Impedance Analysis of Working PEMFCs in the Presence of Carbon Monoxide

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The polymer electrolyte membrane fuel cell (PEMFC) has attracted worldwide interest in the development and commercialization of vehicular and stationary applications. These power devices operate at high efficiency with pure hydrogen but degrade when using hydrogen from hydrocarbons or methanol reforming. This decline of performance is caused by the deactivation of the Pt anode catalyst due to trace levels of CO as low as 10–100 ppm. Mitigating such a poisoning effect has been an ongoing task which challenges scientists and engineers in this field. One of the solutions is to employ alloy catalysts such as Pt/Ru, Pt/Mo, and Pt/Sn, which improve CO tolerance. This improvement is due to either a lowered CO oxidation potential or a weakened adsorption of CO on these catalysts. In the presence of relatively high CO concentration, an additional step involving bleeding an oxidant into the anode compartment has been explored. The bleeding oxidant, which can be air, oxygen, or hydrogen peroxide, chemically oxidizes CO to CO2 and lowers its concentration.

Many attempts to understand the mechanism of CO poisoning have been made by the use of electrochemical technique, in situ infrared spectroscopy, and X-ray absorption spectroscopy. In recent years, impedance spectroscopy has been demonstrated to be a powerful experimental technique to examine the complexity of the different processes that take place in fuel cells and to provide better insight into the reaction mechanism of the electrode system and a systematic investigation of the roles of each parameter. Suitable modelistic treatments have been developed for the impedance response of gas diffusion electrodes. Furthermore, the electrode structure of cathode and the kinetics of the oxygen reduction have been studied with impedance technique using an H2O2 single cell. When the impedance of a full cell (O2 on cathode and H2 on anode) is analyzed during discharging, the impedance spectrum reveals the combined impedance of cathode and anode. In most studies, neat hydrogen oxidizes so fast that its impedance is negligible and the impedance spectrum of the full cell eventually equals the cathode impedance. While the anode impedance cannot be neglected, e.g., poisoned by CO, the studies were generally carried out in a simulated cell. For practical studies, it is necessary to set up an in situ measuring system to clarify the effect of CO poisoning on the anode. It is possible to eliminate the contribution of the cathode in PEMFC by operating it with a continuous feed of hydrogen to the cathode in a H2 + CO/H2 cell. Recently, Zhigang et al. have found that transport of CO in the fuel through the membrane to the cathode side resulted in a decline in cathode performance. The effect of CO on the cathode could be ignored when the experiments were carried out in an H2 + CO/H2 half-cell.

In this study, we prepared a three-electrode membrane electrode assembly (3E-MEA). Cell performance and ac impedance measurements were performed in a three-electrode mode system to investigate the effect of CO gas in the operation of PEMFC. The anode and cathode impedances were studied individually during the cell discharging. An equivalent circuit model was proposed to explain the results of impedance analysis for the anode and cathode.

Experimental

Catalyst preparation.—Carbon powder of Vulcan XC-72 was used as the catalyst support. Required amounts of H2PtCl6 and RuCl3 (Alfa) were dissolved in distilled water. Different compositions of bimetallic catalysts were prepared by impregnating the carbon supports with solutions of Pt and Ru stirred for 4 h. Then methanol was added to reduce Pt and Ru at 70°C for 5 h. After the reduction, the catalyst was filtered, washed with distilled water, and dried at 60°C. In this study, four atomic ratios of Pt/Ru were obtained as 0.12, 0.38, 1.13, and 3.33. The weight percentage of Pt in summation of Pt and carbon is 20% in all catalysts. The catalyst was observed with a transmission electron microscope. The metal particles were uniformly dispersed on the carbon support, and the particle diameter was in the range of 3–7 nm.

Gas diffusion electrode.—Catalyst mixtures were prepared by directly mixing Pt–Ru/C catalysts with Nafion solution (5%, Aldrich) at a mass ratio of carbon/Nafion (dry) = 70:30. Some water was added to dilute the mixture. The mixture was stirred for 1 h, followed by sonication for 1 h. The mixture was kept under stirring prior to application onto Teflon-treated carbon paper (Electrochem), and the gas diffusion medium was used as the anode or cathode substrate. The electrode was dried at room temperature for 30 min and then at 135°C for another 30 min to form the gas diffusion electrode. All the Pt/Ru/C catalysts used for cathode had a Ru/Pt atomic ratio of 0.12. The Ru/Pt atomic ratios of Pt–Ru/C catalyst used for anode were 0.12, 0.38, 1.13, and 3.33. The Pt loading in the gas diffusion electrodes was fixed to 0.8 mg/cm2, and all the Ru loadings in the gas diffusion electrodes depended on the Ru/Pt atomic ratio. The exposure area of the electrodes was 2.5 × 2.5 cm².

3E-MEA.—A platinum film of 1.0 × 2.5 cm² with an electrical contact strip was deposited on a Nafion 117 membrane (DuPont) as a pseudoreference electrode in the form Pt/Nafion assembly by impregnation method. A solution of 0.02 M Pt(NH3)4Cl2 (Aldrich) was first put on one side of the Nafion membrane at 40°C for 2 h to allow Pt(II) ions to permeate the membrane. After the Nafion membrane was rinsed with deionized water, a solution of 0.2 M NaBH4 (Ferak) was placed in contact with the Nafion membrane on the same side that had been impregnated with Pt(NH3)4Cl2. The Pt was reduced on the membrane surface by NaBH4 at 40°C for 0.5 h. 3E-MEA was made by hot-bonding gas diffusion electrodes on the...
Pt/Nafion assemblies, as shown in Fig. 1, at 120°C for 90 s. The anode gas diffusion electrode and the deposited Pt electrode were on the same side of Nafion, and the cathode gas diffusion electrode was on the other side. The spacing between anode electrode and pseudoreference electrode was 2 mm.

Polymer electrolyte membrane fuel cell measurement.—The 3E-MEAs were tested in a single cell. The deposited Pt electrode contacted with the anode gas which diffused from the flow-field plate. The anode shared the same gas with the pseudoreference Pt electrode. This Pt electrode needed to avoid contact with the anode gas diffusion electrode and the deposited Pt electrode were 70, 95, and 40°C, respectively.

The polarization curves of the cell (cathode against anode) at steady state were collected using an electronic load were 70, 95, and 40°C, respectively. The polarization curves of the cell (cathode against anode) at steady state were collected using an electronic load. This Pt electrode needed to avoid contact with the anode gas diffusion electrode. Oxygen was the cathode gas, and neat H2, 25 ppm CO in H2, 100 ppm CO in H2, or 100 ppm CO and 2% O2 in H2 was used as the anode gas. All of the gases were humidified by a humidifier, and the gas flow rates were all 100 mL/min. The temperatures of the cell, anode gas humidifier, and cathode gas humidifier were 70, 95, and 40°C, respectively.

The polarization curves of the cell (cathode against anode) at steady state were collected using an electronic load (model 63010 from Autolab), and the anode and cathode polarization curves were measured against the pseudoreference electrode using a multimeter (model 6001 from Prema) at the same time. An impedance analyzer (PGATAT-30 from Autolab) was used to carry out the ac impedance measurements over the frequency range of 5 kHz–10 mHz in three-electrode mode at constant potential. The corresponding current was recorded according to polarization curve. A small signal, 10 mV in amplitude, was applied to the system throughout the experiments.

Results and Discussion

In a fuel cell, the cell potential (E) can be expressed by reversible potential (E0) and overpotentials (\( \eta \))

\[
E = E_0 - \eta_{ct,e} - \eta_{ct,a} - \eta_{int,e} - \eta_{int,a} - \eta_b
\]

[1]

The subscripts ct, e, ct,a, and mt,a denote the charge-transfer and mass-transport overpotentials at the cathode and anode, and \( \eta_b \) denotes the ohmic potential drop. The overall cell resistance, composed of several resistances, can be calculated from the first derivation of the polarization curve

\[
R'_{\text{overall}} = \frac{dE}{d|\eta|} = R'_{c,t,e} + R'_{c,t,a} + R'_{c,\text{int,e}} + R'_{c,\text{int,a}} + R'_{s}
\]

[2]

The superscript ‘ ‘ denotes the resistances calculated from polarization curves. To study the behavior of the electrode of interest, a three-electrode cell is preferable. The expressions for the potential and resistance of the working electrode are

\[
E_{wk} = E_{c,wk} - \eta_{c,wk} - \eta_{int,wk} - \eta_b
\]

[3]

\[
R'_{\text{overall,wk}} = \frac{dE_{wk}}{d|\eta|} = R'_{c,wk} + R'_{c,\text{int,wk}} + R'_{s,wk}
\]

[4]

The potential (\( E_{wk} \)) and reversible potential (\( E_{c,wk} \)) of the working electrode are referred to the reference electrode, and \( \eta_{c,wk} \) and \( R'_{c,wk} \) are the uncompensated overpotential and resistance between the working and reference electrodes.

Analysis with polarization curves.—The performance of a single cell with 3E-MEA was measured in the two-electrode and three-electrode modes simultaneously. Figure 2 shows the typical polarization curves of the cell (cathode vs anode), cathode (vs reference electrode), and anode (vs reference electrode). The cell potential was confirmed to be equal to the potential difference between cathode and anode at each controlled current experimentally. In the cell polarization curve, the potential decreased with increase of current density and can be fitted into the following equation

\[
E = E^o - b \log i - iR'_{s}
\]

[5]

where \( b \), \( R'_s \), and \( E^o \) are Tafel slope, electrolyte resistance, and open-circuit potential, respectively. The second and third terms on the right refer to charge transfer on the electrodes and ion transport in the electrolyte, respectively. The corresponding impedance can be obtained from the derivation. Below 50 mA/cm², the rapid decrease in cell potential was mainly due to charge-transfer overpotential. Between 50 and 464 mA/cm², the linear decrease in cell potential was mainly due to ohmic resistance, and the constant slope of the curve was equal to the cell resistance \( R'_s \). The rapid decrease of potential due to mass-transfer overpotential did not appear in the measured range of current density. On the anode polarization curve, the anode potential increased linearly with current density. This behavior depicted that the anode charge-transfer resistance was negligible and that the resistance of electrolyte between anode and pseudoreference electrodes was constant. The slope of the anode polarization curve is equal to uncompensated anode resistance.
Ru, a/H11032. The cathode polarization curve was close to the cell polarization curve. Apparently, below 50 mA/cm², the rapid decrease in cathode potential was due to the charge-transfer overpotential of oxygen reduction. This means the cell charge-transfer overpotential was mainly from oxygen reduction. In the range of 50–464 mA/cm², the linear decrease in cathode potential was mainly due to the ohmic resistance of electrolyte between cathode and pseudoreference electrode, and the constant slope of curve was equal to Ru,c/H11032.

Clearly, the behavior of anode or cathode can be effectively studied individually in the three-electrode cell.

The influence of CO content in hydrogen on the polarization curves of cell and individual electrodes is shown in Fig. 3 and 4, respectively, with the electrode catalyst of Ru/Pt 0.12. The open-circuit potential with fuels of neat H₂, CO/H₂, and O₂/CO/H₂ was 1.05 V, independent of the CO concentration in the hydrogen. This phenomenon suggested that the equilibrium potential of the anode was predominantly determined by the equilibrium of H₂/H⁺. Comparing the polarization curves of cell and cathode in Fig. 3 and 4, respectively, the cell potential decreased rapidly when current density increased up to 30 mA/cm² due to charge-transfer overpotential of oxygen reduction, as described above. In the current density range of 30–120 mA/cm², the sharp decrease in the cell potential in 25 and 100 ppm CO/H₂ was mainly due to the increase in anode overpotential as a result of CO poisoning. At current density higher than 120 mA/cm², the slope with CO content decreased to that without CO and can be rationalized by oxidation of CO on the anode. A significant improvement in the CO tolerance was observed by addition of O₂ into the inlet gas of 100 ppm CO/H₂.

The effect of anode composition on the curve of anode charge-transfer resistance vs current density in 25 ppm CO/H₂ is shown in Fig. 5. The anode charge-transfer resistance Rₗct,a/H11032, calculated from anode polarization curves, increased with current density and declined after a maximum value. Above the current with the maximum charge-transfer resistance, the anode potentials were positive enough to oxide the adsorbed CO to CO₂ and thus, led to higher reaction rates, with smaller Rₗct,a/H11032, for hydrogen adsorption and oxidation. With higher atomic ratios of Ru/Pt in the anode catalysts, the effect of current density on reaction rate was weaker and the maximum values of Rₗct,a/H11032 were smaller. These phenomena were consistent with the results, showing that addition of Ru into Pt anode catalysts was able to significantly increase the tolerance of CO. However, the atomic ratio of Ru/Pt of the prepared catalyst which gave the best performance was 3.33 in this study.

Analysis with ac impedance spectra.—The electrode of the PEMFC was porous, and only the three-phase active sites were reactive. The active sites were the junctions of catalyst, electrolyte, and gaseous reactants. An equivalent circuit model for ac impedance analysis of the electrodes was proposed as shown in Fig. 6. Rₜ is the uncompensated resistance of the Nafion membrane between working and reference electrodes. Rₗ and Rₜ are the charge-transfer resistance on the catalyst and the ohmic resistance of the electrolyte in the catalytic layer, respectively. Cdl and CN are the capacitance on the catalyst and carbon support, respectively.

The ac impedance spectra were obtained with constant potential mode in the frequency range of 5 kHz–0.01 Hz. The applied potentials were correlated to loading currents with the polarization curve. For comparison, the controlled condition was reported in terms of the corresponding current. Figure 7 shows the Nyquist plots for both cathode and anode under various currents (or potentials). The currents of 50, 100, 500, and 900 mA corresponded to the applied
cathode potentials 851, 797, 552, and 325 mV and the applied anode potentials of 1, 15, 130, and 249 mV, respectively. Each Nyquist plot in Fig. 7 shows two capacitive loops. When the loading current (or overpotential) increased, the capacitive loop at low frequency shrank but the capacitive loop at high frequency remained the same. That meant that the capacitive loops at low and high frequency corresponded to the charge-transfer reaction \( (R_{ct}, C_{dl}) \) and the ohmic resistance of the catalytic layer \( (R_N, C_N) \) in the equivalent circuit model, respectively.

Figure 7 shows that the experimental data were well fitted to the equivalent circuit in Fig. 6, except the inductive loops at very low frequency in anode Nyquist plots as shown in Fig. 7b. The inductive loop was typical of a system with adsorbed intermediates and was not simulated in this study. From Fig. 7, the uncompensated resistance, \( R_u \), was reasonably found independent of current density.

The influence of the CO content in the hydrogen on the resistances, \( R_{ct, c} \) and \( R_N, \) of cathode and anode with anode catalyst of Ru/Pt 0.12 is shown in Fig. 8. Figure 8a shows that the cathode charge-transfer resistance \( R_{ct,c} \) was large in the low-current-density region and decreased rapidly with increasing current density, as commonly found on most electrodes. However, Fig. 8a also shows that the anode charge-transfer resistance \( R_{ct,a} \) increased with current density. This behavior can be depicted from the slope of corresponding curves at current density lower than 120 mA/cm\(^2\) in Fig. 4. Higher concentration of CO gave stronger dependence. The addition of oxygen into CO/H\(_2\) effectively mitigated the anode charge-transfer resistance \( R_{ct,a} \). Therefore, the value of \( R_{ct,a} \) in 2% O\(_2\)/CO/H\(_2\) was about the same as that in neat H\(_2\). The presence of CO in hydrogen weakly affected \( R_{ct,c} \), similar to the observation in the cathode polarization curve in Fig. 4.

For 100 ppm CO, unusual impedance spectra were observed at current densities higher than 112 mA/cm\(^2\), as shown in Fig. 9. The capacitive loop at medium frequency appeared in the second quadrant and the low inductive loop appeared in the third quadrant. Similar impedance spectra were found in the corrosion studies when metals were in a transpassive dissolution region. When the anode potential is more positive than a particular value, the passive layer on the metal surface breaks down and the anodic current increases rapidly. This phenomenon is similar to that in the presence of CO in this study. Generally, most of the active sites were covered with an adsorbed CO layer, in analogy to the passive layer of metals. When anode potential became more positive, adsorbed CO was oxidized and gave a free metal surface for hydrogen adsorption. The oxidation rate of hydrogen increased rapidly when the potential became more positive. In Fig. 9, the capacitive loop started to bind toward the negative real part at 112 mA/cm\(^2\), which implies that the adsorbed CO was reacted to CO\(_2\) at current density above 112 mA/cm\(^2\). The result was confirmed in the anode polarization curve for 100 ppm CO in Fig. 4. In this polarization curve, current density increased tremendously with potential when current density was larger than 112 mA/cm\(^2\).
Figure 8b shows the dependence of the ohmic resistance in the catalytic layer \( R_{N,C} \) on current density. The cathode resistance \( R_{C,N} \) was not affected significantly in the presence of CO in hydrogen. However, the anode resistance \( R_{N,A} \) increased with the concentration of CO in hydrogen, which is a similar trend to \( R_{C,A} \). This result should not be explained from the point of view of the Nafion polymer electrolyte in catalytic layer, because the concentration of CO was too low to affect the conductivity of the Nafion polymer electrolyte. A proper explanation can be based on the structure of the catalytic layer, which was porous. As a binder, the Nafion polymer electrolyte was distributed in the catalytic layer to form an electrolyte net. Figure 6 is the equivalent circuit for the reaction behavior on a single active site. This equivalent circuit was successfully applied to explain the reaction behavior of the electrode without CO poisoning. However, as the CO poisoning occurred, it failed to explain the increase of ohmic resistance in the catalytic layer with current density. The reaction behavior of the electrode might be explained with the complex equivalent circuit in Fig. 10. In each Nafion polymer electrolyte channel in the catalytic layer, the ohmic resistance connected with the charge-transfer resistance in series, as shown in Fig. 10a. There were numerous Nafion polymer electrolyte channels in the catalytic layer. All of these electrolyte channels formed a proton conductive net with multiple channels and basically connected in parallel. \( R_N \) and \( R_a \) in Fig. 6 may be considered the sums of the parallel connection for the ohmic and the charge-transfer resistances in series, as shown in Fig. 10b. There were numerous Nafion polymer electrolyte channels in the catalytic layer. They were porous and served as a binder for the catalyst. The proton conductivity of the Nafion polymer electrolyte was distributed in the catalytic layer to form an electrolyte net. The active sites were adsorbed CO and became inactive. The Nafion polymer electrolyte connected to the inactive sites also became nonconductive, because the proton did not transport in this path to participate in any reaction. Therefore, parts of the parallel connections in the equivalent circuit disappeared due to the CO poisoning, as shown in Fig. 10b. Therefore, \( R_{N,a} \) (the sum of parallel connection for ohmic resistance in each electrolyte channel) increased with \( R_{C,a} \) in the presence of CO, as shown in Fig. 8.

The effect of the composition of anode catalyst on the relationship of anode resistance vs current density in 25 ppm CO/H\(_2\) is shown in Fig. 11. The charge-transfer resistances \( R_{C,A} \) and the ohmic resistances in catalytic layer \( R_{N,C} \) were calculated from impedance spectra. Figure 11 shows that \( R_{C,A} \) and \( R_{N,C} \) increased with current density due to the presence of CO. With a higher atomic ratio of Ru/Pt in anode catalysts, the increase in the resistance was smaller. The addition of Ru into the Pt anode catalyst significantly improved the CO tolerance.

Results from two analytical methods.—The comparison between the resistances obtained from polarization curves and impedance spectra is shown in Fig. 12. \( R_{C,A} \) is the charge-transfer resistance obtained from an anode polarization curve. \( R_{C,A} \) and \( R_{N,a} \) are the charge-transfer and the ohmic resistances in catalytic layer ob-
tained from an anode impedance spectra. It is observed that the curves of $R'_{ct,an}$ and $R_{ohm} + R_{Na}$ are comparable. In the presence of CO, the increase of anode overpotential observed in the polarization curve was attributed to the increase of charge-transfer resistance. The ac impedance analysis provided a better indication that the increase of anode overpotential was contributed by the increase of both charge-transfer resistance and ohmic resistance in the catalytic layer.

Conclusions

In general, the membrane electrode assembly of PEMFCs includes only two electrodes, anode and cathode. A third Pt electrode on Nafion membrane, prepared by the impregnation-reduction method, was used as the pseudoreference electrode to form a 3E-MEA. The performance of the cell was carried out in three-electrode mode system. During the cell discharging, the reaction behaviors of the anode and cathode could be studied in the three-electrode cell separately. The behavior of CO in PEMFC was investigated by a polarization curve and ac impedance analysis. An equivalent circuit model was proposed to explain the impedance spectra for the anode and cathode. In the presence of CO, the experimental results of ac impedance analysis suggest that the overpotential due to CO poisoning of the anode was contributed by the increasing of both charge-transfer resistance and the ohmic resistance in the catalytic layer.

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List of Symbols

- $b$: Tafel slope
- $C_{cat}$: capacitance of the catalyst
- $C_{N}$: capacitance on the carbon support
- $E$, $E'$: cell potential and reversible cell potential
- $E^o$: open-circuit potential of cell
- $R_{ct}$, $R_{ohm}$: charge-transfer resistance on the catalyst and ohmic resistance of electrolyte in a catalytic layer of an individual electrode calculated from ac impedance analysis
- $R_{ct,an}$, $R_{ct,cath}$: charge-transfer resistance at anode and cathode calculated from ac impedance analysis
- $R_{ct,an}$, $R_{ct,cath}$: uncompensated resistance of Nafion membrane between individual electrode and reference electrodes calculated from ac impedance analysis
- $I_R$: charge-transfer resistance at anode, cathode, and working electrodes calculated from polarization curves
- $R^{'}_{ct,an}$, $R^{'}_{ct,cath}$: mass-transport resistance and working electrodes calculated from polarization curves
- $R_{ct,wk}$: electrolyte resistance in a cell calculated from polarization curves
- $\eta_{ct}$, $\eta_{ct,an}$, $\eta_{ct,cath}$: charge-transfer overpotential at anode, cathode, and working electrodes
- $\eta_{wk}$, $\eta_{wk,an}$, $\eta_{wk,cath}$: mass-transport overpotential at anode, cathode, and working electrodes
- $\eta_{ohm}$: uncompensated overpotential between working and reference electrodes
- $\eta_e$: ohmic potential drop in a cell

References