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Quantitative Solid-State NMR Spectra of CO Adsorbed from Aqueous Solution onto a Commercial Electrode

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Solid-state nuclear magnetic resonance (NMR) spectroscopy is a powerful probe of local atomic structure and dynamics; it has been exploited extensively in studies of gas phase adsorption and catalysis.[1] The CO molecule in particular has been the subject of extensive NMR studies,[2] in part because of its ubiquity in vibrational spectroscopic studies of supported and single crystal metal surfaces. Carbon monoxide is also an important molecule in studies of the oxidation of organic fuels in *electrochemical* catalysis: the oxidation of methanol in fuel cells is an excellent example.[3] NMR studies of electrochemical systems are quite challenging, however, owing to the inherent difficulties in executing high-power, solid-state NMR spectroscopy on conducting samples immersed in electrolyte[4] as well as the complexity of electrochemically preparing and characterizing the adsorbed state. In this Communication we present quantitative, solid-state NMR spectra of CO adsorbed from solution onto a *commercial Pt/C fuel cell electrode*; the CO spectra are presented as a function of surface coverage, as modified by electrochemical oxidation of surface-bound CO. These data clearly portend the widespread application of quantitative solid-state NMR techniques for studies of practical electrochemical processes.

NMR spectra were acquired at ambient temperature with a home-built spectrometer and probe operating with a ^{13}C resonance frequency of 67.17 MHz. Data were typically acquired with a phase-cycled, spin-echo pulse sequence with an echo delay of 30 μs and a recycle delay of 2 s, where both time constants were optimized for quantitation and maximum sensitivity of the CO peak relative to the background signal (see below). The NMR probe was designed to afford *in situ* connection to a potentiostat, as described in ref 4; the NMR data presented herein, however, were obtained under open-circuit conditions: the potentiostat was connected only while the probe was outside the magnet. The commercial electrode material was purchased from E-TEK Inc. and consisted of 20 wt % platinum supported on carbon black (Vulcan XC-72) and pressed into graphitized carbon cloth. Sufficient material was placed in the NMR coil so as to achieve approximately 3 square meters of Pt surface. ^{13}CO-saturated Pt surfaces were prepared in a sealed system by circulation of distilled water containing dissolved CO gas through the porous electrode structure for 10 h. Submonolayer coverages were prepared by galvanostatic partial oxidation of the surface layer. Since carbon monoxide strongly and irreversibly adsorbs to the Pt surface, thereby precluding adsorption of hydrogen ions, voltammetric sweeps through the hydrogen desorption region were used to determine the fraction of surface Pt atoms not covered by CO. All electrochemical experiments were carried out using a 3 M H_2SO_4 electrolyte; for the NMR experiments, the electrolyte was replaced with D_2O. The measured ^{13}CO spectra were obtained under nitrogen-blanketed aqueous conditions. Figure 1 shows representative ^{13}C NMR data. Spectrum A shows the sample with saturation coverage of CO; spectrum B shows the same sample with no CO adsorbed. The latter spectrum is a "background" signal and is consistent with the known NMR parameters of graphite (the electrode materials) and PTFE (from probe components). Spectra C−I show background-subtracted data for CO adsorption at different coverages. Figure 2 shows the integrated (background-subtracted) CO signal intensity versus the number of surface carbon monoxide molecules obtained by coulometry. Since the NMR signal should be proportional to the number of NMR-active nuclei and the coulometry should quantitatively measure the number of surface molecules after oxidation, we expect this plot to be linear and go through the origin. Examination of Figure 2 shows excellent agreement between the purely spectroscopic data and the electrochemical data.

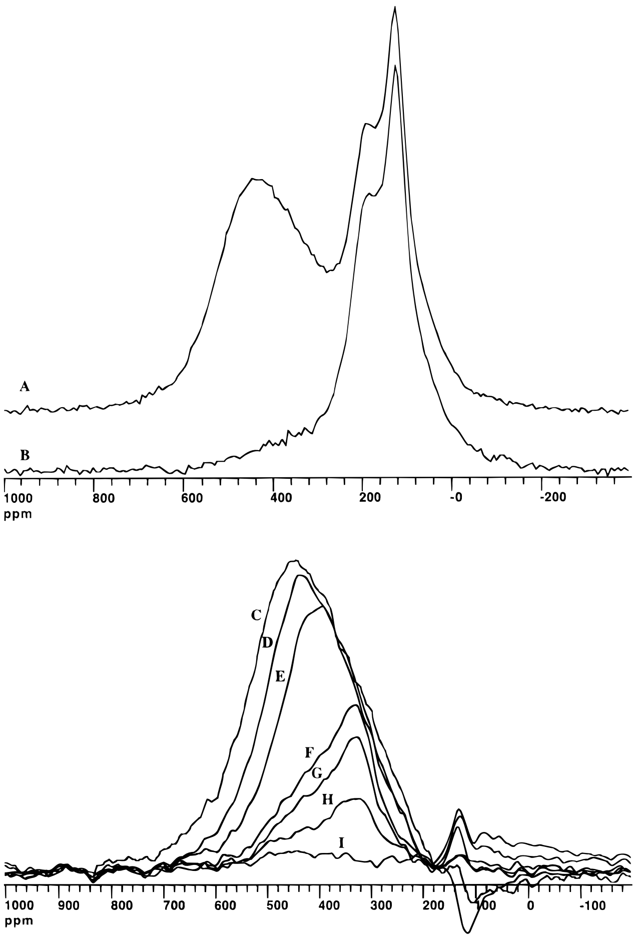

Figure 1. Carbon-13 NMR spectra of Pt/C electrodes. A. Electrode with saturation coverage of ^{13}CO. B. Electrode with no CO adsorbed. C−I. Spectra obtained as a function of ^{13}CO coverage after background subtraction. NMR data in C−I represent 25 000 acquisitions with a 750 Hz line broadening used to present the Fourier-transformed spectra. Data upfield of 180 ppm represent inadequate background subtraction of PTFE probe components (due to varying alignment of the probe assembly in the NMR coil after each oxidation) and dissolved CO_2 in the aqueous phase.

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(1) See, for example: Bell, A. T.; Pines, A. *NMR Techniques in Catalysis*; M. Dekker: New York, 1994.

(2) Recent reviews include: Duncan, T. M. *Colloids and Surfaces* **1990**, *45*, 11. Ansermet, J. P.; Slichter, C. P.; Sinfelt, J. H. *Prog. Nuclear Magn. Reson. Spectrosc.* **1990**, *22*, 401. Duncan, T. M. In *Nuclear Magnetic Resonance Probes of Molecular Dynamics*; Tycho, R., Ed.; Kluwer Academic Publishers: Dordrecht, Boston, 1994; p 525.

(3) Iwasita-Vielstich, T. In *Advances in Electrochemical Science and Engineering*; Gerischer, Tobias, Eds.; 1990; Vol. 1, p 128.

(4) Chan, K. W. H.; Wieckowski, A. *J. Electrochem. Soc.* **1990**, *137*, 367. Slezak, P. J.; Wieckowski, A. *J. Electrochem. Soc.* **1992**, *339*, 401. Slezak, P. J.; Wieckowski, A. *J. Magn. Reson.* **1993**, *102A*, 166.

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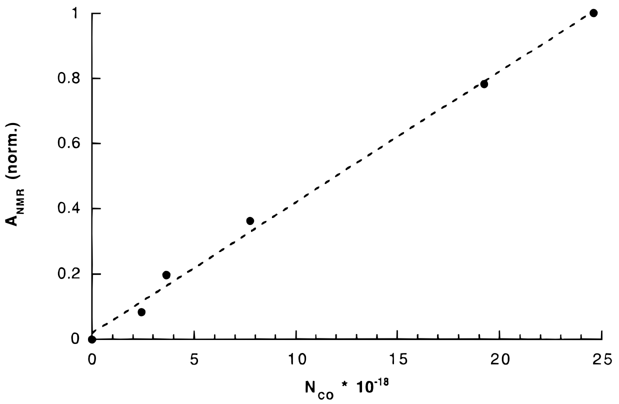

Figure 2. Integrated area of the NMR data shown in Figure 1 versus total number of surface molecules, as determined coulometrically. The numbers on the abscissa were obtained by coulometric titration, correcting for double layer charging and other effects. Coulometric data associated with NMR spectra E and G were not available.

Previously reported NMR spectra of adsorbed CO from the gas phase onto supported-Pt particles are broad and featureless.[5] Chemical and Knight shifts account for the observed resonance frequencies, whereas line widths are governed by three factors: multiple shifts resulting from a distribution of spins between linear and bridged adsorbates; the large anisotropy of the ^{13}C chemical shift tensors; and further broadening of the chemical shift powder patterns by the large magnetic susceptibility of the metal particles. Our data from the solid−liquid interface appear featureless at high coverages but undergo significant changes as surface coverage decreases; indeed at low coverages the observed ^{13}CO line shape is well fit to a chemical shift powder pattern having an anisotropy of about 100 ppm, virtually identical to the anisotropies reported for bridge-bonded CO on supported Ru and Rh particles.[6] Thus our observations appear to be consistent with changing populations of linear and bridge-bonded CO with surface coverage. A further analysis of these spectra will be published soon.

In conclusion, we report quantitative ^{13}C NMR spectra for CO adsorbed onto commercial Pt/C fuel cell electrodes. Each spectrum shown in Figure 1 required approximately 14 h of instrument time to acquire; we are further optimizing both the NMR parameters and probe configuration for improved signal-to-noise ratios. The number and character of CO adsorption sites are clearly accessible via this approach; if used in conjunction with *in situ* potential control,[4] the number of possible studies of potential-dependent processes appears to be vast.

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[5] See, for example: the second reference listed in ref 2, above.

[6] Duncan, T. M.; Root, T. W. *J. Phys. Chem.* **1988**, *92*, 4426.