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The Application of Solid-State NMR Spectroscopy to Electrochemical Systems: CO Adsorption on Pt Electrocatalysts at the Aqueous- Electrode Interface

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by

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CHAPTER 1

INTRODUCTION

A *fuel cell* is an electrochemical energy conversion device, the continuous-flow analogue of the popular electrochemical storage device known as the battery.⁽¹⁻⁵⁾ While the potential of fuel cells as power sources was recognized well over a century ago, they have since found limited application; a myriad of chemical, engineering and materials issues can be cited for this disappointing showing. Recent growing concern over the fate of the environment, however, has helped to renew interest in fuel cell research. The possible benefits are certainly impressive: vast reduction in emissions of poisonous by-products of combustion (NO_x , SO_2 and CO), utilization of non-petroleum fuels such as methanol, and a decrease in levels of the "greenhouse gas" CO_2 . Furthermore, since thermo-electric and thermo-mechanical processes such as present-day power plants and internal combustion engines are Carnot-limited, conversion to fuel cell-based technology represents an enormous opportunity for improvement in efficiency.

A considerable research effort has been made into fuel cells utilizing small organic molecules as the fuel source.⁽⁶⁻⁸⁾ These systems are under development for use as both large, stationary power plants in the megawatt range, and as smaller mobile sources for transportation applications. Building on the proven success of the H_2/O_2 fuel cell, some organic fuel cells incorporate a steam reformer for conversion of the fuel into gaseous hydrogen and product CO_2 prior to being fed to the anode. However, electrochemical oxidation of the organics themselves has also been observed, thus suggesting possible improvements in the cell by eliminating the weight, bulk and slow dynamic response of the reformer. Of the candidate fuels for this direct energy conversion, methanol has shown the most promise.

1.1 Direct electrochemical oxidation of methanol

1.1.1 *The direct methanol fuel cell (DMFC)*

Figure 1.1 shows a schematic of a low-temperature direct methanol fuel cell. Methanol can be fed to the high surface area anode in either liquid or vapor form, with oxidation yielding six electrons per molecule. Oxygen is reduced at the cathode, a gas diffusion electrode requiring a metal-gas-electrolyte interface. A selective membrane is required in the electrolyte phase to keep the cathode inaccessible to fuel molecules, and hence prevent chemical short-circuiting. Whereas the half-cell reactions in Figure 1.1 are shown for an aqueous acid electrolyte, the DMFC will operate with alkaline electrolytes as well, and actually performs better electrochemically under these conditions. However, the accumulation and eventual precipitation of carbonate salts is a catastrophic problem in these systems. While some work has been done using invariant carbonate electrolytes⁽⁹⁻¹¹⁾, the majority of work is currently done in acid.

1.1.2 *Catalytic problems associated with the DMFC anode*

Central to the development of fuel cells is the field of *electrocatalysis*.^(8,12-15) Inherently a heterogeneous phenomenon, electrocatalysis can be defined as the relative ability of electrode surface materials to accelerate the rate of a given electrochemical process. In order to extract the maximum energy available from the fuel in the DMFC, and thus maximize efficiency, the rate of conversion into CO_2 must be as high as possible. Any kinetic limitations will be manifest under an applied load, resulting in deviation of the electrode potential from its open-circuit (thermodynamic) value, and ultimately a lower cell potential. Stated another way, if the overall reaction has a rate-determining step, this step eventually determines the electrode potential as well. Of course, the electrode surface plays the major role in determining the reaction rate in electrocatalysis, much as in heterogeneous catalysis. While platinum remains the most active single-component surface for the methanol reaction, large overpotentials are observed nonetheless. Typical data are shown in Figure 1.2.

Figure 1.1 Generalized schematic of direct methanol fuel cell. Half-cell reactions are shown for acid electrolyte.

Figure 1.2 Typical behavior of platinum DMFC electrodes under applied load in acid electrolyte. The deviation of the electrode potentials from their open-circuit values (overpotential) reflects kinetic limitations, resulting in decreased cell potential and power.

A comparison of hydrogen and methanol oxidation illustrates the major reason for the vast kinetic differences between the two reactions (Figure 1.3). The hydrogen reaction requires only dissociative adsorption of molecular hydrogen on the Pt surface, with subsequent ionization and desorption of product protons. Both of these steps are fast, and very little kinetic overpotential is observed. Methanol also adsorbs dissociatively, shedding hydrogen atoms which are ionized rapidly, as in the hydrogen reaction. This leaves an adsorbed residue containing carbon, oxygen, and perhaps hydrogen. A large research effort has concentrated on the identification of this intermediate(s) and will be addressed in the following section. The final reaction of this adsorbate to CO_2 requires an additional oxygen atom, provided by a water molecule. It is generally agreed that the water molecule must first dissociate on the electrode surface on a site adjacent to the $-(\text{C},\text{O},\text{H}_x)$ moiety, a process that occurs at an appreciable rate on platinum at ambient temperatures only above 0.7 V/RHE.⁽¹⁶⁻¹⁸⁾ At potentials much lower than this, the surface population of $-\text{OH}_{\text{ad}}$ is infinitesimally small, and the oxidation of the residue proceeds very slowly. Another school of thought is that the water molecule oxidizes the adsorbate without becoming strongly adsorbed, but is rate-limiting nonetheless. In either case, the surface becomes overpopulated with $-(\text{C},\text{O},\text{H}_x)$ and is hence deactivated, or "poisoned."

To overcome these kinetic limitations many researchers have been searching for appropriate "bifunctional" electrodes, i.e., surfaces that possess the ability to dissociatively adsorb both methanol and water at reasonably low potentials while catalyzing the oxidation at a high rate. Platinum alloys, most notably with Ru or Sn, have received a great deal of attention.^(19,20) Platinum surfaces modified with adatoms are also strong candidates for this purpose.⁽²¹⁾

1.1.3 Toward identification of the poisoning intermediate(s)

A common goal of the electrocatalysis community has been the identification of the nature of the deactivating species on the anode surface. It is hoped that such knowledge will provide direction in the search for better catalysts which either facilitate oxidation of the

Figure 1.3 Electrocatalytic oxidation mechanisms for hydrogen and methanol on platinum in acid electrolyte.

Figure 1.4 Proposed structures for the stable intermediate in the electrochemical oxidation of methanol on platinum.

adsorbate, such as bifunctional electrodes, or avoid its formation altogether through promotion of alternative reaction pathways. To this end, a variety of analytical techniques traditionally employed in the fields of heterogeneous catalysis and surface science have recently found utility in studies of the electrode-electrolyte interface.^(8,22-24)

Four main structures have been proposed for the methanol adsorbate as shown in Figure 1.4. Interestingly, evidence for each has been obtained from various techniques. Thermal desorption studies of a polycrystalline Pt electrode upon transfer to a UHV environment suggest a mixture of particles of composition (C,O) and (C,O,H), with the actual ratio depending on concentration and total coverage.^(25,26) The formation of such an admixture is in agreement with purely electrochemical information which indicates that the average number of Pt sites occupied per adsorbate molecule varies between 1 and 2. The actual position of the hydrogen atom in the (C,O,H) species could not be determined from the thermal desorption data, however. On-line electrochemical mass spectrometry with a low surface area porous electrode has revealed that oxidation of the predominant adsorbate requires 3 electrons per CO₂ molecule formed, indicative of a composition (C, O, H).⁽²⁷⁾ Further studies with isotope labeling were able to conclude that the hydrogen atom is free to exchange with protons from the bulk electrolyte, suggesting bonding to oxygen and a -COH structure. *In situ* reflectance infrared experiments on mirror-smooth Pt electrodes identified adsorbed CO in both linear and bridged structures.⁽²⁸⁾ The position of the expected C-O stretch for the -COH structure is located in a noisy region occupied by various electrolyte components, and therefore its identification via IR was inconclusive. A later study showed a feature in this region tentatively identified as -COH.⁽²⁹⁾

1.2 Application of NMR spectroscopy to studies of supported catalyst surfaces

The ability to elucidate the structure and dynamics of adsorbates on catalyst surfaces with nuclear magnetic resonance (NMR) spectroscopy has become well established over

the past two decades.⁽³⁰⁻³⁴⁾ With the lowest excitation energy of all spectroscopic methods, NMR is especially attractive for *in situ* studies as a non-intrusive probe of the chemical environment of spin-active nuclei. The flexibility afforded by nuclear specificity has ensured its application to a wide variety of catalytic systems; indeed, the literature are rich with results from ^1H , ^2H , ^{13}C , ^{14}N , ^{15}N , ^{17}O and so on. Furthermore, the vast number of NMR techniques that have been developed has served to increase the range of available spectroscopic information.

However, the low energy of nuclear magnetic transitions places limits on minimum sample size, and sensitivity remains the major drawback in NMR studies of adsorbates on supported metal catalysts. Given the current state-of-the-art instrumentation, these experiments require roughly 10^{18} - 10^{20} nuclei. A 1 cm^2 surface of metal corresponds roughly to 10^{15} surface atoms; hence, for the observation of surface species with NMR one needs 0.1 - 10 m^2 of metal surface contained within a sample coil volume of no more than a few cm^3 . This limits NMR to studies of high surface area catalysts typically found in industrial practice.

1.3 Carbon monoxide as a model adsorbate on catalyst surfaces

Carbon monoxide has found great utility as a model adsorbate, particularly in vibrational spectroscopy, where the C-O stretching frequency is quite sensitive to the surface binding geometry and local chemical environment.^(35,36) This role has been extended to surface NMR, where studies of CO structure and dynamics have set the precedent for research on more technologically relevant adsorbates.⁽³²⁾ The identification of surface CO in the electrocatalytic oxidation of small organic molecules points toward the specific significance of CO adsorption and oxidation in the field of electrochemistry. The apparent presence of only linear and bridged binding geometries on platinum (Figure 1.4) suggests the simplicity desired of a model system.

1.3.1 ^{13}C NMR lineshapes of adsorbed CO on supported metal catalysts

The chemical shift of a nucleus arises from the interaction of the nucleus with its surrounding electron cloud.⁽³⁷⁾ Specifically, when the orbital angular momentum of an electron is perturbed by an external magnetic field, local magnetic fields are produced which influence the nuclear magnetic energy levels. This in turn "shifts" the resonant frequency of the nucleus. This shift is a sensitive indicator of local chemical environment, such that linear and bridged CO have different peak positions in ^{13}C NMR spectra, much as they do in vibrational spectra. For transition metal carbonyls in solution, often cited as model compounds for CO adsorption, the peak for linear CO is generally detected at 170-200 ppm (depending on the metal center), whereas bridged appears at 235-265 ppm.⁽³⁸⁾ In contrast to IR spectra, however, line broadening occurs when observing nuclei in the solid-state, hence the term "broadline NMR" for such studies. The orientational dependence of the chemical shift, or chemical shift anisotropy (CSA), is the principal solid-state broadening mechanism for CO, and reported anisotropies are about 280 ppm for linear and 130 ppm for bridged CO.^(39,40) In studies of CO adsorption on supported Ru and Rh catalysts, both of these species were identified and fit with theoretical lineshapes.^(41,42)

The metallic nature of the particle surface can play a strong role in the interactions experienced by the carbon nucleus.⁽³⁴⁾ The magnetic susceptibility of the metal serves to distort the magnetic field in the vicinity of the particle; this broadens the CSA powder pattern associated with a nucleus directly bonded to the surface. For example, such broadening renders the ^{13}C spectra from CO on metals such as Pt and Pd broad and featureless.⁽⁴³⁻⁴⁵⁾ Furthermore, the difference in energies between the CO molecular orbitals and the work function at the particle surface produces a finite density of conduction electrons at the nucleus; this altered electronic environment yields an additional shift in resonant frequency, termed the Knight shift, to higher frequencies for ^{13}C . Particle size effects contribute to both mechanisms, having been observed and interpreted in terms of a transition between the particle behaving as a "pseudo-molecular" cluster and a bulk

metal.⁽⁴⁵⁾

Molecular motions with time constants less than or comparable to the inverse linewidth manifest themselves as changes in the lineshape. A variable temperature study of CO on Pd/alumina showed line narrowing as temperature was increased, illustrating the effects of surface diffusion on the lineshape.⁽⁴⁶⁾ More complex motions have been observed on Ru and Rh catalysts.^(32,33) Spinning multicarbonyls on isolated metal atoms appeared as Lorentzian features, whereas slower "flipping" motions at these sites resulted in modified powder patterns. The use of additional NMR techniques, such as relaxation studies and spin-population labeling, extends the ability of NMR to characterize molecular motions with time constants ranging from 10^{-9} to 1s.

1.3.2 CO adsorption and oxidation on Pt electrode surfaces

Anodic voltammetry of clean platinum electrodes in acid shows three distinct regions corresponding to hydrogen desorption (0.05-0.35 V/RHE), double layer charging (0.4-0.8 V), and Pt surface oxidation (> 0.8 V).⁽¹⁶⁾ The hydrogen reaction, shown schematically in Figure 1.3, provides a means by which to quantitatively probe the surface. The quantity of charge passed in the hydrogen region is directly proportional to the exposed metal surface area; note the similarity to the use of hydrogen adsorption isotherms in gas phase systems to characterize the catalyst. Aqueous carbon monoxide undergoes irreversible adsorption, thereby displacing or blocking the reversibly adsorbed hydrogen atoms from the electrode surface. This results in the suppression of hydrogen desorption currents, as shown in Figure 1.5. Electrochemical oxidation of CO occurs at potentials above ~ 0.7 V, as indicated by the anodic peak centered near 0.75 V. The reaction is highly dependent on the electrode surface structure, as confirmed by studies on single crystal Pt electrodes, with multiple oxidation peaks observed anodic of about 0.6 V.⁽⁴⁷⁾ Resolution of these peaks is not typically seen on high surface area electrocatalysts, however.⁽⁴⁸⁾

Figure 1.5 Voltammetric sweeps of platinized platinum electrode at 20 mV/s in 0.5 M H_2SO_4 . A: clean surface, B: following adsorption of partial monolayer of CO and elimination of CO from aqueous phase.

1.4 Objectives of this work

While it is certainly tempting to draw from the vast body of knowledge of the metal-vacuum interface, it must be recognized that any analogies between the surface processes in heterogeneous catalysis and electrocatalysis are limited both by the presence of the electric double layer at the electrode surface and the dependence of electrochemical reaction rates on the electrode potential.⁽⁴⁹⁻⁵¹⁾ This situation necessitates the extension of such powerful analytical probes as IR and NMR spectroscopy to studies of the electrochemical interface. It should be noted here that none of the techniques mentioned in section 1.1.3 are applicable to practical electrocatalysts, i.e. supported metal electrodes of high specific surface area. Whereas the extension of results from single-crystal and bulk metal surfaces to small metal particles remains questionable, NMR spectroscopy has been proven as a reliable technique to study high surface area catalysts. As such, the development of solid-state NMR spectroscopy as a flexible probe for the study of electrochemical and potential-dependent processes constitutes the major goal of the research presented in this thesis. A model system of adsorbed CO on a commercially-available Pt/C electrocatalyst has been chosen for this purpose, based on its relevance to the electrooxidation of methanol.

There are certain inherent challenges of performing NMR experiments on electrically-conductive materials. These are discussed in some detail in Chapter 2, along with the experiments which led to the optimization of the system used in this work. The experimental methods relevant to sample preparation and characterization, such as CO adsorption and oxidative stripping, are fully described in Chapter 3. ¹³C NMR spectra of adsorbed CO at the metal-aqueous interface are presented in Chapter 4 as a function of surface coverage.

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CHAPTER 2

EXPERIMENTAL STUDIES OF ELECTRONIC COUPLING BETWEEN ELECTRODES AND THE NMR SAMPLE COIL

The physics of magnetic resonance places restrictions on the physical properties of the sample, in effect turning the study of entire classes of materials into highly specialized fields. Magnetic susceptibility is a good example of such a property, NMR being largely confined to diamagnetic materials. The electrical conductivity of the sample is another restricted property, one which unfortunately makes electrochemistry and NMR spectroscopy ostensibly incompatible fields of scientific endeavor. This chapter addresses the fundamental barriers to be overcome in the *in situ* application of NMR to electrochemical systems, the specific indicators that can be used to help gauge these problems, and the design and implementation of an experimental system for obtaining quantitative NMR spectra from a functioning electrode.

2.1 NMR and conductive samples

2.1.1 Theoretical introduction

A nuclear spin population is split into discrete energy levels by a static magnetic field H_0 - the classical Zeeman interaction. In the NMR experiment, an alternating magnetic field of well-defined phase is applied orthogonally to H_0 , simultaneously promoting spins to higher energy levels and imparting phase coherence to the spin system. This H_1 field is effectively produced by an alternating current flowing through a solenoid at radio frequencies (rf $\sim$ 1-500 MHz), with the sample occupying the interior of the coil (Figure 2.1A). It is the interaction of the sample with H_1 , as described by Maxwell's equations, that underlies the complexity of NMR studies of electrically-conducting materials. In particular, a loss mechanism is introduced as the time-dependent magnetic

Figure 2.1 A: NMR sample coil showing orientation of static and rf magnetic fields, H_0 and H_1 , respectively. End view shows eddy currents induced in conductive sample during application of H_1 . B: Vector representation of pulse NMR experiment.

field induces circular currents in the sample about the H_1 axis. Since this is a dissipative process, the field becomes attenuated as it penetrates the sample; the phase of the field may also be affected, such that it becomes position-dependent as well.

The consequences of a non-uniform rf field can be severe. Consider that modern NMR spectroscopy is largely performed with pulse methods, the time and frequency domains of which are related via the Fourier transform.⁽¹⁾ At equilibrium, the macroscopic magnetization from the sample, M , is aligned parallel to H_0 in the z direction (Figure 2.1B). In a pulse experiment, the H_1 field is applied for a time t_p to create a transverse component of M in the x - y plane, M_{xy} . Immediately after the pulse is turned off, this component has a magnitude given by equation 2-1:

$$M_{xy} = M \sin\theta = M \sin(\gamma H_1 t_p) \quad (2-1)$$

where γ is the magnetogyric ratio of the nucleus. As M_{xy} decays it is detected as an induced current in the coil. The amplitude of the signal is directly proportional to the number of spin-active nuclei in the sample (through M), and is dependent on both t_p and H_1 (see section 2.4). Hence, as H_1 varies within the sample due to conduction losses, the local contribution to the bulk magnetization varies over the sample volume. In the extreme case of high conductivity, the rf field completely vanishes toward the center of the sample and a volume of spins becomes essentially "invisible" to the coil. In any case, the quantitative relationship between the observed signal and the number of spins in the sample becomes complicated, and, since fewer nuclei are accessible in the experiment, the signal-to-noise ratio (S/N) decreases. Furthermore, the ability to perform experiments in which multiple pulses of well-defined phase and amplitude are applied, such as the spin echo, is compromised due to the variation of the phase and amplitude of the field within the sample.

2.1.2 Experimental observations with conductive samples

The difficulty of performing NMR experiments on conductors was recognized soon after its discovery, since metals were among the first materials to be studied with magnetic resonance techniques.⁽²⁾ In early work with metallic copper, for example, it was noticed that the geometry of the sample had a profound effect on the measured NMR absorption.⁽³⁾ A derivation of the power absorbed by the sample revealed that if its characteristic dimensions were small compared to a constant called the *skin depth*, then the rf field will penetrate the sample completely. The skin depth is given by equation 2-2:

$$\delta = \sqrt{\frac{2}{\sigma\mu\mu_0\omega}} \quad (2-2)$$

where σ is the sample conductivity, μ is the magnetic permeability of the sample, μ_0 is the permeability of free space, and ω is the frequency of the applied field. For pure copper at room temperature, $\delta \approx 20 \mu\text{m}$ in an H_0 field in which the Cu resonance is at 10 MHz. The condition for complete penetration was at least approximately fulfilled by converting the metallic sample to a fine powder, each particle having a diameter less than δ and covered with a thin insulating oxide layer. However, in the case of thick Cu foils, the expected attenuation and phase changes of H_1 as it penetrates the sample were observed as distorted and shifted absorption spectra compared to those from the powdered metal. Thus, the important parameter in the coupling between sample and coil was shown to be the *effective* conductivity of the sample, not the local conductivity of each particle. The use of powders dispersed in insulating media such as silica has since become standard methodology for NMR work with conducting solids. Interparticle electron mobility is completely restricted in these samples and, in turn, the coupling between sample and coil is virtually eliminated.

In a later study, it was demonstrated that only a single dimension of the sample needs to be smaller than the skin depth of the material in order for conduction losses to be

minimized. Aluminum foils of various thicknesses, w , were oriented with their planar surface parallel to H_1 , thereby confining eddy currents to the smallest dimension. Distortion of the lineshape was observed only in the cases where $w > \delta$; spectra from foils thinner than the skin depth showed no distortion.⁽⁴⁾

With the advent of magnetic resonance imaging (MRI) in the late 1970's, and particularly its applications to living subjects, researchers have begun to consider the consequences of electrical conductivity on experimental results in more detail.^(5-8,19) Metals, of course, are materials of high *electronic* conductivity which had been seen to have a tremendous influence on the NMR experiment. A biological specimen, on the other hand, is a system with appreciable *ionic* conductivity, and will couple to an NMR coil as well. Since conductivities of electrolyte solutions are typically orders of magnitude lower than those of metals, these effects are much less pronounced. In the case of the metals, however, it is possible to use powders or very thin foils, thereby eliminating the loss mechanisms in the sample. This approach has been successful in some studies of biological fluids as well, with losses reduced by dividing a tube into sections of thickness smaller than the skin depth of the ionic solution.⁽⁹⁾ Yet it is not apparent how to eliminate circular current paths in living subjects; thus the losses encountered in these experiments continue to place limits on the hardware and the results obtainable from these types of systems.

2.1.3 NMR studies of electrochemical systems

Electrochemical reactions are potential dependent; hence, any spatial variations of the potential across an electrode will result in a distribution of local reaction rates. Resistive dissipation is one mechanism by which the potential may vary, as expressed by Ohm's law,

$$i = \sigma \frac{d\Phi}{dx} \quad (2-3)$$

where i is the current density, Φ is the potential and x is a spatial coordinate. In order to minimize these IR losses, electrochemists typically work with materials of high conductivity, such as metals and concentrated electrolytes. For example, battery electrodes are often comprised of relatively low conductivity active material supported on a highly conductive metal current collector. In the case of practical electrocatalysts, one must utilize a high surface area support material that is itself electronically conducting. This drastically restricts the choice of supports, with various forms of carbon being quite common.⁽¹⁰⁾

It is clear that electrochemistry and NMR spectroscopy have sharply contrasting requirements for the conductivity of the sample. It is not surprising, then, that experiments combining the two fields are rare. In fact, only recently researchers have begun studying methanol adsorbates on Pt black electrodes with solid-state NMR.⁽¹¹⁻¹³⁾ While their experimental design allows for *in situ* potential control of the anode during NMR acquisition, it is clear that little attention has been paid to the coupling between the NMR coil and the electrode samples. Consequently, the data published thus far have been of poor quality. With a careful consideration of the coupling between NMR coils and conductive samples, however, NMR spectroscopy can be optimized for the study of electrochemical and other potential-dependent processes.

2.2 Electrode geometry and structure

The particular structure of a conductive sample has a tremendous effect on the execution and results of an NMR experiment. Therefore, different cylindrical electrode structures were investigated in the present work in an attempt to eliminate coupling to the coil. The electrode material will be described in detail in Chapter 3, but is essentially a porous graphite cloth 0.05 cm thick and 1.5 cm wide. Its conductivity was determined to be $46.3 \Omega^{-1} \text{ cm}^{-1}$ from the slope of a plot of resistance vs. length (Figure 2.2). The simplest cylindrical structure that can be constructed from this material is a "jellyroll", as illustrated in Figure 2.3. A 36 cm long piece was first threaded with 6 mil Au wire, a

Figure 2.2 Experimental determination of conductivity of electrode material. Resistance measurements were made as a function of length on a long electrode strip using a Keithley model 175 multimeter. The slope yields a conductivity of $46.3 \Omega^{-1} \text{ cm}^{-1}$.

necessary step for current collection and connection to the external hardware of the electrochemical experiment. This piece was then rolled tightly along its length, with a final diameter of about 1.4 cm. A variation on the jellyroll structure involves the inclusion of an insulating material between electrode layers. Various separator materials were investigated, including analytical grade filter paper, polypropylene felt, non-woven fiberglass, and PTFE; these materials differed in thickness and porosity. Strips of separator were cut slightly wider than the electrode piece to prevent contact of the conducting layers at the edges. A 24 cm long electrode strip was threaded with Au wire and rolled tightly into a jellyroll together with the separator, with a final diameter of 1.4 cm.

A second electrode structure investigated was the "laminar" electrode shown in Figure 2.4. This structure is a multilayer sandwich comprised of many individual electrode pieces, in contrast to the single long piece that was used for the jellyroll electrodes. Strips of electrode material 1.5 cm long were cut to dimensions calculated to fit into a 1.4 cm i.d. glass tube when stacked. Each piece was threaded with 6 mil Au wire before being stacked alternately inside the tube with slightly wider layers of separator. The total length of electrode material used was 21.5 cm.

2.3 Probe circuit quality factor as an indicator for coupling

The coupling of a conductive sample to the coil in an NMR experiment has measurable consequences besides the qualitative "distortion of the spectra" mentioned previously. This section is concerned with the simple observations that can help diagnose the nature and degree of coupling before attempting to perform difficult NMR experiments.

NMR probes are resonant RLC circuits tuned such that the imaginary (reactive) impedance disappears at the resonant frequency of the nucleus under study, and matched to the real (resistive) impedance of the spectrometer hardware, $50\ \Omega$.⁽¹⁾ These conditions are very sensitive to the environment of the coil - the inductor of the circuit - and, hence, to the sample itself. In fact, the resonance peak of a well-tuned probe will become shifted,

A. Unrolled, intact pieces for jellyroll structure

B. Finished electrode

Figure 2.3 A: Dimensions of porous graphite electrode material used to construct jellyroll electrode. B: Jellyroll electrode structure. Conductive material is shown in black, with separator in white. The H_1 field is axisymmetric with respect to the cylindrical electrode.

A. Cut pieces for laminar structure

B. Finished electrode

Figure 2.4 A: Pieces of porous graphite electrode material used to construct laminar electrode. B: Laminar electrode structure. Conductive material is shown in black, with separator in white. The H_1 field is axisymmetric with respect to the cylindrical electrode.

attenuated and broadened upon insertion of conductive material into the coil. This can be studied quantitatively through frequency response measurements on tuned probe circuits.

A particular property of a resonant circuit is its quality factor, Q .^(1,14) Although a fairly esoteric parameter, Q is best described as a dimensionless "efficiency factor" - the ratio of the energy stored in the magnetic and electric fields of the reactive components of the circuit to the energy dissipated in the resistive components; a perfect resonant circuit would have an infinite quality factor. Below the self-resonance frequency of the inductor, a high value of Q is indicative of a circuit that efficiently transforms an alternating current into an alternating magnetic field. As such, the value of Q is a very sensitive indicator of the coupling between a conductive sample and the coil; the structure of the sample can be considered optimized when there is little or no deviation in Q from its empty coil value.

Figure 2.5 Parallel-series tank circuit used to study coupling between electrodes and NMR coil.

For this study, a benchtop parallel-series tank circuit (Figure 2.5) was constructed with a 5-turn coil of flattened copper wire (i.d. = 1.6 cm, l = 3.0 cm). Tuning of the circuit to 67.2 MHz, the operating frequency of the spectrometer (see Chapter 4), and matching to 50 Ω were facilitated by the inclusion of both variable and removable capacitors. Measurements of the magnitude and phase of the complex impedance of the circuit were made with

a Hewlett-Packard model 4173A vector impedance meter. The frequency response behavior of the resonant circuit is well represented by its phase. Therefore, the value of Q was calculated from the ratio of the resonance frequency to the width of the phase peak at 3 dB attenuation from the top of the peak.⁽¹⁵⁾ These calculations are described in detail in Appendix A.

Figure 2.6 shows the phase behavior for dry jellyroll electrodes with and without a non-woven macroporous polypropylene separator. Q for the empty coil (the narrowest peak) is 162. When the jellyroll electrode without the separator is inserted into the coil and the circuit retuned and matched, there is an appreciable broadening of the resonance peak. Since Q is inversely proportional to this peak width, this represents an enormous decrease in Q - from 162 to 14.1. The importance of electrode structure become apparent with the addition of the separator layer to the jellyroll: Q recovers to a value of 66.2. This behavior can be explained in terms of field penetration and eddy currents induced in the conductor. The electrode material itself has a calculated skin depth of 0.09 cm, roughly twice the thickness of the individual electrode layers. H_1 can penetrate the region of the separator, and from there, perhaps, can penetrate the conducting layers. Furthermore, eddy currents are restricted to the individual layers of the electrode - there is no interlayer electron mobility. However, there is still significant deviation from the empty coil Q for the separated jellyroll since each layer is roughly axisymmetric with respect to H_1 , such that circular current paths may still exist within a layer. It should be noted that the presence of the Au wire current collector represent only a small perturbation on the value of Q in these studies.

A distinguishing feature of electrochemical systems is the presence of a liquid-solid interface, so it is interesting to observe the change in resonance behavior upon flooding the electrode with water. While this has no effect on the jellyroll without a separator, the improvement in Q for the dry jellyroll with the porous separator is entirely counteracted by flooding of the structure with water (Figure 2.7). Measurements on the coils alone suggest

Figure 2.6 Comparison of frequency response of probe circuit, as typified by the phase of the complex impedance, for dry jellyroll electrodes without ($\blacktriangle$) and with ($\circ$) a porous separator. Also shown is the empty coil response ($\bullet$).

Figure 2.7 Comparison of phase of probe circuit for jellyroll ($\blacktriangle$) and laminar ($\circ$) electrodes with porous separators in water. Also shown is the response of a water-filled coil ($\bullet$).

the addition of a capacitive mechanism to explain this behavior.⁽¹⁶⁾ The laminar structure, on the other hand, shows a great improvement over the jellyroll under the same conditions, with $Q = 103$. This can be attributed to the same effects described above - improved field penetration, and restriction of conduction electron mobility. Furthermore, by aligning the conducting sheets in planes along the H_1 axis, circular current paths about the rf field are eliminated from the laminar electrode structure, and the additional capacitive mechanism seen for the wet jellyrolls is somehow excluded.

Of course, electrochemistry also utilizes electrolytes, and a comparison of the phase behavior of water-filled and acid-filled coils demonstrates the important effect that ionic conductivity has on the coupling to the coil (Figure 2.8). It is not surprising, then, that the value of Q decreases when water is replaced by 0.5 M H_2SO_4 in the laminar electrode. It would appear in this case, comparing the phase peak from the laminar/porous separator structure in acid with that from the acid-filled coil alone, that the ionic conductivity of the electrolyte dominates the resonance behavior, and that the presence of the electrode material has no effect at all. This is confirmed by replacing the porous separator with a non-porous PTFE sheet. In the latter structure, interlayer current propagation via ions is forbidden; correspondingly, Q is seen to recover from 19.7 to 73.5. The numerical results of this study are summarized in Table 2.1.

Table 2.1 Resonant circuit quality factor, Q , for different electrode structures, separator materials, and flooding fluid.

	EMPTY	JELLYROLL		LAMINAR	
		no separator	porous separator	porous separator	non-porous separator
dry	162	14.1	66.2	-	-
water	168	-	11.8	103	-
0.5 M H_2SO_4	21.0	-	12.0	19.7	73.5

Figure 2.8 Phase behavior of probe circuit for laminar electrodes in 0.5 M H_2SO_4 . Electrode with porous polypropylene mat separator (Δ), electrode with non-porous PTFE separator ($\circ$), water only ($\bullet$), acid only ($\blacktriangle$).

2.4 Nutation behavior of ^{13}C magnetization in electrodes

Application of an rf pulse of length t_p causes the bulk magnetization to precess (or "nutate") about the H_1 axis through an angle $\theta = \gamma H_1 t_p$, as depicted schematically in Figure 2.1B. The transverse component of M is therefore proportional to $\sin \theta$ (equation 2-1). In the ideal case, the amplitude of the NMR signal traces out a sine wave as t_p is varied. With appreciable sample conductivity, however, the H_1 attenuation mechanism becomes important, and the precession angle varies locally within the conductor. This has predictable consequences on the nutation of M , and hence serves as an important probe of H_1 penetration of conductive samples.

2.4.1 Nutation function for conducting cylinders

The magnitude of the NMR signal immediately following the application of an H_1 pulse is obtained by integrating equation 2-1 over the volume of the sample:

$$\frac{S(t_p)}{S_0(t_p)} = \frac{\int_0^{R_s} \sin(\gamma H_1(r, \theta, l) t_p) dV}{\int_0^{R_s} dV} \quad (2-4)$$

where R_s is the sample radius. In the general case of a conductive sample, $H_1(r, \theta, l)$ can be calculated from Maxwell's equations.⁽³⁾ However, the specific case of an infinite cylindrical conductor of conductivity σ serves as a useful illustration of the effect of H_1 attenuation on the nutation function, equation 2-4. This derivation neglects any effect the conductor has on the phase of the field; details can be found in Appendix B.⁽¹⁷⁾

The magnitude of the alternating field as it penetrates a one-dimensional conducting cylinder is shown in Figure 2.9, with δ/R_s as a parameter. When $\delta/R_s > 1$, the radius is smaller than the skin depth of the sample, and the rf penetrates the sample with little attenuation. However, as the sample radius becomes larger than the skin depth, power is dissipated by eddy currents within the conductor, and the field strength decreases inside the sample. Based on the conductivity determined from Figure 2.2, the electrode material used

Figure 2.9 Model for 1-D penetration of H_1 field at 67.2 MHz into solid cylinder of skin depth δ . H_1 is normalized by its value at the surface of the electrode.

Figure 2.10 Simulation of nutation function, equation 2-4, for 1-D conductive cylindrical sample; ω_n^* is the nutation frequency, $\omega_n^* = \gamma H_1^*$, where $*$ indicates the limiting case of a non-conductive sample.

in this work has a skin depth of 0.09 cm; hence, for a sample diameter of 1.4 cm, $\delta/R_s = 0.13$. A cylinder of this material, such as a tightly-wound jellyroll, would therefore be expected to severely attenuate the field inside the sample.

The effect of an H_1 distribution on the nutation function is shown in Figure 2.10. The abscissa is normalized by the nutation frequency $\omega_n^* = \gamma H_1^*$, where the * indicates the limiting case of a non-conductive sample. The resulting axis has units of radians, emphasizing the sinusoidal behavior of the magnitude of the NMR signal as the pulse length is increased. This sine wave is altered as the conductivity becomes appreciable. At intermediate values of δ/R_s ($1 \geq \delta/R_s \geq 0.6$), it appears simply to be modified by an exponential envelope. As δ/R_s decreases further, the curves become stretched, indicating a decrease in the effective nutation frequency resulting from dissipated power. More importantly, however, the nutation function no longer crosses the abscissa; that is, it is no longer possible to either null or invert the magnetization. This situation has serious consequences for many multiple pulse NMR experiments.

2.4.2 *Effect of electrode structure on nutation*

Nutation measurements were made for ^{13}C -enriched liquids soaked into different electrode structures by varying the pulse length of a single-pulse NMR experiment and recording the resulting signal amplitude. Figure 2.11 shows the behavior of a non-conductive methanol standard; the data are described well by a sine wave. Also displayed is the identical experiment on acetic acid in the jellyroll electrode without a separator. The magnetization from this sample reaches a maximum well past that of the non-conductor, and never returns to the abscissa, as predicted for in Figure 2.10 for the case of a solid cylinder with $\delta/R_s \ll 1$. The data in Figure 2.11 were obtained with a probe containing a single-turn sample coil tuned to a ^{13}C frequency of 67.2 MHz.⁽¹⁸⁾

The nutation behavior of liquid methanol in both jellyroll and laminar electrode structures constructed with porous separators is shown in Figure 2.12. These data were obtained with a probe containing a 5-turn coil. Sinusoidal behavior is seen in both cases,

Figure 2.11 Nutation behavior of ^{13}C liquid standards: methanol only ($\circ$), and acetic acid soaked into jellyroll electrode structure without separator ($\bullet$). Data were taken with a single-turn NMR coil (see ref. 17), and are normalized by the maximum value of signal amplitude. The line is a fit to a sine wave, equation 2-1.

Figure 2.12 Nutation behavior of $^{13}\text{CH}_3\text{OH}$ soaked into electrodes with porous separators: jellyroll structure (Δ), laminar structure ($\blacktriangle$), no electrode ($\circ$). Data were taken with a 5-turn coil and normalized by maximum signal amplitude. The line is a fit to a sine wave, equation 2-1.

along with inversion of the magnetization and very little decrease in the signal amplitude over a full cycle. Although these electrode structures are by no means solid cylinders of isotropic conductivity, a comparison to Figure 2.10 indicates behavior similar to a conducting cylinder with $\delta/R_s \geq 1$. With the inclusion of the insulator, the H_1 field can access each layer of the electrode structure, and since the thickness of the conducting strip is less than the skin depth of the material at 67.2 MHz, the rf penetrates with little or no attenuation. The data for the electrodes do show some deviation from sinusoidal behavior that is not predicted by the model, most noticeably for the jellyroll with the separator. Such slanting of the sine wave has also been observed in the present studies for a non-conductive standard and hence is not thought to be associated with the conducting material or the electrode structure.

2.5 Conclusions and recommendations

In an NMR experiment the sample couples to the coil through its electronic and ionic conductivity, thus having a tremendous impact on the execution and results of the experiment. This jeopardizes the simple quantitative relationship between the number of spins being observed and the magnitude of the signal. Careful consideration of the sample structure can reduce or even eliminate this coupling, as indicated by minimal deviation of the probe circuit quality factor (Q) from its empty coil value and by sinusoidal nutation behavior. For *in situ* NMR work with electrochemical systems, the construction of electrodes with insulating layers separating thin sheets of electrode material is recommended. For open-circuit experiments where the conductivity of the liquid phase is not important, macroporous separators can be used. However, where the use of high conductivity electrolytes is necessary, the separator should be non-porous. The particular structure of the electrode is very important. A laminar electrode structure (Figure 2.4) was shown to minimize the induction of eddy currents in the conductor, yielding by far the highest values of Q (and hence S/N) in this study. Furthermore, the laminar structure

promoted the complete penetration of the electrode material by the H_1 field, as indicated by the ideal nutation behavior of methanol soaked into the electrode. Therefore, a laminar electrode is used for the NMR experiments described in the remaining chapters of this thesis.

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CHAPTER 3

PREPARATION OF ELECTROCATALYST SURFACES FOR NMR EXPERIMENTS

The preparation of ^{13}CO -covered platinum electrocatalyst surfaces for use in NMR experiments presented numerous design challenges. The details of the adsorption of the low-solubility gas from the aqueous phase to form a monolayer on the electrode are discussed in this chapter, along with the electrochemical characterization of the adlayer and partial stripping of the monolayer to prepare various ^{13}CO coverages.

3.1 Materials and hardware for electrochemical experiments

3.1.1 *Electrode materials and construction*

The supported Pt electrocatalysts used in this work were purchased from E-TEK, Inc.⁽¹⁾ Given the low sensitivity of surface NMR experiments⁽²⁾, it was desired to maximize the Pt surface area inside the NMR sample coil through optimization of the sample size and the platinum content of the electrode. The sample size is restricted by the dimensions of the sample coil, which are in turn limited by such practical considerations as the H_0 field homogeneity, the bore diameter of the magnet, and the resonance behavior of the probe circuit. The coil inner diameter and length were both set to 1.6 cm based on these limitations. Platinum content is governed by two parameters, the weight percent of the metal relative to the carbon black support (Vulcan XC-72), and the platinum loading.⁽³⁾ While increasing each of these two quantities increases the overall platinum surface area, they have different effects on the particle size. It was desired to keep the Pt particle size small, since the metallic nature of Pt is known to affect the NMR signal arising from adsorbed species.⁽²⁾ While particle size increases with weight percent of Pt in the catalyst powder⁽⁴⁾, it is unaffected by metal loading. Thus, 20 wt.% Pt was used, with a 25 Å

particle diameter as determined by transmission electron microscopy.⁽⁴⁾ The loading was chosen to be 2.0 mg Pt/cm², quite high compared to practical fuel cell electrodes.⁽⁵⁾

This electrode material was cut into twenty pieces 1.5 cm long and of the various widths shown in Figure 3.1. Each piece was threaded with 6 mil diameter gold wire. Pieces of non-woven porous fiberglass mat (~6 mil thickness) were cut to slightly larger dimensions than the electrode pieces in order to prevent contact of the electrode layers at the edges. The electrode pieces were then stacked inside a 1.4 cm i.d. glass tube alternately with two layers of the separator material to form the laminar electrode structure discussed in Chapter 2. The Au leads were then bound together with a separate piece of 6 mil Au wire. Based on company specifications of 112 m²/g Pt, this electrode has an estimated Pt surface area of ~3.5*10⁴ cm², or roughly 4.6*10¹⁹ surface Pt atoms.⁽⁶⁾

3.1.2 NMR electrochemical cell

The electrochemical cell was designed for *in situ* studies, combining all the necessary features for both electrochemical and NMR experiments. Foremost among these are control of the working electrode (WE) potential, and capability for flow of the electrolyte through the WE structure. Hence, accommodations were made for the inclusion of a reference electrode (RE) and the requisite connections and plumbing for electrolyte exchange. However, with a spectrometer magnet bore diameter of 5 cm, the sizing of the cell presented a significant challenge for its design. The cell was constructed of Pyrex glass; its design is shown in Figure 3.2.

The reference electrode was a specially designed glass static hydrogen electrode (SHE).⁽⁷⁾ The bottom of the RE chamber was fitted with a Luggin capillary extending from a male 5/12 ground glass taper. This fit into the center arm of the cell, with the capillary opening curved to within a centimeter of the WE. The top of the RE compartment was a 5/12 female ground glass joint; the active surface, a platinized⁽⁸⁾ Pt coil of ~750 cm² real area, was sealed in a 5/12 male joint. Prior to each electrochemical experiment, the RE

Figure 3.1 Width in centimeters of electrode pieces used to construct lamellar electrode. Each piece is 1.5 cm long.

Figure 3.2 Schematic of NMR electrochemical cell

was charged by galvanostatic evolution of H_2 until the RE compartment was half filled with the static gas bubble.

The counter electrode (CE) was a platinized mesh sealed in a 5/12 ground glass joint, and contained in an arm above the WE chamber. Gas evolved at the CE could be vented either through the 5/12 joint or the stopcock directly above the electrode. The CE had a measured real surface area greater than 1000 cm^2 .

The WE chamber was a cylindrical section of 1.6 cm o.d., 1.4 cm i.d. that fit snugly inside the NMR coil. This compartment was closed with a PTFE cap drilled with a Luer taper. For electrolyte exchange, a PTFE male Luer fitting connected to 1/4" PTFE tubing was inserted into this tapered hole. During non-flow situations, the cell was sealed with a PTFE male Luer plug. Liquid entered the cell through a 14/20 joint and a PTFE stopcock.

3.2 Electrochemical preparation and characterization of a clean electrode surface

The laminar electrode was transferred from its assembly tube to the working electrode compartment of the cell with a PTFE plunger, and the end cap was fit on to the opening. External connection to the WE was provided by a thick Au lead hooked to the 6 mil Au wire bundle at the edge of the electrode. This wire was press-fit through a PTFE 5/12 standard taper joint sealed with wax and shrink-fit tubing to prevent leakage. The presence of the PTFE binder in the electrode macrostructure precluded flooding of the pores by aqueous solution. Hence, it was necessary to use a low surface tension liquid such as methanol to flood the pores. Following purging of the electrode and cell with nitrogen, liquid CH_3OH was added to the cell until the electrode was completely submerged. An atmosphere of N_2 was maintained in the cell during flooding to minimize methanol oxidation on the active Pt surface.

After 30 minutes, the methanol was drained from the cell and replaced with N₂-purged deionized water. In order to dilute the methanol in the electrode pores, a bath of hot deionized water equipped with a N₂ bubbler was set up and circulated through the cell with a PTFE bellows pump. After 5 hours, water was replaced by 3 M sulfuric acid (Ultrex grade, J. T. Baker), and circulation continued for 1 hour. 3 M sulfuric acid was used as the electrolyte throughout this work, and was purged of dissolved O₂ by bubbling N₂ for at least one hour before contacting the electrode.

The reference electrode assembly was then inserted into the cell, filled with electrolyte, and charged at 5 mA until the RE compartment was half filled with H₂ (~45 minutes). Surface cleaning sweeps between reductive (0.05 V/SHE) and oxidative (1.20) potentials at 15 mV/s were programmed and applied to the WE using a PAR model 173 potentiostat interfaced to HeadStart electrochemical control software. After eight such cleaning cycles, a sweep at 0.2 mV/s showed a large anodic peak centered at 0.65 V/SHE, indicating the presence of a significant amount of residual methanol in the electrode pores. The electrode was then ramped to 0.70 V/SHE, a potential at which the complete electro-oxidation of methanol occurs, and held as hot electrolyte (~70 °C) was circulated through the cell with N₂ purging. After 8 hours at 0.70 V/SHE, the potential was ramped down to 0.05 V and the anodic sweep repeated. Comparison of the resulting voltammogram, shown in Figure 3.3, to Figure 1.5A reveals a clean Pt surface, all of the methanol having been eliminated from the electrode pores by oxidation at 0.7 V. The small anodic and cathodic peaks at ~0.65 V/SHE indicate the presence of an electroactive quinone/hydroquinone couple on the surface of the carbon support, unrelated to the Pt surface.⁽⁹⁾ The relatively slow sweep speed of 0.2 mV/s was chosen as the maximum rate that yielded resolution of the hydrogen region peaks and alignment of the anodic and cathodic hydrogen peaks to within ~0.05 V.

Figure 3.3 Cyclic voltammetry of the lamellar electrode in 3 M H_2SO_4 before (dashed line) and after (solid line) elimination of residual methanol from pores by potentiostatic hold at 0.7 V/SHE. Sweep rate was 0.2 mV/s.

Figure 3.4 Voltammetric sweep of anodic hydrogen region of the clean lamellar electrode in 3 M H_2SO_4 at 0.2 mV/s. The active Pt surface area calculated from the area of the shaded region, A_H , (equation 3-1) is $2.99 \times 10^4 \text{ cm}^2$.

The integrated area of the anodic hydrogen region from 0.065 to 0.300 V/SHE after correction for the double layer current (the shaded region, A_H , in Figure 3.4) is related to the actual area of the active Pt surface by equation 3-1:

$$A_{Pt} = \frac{A_H}{vQ_H^0} \quad (3-1)$$

where v is the voltammetric sweep rate, and Q_H^0 is the specific capacity for hydrogen adsorption/desorption, $210 \times 10^{-6} \text{ C/cm}^2$ of surface.⁽¹⁰⁾ This yielded a Pt surface area of $2.99 \times 10^4 \text{ cm}^2$, slightly less than the estimated area; this discrepancy likely arises from the presence of the PTFE binder in the macrostructure. Multiplication by an atomic surface density of $1.305 \times 10^{15} \text{ Pt atoms/cm}^2$ gives $N_{Pt}(0) = 3.90 \times 10^{19}$ surface Pt atoms.

3.3 Preparation and characterization of Pt surfaces of varying ^{13}CO coverages

3.3.1 Preparation of monolayer coverages of ^{13}CO

Carbon monoxide is only moderately soluble in aqueous solution, with a solubility of $1.0 \times 10^{-3} \text{ M}$ in water at 25°C . This solubility decreases with increasing sulfuric acid concentration up to about 8 M acid.⁽¹¹⁾ Given such low concentrations of CO, adsorption on the high surface area electrode from quiescent electrolyte would be expected to be diffusion-limited, requiring very long contact times. Hence, for this study, a system in which electrolyte containing dissolved CO is flowed through the porous electrode structure was desired, thereby exposing the electrode surface to a constant source of adsorbate. Further improvements were made by ensuring that the concentration of gas in the liquid was as high as possible, i.e., the liquid was saturated. A factor of 2 increase in CO concentration was obtained by adsorbing from water instead of electrolyte, requiring open circuit conditions. Saturation of the liquid, however, was complicated by the cost and toxicity of the solute gas - it was too expensive and hazardous to simply bubble the gas

through the liquid in an open system. To facilitate the process, therefore, a closed saturation loop was fabricated consisting of a 250 mL glass bulb with various sidearms and PTFE valves. The gas space was open to a metal bellows pump, which circulated the gas through a porous glass frit submerged in the liquid. The liquid was drawn through the cell by a PTFE bellows pump and returned to the top of the bulb. This dual flow configuration is shown in Figure 3.5.

The bulb was filled with 150 mL of distilled, deionized water and purged with nitrogen for 1 hour. After the system was sealed and evacuated to the vapor pressure of water, 760 Torr of 99% ^{13}C -enriched carbon monoxide (Cambridge Isotope Laboratories) was introduced into the bulb through a FeCO_x trap consisting of glass beads at 300 °C. Gas and liquid were circulated simultaneously for 10 hours, after which the cell was flushed with 100 mL of 3 M H_2SO_4 . Upon insertion of the reference electrode, measurement of the open circuit potential E° showed a slight cathodic drift from 0.35 to 0.29 V/SHE over the 10 hours of adsorption, confirming the absence of oxygen in the system. The potential was then ramped down to 0.05 V at 0.2 mV/s and held for 10 minutes before sweeping the anodic hydrogen region from 0.05 to 0.35 V/SHE at the same rate. The resulting current was essentially constant over this range and of a magnitude comparable to those observed for the double layer charging process on this electrode (Figure 3.6). This was indicative of the complete blocking of reversible hydrogen adsorption on the platinum surface by a monolayer of irreversibly-bound ^{13}CO . A control circulation experiment on the clean surface with N_2 instead of ^{13}CO in the bulb showed no change in the surface area as determined from the anodic hydrogen capacity.

The amount of ^{13}CO in a monolayer was determined by slow galvanostatic oxidation of the surface layer; the details of this calculation can be found in Appendix C. The saturation coverage, defined as the ratio of the number of ^{13}CO molecules in the complete monolayer to the total number of surface platinum atoms, was determined to be

Figure 3.5 Schematic of configuration for simultaneous circulation of gas (through liquid) and liquid (through cell). This design results in efficient adsorption of ^{13}CO on electrode surface.

Figure 3.6 Voltammetric sweeps of anodic hydrogen region in 3 M H_2SO_4 at 0.2 mV/s. A: Clean electrode surface, B: after circulation of N_2 -saturated distilled water for 4 hours (blank experiment), C: after circulation of ^{13}CO -saturated distilled water for 10 hours.

0.682, comparable to the value of 0.70 commonly reported in the literature for carbon monoxide on supported platinum catalysts.

3.3.2 Preparation of sub-monolayer coverages of ^{13}CO

Sub-monolayer coverages were prepared by partial oxidation of the ^{13}CO adlayer, starting with the full monolayer and stepping down incrementally to the bare surface. Immediately following NMR spectral acquisition (see Chapter 4), the cell was flushed with 100 mL of electrolyte and the RE was inserted. A sweep of the anodic hydrogen region was done to determine the area of Pt covered by ^{13}CO . As the monolayer is oxidized, more surface becomes available for hydrogen adsorption, and a gradual recovery of the anodic hydrogen currents should be seen. This behavior was in fact observed, with representative data shown in Figure 3.7. Subtraction of the surface area available to hydrogen adsorption, $A_{\text{Pt}}(\text{H})$, from that of the clean surface, $A_{\text{Pt}}(0)$, yielded the area of platinum blocked by the partial monolayer, $A_{\text{Pt}}(\text{CO})$. Using a surface atomic density of 1.305×10^{15} Pt atoms/cm², $A_{\text{Pt}}(\text{CO})$ was converted to $N_{\text{Pt}}(\text{CO})$, the number of surface Pt atoms blocked by the CO adlayer.

A constant anodic current was then applied to the electrode over a period of ≥ 2 hours to oxidize a desired amount of adsorbed ^{13}CO . Estimation of the charge required for partial oxidation of the adlayer was complicated by the requirements of the coverage-dependent double layer charging process; this situation resulted in overshoot of desired coverages on more than one occasion. Hence, two separate runs were performed, with a different set of coverages obtained for each. Unfortunately, the quality of the data from the partial oxidation runs was poor, rendering quantitative information on the ^{13}CO content of each partial monolayer unavailable. However, a third run was done to determine the number of ^{13}CO molecules in a complete monolayer, as discussed in section 3.3.1. Table 3.1 lists the data obtained from the electrochemical measurements described in this chapter.

Following partial oxidation, the RE was removed and the cell was flushed with 100 mL of H_2O , followed by 100 mL of D_2O (both N_2 -purged). Deuterium oxide was used to

Figure 3.7 Representative voltammetric sweeps of anodic hydrogen region in 3 M H_2SO_4 at 0.2 mV/s showing suppression of hydrogen desorption currents by adsorbed ^{13}CO . A: Clean surface, E: ^{13}CO -saturated surface, B-D: surfaces with sub-monolayer coverages of ^{13}CO .

ensure that dipolar coupling between the ^{13}C nuclei of the adsorbed molecules and the protons in solvent molecules immobilized in the electrical double layer near the Pt surface was not significant in the NMR experiments. The stopcock on the liquid inlet joint was then closed and the WE chamber inserted into the NMR sample coil. Once the cell was secured inside the NMR probe, the probe was inserted into the bore of the magnet and flushed with N_2 over the entire course of the NMR experiment. Details of the NMR experiments are discussed in the next chapter.

Table 3.1 Electrochemical data for the 7 samples studied in this thesis.

sample	$\text{N}_{\text{Pt}}(\text{CO})^* 10^{-19}\dagger$	$\text{N}_{\text{CO}} * 10^{-19}\dagger\dagger$
1.1	3.876	-
1.2	2.001	-
1.3	0.876	-
2.1	3.902	-
2.2	3.316	-
2.3	1.684	-
3.1	3.902	2.661

$\dagger$ $\text{N}_{\text{Pt}}(\text{CO})$ is the number of surface Pt atoms blocked by the adsorbed ^{13}CO layer.

$\dagger\dagger$ N_{CO} is the number of CO molecules in a monolayer, and was determined only for sample 3.1.

3.4 References

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CHAPTER 4

^{13}C NMR STUDY OF CO ADSORPTION ON SUPPORTED Pt ELECTROCATALYSTS

^{13}C NMR spectra are presented in this chapter for different coverages of ^{13}CO on a Pt electrocatalyst surface. The spectra are interpreted quantitatively in terms of changing populations of linear and bridge-bonded molecules on the metal surface using lineshape simulations and the electrochemical measurements described in Chapter 3.

4.1 Equipment and procedures for NMR experiments

NMR spectra were acquired on a home-built spectrometer operating at 67.17 MHz for ^{13}C . The sample coil was a 5-turn solenoid with 1.60 cm i.d. and 1.65 cm length wound with flattened copper wire. This coil was tuned and matched in the parallel-series resonance probe circuit shown in Figure 4.1. This circuit design allowed for application of high power rf pulses by splitting the tuning capacitance between the two sides of the coil, thereby reducing the maximum voltage in the circuit and eliminating arcing.

Since the presence of the conducting material in the coil perturbs the resonance behavior of the circuit, it was crucial to have a laminar electrode inside the coil when the circuit was tuned and matched. The same held true for the general set-up of the spectrometer transmitter; recall the effect of electrode structure on nutation behavior. Hence, a standard was prepared by soaking liquid ^{13}C -enriched methanol into a laminar electrode identical to that constructed for the study of adsorbed ^{13}CO . The phase behavior of the probe tuned to 67.2 MHz and matched to $50\ \Omega$ with this electrode standard inside the coil is shown in Figure 4.2. This circuit had a measured quality factor of 135, higher than Q obtained for a similar laminar electrode with the test circuit (section 2.3). Also shown in the figure is the change in behavior observed when the standard is removed from the coil -

Figure 4.1 Parallel-series probe tank circuit used for ^{13}C NMR experiments with supported Pt electrocatalysts.

Figure 4.2 Phase behavior of probe tuned and matched with laminar electrode standard in coil (◊). Change upon removing standard from coil is also shown (•).

the resonance shifts to a higher frequency, the matching condition is no longer fulfilled, and the quality factor increases to 150.

The Hahn spin echo sequence^(1,2) was used with a $4.6\ \mu\text{s}$ $\pi/2$ pulse length to acquire the NMR spectra. A second pulse length of $12.5\ \mu\text{s}$ yielded the maximum amplitude of the echo. Transmitter power was 910 W. The ^{13}C reference frequency, ν_{ref} , was set by adjusting the carrier frequency until the CH_3OH resonance was centered 52 ppm downfield of tetramethylsilane (TMS). Since the signal arising from adsorbed ^{13}CO is expected to be shifted well downfield of the ^{13}C reference, the spectrometer carrier frequency, ν_0 , was adjusted to $\nu_{\text{ref}} + 25\ \text{kHz}$ (372 ppm relative to TMS). This value was chosen based on reported spectra for ^{13}CO on supported Pt catalysts.^(3,4)

4.2 Optimization of the NMR experiment

Estimation of the number of ^{13}C nuclei from different sources in or near the sample coil (Appendix D) reveals a possible drawback of these NMR experiments. A saturated electrode surface can be expected to contain $\sim 3 \times 10^{19}$ ^{13}CO molecules, as determined by galvanostatic oxidation of a complete monolayer (section 3.3.1). The electrode support materials and the PTFE endcap of the cell, on the other hand, each contain roughly an order of magnitude more ^{13}C in natural abundance than the enriched surface monolayer. Fortunately, the interaction of the conduction electrons with the metal-bonded ^{13}C nuclei ensures that the characteristic relaxation times of the magnetization arising from the surface spins are very short - much shorter, in fact, than the background components of the raw signal. For example, the spin-lattice relaxation time, T_1 , of graphite has been determined to be greater than 100 s⁽⁵⁾, whereas $T_1 \approx 100\ \text{ms}$ for ^{13}CO on Pt/alumina.⁽³⁾ Hence, it is possible to maximize the amplitude of the ^{13}CO signal relative to the background signal through judicious choice of the timing parameters of the NMR pulse sequence, including the echo delay, τ , and the recycle delay, t_r (Figure 4.3).

^{13}C NMR spectra for a ^{13}CO -saturated electrode are presented in Figure 4.4 as a

Figure 4.3 Schematic of NMR pulse sequence showing parameters to be optimized.

Pulse lengths: $t_{p1} = 4.6 \mu\text{s}$, $t_{p2} = 12.5 \mu\text{s}$.

function of the recycle delay. Based on its large downfield shift, the broad peak centered at 415 ppm can be confidently assigned to adsorbed ^{13}CO ; ^{13}C shifts greater than 250 ppm are encountered only in cases where the carbon nucleus is bonded directly to a metal surface. As will be seen, this peak is not present in spectra of the bare electrode and undergoes significant changes as the adsorbed layer is oxidized. The peak at 175 ppm is assigned to the perpendicular component of the graphite chemical shift powder pattern by comparison with spectra from the literature⁽⁶⁾, whereas the peak at 135 ppm is attributed to PTFE.

These background components prevented the full resolution of the signal from adsorbed ^{13}CO , requiring subtraction of a background spectrum from each experiment. Given these circumstances, it was desired to minimize the magnitude of the background signal relative to the surface signal. Figure 4.4 illustrates the vast difference in spin-lattice relaxation rates of the surface and background components. In the extreme case, where t_r is much longer than the longest T_1 (not shown), all three signal components would be allowed to fully relax between acquisitions and the background signal would appear to completely overwhelm the surface signal. This is apparent even at a recycle delay of 20 s.

Figure 4.4 NMR spectra of ^{13}CO -saturated electrode as a function of recycle delay, t_r . Components of the spectra are A: ^{13}CO , B: carbon/graphite, C: PTFE. Each spectrum is the Fourier transform of the sum of 1008 echoes ($\tau = 30 \mu\text{s}$) with 750 Hz line broadening. All NMR spectra are reported using the δ scale, with downfield to the left.

However, as the recycle time is decreased, the background magnetization no longer fully relaxes between experiments, becoming partially saturated. The magnetization from the surface species, on the other hand, does fully relax; hence, the ratio of the surface to background signal increases.

For quantitative analysis of the ^{13}C O signal, care must be taken to ensure that it is fully relaxed, with $t_r \geq 5T_1$ being a commonly used criterion for full relaxation.⁽⁷⁾ T_1 was estimated from a plot of the amplitude of the ^{13}C O signal versus recycle time (Figure 4.5); assuming single exponential relaxation, a least-squares fit yields $T_1 = 0.33$ s. Thus, the optimal recycle delay is ≈ 1.7 s. A value of 2 s was used for the remainder of the experiments.

A similar optimization procedure was used to set the echo delay, τ . Figure 4.6 shows that the ratio of the ^{13}C O and background signals increases as τ decreases. The lower limit is governed by the ringdown time of the spectrometer receiver, provided that the free induction decay (FID) from the second pulse does not interfere with the formation of the echo. This situation can be avoided with the phase cycling scheme shown in Figure 4.7. An echo delay 30 μs yielded both the maximum ^{13}C O signal amplitude and the largest ratio of surface to background signals (Figure 4.8), with lower values of τ introducing significant ringdown to the echoes. A 30 μs delay was used in all subsequent experiments.

4.3 ^{13}C NMR spectra as a function of ^{13}C O coverage on Pt/C fuel cell electrodes

Figure 4.9 shows a ^{13}C NMR spectrum of the ^{13}C O-saturated Pt/C electrode surface (spectrum A), along with the spectrum of the electrode acquired after the oxidation of the entire ^{13}C O monolayer (B). Subtraction of this background signal from spectrum A yields a difference spectrum (C) attributed solely to the ^{13}C O adlayer. Four difference spectra corresponding to sub-monolayer coverages were similarly obtained and are presented in Figure 4.10 along with a saturation coverage spectrum. The narrow peak at

Figure 4.5 Magnitude of the ^{13}CO signal at 415 ppm as a function of recycle delay. The line is a least squares fit assuming single exponential relaxation, yielding $T_1 = 0.33$ s.

Figure 4.6 NMR spectra of ^{13}CO -saturated electrode as a function of echo delay, τ . Components of the spectra are A: ^{13}CO , B: carbon/graphite, C: PTFE. Each spectrum is the Fourier transform of the sum of 1008 echoes acquired at 2 s recycle delay with phase cycling to remove the free induction decay. Line broadening was 750 Hz.

Figure 4.7 Phase cycling scheme used to subtract the FID from the acquired signal. Such a scheme becomes necessary at low values of the echo delay to eliminate interference with the formation of the echo. Entries under pulse steps refer to the phase of the rf pulse. For the acquisition step, entries describe the manner in which the signal acquired in that step is combined with the accumulated signal. This is clarified in the inset: "A" and "B" are the spectrometer channels, with the sign indicating whether the signal is added or subtracted from the accumulated signal. "Re" and "Im" are the real and imaginary components of the accumulated signal, respectively.

Figure 4.8 Amplitude of the signal from adsorbed ^{13}CO and ratio of ^{13}CO and graphite peak amplitudes as a function of the echo delay. The optimum delay time is $30\ \mu\text{s}$, for which both quantities are maximized. Below $30\ \mu\text{s}$, receiver ringdown interferes with the echo.

Figure 4.9 A: ^{13}C NMR spectrum of ^{13}CO on Pt/C electrode. B: Background spectrum of electrode after complete oxidation of ^{13}CO monolayer. These two spectra represent the Fourier transform of the sum of 25008 and 50000 echoes, respectively, acquired with a 30 μs echo delay and 2 s recycle delay. No line broadening function was applied to these data. C: Difference spectrum obtained by subtraction of B from A.

Figure 4.10 Coverage-dependent ^{13}C NMR spectra of ^{13}CO on Pt/C electrode. Each spectrum represents the Fourier transform of the sum of 25008 echoes acquired with a $30\ \mu\text{s}$ echo delay, 2 s recycle delay, and phase-cycling to remove the FID. A background spectrum acquired under identical conditions with a bare electrode surface was subtracted from the raw spectra to obtain the difference spectra shown above. 750 Hz line broadening was applied to the difference spectra.

133 ppm is attributed to residual dissolved CO₂ from the partial oxidation procedure, with background-subtraction artifacts evident in some of the spectra in the range of 0-200 ppm. These do not interfere with the signal from the carbon monoxide layer, however. The magnitude of the observed shifts arising from the surface layer are well outside the range of isotropic chemical shifts observed for ¹³C compounds⁽⁸⁾, suggesting the contribution of an additional shift mechanism. For nuclei directly bonded to a metallic particle, the Knight shift provides such a mechanism. Indeed, for ¹³CO on supported platinum particles, lineshapes centered at 340-380 ppm have been reported.^(3,4)

The integrated intensity of an NMR spectrum is directly proportional to the number of spin-active nuclei in the sample, provided the issues of probe Q and rf penetration have been properly addressed (Chapter 2).⁽⁹⁾ Thus, the number of molecules in a monolayer as determined electrochemically (see section 3.3.1 and Appendix C) serves as a calibration standard for the NMR data. The areas of each difference spectrum were obtained by integration over the range 200-800 ppm after baseline correction. Due to slight variations in the probe Q between experiments, it was also necessary to apply a correction factor to each spectrum. The details of this procedure are discussed in Appendix E. The amount of ¹³CO on each surface was then calculated from the areas of their NMR spectra from equation 4-1:

$$\frac{N_{\text{CO}}(\Theta_{\text{CO}})}{N_{\text{CO}}(\Theta_{\text{COsat},3.1})} = \frac{A_{\text{NMR}}(\Theta_{\text{CO}})}{A_{\text{NMR}}(\Theta_{\text{COsat},3.1})} \quad (4-1)$$

where the subscript "3.1" refers to the particular sample for which these quantities apply. The coverages corresponding to each spectrum were then obtained as the ratio of N_{CO} to the number of electrochemically-active surface platinum atoms in the electrode, N_{Pt(0)}, determined from anodic hydrogen voltammetry of the clean electrode (section 3.2). Table 4.1 lists the Q-corrected integrated areas of the NMR lineshape for each sample, along with the calculated values of N_{CO} and Θ_{CO}.

Table 4.1 Integrated intensities of ^{13}C NMR spectra at various coverages.

sample	$A_{\text{NMR}} * 10^{-6}$	$N_{\text{CO}} * 10^{-19} \dagger$	$\Theta_{\text{CO}} \dagger\dagger$
1.1	3.178	2.633	0.675
1.2	1.311	1.094	0.280
1.3	0.776	0.657	0.168
2.1	3.450	2.872	0.734
2.2	2.405	1.996	0.511
2.3	1.050	0.879	0.225
3.1	3.197	2.661	0.682

$\dagger$ The number of CO molecules on the electrode surface, as determined from equation 4-1.

$\dagger\dagger$ The coverage, Θ_{CO} , is defined as the ratio of the number of CO molecules on the surface, N_{CO} , to the total number of surface Pt atoms, $N_{\text{Pt}}(0)$.

Three different saturation coverage experiments are represented by spectra n.1, acquired following saturation of the surface starting from the bare electrode (section 3.3.1). Anodic hydrogen voltammetry of each saturated surface yielded a flat baseline consistent with double-layer charging currents, indicating the complete blocking of hydrogen adsorption by ^{13}CO . Comparison of the areas and shapes of spectra 1.1 and 3.1 in Figure 4.11 shows excellent reproducibility. Spectrum 2.1, however, has a significantly larger integrated area and is shifted downfield from the other two spectra.

Similar changes in the lineshape with coverage are readily apparent from Figure 4.10, and the shift in the center of mass of the spectra is one quantitative indication of this phenomenon (Figure 4.12). It can be seen that the ^{13}C shift decreases monotonically as the coverage decreases to approximately 0.3, at which point a constant shift is observed. In this context, the variability in the data from the saturated surfaces is consistent with the trends in the rest of the data. Such coverage dependence has not been reported previously for carbon monoxide on platinum surfaces; indeed, only broad, featureless spectra of

Figure 4.11 Comparison of ^{13}C NMR spectra of three different ^{13}CO -saturated surfaces of the same Pt/C electrode. Spectra were obtained as described in Figure 4.10.

Figure 4.12 Coverage dependence of the center of mass of ^{13}C NMR spectra of ^{13}CO adsorbed on Pt/C electrodes.

saturated or nearly-saturated surfaces are found in the literature.^(3,4) The coverage dependence of the lineshapes and their deconvolution will be addressed in the remaining portion of this chapter.

4.4 Deconvolution of spectra with lineshape simulations

4.4.1 Chemical shift powder patterns^(8,10,11)

The chemical shift shielding is dependent on the orientation of the molecule relative to the external magnetic field. For an axially-symmetric molecule such as CO, this dependence is given to first order by

$$\omega = \omega_0 \left(1 - \langle \delta \rangle - \frac{1}{2} \eta (3 \cos^2 \theta - 1) \right) \quad (4-2)$$

where $\langle \delta \rangle$ is the isotropic chemical shift and η is termed the shielding anisotropy. The angle θ is that formed by the molecular axis of symmetry and the direction of the external field. In liquids, thermal motion is rapid on an NMR timescale, such that the molecule samples all orientations relative to H_0 during the experiment. The term $(3 \cos^2 \theta - 1)$ averages to zero under such conditions, and a single sharp resonance is observed at the isotropic shift. For a randomly oriented ensemble of rigidly adsorbed molecules, however, the orientation dependence is retained, and the chemical shift lineshape is obtained by integration of equation 4-2 over spherical space. Hence, the probability associated with a molecular orientation of $\theta = 90^\circ$ is much greater than that of $\theta = 0^\circ$, and the lineshape takes on the asymmetric shape known as a "powder pattern" shown in Figure 4.13.

4.4.2 Low coverage lineshapes

Figure 4.12 indicates that the center of mass of the NMR spectra below $\Theta_{CO} \approx 0.3$ remains constant; visual inspection of the three low coverage spectra suggests that their shape also remains constant and, furthermore, resembles that of an axially-symmetric powder pattern. Hence, these data were each fit to powder patterns convoluted with a

Figure 4.13 A. Spherical distribution of possible orientations of CO molecule with respect to external magnetic field, H_0 . Integration of $\omega(\theta)$, equation 4-2, over a sphere yields an axially-symmetric powder pattern, B.

Table 4.2 Results of lineshape simulations for the three low coverage spectra.

	$\Theta_{\text{CO}} = 0.280$	$\Theta_{\text{CO}} = 0.225$	$\Theta_{\text{CO}} = 0.168$	avg. $\pm$ std.dev.
<u>powder pattern</u>				
$\langle\delta\rangle$, ppm	378.0	380.7	379.7	379.5 ± 1.4
η , ppm	-134.2	-137.1	-147.7	-139.7 ± 7.1
broadening, ppm	46.0	46.5	48.9	47.1 ± 1.6
<u>Gaussian</u>				
$\langle\delta\rangle$, ppm	255.5	256.5	242.0	251.3 ± 8.1
FWHM, ppm	24.0	17.6	18.4	18.4 ± 3.5
amplitude [†]	0.0102	0.0065	0.0134	-

[†] Amplitude of Gaussian component is the integrated intensity relative to the powder pattern.

Gaussian broadening function using a least-squares algorithm. The powder patterns were produced by interpolation using 64 grid points.⁽¹²⁾ The broadening likely arises from the magnetic susceptibility of the metal particles: circulating conduction electrons in the metal alter the z-component of the magnetic field experienced by the adsorbed ^{13}CO molecule; this effect is expected to vary substantially both across the face of a particle⁽¹³⁾ and with position relative to the static field, thereby broadening the NMR spectra. An improved fit was obtained with the addition of a small Gaussian component near 250 ppm, as suggested by the high coverage data (section 4.4.3).

The results of the low coverage fits are shown in Figure 4.14 and Table 4.2. All three parameters - $\langle\delta\rangle$, η , and Gaussian broadening - were allowed to vary in the fits, and very good agreement between the data sets was obtained. This provides strong evidence that the carbon monoxide at low coverage is relegated to a single type of surface site characterized by a single broadened powder pattern.

A comparison of the anisotropy of the chemical shift powder pattern to that of a

Figure 4.14 Results of least-squares fits of the low coverage ^{13}C NMR lineshapes to a Gaussian-broadened powder pattern plus a small Gaussian component. Each component is shown separately, with the data as points and the difference between the fit and the data given by the gray line.

model compound could provide valuable evidence for the identity of the surface carbonyl species. Unfortunately, however, no solid-state NMR studies have been reported for platinum carbonyls, although compounds such as $[\text{Pt}(\mu\text{-CO})_3(\text{CO})_3]^{2-}_n$ clusters have been synthesized in recent years.⁽¹⁴⁾ Anisotropies ranging from 220 to about 295 ppm have been observed for terminally-bound CO in transition metal carbonyl compounds.^(8,11) Whereas there are far fewer reported spectra for bridge-bonded CO, those powder patterns that have been observed have anisotropies of 90-140 ppm.^(8,11)

4.4.3 High coverage lineshapes

At Θ_{CO} values greater than about 0.3, the center of mass of the lineshape shifts downfield from 380 ppm (Figure 4.12). Furthermore, the upfield shoulder of the high-coverage lineshapes appears to remain intact, suggesting the presence of the same low coverage species at high coverages. This is shown in Figure 4.15, which compares the lineshape at $\Theta_{\text{CO}} = 0.280$ to those at two representative higher coverages, $\Theta_{\text{CO}} = 0.511$ and 0.675. Subtraction of the analytical form of the low coverage powder pattern from the high coverage lineshapes suggests the presence of at least two additional components at high coverage - a Gaussian-like contribution centered around 250 ppm, and a downfield component, as illustrated in Figure 4.16.

It is the downfield component that dominates the shift in the center of mass of the lineshape with coverage. In order to isolate this component, the low coverage powder pattern and the Gaussian were subtracted from the lineshapes using the parameters determined from the low coverage data (see Table 4.2); the amplitudes of the two analytical components were optimized by minimization of the baseline error in the region 200-350 ppm. The resulting high coverage components are shown in Figure 4.17. From these difference spectra it is clear that the high coverage component can not be described by a single chemically-distinct species, since its center of mass increases with increasing coverage (Figure 4.18). This is in contrast to the low coverage spectra, which were shown to have a constant center of mass near 380 ppm. The contributions of each component to

Figure 4.15 Comparison of ^{13}C NMR spectra of ^{13}CO on Pt/C electrode. Spectrum C ($\Theta_{\text{CO}} = 0.280$) represents the upper limit at which a single powder pattern fits the lineshape. Spectra A and B (A, $\Theta_{\text{CO}} = 0.675$; B, $\Theta_{\text{CO}} = 0.511$) can not be described by a single powder pattern, but appear to retain the low coverage component in the lineshape.

Figure 4.16 A. ^{13}C NMR spectrum of ^{13}CO on Pt/C electrode, $\Theta_{\text{CO}} = 0.675$. B. Residual components of lineshape following subtraction of low coverage powder pattern. C. Residual component of lineshape following subtraction of low coverage powder pattern and Gaussian.

Figure 4.17 Downfield component of lineshape following subtraction of low coverage powder pattern and Gaussian. A. $\Theta_{\text{CO}} = 0.734$, B. $\Theta_{\text{CO}} = 0.682$, C. $\Theta_{\text{CO}} = 0.511$.

Figure 4.18 Center of mass of downfield component of lineshape as a function of coverage.

Figure 4.19 Relative contributions of the three components of the lineshape: (●) = low coverage powder pattern, (○) = high coverage downfield component, (▲) = Gaussian centered near 250 ppm.

the total lineshape are plotted as Figure 4.19.

While the presence of multiple components in the NMR lineshapes suggests that the surface carbonyls are distributed over a variety of bonding environments, the issue of whether the species are linear or bridged has yet to be addressed. The next section considers the evidence toward answering this question.

4.5 Identification of linear and bridged ^{13}CO populations as a function of coverage: assignment of spectral components

Linear and bridged CO are distinguished by the number of metal atoms to which the carbon atom is bonded - bridged CO to two metal atoms, and linear to a single atom. Hence, the average ratio of blocked platinum atoms to adsorbed CO molecules for a mixed population of the two species would be expected to lie between 1 and 2; a quantitative measure of this ratio could provide valuable information relevant to the assignment of the lineshape components. Such information is accessible with voltammetry, as described in section 3.3. Specifically, voltammetric sweeps of the anodic hydrogen region yield the total number of platinum atoms blocked by the ^{13}CO adlayer, $N_{\text{Pt}}(\text{CO})$ (Table 3.1). The ratio of $N_{\text{Pt}}(\text{CO})$ to N_{CO} - the latter provided by the relative areas of the NMR spectra (Table 4.1) - is shown in Figure 4.20. At low coverages the data tend towards a value of $N_{\text{Pt}}(\text{CO})/N_{\text{CO}} = 2$, indicating the predominance of bridged species as coverage decreases. Thus, the low coverage powder pattern is assigned to bridged CO.

The corollary is that the population of linear CO on the platinum surface increases with coverage. An assignment of the downfield component of the high coverage spectra to linear CO based on this trend alone is rather dubious since it appears that this component may not correspond to a single species. However, if it is assumed that only the two species are present on the electrode, and that bridged and linear CO block the adsorption of two and one hydrogen atoms, respectively, then the data in Figure 4.20 can be used to calculate the absolute populations of the two CO structures from equations 4-3 and 4-4:

Figure 4.20 Average ratio of the number of platinum atoms per CO molecule as a function of coverage. A ratio of 2 corresponds to an entire population of bridged CO, whereas a ratio of 1 corresponds to all linear CO.

$$N_{\text{CO}}^b = N_{\text{CO}} \left[\left(\frac{N_{\text{Pt}}(\text{CO})}{N_{\text{CO}}} \right) - 1 \right] \quad (4-3)$$

$$N_{\text{CO}}^l = N_{\text{CO}} - N_{\text{CO}}^b \quad (4-4)$$

where N_{CO}^b and N_{CO}^l are the bridged and linear CO populations, respectively.

Such a determination has already been attempted from the lineshape analysis in section 4.3, although no assignment of the spectral components was made at that time. Comparison of the data in Figure 4.19 to the linear and bridged populations calculated using the voltammetry data reveals striking similarities. Figure 4.21 compares the bridged CO population as determined from equation 4-3 with the CO population corresponding to the area of the low coverage powder pattern. The numbers and their trend with coverage are both consistent between the data sets. Likewise, the linear CO population calculated from equation 4-4 is compared with the number of CO molecules in the downfield component of the spectra in Figure 4.22. Again, the trends and the numbers themselves show remarkable consistency between data sets.

At this point, it is worth reexamining the origins of each set of numbers. The "NMR" data in Figures 4.21 and 4.22 were generated via deconvolution of the spectral lineshapes; the total CO population was determined by the relative area of the integrated intensity of the spectra as calibrated by coulometry. The "electrochemical" data were determined from equations 4-3 and 4-4, where the number of surface platinum atoms blocked by adsorbed CO, $N_{\text{Pt}}(\text{CO})$, was obtained voltammetrically. The total CO population was obtained in the same way as for the "NMR" data set. Hence, while neither set of CO populations are based on purely electrochemical or NMR information, they are based on two sets of data - lineshape deconvolution and N_{Pt} - which are completely independent of one another. The favorable comparison of the calculations resulting from each provides compelling evidence for the assignments of the low coverage powder pattern to bridged CO and the downfield component to linear CO.

Figure 4.21 Comparison of the amount of CO on the electrode surface determined from the area of the low coverage powder pattern component of the NMR spectra ($\circ$) with the amount of bridged CO calculated via voltammetric sweeps of the anodic hydrogen region ($\bullet$) from equation 4-3.

Figure 4.22 Comparison of the amount of CO on the electrode surface determined from the area of the high coverage downfield component of the NMR spectra ($\circ$) with the amount of linear CO calculated via voltammetric sweeps of the anodic hydrogen region ($\bullet$) from equation 4-4.

4.6 Discussion

4.6.1 Quantitative considerations

Whereas the agreement in the trends shown in Figures 4.21 and 4.22 provides the necessary evidence for the spectral assignments, the good quantitative agreement between the electrochemical and NMR data sets suggests that quantitative NMR spectroscopy can indeed be performed with materials of appreciable conductivity. The results of section 4.5 are a step towards confirming the assertion made in Chapter 2 that minimal deviation of the probe circuit quality factor and nutation behavior from "empty coil conditions" assures the quantitative nature of the experiment. Figure 4.2 shows that Q for the empty and laminar electrode-filled coils differs by only $\sim 10\%$, while the nutation of a ^{13}C liquid standard soaked into the laminar electrode structure shows little deviation from sinusoidal behavior (Figure 2.12). Care must be taken to include the necessary corrections discussed in Appendix E, since the magnitude of the NMR signal is sensitive to even slight changes in the resonance condition of the experiment. Furthermore, the assumption inherent in equation 4-1 is not a suitable substitute for coulometry data, and future studies should include good quality data of this type as an independent measure of N_{CO} .

4.6.2 Coverage dependence of CO surface populations

The trends in the ^{13}C NMR data with coverage are supported by recent IRRAS (infrared reflection-absorption spectroscopy) spectra on low index single crystal Pt electrodes.⁽¹⁵⁻¹⁸⁾ Under potential control at 0.34 V/RHE, very close to the open circuit potentials measured for the NMR data set, IRRAS indicates the presence of the bridged structure at low coverages on those crystal planes thought to compose small platinum particles - namely the (100) and (111) faces - whereas high coverage favors the formation of linear CO. This disproportionation was especially evident on the (100) face⁽¹⁷⁾, where CO was shown to be almost exclusively bridge-bonded at $\Theta_{\text{CO}} = 0.2$, and mostly linear-bonded near saturation coverage. A quantitative comparison with the NMR results is not possible, however, since the dependence of the infrared absorptivity on coordination

geometry and coverage is uncertain. UV-Vis reflectance spectra on polycrystalline electrodes also support the formation of linear CO at high coverages and bridged CO at low coverages.^(19,20)

This same coverage dependence has been reported in electrochemical studies of polycrystalline platinum electrodes. Under certain conditions, the voltammetric oxidation peak for CO is resolved into two components, which were attributed to linear and bridged CO.⁽²¹⁾ By relating their relative integrated intensities to the amount of platinum surface covered by the adlayer, the authors were able to calculate both the total coverage by CO and the fractional coverage of each structure. These data are cross-plotted in Figure 4.23; note the identical trends of the linear and bridged populations with coverage to those shown in Figures 4.21 and 4.22. These researchers also observed that as the time of contact between dissolved CO and the electrode surface increased, the linear CO population dominated the surface until eventually bridged CO disappeared altogether ($\Theta_{\text{CO}} > 0.8$, not shown). Hence, seemingly "saturated" surfaces are able to crowd more CO on through conversion of bridged to linear structures. The changes in the lineshape of the saturated surfaces in Figure 4.11 are entirely consistent with this hypothesis - as CO is converted from the bridged to the linear structure, the center of mass of the spectrum moves downfield; with more CO able to occupy the surface, the area under the spectrum increases.

Consider also a previous study of adsorbed CO (ex-CH₃OH) on a fuel cell grade Pt black electrode in 0.5 M H₂SO₄.^(22,23) In this work, ¹³C NMR spectra of the surface adlayer were reported with an apparently potential-dependent center of mass and linewidth. Upon closer inspection, the surface coverage is seen to decrease as the potential becomes more anodic; hence, it can not be discerned whether the changes in the spectrum are potential- or coverage-induced. However, assuming minimal potential dependence (as supported by IRRAS on Pt(100)⁽¹⁷⁾), the trends with coverage are consistent with those observed in the present work - the center of mass shifts downfield and linewidth increases with increasing coverage. Those authors claimed the presence of two spectral components

Figure 4.23 Relative populations of linear (●) and bridged (○) CO on the surface of a polycrystalline Pt electrode as determined from multiple voltammetric oxidation peaks in reference 21.

based solely on the potential-dependence of the linewidth, and assigned the upfield component to linear CO, in contrast to the assignments made in section 4.5. However, since the surface adlayer was prepared by electrochemical decomposition of methanol, not by adsorption of dissolved CO, a direct comparison of the results is not advised. Furthermore, the apparent hysteresis observed in the literature when dosing surfaces with adsorbate and oxidatively stripping the surface of adsorbate should be acknowledged.^(16,17)

The difference in the lineshape behavior of the linear and bridged components may be indicative of the adsorption sites available to each structure. Studies of supported platinum particles have identified a distribution of Knight shifts across the particle surface, suggesting variations in the surface conduction-electron density.^(3,13,24) Thus, a distribution of ^{13}C Knight shifts for molecules in which the ^{13}C nucleus is bonded to the metal surface should also be expected. The lack of any discernible analytical form for the linear CO lineshape, as well as the variability of its center of mass with coverage, may point to such a distribution. The bridged structure, however, can be fit to a single chemical shift powder pattern Knight-shifted by ~ 150 ppm. This is consistent with the exclusive bonding of bridged CO on very well-defined sites, e.g. terraces, with the "filling in" of the remaining site population by the linear structure.

4.6.3 *Knight shifts and relaxation*

Linear and bridged carbonyls in organometallic platinum cluster compounds show ^{13}C NMR chemical shifts of 168 and 228 ppm, respectively.⁽²⁵⁾ Thus, given that the total shift is a sum of the chemical and Knight shifts, the latter can be estimated for the two structures to be around 150 ppm for bridged and 265-320 ppm for linear. This large difference between the two structures can be interpreted in terms of different degrees of mixing of the wave functions of the nucleus and the conduction electrons in the metal. One manifestation of this "Fermi contact interaction" is the spin-lattice relaxation; the Korringa equation^(26,27) provides the relationship between the Knight shift, K , and the relaxation

that must accompany it, characterized by T_1 :

$$T_1 T K^2 = \frac{h}{4\pi k_B} \left(\frac{\gamma_e}{\gamma_n} \right)^2 B \quad (4-5)$$

where k_B is Boltzmann's constant, T is the temperature, and γ is the magnetogyric ratio for the electron (e) and the nucleus (n). B is a correction factor for electron-electron interactions, typically close to unity. For ^{13}C , with $B=1$ and K expressed in ppm,

$$T_1 T K^2 = 4.16 \times 10^6 \text{ s K} \quad (4-6)$$

Values of T_1 calculated from equation 4-6 at 293 K are 0.63 s for the bridged component, and 0.14-0.20 s for the linear component. These relaxation times are close to the spin-lattice relaxation time of 0.33 s determined from a fit to the data in Figure 4.5. Using the T_1 values from equation 4-6 along with the relative fractions of linear and bridged CO from the NMR lineshape deconvolution, the relaxation behavior can be calculated with no adjustable parameters. Figure 4.24 shows that this calculated relaxation fits the data at least as well as the single exponential least-squares fit, suggesting that the Fermi contact interaction is indeed responsible for relaxation. The larger Knight shift for linear CO is consistent with a higher density of states at the Fermi level at the carbon nucleus for linear than for bridged CO at the aqueous-metal interface.⁽²⁷⁾ This fact may help explain why the linear structure is oxidized before the bridged structure in the partial stripping experiments. A more detailed look at the relaxation behavior, particularly its coverage-dependence, could both confirm the surface populations proposed from the lineshape data and yield further information on the nature of the bonding between the C and Pt nuclei.^(28,29)

4.6.4 Gaussian peak

The Gaussian component has until now been excluded from the discussion of CO

Figure 4.24 Comparison of best fit to single exponential relaxation, with $T_1 = 0.33$ s (solid line), to two component relaxation calculated using $T_{1,b} = 0.63$ s and $T_{1,l} = 0.17$ s, as determined from equation 4-6 (dashed line). Relative fractions of linear and bridged CO were obtained from lineshape deconvolution to be 0.568 and 0.432, respectively (data is from sample 1.1).

populations, primarily because of its relatively small contribution to the total intensity. This peak is centered near 250 ppm, shifted downfield from unbound CO (181 ppm) and CO₂ (133 ppm), and is seen in significant quantities only in the high coverage spectra.

Typically only the two CO structures are observed on platinum surfaces in electrochemical and UHV environments alike. Recently, however, evidence has begun to appear in the literature for a high coverage structure termed "weakly-" or "loosely-" bound on Pt-Sn alloy surfaces⁽³⁰⁻³³⁾; it has been proposed that this species results from the repulsive interactions of molecules on neighboring Pt atoms. Decreased heats of adsorption at high coverage indicate a weakened Pt-C bond, and the species would be expected to be highly mobile on the surface as a consequence. The Gaussian peaks in the present NMR spectra are wholly consistent with such a weakly bound CO species - a smaller Knight shift would be expected in the case of a weakened Pt-C bond, and the narrow peak width suggests a motional narrowing mechanism consistent with fast (on an NMR timescale) surface diffusion. It has also been proposed that the electrooxidation of the weakly-bonded species is facile, such a situation being of obvious interest for fuel cell research. Future NMR studies of adsorption on fuel cell electrocatalysts should pay close attention to the presence of this peak.

4.6.5 *Dynamics of the surface layer*

The ¹³C NMR spectra show some evidence of molecular motion of the adlayer that deserves further investigation. Most interestingly, the powder pattern assigned to bridge-bonded CO is flipped relative to those of solid state carbonyl cluster compounds and frozen carbon monoxide; that is, the sign of the anisotropy is the opposite of what is expected. Such a sign change can be effected by certain types of motion of the population on the surface, in particular, a flipping-type motion where the molecule fluctuates between two states.⁽³⁴⁾ This situation might be encountered in a dynamic exchange between bridged and linear adsorption states. The linear component of the lineshape also shows evidence of motional narrowing. In the absence of the additional broadening mechanisms of a Knight

shift distribution and magnetic susceptibility, the minimum linewidth of the linear component should be on the order of the chemical shift anisotropy. The anisotropy of terminal carbonyls in transition metal cluster compounds ranges from 220-295 ppm, with platinum expected to have a value near the low end of this range.⁽¹¹⁾ However, the approximate half-width of the linear component of the lineshape is on the order of 200 ppm, suggesting mobility of linearly bound CO at room temperature. The presence of both types of motion should be confirmed through low temperature experiments.

4.6.6 *Comparison of ^{13}C NMR spectra of adsorbed carbon monoxide at aqueous-metal and vacuum-metal interfaces*

There is much to be learned from a comparison of the lineshapes for ^{13}CO monolayers on Pt/C at the aqueous-metal interface and on Pt/ η -alumina at the vacuum-metal interface (Figure 4.25).⁽³⁾ The spectrum of the surface layer on the electrode is both narrower than and shifted downfield from the spectrum of the vacuum system. Furthermore, no changes with CO coverage have yet been reported at the Pt-vacuum interface. Possible explanations for these differences may be related to the support materials, the presence of the aqueous phase, and the differences in potentials at the metal surface in the two types of systems.

Additional information is provided by the aforementioned ^{13}C NMR of adsorbed CO (ex- CH_3OH) on fuel cell grade Pt black in aqueous H_2SO_4 .^(22,23) At high coverage, these spectra were centered around 300 ppm; hence, neither the aqueous environment nor the potential seem to be able to account for the difference in the peak positions between the aqueous and vacuum systems. This suggests a strong interaction between the electronically-conducting carbon support and the platinum particles that somehow enhances the metallic character of Pt relative to the alumina-supported catalyst, resulting in increased ^{13}C Knight shifts. ^{195}Pt NMR and ^{195}Pt - ^{13}C SEDOR (spin-echo double resonance) experiments on these materials, with a comparison to the platinum NMR literature on supported Pt catalysts^(24,35,36), could contribute significantly to understanding this issue.

Figure 4.25 Comparison of ^{13}C NMR lineshapes of CO on supported Pt catalysts at saturation coverage: Pt/C electrocatalyst in aqueous environment at open circuit potential near 0.35 V/SHE (solid line), Pt/ η -alumina with 76% dispersion (10 Å particle size) in vacuum from reference 3 (dashed line).

The widths of the two spectra in Figure 4.25 are vastly different as well, with the electrochemical system having a full width at half maximum (FWHM) of 210 ppm and the vacuum system having a FWHM of 330 ppm. Comparing the two, it is tempting to argue that this difference is due to differing site heterogeneity, with the conditions of the vacuum system providing an additional upfield component near 200 ppm. This would not sufficiently explain the presence of structure in the coverage-dependent lineshapes of the electrochemical spectra, nor would it address the lack of structure in the corresponding vacuum spectra. The Gaussian lineshapes obtained in the vacuum systems have been attributed to the magnetic susceptibility of the metal particles, as confirmed by the observation of varying ^{13}CO linewidths on particles of different, yet large susceptibility (Pt, Pd, Os, Ir).⁽³⁷⁾ The same mechanism does not appear to obscure the resolution of the lineshapes in the electrochemical system, and it can be argued that the rf-induced motion of conduction electrons in the particle should be strongly affected near the surface by the presence of oriented electric dipoles at the interface (the electrical double layer). Perhaps electronic motion is partially quenched by this strong capacitive element, thereby reducing the magnetic field distribution at the particle surface and reducing the broadening of the spectra. Indeed, in the Pt black study^(22,23) line narrowing was observed upon moving the electrode potential out of the hydrogen region into the double layer region. Again, it is not possible to separate the effects of potential and coverage in their data; susceptibility broadening might be expected to vary with coverage, although this is not apparent in the data in this thesis. However, the ionic strength of the electrolyte affects the properties of the double layer as well, such that susceptibility broadening should depend on acid concentration. A series of experiments with different electrolyte concentrations could be a key to settling this question.

4.7 Conclusions and recommendations for future work

The work contained in this thesis represents the first quantitative application of solid-state NMR spectroscopy to electrochemical systems. The key to the success of this study lies in the acknowledgment of the sensitivity of the NMR experiment to the conditions present inside the sample coil, specifically the consideration of the interaction of the magnetic field inside the coil with the conductive sample. Measurements of the probe circuit quality factor, Q , and the nutation of ^{13}C magnetization proved to be reliable indicators for the degree of coupling between the two. An electrode structure was introduced to minimize this coupling by eliminating azimuthal current paths within the coil volume.

This laminar electrode structure was utilized with a commercial supported platinum electrocatalyst to study carbon monoxide adsorption at the aqueous-metal interface at open-circuit potentials near 0.35 V/SHE. ^{13}C NMR of the adlayer at coverages below 0.3 yielded chemical shift powder patterns with a constant anisotropy and center of mass, suggesting the presence of a single CO structure at low coverages. The lineshapes broadened and shifted downfield with increasing coverage above 0.3, but could not be described by a combination of the low coverage powder pattern and a single additional component. The data are instead consistent with the introduction of an additional high-coverage structure subject to a Knight shift distribution, and quantitative analysis of the lineshapes provided coverage-dependent populations of the two structures.

The spectral components were assigned to bridged and linear CO by consideration of the coverage dependence of the anodic hydrogen voltammetry data. The bridged CO population calculated from these data compared well both qualitatively and quantitatively with the amount of adsorbate corresponding to the low coverage powder pattern. Likewise, the amount of linear CO determined using the electrochemical data and the amount of CO in the downfield spectral component showed excellent agreement.

This result demonstrates the potential power of combined electrochemical and NMR

measurements. The logical next step in experimental methodology is the control of the electrode potential during NMR acquisition, thus eliminating any ambiguity regarding potential and coverage effects while establishing NMR as a truly *in situ* tool for electrochemical systems. Extension of the present CO adsorption study to supported Pt-Ru and Pt-Sn electrodes could provide insight into the increased CO electrooxidation activity observed on these surfaces, while comparison to studies of adsorbates in the electrochemical oxidation of other oxygenated carbonaceous fuel molecules could provide a basis on which to interpret the results of the latter. The ultimate goal of electrocatalysis research is the design of better catalysts for electrochemical reactions; given its sensitivity to the electronic properties of the catalyst surface, and adsorbate structure and dynamics, NMR spectroscopy is now poised to play an important role in this respect.

4.8 References

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APPENDIX A

DETERMINATION OF PROBE CIRCUIT QUALITY FACTOR

Below the self-resonance frequency of the NMR sample coil, a simple analytical expression for the quality factor of the probe circuit, Q , is given by equation A-1:

$$Q = \frac{\omega L}{R} \quad (\text{A-1})$$

where ω is the angular frequency of the current, L is the inductance of the coil and R is the real resistance of the circuit.⁽¹⁾ Calculation of Q from equation A-1, however, is not possible without the additional measurements and assumptions required to determine L and R . For the case of conductive samples, the situation is further complicated by the dependence of both of these parameters on the sample conductivity.

A much easier determination of Q can be made from the behavior of a tuned, matched resonance circuit. A probe circuit is tuned such that the reactive component of the complex impedance disappears at or near the resonance frequency; thus, the phase of the circuit goes through a peak. Q is the ratio of the frequency at the peak maximum to the width of the resonance peak at 3 dB attenuation.⁽²⁾ By definition,

$$-3\text{dB} = 20\log\left(\frac{\Delta\Phi_{3\text{dB}}}{\Delta\Phi_{\text{max}}}\right) \quad (\text{A-2})$$

where the quantities $\Delta\Phi_{3\text{dB}}$ and $\Delta\Phi_{\text{max}}$ are defined in Figure A.1. For a $+90^\circ$ baseline, the values of the -3 dB phase points are given by equation A-3:

$$\Phi_{3\text{dB}} = 90 - 0.708\Delta\Phi_{\text{max}} \quad (\text{A-3})$$

Figure A.1 Definition of parameters used to calculate Q

The values of the upfield and downfield frequencies corresponding to Φ_{3dB} , v_1 and v_2 , were obtained using a Hewlett-Packard model 4173A vector impedance meter. The quality factor was then calculated from equation A-4:

$$Q = \frac{v_{max}}{\Delta v_{3dB}} = \frac{v_{max}}{v_2 - v_1} \quad (A-4).$$

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APPENDIX B

DERIVATION OF NUTATION FUNCTION FOR A CONDUCTING CYLINDER

The nutation function for a conducting cylinder is given by equation 2-4:

$$\frac{S(t_p)}{S_o(t_p)} = \frac{\int_0^{R_s} \sin(\gamma H_1(r, \theta, l) t_p) dV}{\int_0^{R_s} dV} \quad (2-4)$$

The field distribution inside the sample, $H_1(r, \theta, l)$, can be derived from Maxwell's equations. Faraday's and Ampere's laws are written in MKSA units as

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (B-1)$$

$$\nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} \quad (B-2)$$

The displacement field, $\vec{D}$, and the current density, $\vec{J}$, are both related to the electric field, $\vec{E}$:

$$\vec{D} = \epsilon \vec{E} \quad (B-3)$$

$$\vec{J} = \sigma \vec{E} \quad (B-4)$$

where ϵ is the dielectric constant, and σ is the electrical conductivity. Similarly, the magnetic induction, $\vec{B}$, is related to the magnetic field, $\vec{H}$, through the magnetic permeability, μ :

$$\vec{B} = \mu \vec{H} \quad (B-5)$$

In the general case, the properties ϵ , σ , and μ are tensors. For this derivation, however, the sample was assumed to be isotropic, reducing the tensors to scalar quantities.

The alternating fields in the conductor can be separated into spatial and time-dependent components:

$$\bar{E} = \bar{E}(r)e^{i\omega t} \quad (B-6)$$

$$\bar{H} = \bar{H}(r)e^{i\omega t} \quad (B-7)$$

Equations B-5, B-6 and B-7 can then be substituted into B-1, and equations B-3, B-4, B-6 and B-7 substituted into B-2. Combination of the two resulting equations yields a second-order equation in the spatial coordinates:

$$\nabla^2 \bar{H}(r) = (i\omega\mu\sigma - \mu\epsilon\omega^2)\bar{H}(r) \quad (B-8)$$

For a conductor, the displacement currents described by the real term in equation B-8 are usually negligible compared to the electrical currents given by the imaginary term.

Furthermore, the sample was assumed to be an infinite cylinder of angular symmetry; these considerations reduce the problem to a second order ODE in the radial coordinate, r :

$$r^2 H'' + rH' + r^2(-i\omega\mu\sigma)H = 0 \quad (B-9)$$

Equation B-9 is a form of Bessel's equation of order 0, with an imaginary parameter λ . A general solution is given as

$$H(r) = C_1 J_0\left(\frac{\sqrt{2}}{\delta} r e^{-i\frac{\pi}{4}}\right) + C_2 K_0\left(\frac{\sqrt{2}}{\delta} r e^{-i\frac{\pi}{4}}\right) \quad (B-10)$$

where J_0 and K_0 are Bessel functions of order zero, and δ is the skin depth. With the boundary conditions that $H_1(0)$ must be finite and $H_1(R_s)$ is equal to the field in an equivalent coil in the absence of the conductor, the solution for the field distribution inside the conductor becomes

$$\frac{H_1(r)}{H_1(R_s)} = \frac{J_0\left(\frac{\sqrt{2}}{\delta} r e^{-i\frac{\pi}{4}}\right)}{J_0\left(\frac{\sqrt{2}}{\delta} R_s e^{-i\frac{\pi}{4}}\right)} \quad (\text{B-11})$$

This function is plotted as Figure 2.9.

Substitution of equation B-11 into the nutation function, equation 4, yields

$$\frac{S(t_p)}{S_o(t_p)} = \frac{2}{R_s^2} \int_0^{R_s} \sin(\omega_n^* t_p) \frac{H_1(r)}{H_1(R_s)} dV \quad (\text{B-12})$$

where ω_n^* is the nutation frequency in the absence of the conductor, equal to $\gamma H_1(R_s)$.

This function is plotted as Figure 2.10.

APPENDIX C

DETERMINATION OF THE NUMBER OF ¹³CO MOLECULES IN A MONOLAYER

Following acquisition of the NMR spectrum of the saturated electrode (sample 3.1), the monolayer was oxidized galvanostatically at a current of 200 μ A while the electrode potential was monitored. Assuming a single oxidation reaction - that of CO to CO₂ - the current is divided between the oxidation reaction and the charging of the electrical double layer. These two processes show different E(t) behavior at constant current. In the absence of the faradaic reaction, double layer charging is characterized by a region of linearly increasing potential. When a potential is reached at which CO oxidation is kinetically favorable, the reaction becomes potential-controlling; ideally, E remains constant until the entire population of reactant is consumed.

This behavior is illustrated in the plot of E vs. t, Figure C.1. The amount of charge required for the double layer charging process, Q_{dl}, is determined from the slope of the linear region and is given by equation C-1:

$$Q_{dl} = \frac{I \cdot \Delta E}{\left(\frac{dE}{dt}\right)_o} \quad (C-1)$$

where I is the current, ΔE is the change in electrode potential over the course of double layer charging, and $\left(\frac{dE}{dt}\right)_o$ is the initial slope of the E(t) curve. Hence, any deviation from linearity is attributed to oxidation of the adsorbate. A least-squares fit to the first 30 minutes of data in Figure C.1 yields a slope of 2.0367 mV/min. The difference between Q_{dl} and the total amount of charge passed in the hold, I*t, yields the quantity of charge consumed by the oxidation of CO to CO₂, Q_{CO} (equation C-2):

$$Q_{CO} = Q_{tot} - Q_{dl} = I \left(t - \frac{\Delta E}{(dE/dt)_o} \right) \quad (C-2)$$

For CO oxidation, this amount of charge is converted by equation C-3 into the number of CO molecules consumed in the reaction:

$$N_{CO(ox)} = \frac{Q_{CO} N_A}{2F} = \frac{I * N_A}{2F} \left(t - \frac{\Delta E}{(dE/dt)_o} \right) \quad (C-3)$$

where N_A is Avogadro's number, and F is Faraday's constant, 96485 C/equiv. The factor of 2 is required since oxidation of a CO molecule requires 2 electrons. From the raw data, $\Delta E = 202$ mV and $t = 34200$ s, yielding $N_{CO(ox)} = 1.763 * 10^{19}$ molecules.

Upon complete oxidation of the monolayer, the potential should resume increasing linearly. However, this linear trend is not observed in Figure C.1, suggesting that the monolayer was not completely oxidized. Hence, the electrode was held at 200 mA for an additional nine hours. The $E(t)$ curve for this second hold experiment is shown in Figure C.2. Two linear regions are seen, separated by a potential plateau. From the first linear region, $(dE/dt)_o = 1.3326$ mV/min. The potential at which the second linear region is established is taken as the endpoint of CO oxidation. This occurs at 560 mV ($t = 338$ min), such that $\Delta E = 560 - 429$ mV = 131 mV. From equation C-3, the number of CO molecules oxidized in the second galvanostatic hold is $N_{CO(ox)} = 0.898 * 10^{19}$ molecules.

Hence, the total number of CO molecules oxidized from the surface of the saturated electrode is

$$N_{CO(ox)} = (1.763 + 0.898) * 10^{19} = 2.661 * 10^{19} \text{ molecules} \quad (C-4).$$

Figure C.1 Electrode potential during first galvanostatic hold at 200 μA .

Figure C.2 Electrode potential during second galvanostatic hold at 200 μA . Cut-off for CO oxidation was estimated to be 560 mV at $t=338 \text{ min}$.

APPENDIX D

ESTIMATION OF SPIN POPULATIONS

The raw ^{13}C NMR spectra presented in Chapter 4 consist of contributions from the ^{13}C -enriched surface adlayer as well as natural abundance carbon in the electrode materials and cell parts. Three main components have been identified and can be attributed to ^{13}CO adsorbed on the platinum particles, graphitized and partially graphitized support materials, and PTFE in the electrode and in the cell endcap.

The surface area of platinum has been determined by voltammetric sweeps of the anodic hydrogen region to be on the order of 3 m^2 . At saturation coverage, the ratio of the number of CO molecules to surface platinum atoms is typically 0.7. Assuming a surface density of 1.305×10^{15} Pt atoms/ cm^2 , this gives

$$N_{\text{CO}}^{\text{sat}} \approx (1.305 \times 10^{15} \frac{\text{surface Pt atoms}}{\text{cm}^2})(3.0\text{ m}^2)(100 \frac{\text{cm}}{\text{m}})^2 (0.7 \frac{\text{CO molecules}}{\text{surface Pt atoms}})(1 \frac{^{13}\text{C nucleus}}{\text{CO molecule}}) \quad (\text{D-1})$$

$$N_{\text{CO}}^{\text{sat}} \approx 2.7 \times 10^{19} \text{ } ^{13}\text{C nuclei}$$

The signal from the support materials arises from two sources, the Vulcan XC-72 carbon black and the graphitized carbon cloth. For simplicity, both are assumed to contribute to the peak at 175 ppm. The electrode contains 32.5 cm^2 of material with a metal loading of 2.0 mg/cm^2 . Since the catalyst powder is 20 wt.% platinum, there must be

$$m_{\text{C}}(\text{Vulcan XC72}) = (2.0 \times 10^{-3} \frac{\text{g Pt}}{\text{cm}^2})(32.5\text{ cm}^2)(4 \frac{\text{g C}}{\text{g Pt}}) \quad (\text{D-2})$$

$$m_{\text{C}}(\text{Vulcan XC72}) = 0.260\text{ g C}$$

assuming it to be 100% carbon. The graphite cloth has a specific mass of 116 g/m^2 , such that 32.5 cm^2 of the cloth has a mass of approximately 0.377 g . Hence, the total spin population of this signal component is

$$N_{\text{C(carbon)}} \approx (0.260 + 0.377 \text{ gC}) \left(\frac{1 \text{ mole}}{12.01 \text{ gC}} \right) \left(6.022 \times 10^{23} \frac{\text{C atoms}}{\text{mole}} \right) \left(0.01 \frac{^{13}\text{C nucleus}}{\text{C atom}} \right) \quad (\text{D-3})$$

$$N_{\text{C(carbon)}} \approx 3.2 \times 10^{20} \text{ } ^{13}\text{C nuclei}$$

PTFE is used as a binder for the electrode material and is present in approximately the same amount by weight as the catalyst powder itself (or, about five times the mass of Pt). Since PTFE is 24% carbon by weight, the mass of carbon in the binder is given by

$$m_{\text{c(PTFE binder)}} = (2.0 \times 10^{-3} \frac{\text{g Pt}}{\text{cm}^2}) (32.5 \text{ cm}^2) (5 \frac{\text{g PTFE}}{\text{g Pt}}) (0.24 \frac{\text{g C}}{\text{g PTFE}}) \quad (\text{D-4})$$

$$m_{\text{c(PTFE binder)}} = 0.078 \text{ g C}$$

The endcap of the cell was machined from PTFE and is situated near the end of the sample coil. The cap weighs approximately 2 g, and hence contains about 0.48 g of carbon. The total number of PTFE spins in the vicinity of the coil is therefore

$$N_{\text{C(PTFE)}} \approx (0.078 + 0.48 \text{ gC}) \left(\frac{1 \text{ mole}}{12.01 \text{ gC}} \right) \left(6.022 \times 10^{23} \frac{\text{C atoms}}{\text{mole}} \right) \left(0.01 \frac{^{13}\text{C nucleus}}{\text{C atom}} \right) \quad (\text{D-5}).$$

$$N_{\text{C(PTFE)}} \approx 2.8 \times 10^{20} \text{ } ^{13}\text{C nuclei}$$

APPENDIX E

CORRECTIONS TO NMR SPECTRA DUE TO VARIATIONS IN Q

The NMR signal amplitude is directly proportional to the field strength inside the sample coil, H_1 . Given that the probe circuit quality factor, Q , is essentially a ratio of the energy stored in the coil as H_1 to energy dissipated through resistance, any changes in H_1 are reflected both in the signal amplitude and Q . As discussed in Chapter 2 (see for example Figure 2.9), the use of electronically- and ionically-conducting materials renders the precise control of H_1 a difficult task in NMR; hence, this becomes a potential error source in the present set of experiments.

The quality factor was indeed observed to vary slightly between experiments, perhaps due to small variations in either the concentration of the residual electrolyte in the cell after exchange for water and D_2O , or the positioning of the electrode relative to the coil. In addition, Q was seen to vary over the course of a single acquisition. Specifically, the frequency response of the probe circuit was typically unstable upon insertion in the magnet, but was stable by the end of an acquisition; this suggests that thermal equilibration of the system be allowed before beginning an experiment. Regardless, the use of Q itself as a scaling factor for the NMR spectra is not appropriate since any correction should be made for variations in signal amplitude (an H_1 effect) and not the noise (a resistance effect). The measurement of Q can not distinguish between the two.

The background subtraction scheme, however, provides an appropriate scaling factor for the results. Difference spectra at each coverage were generated by subtraction of a background signal from a spectrum corresponding to the ^{13}CO -covered Pt surface. This background spectrum was the sum of 50,000 acquisitions - twice as many as for each coverage - and was necessarily scaled by a factor k , as determined by minimization of the

baseline error in the difference spectrum. Since the same background spectrum was used for each coverage, the factor k is actually a measure of the variation in signal amplitude between experiments, assuming that the chemical components of the background signal do not change between experiments. Values of k for each spectrum are listed in Table E.1 along with the measured values of Q . Figure E.1 shows the correlation between Q and k . Scatter in these data results from the variation of Q over the course of an experiment as well as the inconsistency of when Q was measured; i.e., at the beginning, middle, or end of an experiment. A trend is apparent nonetheless, justifying the use of k as a scaling factor for the spectra.

Figure E.1 Correlation between probe circuit quality factor, Q , and spectral scaling factor, k .

Table E.1 Scaling factors for each spectrum obtained from background subtraction.

spectrum	scaling factor, k	Q
1.1	0.73	135
1.2	0.72	136
1.3	0.67	134
2.1	0.76	150
2.2	0.79	142
2.3	0.76	150
3.1	0.88	154