SUPPORTING INFORMATION FOR

An NMR Determination of CO Surface Diffusion on Pt Electrocatalysts

Takeshi Kobayashi, Panakkattu K Babu, Lajos Gancs, Jong Ho Chung, Eric Oldfield* and Andrzej Wieckowski*

Department of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Mathews Avenue, Urbana, IL 61801.

EXPERIMENTAL DETAILS

Sample Preparation. About 300 mg of fuel cell grade polycrystalline platinum black (Johnson-Matthey, MA) was electrochemically cleaned in 0.5M H₂SO₄ in D₂O (99% enriched, SIGMA-Aldrich) by holding the electrode potential at 0.46 V (vs. the reversible hydrogen electrode, RHE). CO was adsorbed onto the Pt particle surfaces by admitting ${}^{13}C$ enriched (99%) CO gas (Cambridge Isotopes, MA) to the electrolyte at open circuit potential, followed by purging the electrolyte with ultra-pure argon, to remove excess CO. The sample was then transferred to an NMR ampoule with a portion of the electrolyte, then flame sealed. A small amount of Pt-CO sample was left in the electrochemical cell to determine the CO coverage. The electrochemical potential was varied from 20 mV to 900 mV at a scan rate of 10 mV/minute, during which time the adsorbed CO was completely oxidized. CO coverage was then determined by comparing the CO oxidation charge with respect to the hydrogen adsorption charge. Particle size variations are known to affect CO coverage due to the distribution in the population of edge, vertex and terrace Pt sites on the surface of nanoparticles. Significant differences in the population of various Pt sites have been seen for Pt particles whose average diameters are less than 3 nm (K. Kinoshita, J. Electrochem. Soc. 137 (1990) 845)). The average diameter of the Pt-black used in the present study, as estimated from TEM, is about 7.0 ± 1.8 nm. Therefore, for our samples, the effect of particle size distribution on CO coverage is expected to be very small. The relative standard deviation taken from 5 coverage measurements is 2%. Therefore, the actual CO coverage is 1.00 ± 0.02 .

NMR Experiments. ¹³C and ²H NMR measurements were carried out at 8.47 T using a "homebuilt" NMR spectrometer. ¹³C NMR experiments used the "S-shape" pulse sequence of Becerra et al.² Typical 90° pulse widths were 12 μ s with $T_p = 8 \mu$ s, T_{ev} was varied from 80 μ s to 1 s and a 30 μ s τ value was used for echo detection. ¹³C T_1 values were obtained by using an inversionrecovery technique. Experiments were carried out between 253 and 293 K at intervals of 10 K using an NMR probe housed in a continuous flow cryostat (CF-1200, Oxford Instruments, MA).³ ²H NMR spectra were obtained at various temperatures using a solid echo sequence with 90° pulse width of 3 μ s and $\tau = 30 \ \mu$ s. The ¹³C NMR signal showed a broad, single Gaussian peak from the CO adsorbed on Pt black. There was no indication of any CO present in the electrolyte, which would have resulted in a sharp NMR line at 181 ppm (vs. TMS), which was not seen.

REFERENCES

- (1) K. Kinoshita, K., J. Electrochem. Soc. **1990**, 137, 845.
- (2) Becerra, L. R.; Klug, C. A.; Slichter, C. P.; Sinfelt, J. H. J. Phys. Chem. **1993**, 97, 12014-12019.
- (3) Babu, P. K.; Kim, H. S.; Chung, J. H.; Oldfield, E.; Wieckowski, A. J. Phys. Chem. B **2004**, *108*, 20228-20232.