

AC Impedance Study of Hydrogen Oxidation and Reduction at Pd/Nafion Interface

Seong-Min Song, Il-Gyo Koo and Woong-Moo Lee

Department of Molecular Science and Technology
Ajou University, Suwon 442-749, Korea

Abstract

Electrocatalytic activity of palladium for hydrogen oxidation and reduction was studied using AC impedance method. The system under study was arranged in electrolytic mode consisting of Pd electrode under study, Pt counter electrode and Nafion electrolyte between them. Two types of Pd electrodes were used - carbon-supported Pd (Pd/C) and Pd foil electrode. Pd/C anode contacting pure hydrogen showed a steady decrease of charge transfer resistance with the increase of anodic overpotential, which is an opposite trend to that found with Pd foil anode. But Pd foil cathode also exhibited a decrease of the resistance with the increase of cathodic overpotential. The relationship between imposition of overpotential and subsequent change of the charge transfer resistance is determined by the ratio of the rate of faradaic process to the rate of mass transportation; if mass transfer limitation holds, increase of overpotential accompanies the increase of charge transfer resistance. Regardless of the physical type of Pd electrode, the anode contacting hydrogen/oxygen gas mixture did not reveal any independent arc originated from local anodic oxygen reduction

1. Introduction

Numerous studies have been performed [1-4] to lessen the level of impurities such as CO, H₂S and SO₂ that could be present in hydrogen fuel for proton exchange membrane fuel cell (PEMFC). Besides these impurities there is a rare case in which oxygen could be mixed with hydrogen fuel. If the gas mixture of hydrogen and oxygen is supplied to the anode of PEMFC, the oxygen actually undergoes a local reduction by reacting with the proton generated [5]. The investigation regarding the electrode reaction of the gas mixture was prompted by the following reason. Radiolysis usually cogenerates hydrogen and oxygen and it necessitates utilizing the gas mixture using electrochemical methods. Prompted by these needs, its electrochemistry was well studied in 1940s [6] and the electrochemical system that utilizes such mixture was invented [7].

Our group also has been engaged in a research on plasmolysis of water, studying the possibility of using the gas mixture as the fuel for PEMFC or of its purification [5,8]. In enrichment mode, the electrochemical behavior of hydrogen/oxygen gas mixture was examined by measuring i/V_{appl} curves. The current at a given applied voltage drops sharply as x_{H_2} , the hydrogen mole

fraction in the gas mixture, is decreased. For the case of using H₂/O₂ mixture the local consumption of the protons generated at the anode by oxygen (called anodic oxygen reduction reaction, AOR) was the prime cause for the drastic current reduction. On the other hand, the V_{terminal}/i measurements for a PEMFC using the gas mixture as the fuel show that the overpotential due to AOR is much smaller than the case of the electrolytic anode. It implies that the rate of AOR on Pt anode of fuel cell is much lower than the rate of oxygen reduction at the cathode of the same cell. Its practical implication is that electrochemical purification of the mixture does not have any economical value while use of the mixture, as the fuel for PEMFC is not totally impractical. Our group also has been engaged in a research on plasmolysis of water, studying the possibility of using the gas mixture as the fuel for PEMFC or of its purification [5,8]. In enrichment mode, the electrochemical behavior of hydrogen/oxygen gas mixture was examined by measuring i/V_{appl} curves. The current at a given applied voltage drops sharply as

Compared to Pt electrocatalyst, palladium (Pd) is much poorer catalyst, particularly, toward oxygen reduction. Thus use of Pd electrode can possibly further reduce the power loss due to AOR when the gas mixture is supplied to the anode of PEMFC. In this study we investigated in detail the impedance

response of Pd anode or cathode interfaced with Nafion electrolyte when it oxidizes hydrogen gas molecules or reduces hydrogen ions. Carbon-supported Pd (Pd/C) or Pd foil was used as the Pd electrode. Hydrogen gas molecules can easily access to the catalytic site of Pd/C anode, but in the case of foil anode they have to be oxidized first and then diffuse through the foil to be oxidized at the other side that contacts Nafion. The latter case provides an extreme example of slower mass transfer rate compared to the rate of faradaic process. Thus we hoped through this study to gain some insight for fundamental aspects of the frequency response of hydrogen redox reaction at Pd/Nafion 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 Palladium (Pd) electrodes of high surface area were prepared by

loading carbon supported Pd on gas diffusion backing. The loading level was approximately 0.4 mg cm⁻². Pd foil of 25 m thick 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 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 °C and 70 atm for 90 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°C and 65°C, respectively .

Analyses - A scheme of experimental setup for the impedance measurements is shown in Fig. 1. The electrochemical impedance spectrum was recorded in the 1 mHz ≤ f ≤ 10 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 measuring the ac impedance spectra the palladium/hydrogen electrode [9, 10] was used as the reference electrode.

3. RESULTS AND DISCUSSIONS

Hydrogen oxidation at Pd/C anode

When pure hydrogen molecules contacting Pd/C anode are oxidized, the related AC impedance spectra are shown in Fig. 2 as a function of the anode potential with respect to Pt/C cathode. The small arc shown at high frequency region is believed to be due to the oxidation of dissolved hydrogen. It is interesting to note that the arc radius decreases with the increase of the anodic overpotential, an opposite trend found at Pt/C anode [8]. This is due to lower catalytic activity of Pd for hydrogen oxidation than that of Pt.

The arc diameter reflects the charge transfer resistance R_{ct} . The charge transfer resistance is defined by

$$R_{ct} = RT / nFi_o \quad (1)$$

where i_o denotes the exchange current density of the involved charge transfer reaction. When the impedance measurements are made at potentials

away from the open cell potential (OCV), the effective charge transfer resistance is likewise related to the effective ac exchange current density [11] as follow

$$R_{ct,eff} = RT / nFi_{o,eff} \quad (2)$$

However, the mean surface concentrations for the ac process act like bulk values and thus the effective exchange current density would be given by

$$i_{o,eff} = nFAk_o [C_{O(0,t)_m}]^{(1-\alpha)} [C_{R(0,t)_m}]^\alpha \quad (3)$$

where C_O , C_R denote the surface concentration of oxidizing or reducing species, respectively and α denotes the transfer coefficient. Therefore, whenever a mass transfer limitation holds for any species involving in charge transfer process, the related R_{ct} increases.

Unlike the case of Pt anode the slower faradaic rate at Pd anode does not meet any kind of deficiency in hydrogen molecule concentration at the electrode. Increase of the overpotential then accompanies the increase of the surface concentrations, thus reducing R_{ct} . Fig. 3 (a) and (b) show the same spectra for the case where hydrogen/oxygen gas mixture of different mixing ratio contacts the anode. As already confirmed from the spectra on smooth Pd electrode [8] they do not show any independent arc due to local oxygen anodic oxidation. The decrease of the arc with the increase of the overpotential shows the same trend as

the case of pure hydrogen.

Hydrogen oxidation at Pd foil anode. -

The impedance spectrum of the oxidation of pure hydrogen at the Pd foil electrode is shown in Fig. 4. The radius of arc increases with the increase of anodic overpotential. For the hydrogen gas molecules to reach the Pd/Nafion interface they have two choices. First, they are adsorbed at one surface of the foil, then dissolved as atomic form and diffuse through across the foil and then oxidized at the other surface of the foil contacting Nafion. Or the gas molecules can diffuse through a very narrow space developed between Pd foil surface and Nafion. Depending upon the tightness of the channel, the mass transfer rate can be very low. Therefore, increase of the overpotential, as the case of Pt/C anode, can develop deficiency of the species at the interface, thus increasing the charge transfer resistance.

Hydrogen reduction at Pd foil cathode

The spectra for hydrogen reduction at Pd foil cathode are shown in Fig. 5. When the foil is used as the cathode it has direct contact with hydrogen ions that are transported from the other electrode through the polymer electrolyte. Thus we do not anticipate any kind of mass transfer limit and thus the radius of arc decreases with the increase of the cathodic overpotential. The uniqueness of Pd electrode is demonstrated in this example too. Usually fuel cell electrodes develop three-phase region, the catalyst in

solid phase, fuel gas or oxygen in gas phase and a solution phase (electrolyte). But, the Pd foil cathode can perform its role without the presence of the gas phase. When the Pd is saturated with hydrogen, it should have an adverse effect on the charge transfer rate.

4. Conclusions

The hydrogen oxidation and reduction at Pd/Nafion interface was studied using AC impedance method. The electrochemical system arranged in electrolytic mode included carbon-supported Pd or Pd foil electrode, Pt/C counter electrode and Nafion electrolyte between them. Increase of overpotential brought in opposite trend in change of charge transfer resistance depending on the accessibility of hydrogen gas to the interface. It brought in decrease of the resistance for Pd/C electrode while it resulted in increase of the resistance for Pd foil electrode. For Pd/foil cathode the increase of cathodic overpotential brought in decrease of the resistance. For Pd/C anode or Pd foil cathode, the mass transfer of hydrogen gas molecules or hydrogen ions to the interface is not blocked. But for Pd foil anode the hydrogen molecules either has to be dissolved first in Pd and then be oxidized at the interface or has to diffuse through a tight space region developed between the foil surface and Nafion. The AC impedance spectra of Pd anode in

contact with H₂/O₂ gas mixture did not reveal the independent arc due to local anodic oxygen reduction, confirming its poor catalytic activity towards oxygen reduction.

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REFERENCES

- [1] T. R. Ralph, G. A. Hards, J. E. Keating, S. A. Campbell, D. P. Wilkinson, M. Davis, J. ST-Pierre and M. C. Johnson, *J. Electrochem. Soc.*, **144**, 3845 (1997).
- [2] C. Sischtla, G. Koncar, R. Platon, S. Gamburgzev, A. J. Appleby and O. A. Velev, *J. Power Sources*, **71**, 249 (1998).
- [3] S. Gottesfeld and J. Pafford, *J. Electrochem. Soc.*, **135**, 2561 (1988).
- [4] V. M. Schmidt, H.-F. Oetjen and J. Divisek, *J. Electrochem. Soc.*, **144**, L237 (1997).
- [5] S.Y. Cha, J.M.Song, W.M. Lee, *J. Appl. Electrochem.*, **28**, 1413 (1998).
- [6] W. Vielstich, *Fuel Cells*, Wiley-Interscience, New-York, 1970.
- [7] G. Grüneberg, W. Wicke and E. Justi, French Pat. 1321373
- [8] S.M. Song and W.M. Lee, J. of the Korean Hydrogen Energy Society, **11**, 179 (2000)
- [9] G. J. Janz, *Reference Electrode*, p. 111, Academic Press, New York and London, 1961.
- [10] J.M. Song, S.Y. Cha and W.M. Lee, *J. Power Sources*. **94**, 78 (2001).
- [11] A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, p. 335, John Wiley & Sons, New York, 1976.

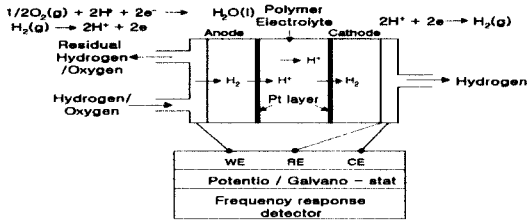
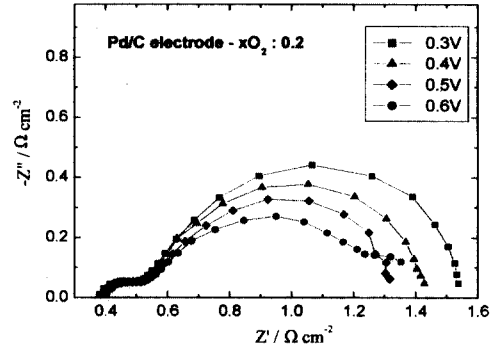


Fig. 1. Schematic experimental setup and instrumentation system



(a)

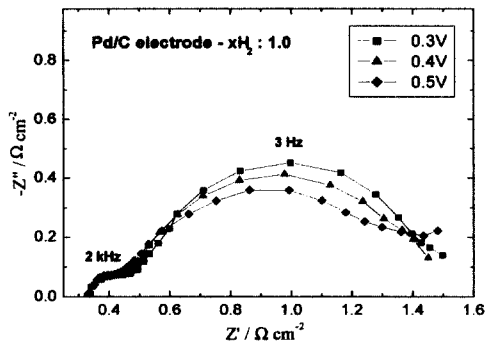
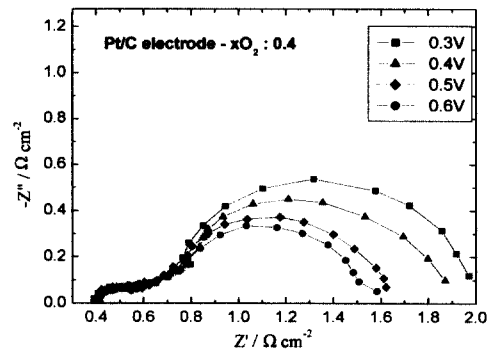


Fig. 2. AC impedance spectra for hydrogen oxidation at Pd/C anode in contact with pure hydrogen



(b)

Fig. 3. AC impedance spectra for hydrogen oxidation at Pd/C anode in contact with H_2/O_2 gas mixture in which the hydrogen mole fraction is (a) 0.2 and (b) 0.4.

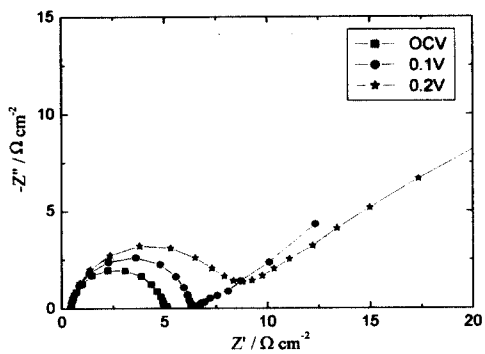


Fig. 4. AC impedance spectra for hydrogen oxidation at Pd foil anode in contact with pure hydrogen.

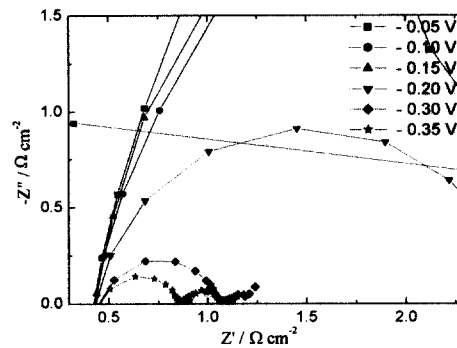


Fig. 5. AC impedance spectra for hydrogen reduction at Pd foil cathode in contact with pure hydrogen.