

The Effect of Low Concentrations of CO on H₂ Activation on Pt/C

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Introduction

The electrooxidation of H₂ on Pt is the first step in a series of reactions that ultimately generates the current produced from a proton electrolyte membrane fuel cell (PEMFC). The reaction itself follows the Tafel-Volmer sequence [1] in which the activation of H₂ on Pt is the rate limiting step. During fuel cell operation, when pure H₂ feed is used, H₂ activation occurs very rapidly and is much faster than both H⁺ transport across the membrane and O₂ reduction at the cathode. However, the presence of CO in the reformed H₂ feed, even at ppm levels, has detrimental effects on this process. Proper kinetic measurements of H₂ activation on Pt and the effect of CO at fuel cell operating conditions are lacking due mainly to the reaction reaching equilibrium with even very small amounts of Pt. Even measurements such as surface coverage are hard to obtain using traditional experimental methods. Many groups have tried to get around this problem through surface science techniques. However, it is important to note that these experiments are far removed from actual operating conditions of a PEMFC and from PEMFC catalysts.

Investigation of H₂ activation on Pt using a fuel cell is complex and prone to unaccountable variables. Thorough work has been done showing similar reaction rate constants between the electrooxidation of H₂ and H₂-D₂ exchange on Pt at temperatures close to 60°C [1]. Due to the nature of the study and the simplicity of H₂-D₂ exchange, the present study investigates the effect of CO on H₂ activation on Pt/C catalysts at fuel cell operating conditions via the exchange reaction and modified experimental techniques.

Materials and Methods

For the present study, 20 wt% Pt/C catalysts were obtained from E-TEK and were used as is. For the Nafion-Pt/C, Nafion® solution was obtained from Ion Power and impregnated on the 20 wt% Pt/C via incipient wetness to achieve a loading of 30 wt%. The catalysts were characterized by BET, TEM, EDX, and H₂/CO chemisorptions. Experimental data were obtained by following H₂ (m/z = 2), D₂ (m/z = 4), and the product HD (m/z = 3) via a mass spectrometer (MS).

Results and Discussion

Results from TEM showed the average Pt particle size to be 2.9 ± 0.45 nm, which is similar to that obtained from H₂ chemisorption. Aside from C, Pt, and O present on the surface, EDX determined trace amounts of S, which may affect the activity of Pt/C. Apparent activation energies of H₂-D₂ exchange in the absence of CO cannot be obtained due to reaction reaching equilibrium. In the presence of CO, the apparent activation energy was found to be 19.5 ± 1.3 kcal/mol regardless of the CO concentration (10–40 ppm). For surface science studies of H₂-D₂ exchange on Pt(111), the apparent activation energy for H₂-D₂ exchange in the absence of CO was calculated to be 5.3 kcal/mol but increased to 17.4 kcal/mol in the presence

of small amounts of CO [2]. The apparent activation energy behavior in the presence of CO for both single crystal Pt surfaces and Pt/C are very similar.

Table 1. Effect of CO on E_a of H₂-D₂ Exchange

CO (ppm)	E _a (kcal/mol)
10	20.6
20	18.0
40	19.8

Due to the low concentrations of CO used and high detection limit of a MS, surface coverage of CO was measured indirectly from the amount of HD formed following reaction of D₂ in the gas-phase with a surface covered with H. In the presence of 70 ppm CO, surface coverage of CO was approximately 0.5 monolayer (ML) at typical fuel cell operating conditions (T = 80°C and P = 2 atm). Saturation surface coverage of CO was determined to be 0.7 ML in the presence of 1 atm of CO [3]. Reasons for the lower surface coverage of CO in the presence of H₂ may be due to the elevated temperature and the large amount of H₂ present (P_{H2} = 0.4 atm, P_{CO} = 0.00014 atm at 70 ppm).

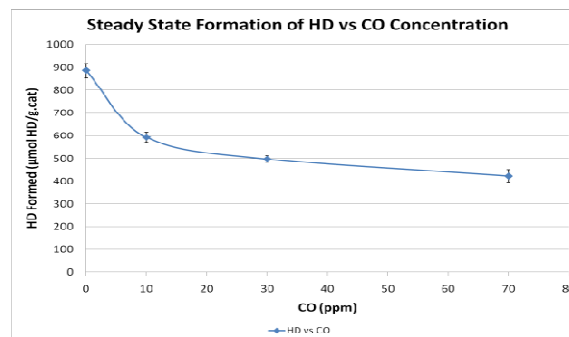


Figure 1. Steady-state formation of HD as a function of CO concentration at T = 80°C and P = 2 atm. Fresh catalyst was used in between each CO concentration measurement.

Significance

This work is important in furthering the goal of developing an economical fuel cell powered automobile by investigating the poisoning mechanisms of CO and other impurities affecting fuel cell performance and by determining means to mitigate their effects.

References

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