RATES OF ADSORPTION, DESORPTION, AND OXIDATION OF CO ON PEM ELECTRODES

Balasubramanian Lakshmanan, and John W. Weidner
Center for Electrochemical Engineering
Department of Chemical Engineering
University of South Carolina
Columbia, SC 29208

Abstract

The rates of CO adsorption, desorption, and oxidation on proton exchange membrane fuel cells (PEMFC) electrodes are determined. Desorption was controlled by the parallel desorption of CO from linear bridge bonded sites and rearrangement between them. The kinetic rate constant for rearrangement from linear to bridge bonding is 3 to 4 orders of magnitude higher than either of the two desorption rate constants. Adsorption was significantly influenced by convection of the gas along the flow channel and diffusion of CO into the catalyst layer. Oxidation of preadsorbed layer of CO followed a dual path mechanism as well. However, rearrangement between the two types of bonding was negligible since the time duration of CO oxidation was 2 to 3 orders of magnitude smaller than the desorption time. Hence oxidation rates were determined by the sum of two exponential terms corresponding to linear and bridge bonded CO molecules.

Introduction

Proton exchange membrane fuel cells (PEMFC) operating on pure hydrogen show very good polarization characteristics over a wide range of load and temperature conditions. However, the use of reformate gas (a mixture of nitrogen (40 -50%), hydrogen (35 – 45%), CO2 (10 –20%), CO, water vapor and traces of other gases) causes a drop in Fuel Cell performance due to CO poisoning.

Study of CO poisoning of platinum and other alloy electrodes are usually carried out in aqueous electrolyte on a pre-adsorbed monolayer of CO.\textsuperscript{1,2} However, these techniques have their own limitations in estimating the rates of CO adsorption, desorption, and oxidation on composite electrodes. In this study, we conduct experiments on a conventional fuel cell membranes electrode assembly (MEA) to estimate the rates of CO adsorption, desorption and oxidation under different temperature conditions.
Experimental

Flow Cell

Catalyzed membranes were prepared using a procedure similar to the steps described in patent # 5211984. The active area of the electrodes was 50 cm², the anode side had a catalyst loading of 0.45 mg/cm² of 1:1 atomic ratio Pt-Ru catalyst or 0.5 mg/cm² of Pt, while the cathode was made of 0.5 mg/cm² of Pt. The membrane was catalyzed by hot pressing at 140 °C under 1000 psig pressure for 2 minutes against Teflon® decals sprayed with catalyst ink. The catalyzed membrane was then bonded to carbon cloth gas diffusion layers (GDL) at 140 °C under 500 psig pressure for 2 minutes to form a membrane electrode assembly (MEA). The MEA was assembled into a fuel cell with single channel serpentine flow field plates bought from Fuel Cell Technologies. The cathode side had H₂ flowing at 0.05 standard liters per minute (SLM). The cathode side was used as the counter and reference electrode (i.e., dynamic hydrogen electrode DHE) such that all the potentials reported here are referred to the H₂ cathode. The anode side had a flow of N₂, or CO/N₂ (476 ppm). All the gases were obtained from Air Products and the concentrations certified by the manufacturer. All the pure gases used were certified ultra high purity (UHP).

Cyclic voltammetry

For electrochemical characterization of the MEA, N₂ was first flowed at 0.10 SLM through the anode side, and the cell was left at open circuit. The N₂ flow was switched to a flow of 476 ppm CO in N₂ with a total flow rate of 0.10 SLM for a specified period of time (referred as exposure time) after which N₂ flow was restored. The cell was held at a constant potential of 50 mV for 15 seconds, which was followed by a cyclic voltammetry (CV) for three cycles, at a scan rate of 20 mV/s from 50 to 1150 mV and back to 50 mV. Experiments were conducted using a M263A potentiostat/galvanostat and ECHEM software made by EG&G. The area under the CO oxidation peak relative to the background current was used to calculate the amount of CO oxidized, which is reported as the amount of CO adsorbed. The experiment was repeated for various durations of CO/H₂ exposure. Between each experiment, the electrode was polarized at 0.9 V for 2 minutes to oxidize any remaining pre adsorbed CO on the catalyst layer.

Desorption

For determining the rate of desorption of CO from a Pt MEA, the electrode was saturated with CO by exposing it to 476 ppm CO for 300 s after which N₂ flow was restored. A cyclic voltammetry was conducted after a specified period of time (referred as desorption time) as per the procedure discussed above. The experiment was repeated for various durations of CO desorption at different temperatures.

Oxidation

For determining the rate of oxidation of CO on a Pt MEA, the electrode was saturated with CO by exposing it to 476 ppm CO for 300 s after which N₂ flow was restored. The electrode was polarized to a specific potential, (referred as oxidation potential) for a specific duration of time (referred as oxidation time), followed
immediately by a cyclic voltammetry as per the procedure discussed above. The experiment was repeated for various durations of CO oxidation at different oxidation potentials and temperatures.

Model development

Reactions

Adsorption, desorption, and oxidation of CO occur through the following reactions:

\[
\begin{align*}
\text{CO} + \text{Pt} & \rightleftharpoons \text{Pt-CO} \quad [1] \\
2\text{Pt} + \text{CO} & \rightleftharpoons \text{CO} \quad [3] \\
\text{Pt-CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- + \text{Pt} \quad [4] \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- + 2\text{Pt} \quad [5]
\end{align*}
\]

where \( k_1 \), \( k_2 \), \( k_3 \), \( k_4 \), and \( k_5 \) are the rate constants for reactions 1, 2, 3, 4, and 5, respectively.

Reaction [1] corresponds to the adsorption of CO onto the Pt catalyst (i.e., CO poisoning) through linear bonding. Reaction [2] corresponds to rearrangement of CO between linear and bridge type bonding and reaction [3] corresponds to the CO adsorption through bridge bonding. Reactions [4] and [5] correspond to the electrochemical oxidation of linear and bridge bonded CO molecules, respectively.

Desorption

During desorption since the gas phase CO concentration is zero, the material balance for pre adsorbed CO layer during desorption time can be given as

\[
\begin{align*}
\rho \frac{\partial \theta_{\text{CO}}^{\text{C}}}{\partial t} & = -k_1 \theta_{\text{CO}}^{\text{C}} - k_2 \theta_{\text{CO}}^{\text{C}} (1 - \theta_{\text{CO}}^{\text{C}} - \theta_{\text{CO}}^{\text{B}}) + k_3 \theta_{\text{CO}}^{\text{B}} \quad [6] \\
\rho \frac{\partial \theta_{\text{CO}}^{\text{B}}}{\partial t} & = k_2 \theta_{\text{CO}}^{\text{C}} (1 - \theta_{\text{CO}}^{\text{C}} - \theta_{\text{CO}}^{\text{B}}) - k_3 \theta_{\text{CO}}^{\text{C}} - k_3 \theta_{\text{CO}}^{\text{B}} \quad [7]
\end{align*}
\]

where \( \rho \) is the molar density of catalyst sites in the electrode. Equation [6] and [7] represent the site balance for linear (\( \theta_{\text{CO}}^{\text{C}} \)) and bridge (\( \theta_{\text{CO}}^{\text{B}} \)) bonded platinum sites, respectively. Equations [6] and [7] were solved simultaneously with \( k_1 \), \( k_2 \), \( k_3 \) as parameters using the principles of parameter estimation described by Constantinides et al. along with confidence interval analysis. The total CO coverage is calculated by using equation [8]

\[
\theta_{\text{CO}} = \theta_{\text{CO}}^{\text{C}} + \frac{\theta_{\text{CO}}^{\text{B}}}{2} \quad [8]
\]
**Adsorption**

Adsorption of CO in the platinum catalyst is limited by both diffusion of CO into the catalyst layer and convection along the flow channel. Figure 1 shows a schematic of the flow channel and the catalyst region. The material for CO in the flow channel is given by equation [9]

$$\frac{\partial C_{CO}}{\partial t} = -u \frac{\partial C_{CO}}{\partial z} - \frac{a}{\text{area}} N_x$$  \[9\]

where $C_{CO}$ and $u$ refer to the concentration of CO and velocity of the gas in the flow channel, respectively, $a$ refers to the equivalent area of the catalyst layer based on roughness and $N_x$ is the flux of CO into the catalyst layer evaluated at the channel – catalyst layer interface.

The material balances for CO both in dissolved phase and adsorbed phase (catalyst sites) are given by equations [10] and [11]

$$\frac{\partial C_{CO}}{\partial t} = D_{CO} \frac{\partial^2 C_{CO}}{\partial x^2} - k_1 C_{CO} (1 - \theta_{CO}) - k_2 \theta_{CO} + k_3 C_{CO} (1 - \theta_{CO})^2 - k_4 \theta_{CO}$$  \[10\]

$$\rho \frac{\partial \theta_{CO}}{\partial t} = k_1 C_{CO} (1 - \theta_{CO}) - k_2 \theta_{CO} + k_3 C_{CO} (1 - \theta_{CO})^2 - k_4 \theta_{CO}$$  \[11\]

In equation [10], $D_{CO}$ is the diffusion coefficient of CO in Nafion® ionomer in the catalyst layer. Equations [9], [10], and [11] were solved using Femlab in a pseudo 2-dimensional domain.

**Oxidation**

The material balances for linear and bridge bonded Pt sites during electrochemical oxidation are given by equations [12] and [13], respectively. Once again the total coverage is calculated using equation [8].

$$\frac{\partial \theta_{CO}^l}{\partial t} = -k_6 \theta_{CO} - k_7 \theta_{CO} (1 - \theta_{CO} - \theta_{CO}^b) + k_8 \theta_{CO}^b$$  \[12\]

$$\frac{\partial \theta_{CO}^b}{\partial t} = k_6 \theta_{CO} + k_7 \theta_{CO} (1 - \theta_{CO} - \theta_{CO}^b) - k_8 \theta_{CO}^b$$  \[13\]

However, rearrangement between the two types of bonding was negligible since the time duration of CO oxidation was 2 to 3 orders of magnitude smaller than the desorption time. Hence oxidation rates were determined could be predicted by the sum of two exponential terms corresponding to linear and bridge bonded CO molecules.

**Results and Discussion**

Figure 2 shows the data from the first cycle of CV’s obtained from the CO adsorption experiments for different durations of CO bleed. The area under the CO peak is used to calculate the surface coverage of CO. CO oxidation shows two overlapping peaks. These peaks were deconvoluted using a bimodal Gaussian distribution and the areas under each peak were determined independently. For example, the CV after 300 s of CO exposure normalized for the back current is shown in Figure 3. The area under the first peak corresponds to 52 percent of the total area under the experimental curve. This
fraction was assumed to be the initial fraction of bridge bonded CO sites after 300 s of CO exposure and used in the analysis of CO desorption and oxidation. Figure 4 shows the cyclic voltammetry on a Pt electrode at 50 °C under 0.10 SLM flow of N₂ after different durations of CO desorption from a saturated electrode. The area under the curve gives the amount of CO remaining in the Pt electrode after desorption time. The surface coverage as a function of desorption time was used to determine the rate of CO desorption. CO desorption cannot be predicted by a simple exponential decay of surface coverage. Hence the mechanism involving parallel desorption from linear and bridge bonded sites along with rearrangement of both species is needed for better prediction.

Figure 5 shows the surface coverage as a function of desorption time the symbols and the dotted line correspond to the experimental data and model prediction, respectively. The initial coverage of bridge bonded sites was determined to be 57 % by deconvoluting the peaks from a cyclic voltammetry conducted after 300 seconds CO exposure. The surface coverage of linear and bridge bonded sites as a function of time predicted by the model is shown as an inset. The coverage of linear sites decreases throughout desorption time. However, the coverage of bridge bonded sites increases initially, attains a peak, and starts to decrease. The initial increase in surface coverage of bridge bonded sites is due to the rearrangement of linear bonded CO through reaction [2].

Figure 6 shows the surface coverage as a function of exposure time the symbols and the dotted line corresponds to the experimental data and model prediction, respectively. The pseudo two dimensional model was used to predict the experimental data. The model predictions show that the adsorption is significantly influenced by the convection along the flow channel and the diffusion of CO into the catalyst layer.

Figure 7 shows some of the cyclic voltammograms conducted on a Pt electrode after different durations of CO oxidation at 650mV under 0.10 SLM of N₂ at room temperature. Prior to oxidation the electrode was saturated with CO by 300 s exposure to 476 ppm CO in N₂. The symbols correspond to different duration of CO oxidation. The peak at the lower potentials (600 – 750 mV) CO and it oxidizes faster than the peak at higher potentials (750 – 850 mV) corresponding to bridge bonded and linear bonded CO sites, respectively. It should be noted that no CO was remaining on the electrode surface after 300 seconds of oxidation.

Figure 8 shows the surface coverage of CO as a function of oxidation time on a Pt electrode at room temperature. The symbols and the dotted line correspond to experimental data and model prediction, respectively. The experimental data is the area under the CV after different durations of CO oxidation shown in figure 7. The rate of CO oxidation was determined by the sum of two exponential corresponding to the linear and bridge bonded CO sites. The dependence of the oxidation rate constants is shown in figure 9. The experimental data is the summary of rate constants determined using the exponential fits at various potentials. At 25 °C the pre exponential for CO oxidation on bridge bonded sites is nearly 3 orders of magnitude higher than the linear bonded sites. However, the exponential factor for the oxidation of both bridge bonded and linear CO molecules are nearly equal at 0.025 decades/mV corresponding to a Tafel slope of 40 mV/decade.
Conclusions

Experiments were conducted to study the rate of CO adsorption, desorption, and oxidation in PEM electrodes. Mathematical models were developed to analyze the experimental results. Table I summarizes the rate constants for various reactions.

Table 1: Summary of determined parameters

| Kinetic Constant | Value (Units) | Kinetic Constant | Value |
|------------------|---------------|------------------|-------|
| $k_1$            | 1300/s        | $k_3$            | $9.0 \times 10^{-9}$ mol/s |
| $k_{-1}$         | $2.1 \times 10^{-6}$ mol/s | $k_{-3}$         | $9.0 \times 10^{-9}$ mol/s |
| $k_2$            | $2.0 \times 10^{-3}$ mol/s | $k_4(V)$         | $6.8 \times 10^{-11}$ e $^{(0.0287V)}$ |
| $k_{-2}$         | $3.6 \times 10^{-5}$ mol/s | $k_5(V)$         | $1.2 \times 10^{-8}$ e $^{(0.0253V)}$ |

Desorption was controlled by the parallel desorption of CO from linear bridge bonded sites and rearrangement between them. The kinetic rate constant for rearrangement from linear to bridge bonding is 3 to 4 orders of magnitude higher than either of the two desorption rate constants. Adsorption was significantly influenced by convection of the gas along the flow channel and diffusion of CO into the catalyst layer. Oxidation of preadsorbed layer of CO followed a dual path mechanism as well. However, rearrangement between the two types of bonding was negligible since the time duration of CO oxidation was 2 to 3 orders of magnitude smaller than the desorption time. Hence oxidation rates were determined by the sum of two exponential terms corresponding to linear and bridge bonded CO molecules.

References

1. H. A. Gasteiger, N. Markovic, P. N. Ross, and E. J. Cairns. J. Phys Chem, 98, 617, (1994)
2. R. J. Bellows and E. Marcuchi-Soos, in Proton Conducting Membrane Fuel Cells II, S. Gottesfield and T. F. Fuller, Editors, PV 98-27, p.218, The Electrochemical Society Proceedings Series, Pennington, NJ (1998).
3. M. S. Wilson. United States Patent #5211984. May 18, 1993
4. A. Constantinides, and N. Mostoufi, Numerical Methods for Chemical Engineers with MATLAB Applications, p.522, Prentice Hall PTR, New Jersey (1999).

Acknowledgement

The authors acknowledge the support from the National Reconnaissance Office for Hybrid Advanced Power Sources under grant # NRO-00-C-1034.
**Figure 1:** Schematic of the flow channel and the catalyst layer in a fuel cell. The channel and the catalyst layer are not drawn to scale.

**Figure 2:** Cyclic voltammetry on a Pt composite electrode at room temperature under atmospheric N\textsubscript{2} flow after various exposure times to CO. The total flow rate was 0.1 SLM. The symbols correspond to time duration indicated by the legend.

**Figure 3:** The CV on electrode conducted after an exposure time of 300 s normalized for the background current is shown (●). The deconvoluted peaks using a bimodal Gaussian distribution along with the sum of the two peaks are also shown. The symbols ▲, ■, and ♦ show peaks 1, 2 and sum of 1 and 2, respectively. The experimental data is the CV after 300s exposure time shown in figure 2.
Figure 4: Cyclic voltammetry on a Pt composite electrode at 50 °C under atmospheric N₂ flow following saturated coverage. The total flow rate on the anode side was 0.1 SLM. The symbols correspond to different duration of CO desorption indicated by the legend.

Figure 5: Surface coverage of CO as a function of time on a Pt electrode at 50 °C. The symbols and the dotted line correspond to experimental data and model prediction, respectively. The predicted surface coverage of bridge and linear bonded sites is shown on the inset.
Figure 6: Surface coverage as a function of time during adsorption of CO. The symbols and the line correspond to the experimental data and model prediction, respectively. The experimental data is the summary of the results shown in figure 2.

Figure 7: Cyclic voltammetry on a Pt composite electrode at room temperature under atmospheric N₂ flow after various duration of CO oxidation. The total flow rate was 0.1 SLM, Co exposure time was 300 s and a potential of 650 mV was used during the oxidation step. The symbols correspond to time duration indicated by the legend.
Figure 8: Surface coverage of CO as a function of oxidation time on a Pt electrode at room temperature after CO oxidation at 650 mV. The symbols and the dotted line correspond to experimental data and model prediction, respectively. The data is the summary of the area under the cyclic voltammograms shown in figure 7.

Figure 9: Rate constants as a function of the applied potential. The ▲ and ● symbols correspond to bridge and linear bonded CO sites. The experimental data is the summary of rate constants determined using the exponential fits at various potentials.