Rates of Adsorption, Desorption and Oxidation of CO on PEM electrodes

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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%), CO_2 (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 [1]. The effect of CO poisoning on the performance of Fuel Cells have been studies previously [2]. However, both 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 fully assembled fuel to estimate the rates of CO adsorption, desorption and oxidation under different temperature conditions.

Experimental

Catalyzed membranes were prepared using a procedure similar to the steps described in patent # 5211984 [3]. The active area of the electrodes was 10 cm^2, the anode side had a catalyst loading of 0.45 mg/cm^2 of 1:1 atomic ratio Pt-Ru catalyst or 0.5 mg/cm^2 of Pt, while the cathode was made of 0.5 mg/cm^2 of Pt. The catalyzed membranes were then bonded to carbon cloth gas diffusion layers (GDL) at 140 °C under 500 psig pressure for 2 minutes to form a membrane electrode unit (MEU). The MEU was assembled into a fuel cell with single channel serpentine flow field plates bought from Fuel Cell Technologies. The cathode side had H_2 flowing at 0.05 standard liters per minute (SLM). It 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 H_2 cathode. The anode side had a flow of N_2, or CO/N_2 (496 ppm). All the gases were obtained from Air Products and the concentration certified by the manufacturer, all the pure gases used were certified ultra high purity (UHP).

Model development

Electro oxidation of CO occurs through the following reactions (M refers to either Pt or Ru metal catalysts sites)

$$CO + * \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CO_{ads} \qquad [1]$$

$$H_2O + * \underset{K_{-2}}{\overset{K_2}{\rightleftarrows}} OH_{ads} + H^+ + e^- \qquad [2]$$

$$CO_{ads} + OH_{ads} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CO_2 + H^+ + e^- + 2* \qquad [3]$$

The rate of CO adsorption and the rate of change of the concentration of CO in the gas phase can be given by

$$\frac{\partial X_{CO}}{\partial t} = -u\frac{\partial X_{CO}}{\partial z} - \frac{K_1}{d} X_{CO}(1-\theta_{CO}) - \frac{K_{-1}}{d}\frac{\theta_{CO}}{c} \qquad [4]$$

$$\frac{\partial \theta_{CO}}{\partial t} = -\frac{K_{-1}}{\rho}\theta_{CO} + K_1 X_{CO}(1-\theta_{CO})\frac{c}{\rho} \qquad [5]$$

Figure 1 shows the data from the first cycle of CV's obtained from this experiment for different duration of CO bleed. The area under the CO peak is used to calculate the surface coverage of CO, which in turn is, used to estimate the adsorption and desorption rate constants used in equations 4 and 5.

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*, **PV98-27** ,218, The Electrochemical Society Proceedings Series, Pennington, NJ (1999)
3. M. S. Wilson. United States Patent #5211984. May 18, 1993

Figures

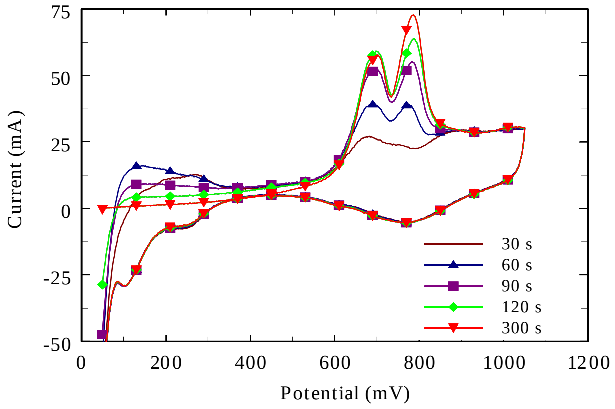

Figure 1: Cyclic voltammetry on a Pt composite electrode at room temperature under atmospheric N_2 flow after various exposure times to CO. The total flow rate was 0.1 SLM. The symbols correspond to time duration indicated by the legend.