

THE EFFECT OF CARBON MONOXIDE CONTAMINATION ON ANODE EFFICIENCY IN PEM FUEL CELLS

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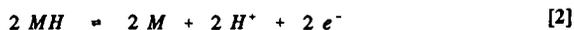
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ABSTRACT

Carbon monoxide (CO) contamination in the anode feed acts as a poison to platinum electrodes in proton exchange membrane (PEM) fuel cells. The CO is preferentially adsorbed onto the platinum, blocking active catalyst sites which are required for hydrogen oxidation. An empirical model of the performance of a Ballard PEM fuel cell based on a mechanistic analysis of the gas-electrode-interface has been developed by our group. This model was modified with a CO surface coverage term to account for the effect of CO contamination on the fuel cell output voltage. The effect of CO enters the model as a reduction in the exchange current which results in an increase in activation voltage losses.

A proton exchange membrane (PEM) fuel cell system combines hydrogen and oxygen electrochemically via catalyzed reactions. The products of these reactions are electrochemical energy and water. Hydrogen can be obtained by steam reforming methanol or other light hydrocarbon fuels. The reformat feed gas may contain up to 5 % carbon monoxide (CO) by volume, which can be reduced to 100 ppm using a selective oxidizer^{1,2}. Even small traces of CO, however, can cause significant reductions in fuel cell performance. It has been shown³ that even 30 ppm of CO can cause a 48 % drop in the output cell voltage of a PEM fuel cell lowering it from 0.60 V to 0.31 V at 150 Amps. Other researchers² have reported output voltage drops up to 90 % for 100 ppm of CO at a current density of 650 ASF.

Adsorption of carbon monoxide greatly reduces the activity of the platinum electrocatalyst by blocking active catalyst sites¹. CO poisoning thus reduces the voltage output of a PEM fuel cell by limiting the number of catalyst sites available for the hydrogen oxidation reaction. The mechanism for the electrochemical oxidation of molecular hydrogen on platinum is believed to proceed according to the Tafel-Volmer Sequence^{4,5,6}:



The rate controlling reaction step is the dissociation of the adsorbed hydrogen molecule to two hydrogen atoms (shown in reaction [1]). CO impurities in the hydrogen feed, may result in another competitive adsorption process:



where n is the average number of platinum sites occupied by each carbon monoxide molecule. It has been reported⁷ that $1 \leq n \leq 2$. These inhibiting effects of CO can be explained through the kinetics of the anode reaction in the fuel cell.

The output voltage of a PEM fuel cell consists of three terms: the thermodynamic potential, the activation overvoltage, and the ohmic overvoltage, with mass transport losses incorporated into each of the terms⁸:

$$V = E + \eta_{act} + \eta_{ohmic} \quad [4]$$

where η_{act} and η_{ohmic} are both negative terms which decrease the total output voltage. The polarisation due to kinetic losses at the anode has been defined by Berger⁸:

$$\eta_{act} = \frac{RT}{2F} \ln \frac{I^o}{I} \quad [5]$$

where the exchange current density, I^o , is always less than the actual current density, I . The exchange current density for a fuel cell is defined as the current density in either direction at reversible conditions⁸. This occurs at zero overvoltage when the anodic and cathodic currents are equal.

DERIVATION OF A PERFORMANCE MODEL INCORPORATING THE EFFECTS OF CO

The rate limiting process for the kinetics of the anode reaction is the chemisorption of hydrogen onto active catalyst sites⁵. The exchange current density is thus dependent upon the rate of chemisorption. As CO is preferentially adsorbed onto the platinum, the rate of hydrogen chemisorption will decrease, lowering values of current density and increasing the activation overvoltage. The fraction of the total platinum sites that are available, θ_M , will be reduced by the fractional CO surface coverage, θ_{CO} , so that the fraction of the catalyst that is available for hydrogen chemisorption becomes:

$$\theta_M = 1 - \theta_H - \theta_{CO} \quad [6]$$

A special case of this conservation equation applies at zero current when all values are at an steady-state, zero overvoltage condition:

$$\theta_{M,p} = 1 - \theta_{H,p} - \theta_{CO,p} \quad [7]$$

The electrode potential in the presence of CO can be expressed as^{5,6,9}

$$E = E^* + \frac{RT}{F} \ln \left(\frac{1 - \theta_{H,p} - \theta_{CO,p}}{\theta_{H,p}} \right) \quad [8]$$

Vogel and co-workers⁵ proposed that the exchange current density for pure hydrogen (no CO contamination) be defined as:

$$I^o = 2FkC_{H_2}(1-\theta_{H_2})^2 \quad [9]$$

and the exchange current density with CO contamination be defined as⁵

$$I_{CO}^o = 2FkC_{H_2}(1-\theta_{H_2})^2(1-\theta_{CO,\rho})^2 \quad [10]$$

Therefore, the effects of CO can be expressed by combining Equations [9] and [10]^{5,6,9}:

$$I_{CO}^o = I^o(1-\theta_{CO,\rho})^2 \quad [11]$$

where I_{CO}^o is the exchange current density for a CO site coverage of $\theta_{CO,\rho}$ and I^o is the exchange current density with no CO contamination. Combining Equations [5] and [11] yields the following expression for the activation overvoltage with CO effects:

$$\eta_{act,CO} = \frac{RT}{2F} \ln \frac{I^o(1-\theta_{CO,\rho})^2}{I} \quad [12]$$

Rearranging Equations [4] and [12] produces a relationship between the steady-state (ie. zero current) fractional surface coverage of CO and overvoltage:

$$\theta_{CO,\rho} = 1 - \exp \left[\frac{-F}{RT} (\eta_{act} - \eta_{act,CO}) \right] \quad [13]$$

Now that the CO concentration can be expressed as a surface coverage, the next step is to incorporate the CO surface coverage term into a fuel cell performance model. Combining Equations [4], [12], and [13] will yield the simple expression for the fuel cell output voltage:

$$V_{CO} = V + \frac{RT}{F} \ln(1 - \theta_{CO,\rho}) \quad [14]$$

as the general case for any PEM fuel cell where V is the cell voltage for a zero CO content.

A model predicting the output voltage of a PEM fuel cell (a Ballard Power System Mark IV single cell with NafionTM membrane, Pt catalyst and an active surface area of 50.56 cm²) has been developed by our group^{10,11}. Mechanistic expressions were developed for each term in Equation [4], leading to an expression with seven unknown coefficients. These model parameters were determined by least squares linear regression using the experimental data based on the Ballard single cell. The following empirical expression was obtained:

$$\begin{aligned} V = & 1.23 - 0.85 \cdot 10^{-3}(T-298.15) + 4.31 \cdot 10^{-5} \cdot T[\ln(p_{H_2}) + \frac{1}{2} \ln(p_{O_2})] \\ & - 0.951 + 3.12 \cdot 10^{-3} T - 1.87 \cdot 10^{-4} T[\ln(i)] + 7.40 \cdot 10^{-3} T[\ln(c_{O_2})] \\ & + 0.016 - 3.5 \cdot 10^{-3} T + 8.0 \cdot 10^{-5} i \end{aligned} \quad [15]$$

The operating range for each experimental variable were as follows: 50 ASF $\leq I \leq$ 300 ASF, 328 K $\leq T \leq$ 300 K, 0.64 atm $\leq p_{O_2} \leq$ 3.06 atm, and 1.99 atm $\leq p_{H_2} \leq$ 3.06 atm. By combining Equations [14] and [15], the effect of CO contamination can be incorporated into the performance model of the PEM fuel cell.

APPLICATION OF THE MODIFIED PERFORMANCE MODEL TO PUBLISHED DATA

Figure 1 shows the experimentally measured effect of CO contamination on the output voltage of a PEM fuel cell as reported by Lemons². The derivation of Equation [13] implies that $\theta_{\text{CO},o}$ does not vary with current density (based on the definition of exchange current). Equation [13] therefore predicts that the decrease in the output cell voltage, $(V - V_{\text{CO}})$, should be uniform over the polarization curve as shown in Figure 2. The values of $\theta_{\text{CO},o}$ used to generate Figure 2 are based on the values of $(V - V_{\text{CO}})$ at 700 ASF for each level of CO contamination shown in Figure 1. These values of $\theta_{\text{CO},o}$ are given in Table 1. A current density of 700 ASF was chosen, since the high current density end of a polarization curve is more likely to be at steady-state during an experiment than the low current density end.

DISCUSSION

Comparing Figures 1 and 2, it is clear that the modified performance model, incorporating the effect of CO based on the analysis of Dhar and Vogel, does not predict the observed variation in fuel cell performance reported by Lemons. Assuming $\theta_{\text{CO},o}$ does not vary with current density, Equation [14] is not able to account for the points of inflexion seen in Figure 1. Several explanations for this disagreement are possible.

It is commonly known that the complex multi-phase system at the electrolyte-electrocatalyst-gas interface is very slow in reaching steady-state. The processes involved, such as membrane hydration, catalyst surface equilibration and water removal, can undergo very slow transients as operating conditions are changed. It is possible, therefore, that there is a systematic error in the measured output cell voltage which varies with current density in the data reported in Figure 1 because steady-state was not fully attained. If Figure 1 is compared with Figure 2, it is clear that the experimental values of $\theta_{\text{act,CO}}$ are lower than that of the predicted values. This could imply that the CO poisoning process is still underway, perhaps too slowly to be evident, and that the experimental values of $\theta_{\text{act,CO}}$ are still increasing.

A second possible explanation is that the assumption of θ_{CO} remaining constant at $\theta_{\text{CO},o}$ for a particular CO concentration (as concluded by Dhar³) is not valid. A conservation analysis of the concentration of chemisorbed H, θ_{H} , will indicate that the value of θ_{H} is determined by the relative rates of H atoms occupying vacant sites and vacating occupied sites. If the removal rate increases, θ_{H} decreases. When the basic two processes, adsorption and desorption, are joined by a third, the movement of protons from platinum sites into the membrane toward the cathode, θ_{H} should decrease. The greater the cell current density, such that the greater the required proton flux from the anode to the cathode, the lower θ_{H} should be. Since hydrogen and CO are involved in a competitive chemisorption process, a decrease in θ_{H} should permit a decrease in θ_{CO} . Thus higher currents should cause a higher fraction of the Pt sites to be poisoned by CO and the performance of the cell to degrade. This hypothesis can be indirectly tested as follows. As explained earlier, the 700 ASF data from Lemon's paper were used to estimate $\theta_{\text{CO},o}$ at each CO level via Equation [13]. If instead, overvoltages at other current densities are used to make the same estimation, the results in Figure 3 are obtained. Since the choice of 700 ASF data was somewhat arbitrary, it would be expected, for a particular ppm level of CO in the anode gas, that the same value of $\theta_{\text{CO},o}$ would be calculated from Equation [13] for all current densities. Figure 3 makes it clear that this is far from true.

CONCLUSIONS

The model previously proposed^{5,6,9} to account for the effect of CO contamination on the activation overvoltage in PEM fuel cells does not appear to explain the one available set of published data². It is possible that either the model or the data are at fault. More work, both theoretical and experimental, is required.

Table 1. The surface coverage of carbon monoxide as a function of CO concentration based on Lemons' data at 700 ASF.

| CO concentration (ppm) | θ_{CO} |
|------------------------|---------------|
| 5 | 0.99988109 |
| 10 | 0.99998049 |
| 20 | 0.99999477 |
| 50 | 0.99999927 |
| 100 | 0.99999980 |

Figure 1. Experimental data on the effects of CO impurities on a PEM fuel cell (reconstructed from Lemons, R.A., *J of Power Sources* 29, 251 (1990))²

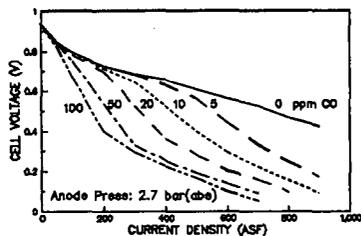


Figure 2. The predicted effects of CO on the Ballard Mark IV fuel cell performance using θ_{CO} data from Table 1.

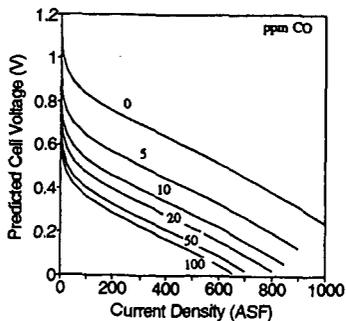
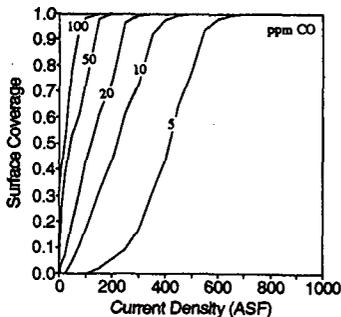


Figure 3. CO surface coverage on a platinum catalyst as a function of current density based on Lemons' data.



NOTATION

| | | |
|------------------|---|------------|
| A | active surface area, cm ² | |
| c _i | concentration of species i at the interface, mol·cm ⁻³ | |
| CO | carbon monoxide | |
| E | thermodynamic potential, V | |
| F | Faraday's Constant | |
| I | current density, ASF | |
| I ^o | exchange current density, ASF | |
| i | current, A | |
| K | adsorption equilibrium constant, bar ⁻¹ | |
| k | reaction rate constant, mol·s ⁻¹ ·bar ⁻¹ | |
| M | available catalyst site | |
| MCO | catalyst site with CO adsorbed | |
| MH | catalyst site with H adsorbed | |
| N | net number of electrons transferred in a reaction | |
| n | average number of platinum sites occupied by the CO molecule | |
| p _i | partial pressure of species i in the fuel cell, bar | |
| R | ideal gas constant, 8.314 J/mol·K | |
| r | reaction rate, mol·s ⁻¹ | Subscripts |
| T | temperature of the fuel cell stack, K | CO |
| V | total cell output voltage, V | H |
| | activation overvoltage, V | M |
| ^{act} | ohmic overvoltage, V | o |
| _{ohmic} | | T |
| θ | fraction of platinum surface sites | |

REFERENCES

1. S. Gottesfeld, S. Pafford. *J. Electrochem. Soc.* **135**, 2651 (1988).
2. R.A. Lemons. *J. Power Sources* **29**, 251 (1990).
3. C.M. Seymour. *J. Power Sources* **37**, 155 (1992).
4. K.J. Vetter. *Electrochemical Kinetics*, p.522. Academic Press, New York (1967).
5. W. Vogel, J. Lundquist, P. Ross, and P. Stonehart. *Electrochim. Acta* **20**, 79 (1975).
6. J. Wang and R.F. Savinell. *Electrochim. Acta* **37**, 2737 (1992).
7. R.P. Eischens and W.A. Pliskin. *Z. Phys. Chem.* **24**, 11 (1960).
8. C. Berger. *Handbook of Fuel Cell Technology*, Prentice-Hall, Englewood Cliffs, NJ (1968).
9. H.P. Dhar, L.G. Christner, A.K. Kush, and H.C. Maru. *J. Electrochem. Soc.* **133**, 1574 (1986).
10. R.M. Baumert. *Performance Modelling of the Ballard Mark IV Solid Polymer Electrolyte Fuel Cell*, Masters Thesis, Queen's University, Kingston, Ont. (1993).
11. J.C. Amphlett, R.M. Baumert, R.F. Mann, B.A. Peppley, P.R. Roberge. "Performance Modelling of the Ballard Mark IV Solid Polymer Electrolyte Fuel Cell", submitted to *J. Electrochem. Soc.* June 1993.
12. T.E. Springer, T.A. Zawodzinski, and S. Gottesfeld. *J. Electrochem. Soc.* **138**, 2334 (1991).