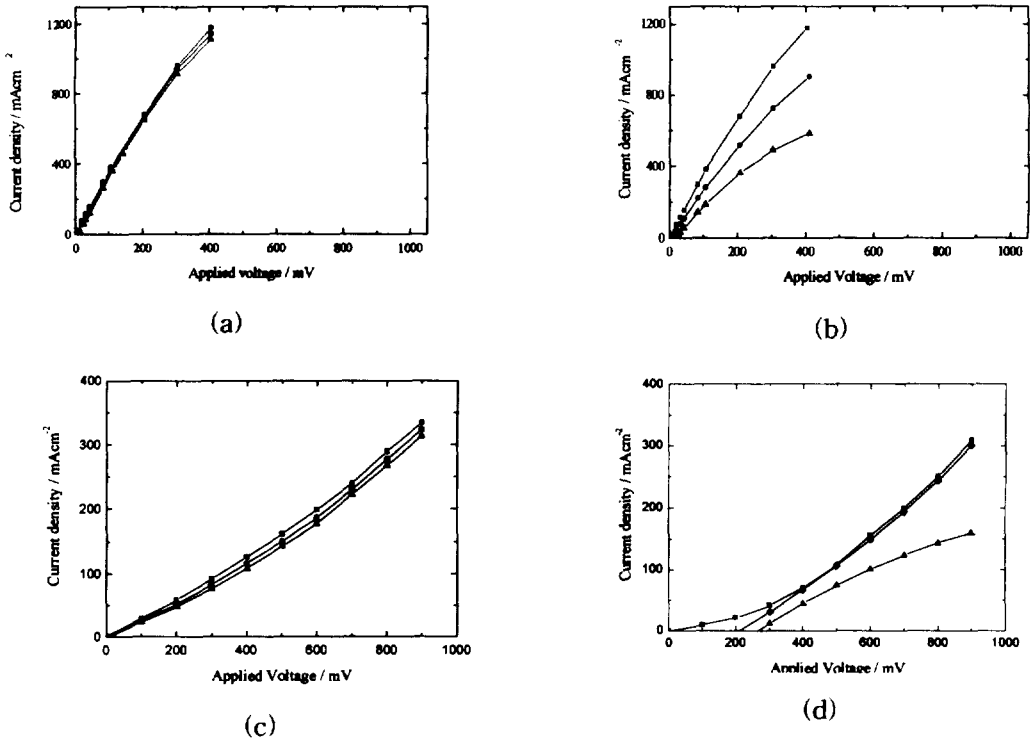
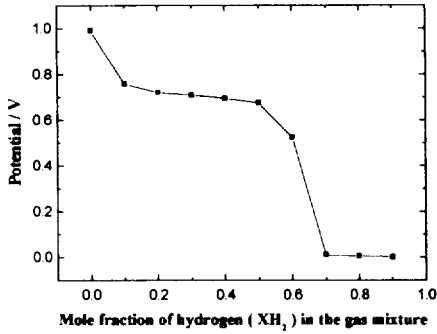
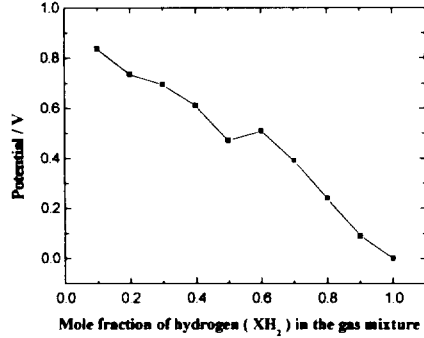


Fig. 2. $V_{app} - i$ characteristics of the hydrogen purifying cell utilizing (a) a H₂/N₂ gas mixture of varying composition on Pt electrode, (b) a H₂/O₂ gas mixture of varying composition on Pt electrode, (c) a H₂/N₂ gas mixture of varying composition on Pd electrode, (d) a H₂/O₂ gas mixture of varying composition on Pd electrode. The hydrogen mole fraction is (■) 1.0, (●) 0.8, (□) 0.6.

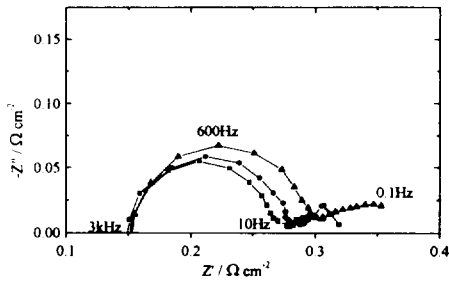


(a)

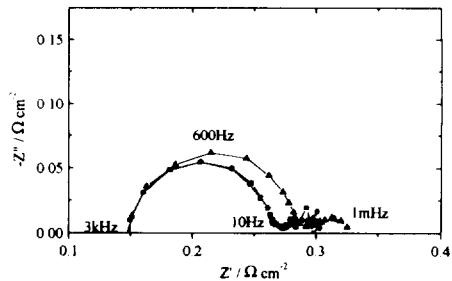


(b)

Fig. 3. The electrode potential of Pt electrode contacting H₂/O₂ gas mixture of varying composition, (a) the electrode having high surface area, (b) the electrode having low surface area. The potential is measured in reference to Pt electrode contacting pure hydrogen gas.



(a)



(b)

Fig. 4. AC impedance spectrum for hydrogen oxidation at Pt anode of high surface area that contacts (a) pure hydrogen or (b) H₂/N₂ gas mixture with as.

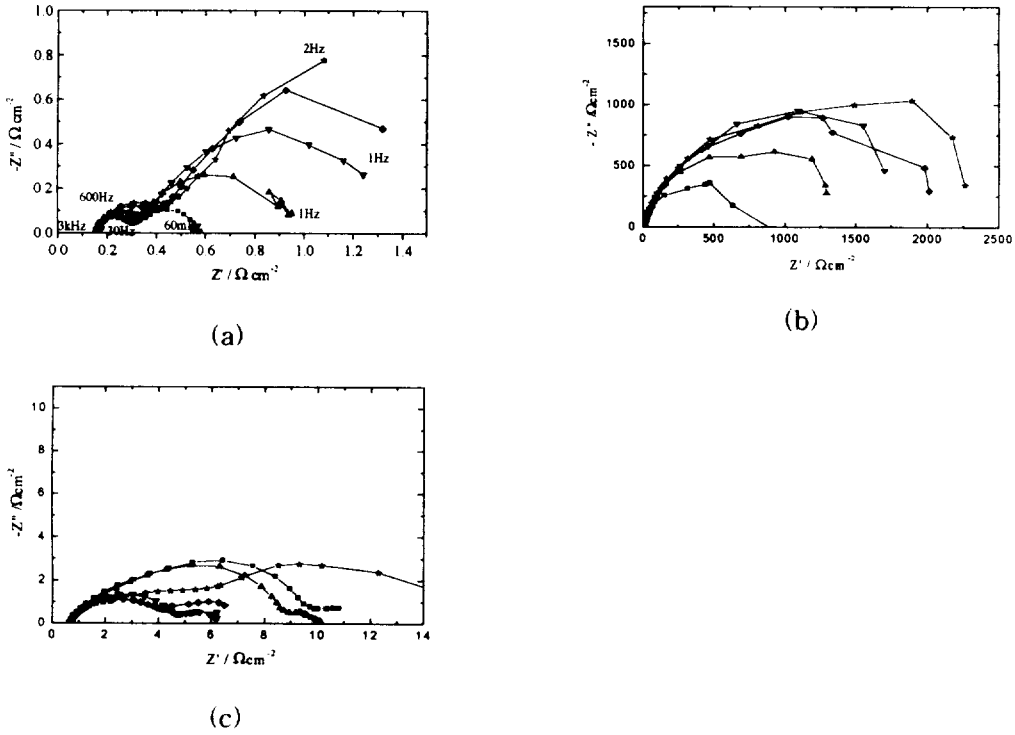


Fig. 5. AC impedance spectra ($\alpha_H = 0.6$) on (a) Pt electrode of high surface area, (b) Pt foil electrode, (c) Pd electrode. The spectra is taken at 0.1V; 0.3V; 0.5V; 0.7V; 0.9V vs spectrum of the electrochemical reactions of H₂/O₂ gas mixture with

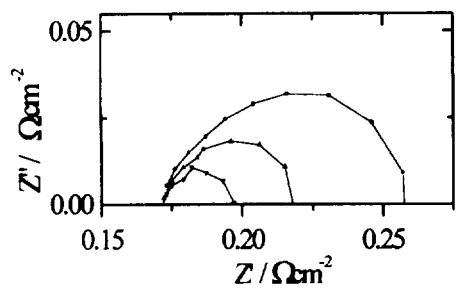


Fig. 6. AC impedance spectrum of hydrogen oxidation of H₂/O₂ gas mixture at the anode of PEMFC, taken at different terminal voltages: (●) 0.8 V, (□) 0.7 V, (□) 0.6V