COMPARISON OF CO TOLERANCE ON Pt and Pt-Ru ANODES IN PEMFCs

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Trace CO impurities can polarize the electro-oxidation of H2 in the proton exchange membrane fuel cell (PEMFC). CO polarization can severely decrease the PEMFC's power and efficiency. CO polarization data from several groups are compared for PEMFCs using Pt and Pt-Ru anodes with impure H2. Anodic polarization, in the presence of ppm levels of CO, shows surprisingly high slopes on semi-logarithmic plots. These polarization slopes exceed typical Tafel slopes and are consistent with a non-Faradaic rate limiting step. The onset of severe anode polarization, Icrit, correlates with noble metal loading, CO concentration level, and temperature. The dependence of Icrit on CO level supports the use Temkin adsorption isotherms for modeling CO tolerance behavior.

INTRODUCTION

The objective of this work was to develop a correlation for CO polarization losses in the proton exchange membrane fuel cell (PEMFC), in order establish a benchmark for anticipated improvements in CO tolerance. The PEMFC has emerged as a promising candidate for distributed power applications and for powering electric vehicles. Many groups are now considering supplying H2 for PEMFCs by reforming natural gas, alcohols or various hydrocarbons fuels (1-4). This "reformate H2" avoids many of the limitations anticipated with storing and distributing pure H2 fuel. Unfortunately, reformate H2 contains CO impurities, which cause large polarization losses, thereby reducing the PEMFC's efficiency and power output.

Several groups have reported PEMFC performance using impure H2 on Pt and Pt-Ru catalyzed anodes (5-12). Typical performance curves for on Pt anodes using impure H2 are shown in Figure 1. The highest performance is always obtained when using pure H2. The performance using impure H2 decreases with both increasing CO and with increasing current density. Interestingly, at low current densities, the voltage can remain close to pure H2, even at the higher CO levels.

Several research groups are trying to develop "CO tolerant" anodes. "CO tolerance" is usually defined as the ability to electro-oxidize H2 in the presence of CO at an acceptable polarization loss. CO tolerance is usually quantified at some current density in terms of the maximum CO concentration (typically ppm) which can be tolerated, as defined by some nominal polarization loss at the anode (typically 20-100 mV). Losses are referenced to performance on pure H2. Pt-Ru anodes are reported to show increased CO tolerance over Pt anodes in PEMFCs (8). Pt3Sn and Pt75Mo25 are reported to oxidize CO at low potentials (13,14). Pt-Ru/WO3 is reported to tolerate higher CO levels than Pt in gas diffusion electrodes (15).

There is a need for a benchmark for comparing CO tolerance data from various sources. This would be especially useful since typically the workers have conducted...
experiments using differing PEMFC designs, materials, noble metal loadings, CO impurity levels and test protocols. In earlier work, the onset of CO polarization on Pt anodes was correlated with noble metal loading, CO concentration level and temperature (11). In this presentation, we extend our correlation to Pt-Ru anodes and we discuss our correlations relative to the modeling of CO tolerance behavior.

**THEORY**

**Anode Surface Chemistry**

Fuel cell performance curves are interpreted using polarization theory (16). At any current density, the terminal voltage is a combination of the theoretical voltage (1.23V) minus various polarization losses attributed to O₂ activation at the cathode, O₂ concentration polarization in air cathodes, internal resistance in the cell and H₂ activation losses at the anode. This paper considers an additional H₂ activation loss which is caused by the presence of CO in the H₂. This loss can be interpreted as an additional polarization term, CO polarization (η_{CO}), which is defined as the difference between cell performance on pure H₂ and that with some level of CO.

The electro-oxidation of H₂ on Pt is a two step reaction which proceeds first by the dissociation of H₂, followed by the discharge of adsorbed monatomic H (17). Dissociation is the rate limiting step and requires two adjacent bare Pt sites. CO is a well known poison for the electro-oxidation of H₂ on Pt. CO binds strongly to Pt sites, thereby blocking the H₂ dissociation reaction, even at trace levels (18). Adsorbed CO can be removed from Pt via electro-oxidization but this is a sluggish reaction which generally occurs only at much higher potentials than H₂ electro-oxidation. H₂ electro-oxidation activity on Pt surfaces in the presence of CO (i_{H2/CO}) is reported by Ross and Stonehart to be a function of anode activity on pure H₂ (i°_{H2} (V, T)) multiplied by a poisoning parameter ([1-Θ_{CO}]²), where V = potential, T = temperature, Θ_{CO} = fraction of Pt surface covered by CO, and [1-Θ_{CO}] = fraction of Pt surface not covered by CO (17,18).

\[
i_{H2/CO} = i°_{H2} (V, T) \cdot [1-Θ_{CO}]^2
\]  

Their interpretation is that the limiting reaction mechanism requires two adjacent sites and that the probability of finding two adjacent sites is reduced by the square of the surface fraction not poisoned by CO. Equilibrium considerations suggest that CO coverage on Pt should be decreased by using lower CO partial pressures and/or higher temperatures.

The activity on gas diffusion electrodes is given by [2], where S = Pt surface area factor in cm² Pt per cm² superficial electrode area, i₀ = exchange current density and b = the Tafel slope for H₂ on Pt. Based on these considerations, an implicit relationship for CO polarization in the H₂ electro-oxidation is given by:

\[
I_{\text{krit}} = S \cdot i_0 \cdot \exp(2.3 \cdot η_{CO}/b) \cdot [1-Θ_{CO}]^2
\]  

**CO Tolerance Correlation for Pt Anodes**

PEMFC performance curves, taken in this laboratory, are shown as a function of CO concentration in Figure 1. At low current densities, performance on impure H₂ is nearly identical to that for pure H₂. At some intermediate current density, the voltage begins to drop below that for pure H₂ and at slightly higher currents, the voltage drops...
quite rapidly. At still higher currents, the slope of the performance curve changes, showing a positive second derivative. After this inflection, the voltage remains relatively constant.

The polarization caused by trace CO, $\eta_{\text{CO}}$, is defined as the difference in cell voltage at constant current, between performance on pure and impure H$_2$. $\eta_{\text{CO}}$ is plotted vs. current density on a semi-logarithmic scale in Figure 2. For each CO level, $\eta_{\text{CO}}$ shows three distinct behaviors: 1) $\eta_{\text{CO}} = 0$, at lower current densities, 2) $\eta_{\text{CO}} = 50-350$ mV, where $\eta_{\text{CO}}$ increases very rapidly with increasing current density and 3) $\eta_{\text{CO}} = \text{constant}$, at higher current densities. Region 2 of Figure 2 is particularly interesting because the slope for each curve is quite large, i.e., about 800-900 mV/decade.

In region "1", the "open CO monolayer region", there is enough bare Pt (i.e., not covered by CO) to support H$_2$ electro-oxidation at low current densities with no polarization losses, because $i_0$ for H$_2$ on Pt is quite high (11).

In region "2", the "non-Faradaic region", the current density for H$_2$ oxidation on bare Pt exceeds $i_0$ and $\eta_{\text{CO}}$ grows rapidly. The slope of the polarization between 50 and 350 mV is much higher than expected electro-chemical Tafel slopes, which are typically 30-120 mV/decade. We believe that these large slopes have not been appreciated previously.

The high slope suggests that a non-Faradaic chemical step is rate limiting, possibly the dissociation of H$_2$ into monatomic H. This is consistent with the two step mechanism proposed previously (17). This high slope is of critical importance in understanding CO tolerance. If the rate limiting step in H$_2$ oxidation was Faradaic, the Tafel slope would be much lower and CO poisoning in PEMFCs might be minor problem.

In region "3", the "CO overpotential region", at higher current densities the high $\eta_{\text{CO}}$ starts to promote simultaneous oxidation of adsorbed CO. CO oxidation on Pt has been reported to start between 150-300 mV/RHE at 60°C (19). CO oxidation rates increase with increasing $\eta_{\text{CO}}$ until CO oxidation starts to exceed the rate of adsorption for incoming CO in the feed. At the potentials in region "3", our interpretation is that CO oxidation begins to decrease $\Theta_{\text{CO}}$, opening additional bare Pt sites so that further increases in current density require almost no increase in $\eta_{\text{CO}}$.

The onset of CO polarization provides a useful basis for correlating various CO poisoning studies. The onset of CO polarization in Figure 2 was defined by extrapolating the steep slope in region "2" back to the intercept where $\eta_{\text{CO}} = 0$ mV for each level of CO. We interpret this intercept as a "critical" H$_2$/CO ($I_{\text{crit}}$), above which the available bare Pt can no longer support reversible H$_2$ electro-oxidation. CO polarization plots (similar to Figure 2) were prepared from CO tolerance studies reported in the literature (5,6,8,9,10,12). The $I_{\text{crit}}$ values estimated from these various studies are plotted in Figure 3 (normalized to a Pt loading of 0.4 mg Pt/cm$^2$). The comparison shows a surprisingly consistent correlation for the onset of the non-Faradaic region, despite differing fabrication procedures, differing experimental conditions and differing CO poisoning protocols.

The normalization to a constant loading improved the correlation, suggesting that the $I_{\text{crit}}$ is proportional to Pt loading (more probably Pt surface area). The outliers in the trend line in Figure 3 (Wilson (ref. 6) and Iwase (ref. 8)) may be caused by differences in Pt surface area, Pt utilization or O$_2$ crossover. (Pt surface areas and other experimental
Details were generally not reported in the original references.) $I_{crit}$ decreases with increasing CO level in Figure 3 because higher CO levels decrease the available bare Pt sites. Figure 3 shows a power law correlation where $I_{crit}$ is proportional to $[\text{CO}]^{0.6}$, ($[\text{CO}] = \text{CO concentration}$). The data at 120°C suggest that $I_{crit}$ has an apparent activation energy $= 100 \text{ kJ/mol}$. (Note: The apparent activation energy was incorrectly stated as 25 Kcal/mol in ref. 11.)

Modeling of CO Polarization at LANL

Los Alamos National Labs (LANL) has published a useful phenomenological model which describes their CO polarization results in PEMFCs (20). Their model assumes a "Tafel" relationship for the electro-oxidation of H$_2$ and CO on Pt, a Langmuir adsorption isotherm for CO on Pt and the poisoning parameter as described above. The LANL interpretation of the CO polarization is generally consistent with our discussion of the three regions in Figure 2. The LANL model predicts that the onset of severe CO polarization decreases as a function of increasing CO. The LANL model can be used to predict how changing significant parameters (increasing CO oxidation rate or decreasing CO adsorption strength) would improve CO tolerance.

EXPERIMENTAL DETAILS

The CO tolerance tests were conducted on a GT-120 test station with a 5 cm$^2$ fuel cell test fixture manufactured by Globetech, Bryan, TX. The membrane electrode assembly (MEA) was fabricated on Nafion™ 112 by General Motors, using a spray technique. Catalysts were 40 wt% Pt and 20 wt% Pt-Ru on Vulcan XC72, as supplied by E-tek (Natick, MA). Both anode and cathode had a loading of 0.3 mg Pt/cm$^2$. For Pt-Ru, the anode loading was 0.225 mg Pt/cm$^2$. The pure H$_2$ feed was passed through a butyl-Li getter to remove trace impurities. Air was provided by Exxon house gas systems. Cylinders containing pre-mixed CO and H$_2$ were supplied by MG Gases. The trace CO levels are based on the manufacturer's analysis, as delivered. Anode and cathode pressure were 10 and 15 psig respectively and anode and cathode flow rates were 0.11 and 0.43 liters/min., under all operating conditions.

The experimental protocol used to evaluate the "CO Tolerance" was as follows (21): 1. Anode feed was held at a constant flow rate during the scan, so that H$_2$ stoichiometry is well above 1.0, especially at low current densities. 2. Each data point in performance scan was recorded after 1 minute at constant voltage. 3. Anode was exposed to impure H$_2$ for at least 1 hour prior to scan (longer for 5 ppm CO).

RESULTS AND DISCUSSION

CO tolerance studies for Pt-Ru anodes were conducted and analyzed in the same manner as those for Pt (11). Representative PEMFC performance curves using Pt-Ru anodes, taken in this laboratory, are shown as a function of CO concentration level in Figure 4. The behavior is qualitatively similar to that observed on Pt anodes.
η_{CO} for Pt-Ru anodes is plotted vs. current density on a semi-logarithmic scale (similar to Figure 2) in Figure 5. As with Pt anodes, η_{CO} shows three distinct behaviors at each CO level: 1) η_{CO} = 0, at lower current densities, 2) η_{CO} = 50-300 mV, where η_{CO} increases very rapidly with current density and 3) η_{CO} = constant, at higher current densities. The slope in Region “2” is again quite large, i.e., about 500-800 mV/decade but somewhat less than the 800-900 mV/decade observed for Pt anodes.

Similar PEMFC performance curves using Pt-Ru anodes with impure H₂, have been reported by other groups (8,9,10). CO polarization curves estimated from published performance, showed regions similar to the three regions seen in Figure 5. Table I summarizes the slopes found in the non-Faradaic region.

The onset of CO polarization, I_{crit} for these various studies is plotted in Figure 6, normalized to a Pt loading of 0.4 mg/cm². The normalization to a constant loading improved the correlation, again suggesting that I_{crit} is proportional to noble metal loading (or probably surface area). The dashed lines in Figure 6 summarize our earlier correlation lines for Pt anodes (Figure 3) and are included for comparison purposes. Generally, Figure 6 suggests that I_{crit} averages about 3-4 fold higher on Pt-Ru than on Pt anodes. The comparison however, shows wider variability than we found with Pt anodes in Figure 3 and therefore we did not attempt to characterize Pt-Ru using a single correlation line. The spread in the Pt-Ru data suggest differences among the Pt-Ru catalysts (or perhaps among MEA fabrication procedures, experimental conditions or CO poisoning protocols). The extent of alloy formation in Pt-Ru catalysts is reportedly variable (22).

In all cases, I_{crit} decreases with increasing CO level. Our Pt-Ru data for I_{crit} vs. CO level show that a power law correlation exponent of -0.6. This is similar to the overall power law dependence on Pt anodes, as shown in Figure 3. However, separate power law correlations for the data of either Schmidt or Acres both show power law exponents of -0.25. The reason for this variability in CO dependence is not understood.

Proposed Improvement in LANL Model for CO Tolerance

Values for I_{crit} were estimated from the LANL model (using Figure 1 in ref. 5) and are plotted vs. CO level in Figure 7 (20). Values of I_{crit} were also estimated from LANL’s experimental data (using Figure 1 from reference 5) and these are also plotted for comparison in Figure 7. The dashed lines again represent our correlation for Pt anodes as shown in Figure 3. A power law fit of I_{crit} vs. CO level, as predicted by the LANL model, shows an exponent of -1.7. It can be shown mathematically that this predicted power law dependence is related to the assumed Langmuir adsorption constant. The inconsistency between the LANL model and our correlation of experimental data as shown in Figure 3 suggests that the LANL model can be further improved by using an isotherm where the adsorption strength varies with CO coverage, such as a Temkin or Freundlich isotherm. Of course, the use of more complicated isotherms has the disadvantage of introducing additional fitting parameters.

CONCLUSIONS

The CO polarization behavior for Pt-Ru catalyzed anodes in PEMFCs at 80°C was analyzed. Data from several sources consistently showed 3 regions of behavior:
1. An "open CO monolayer region" which shows no polarization losses. At low current densities, there is sufficient bare Pt to effectively catalyze H₂ oxidation.

2. A "non-Faradaic region", where ηCO is between 50 and 300 mV, shows surprisingly high "Tafel" slopes. High slopes suggest that the rate limiting step in H₂ electro-oxidation is non-Faradaic, probably the H₂ dissociation step.

3. A "CO overpotential region" which shows a relatively constant ηCO at about 250-400 mV, depending on CO level, which correlates with the onset of significant CO oxidation on Pt-Ru.

The onset of severe polarization, Icrit, correlates with Pt loading and CO impurity level, similar to the correlation previously observed on Pt anodes. In general, Icrit is about 3-4 times higher for Pt-Ru than for Pt anodes. The variability of the Icrit correlation for Pt-Ru is greater than that for Pt. Also the power law dependence for Pt-Ru anodes shows a greater range of CO dependence than Pt. A possible interpretation for this variability is that there was greater variability among Pt-Ru than Pt catalysts.

The CO dependence of Icrit suggests that accurate modeling of CO tolerance should use a coverage dependent isotherm such as the Temkin isotherm.

FUTURE EFFORTS

A series of CO tolerance experiments are planned using Pt anodes where both Pt loading and Pt surface area will be systematically varied.

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Table I: Summary of “Tafel Slopes in the Non-Faradaic Regime”

| First Author | Slope (mV/decade) |
|--------------|------------------|
| Bellows      | 500              |
| Schmidt      | 510              |
| Iwase        | 720              |
| Acres        | 775              |

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Figure 1: PEMFC Performance with H₂/Air on Pt Anodes with Increasing CO, 80°C, 0.3 mg Pt/cm²

Figure 2: CO Polarization with H₂/Air on Pt Anodes with Increasing CO, 80°C, 0.3 mg Pt/cm²
Figure 3: $I_{\text{crit}}$ on Pt for $\text{H}_2/\text{Air}$ PEMFCs increases with Decreasing CO Level and Increasing Temperature.

Figure 4: PEMFC Performance with $\text{H}_2/\text{Air}$ on Pt-Ru Anodes with Increasing CO, 80°C, 0.225 mg Pt/cm$^2$. 

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Figure 5: CO Polarization with H₂/Air on Pt-Ru Anodes with Increasing CO, 80°C, 0.225 mg Pt/cm².

Figure 6: Comparison of \( i_{\text{crit}} \) on Pt-Ru and Pt Anodes vs CO Level

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Figure 7: Comparison of \( I_{\text{crit.}} \) on Pt Anodes and LANL Model vs. CO Level.