First Observation of Platinum-195 Nuclear Magnetic Resonance in Commercial Graphite-Supported Platinum Electrodes in an Electrochemical Environment

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Figure 1. [195]Pt NMR spectra (8.47 T) of a commercial graphite-supported nanoscale platinum electrode (ref 16) under different surface conditions, at 80 K: (A) as-received; (B) electrochemically cleaned in 0.5 M H_2SO_4. The error bars represent the noise level.

There has recently been increasing interest in the use of solid-state nuclear magnetic resonance (NMR) spectroscopic methods to investigate fuel cell related electrocatalytic systems.[1−5] In each case, focus has centered on the investigation of the adsorbate (CO, CN) rather than the actual catalytic surface itself. At first glance this is perhaps surprising since over the past 15 years, [195]Pt NMR studies of oxide-supported platinum-based catalysts have made important contributions to our understanding of the electronic properties of these systems.[6] However, the NMR of platinum supported on a conducting material, like graphite, has been thought to be particularly challenging.[7] Indeed, the spectrum of platinum on carbon black[7] does not show the line shape expected from the corresponding particle size distribution obtained by electron microscopy.[8] Nevertheless, from the standpoint of fuel cell applications, it would be exceptionally desirable to make direct observations of [195]Pt NMR in actual fuel cell catalysts, since this should then lead to future detailed studies of electronic structure and bonding, including topics such as CO poisoning of platinum electrodes, and its improvement by "alloying" ruthenium to platinum.

As a first step toward the long-term goal of achieving a better understanding of CO tolerance in Pt/Ru fuel cell materials, we present the first observation of [195]Pt NMR in commercial, graphite-supported (Vulcan) nanoscale platinum electrodes (Pt/Vul) in an electrochemical environment. Electrochemically cleaned platinum electrodes in electrolyte solutions show [195]Pt NMR spectra characteristic of small platinum particles with clean surfaces, very similar to those obtained from typical gas-phase catalysts,[9−12] but the slow beat observed at the conventional surface peak position (1.100 G/kHz) indicates that the Ruderman−Kittel−Kasuya−Yosida (RKKY)[13−15] *J* coupling is almost twice that seen in the gas-phase case, which suggests a
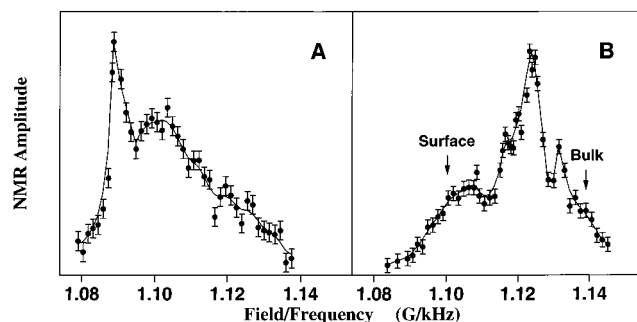
major enhancement of the s-like local density of states at the Fermi level (E_f-LDOS).

We show in Figure 1 the point-by-point [195]Pt NMR spectra of as-received (Figure 1A) and of electrochemically cleaned electrode materials (Figure 1B), obtained by manually sweeping the spectrometer frequency. The effects of surface treatment can be clearly seen from the change in the NMR spectra (Figure 1A,B). We believe that the surfaces of as-received samples, as has been found previously in platinum catalysts on oxidic supports,[17] are completely coated by oxygen and/or OH groups, since the low-field peak in Figure 1A at 1.089 G/kHz coincides exactly with that of PtO_2,[17] and spin−lattice relaxation rate measurements (data not shown) are also very similar.[18] The slowly diminishing tail toward the high-field or bulk platinum position (1.138 G/kHz) suggests that the sample also contains relatively large particles. After electrochemical cleaning, the sample shows an NMR line shape characteristic of (though not exactly the same) those found (in gas-phase studies) for supported Pt catalysts having a similar particle size, about 2.5−4.8 nm, with nominally clean platinum surfaces.[19] This great similarity to the gas-phase results suggests that most likely the interpretation of [195]Pt NMR spectra in electrolyte solutions can follow along the lines developed previously for the gas-phase systems. That is, the low-field signals (around 1.100 G/kHz) come from surface platinum atoms, while the high-field signals come from the atoms *inside* the platinum particles. There is, however, one significant difference: instead of being centered at the bulk Pt position (1.138 G/kHz in the gas-phase case), the bulklike high-field peak in Figure 1B has shifted to a much lower field position, 1.123 G/kHz, and the spectrum shows more structure in this region than in the gas-phase case. Since the Knight shift of a given platinum atom in a small particle is determined by the sum of the positive (s-like) and the negative (d-like) hyperfine interactions,[20] this low-field shift of the bulk peak may be understood as an enhancement of the s-like local density of states at the Fermi level (E_f-LDOS), and/or a de enhancement of the d-like E_f-LDOS.

We show in Figure 2A (solid circles) the results of spin−spin relaxation (T_2) measurements carried out at the surface position, 1.100 G/kHz, also at 80 K. The solid line is the

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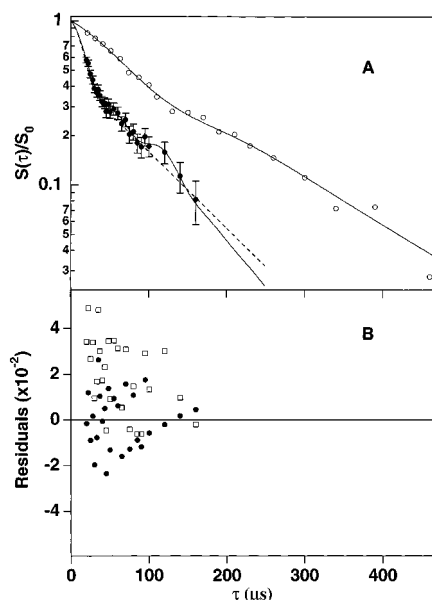(23) Tong, Y. Y.; van der Klink, J. J. Unpublished results.

Figure 2. (A) Spin−spin (T_2) relaxation results at the surface position (1.100 G/kHz) and at 80 K, for ^{195}Pt in the graphite-supported electrochemical environment (Pt/Vul, solid circles) and in a polymer-protected Pt system (Pt/PVP, open circles). The solid lines are the correponding six-parameter fits, and the dashed line is the constrained fit (see text for details). All simulation parameters are shown in Table 1. **(B)** Residuals $(S_{exp}(\tau) - S_{fit}(\tau))/S_0$ for free (solid circles) and constrained (open squares) fits for the electrochemical system (Pt/Vul).

Table 1. Fitting Parameters Used in Data Simulations

sample	$J/2\pi$ (kHz)	T_2 (μs)	T_{2j} (μs)	B_0	B_1	B_2	rms (%)
Pt/Vul	8.0	146	126	0.69	0.21	0.10	1.2
Pt/PVP	3.2	301	178	0.81	0.19	0.0	1.3
Pt/Vul	4.2 (fixed)[a]	187	29	0.50	0.29	0.21	2.5

[a] $J/2\pi$ was fixed at 4.2 kHz, while the other five parameters were freely variable.

theoretical fit to the equation derived in ref 21 , which is

$$S(t)/S_0 = \exp(-2\tau/T_2)\{B_0 + \exp(-(\tau/T_{2j})^2)[B_1 \cos J\tau + B_2 \cos 2J\tau]\} \quad (1)$$

where J is the RKKY coupling constant, τ is the variable interval between the two rf excitation pulses, T_{2j} is the spin−spin relaxation time due to the distribution of J couplings, and B_0, B_1, and B_2 are the fractional amplitudes of different components. The fitted parameters are $J/2\pi = 8.02 \pm 0.28$ kHz, $T_2 = 148 \pm 6$ μs, $T_{2j} = 126 \pm 30$ μs, $B_0 = 0.69 \pm 0.02$, $B_1 = 0.21 \pm 0.02$, and $B_2 = 1 - B_1 - B_0 = 0.10$ (Table 1).

The most remarkable observation is that the RKKY J coupling constant appears to increase from the conventional value of ~4.2 kHz (seen inside Pt particles[21] and some Pt alloys,[22] to ~8 kHz, in the electrochemical environment. Interestingly, we have also deduced a similarly small RKKY J coupling at a clean platinum surface, using a poly(vinylpyrrolidone) (PVP) polymer-protected system.[23,24] This clean surface shows Korringa behavior over the whole spectrum, and yields $T_1/T_2 = 3.70 \pm 0.59$ at 80 K,[23] a value very close to that which has been found for the metallic spectral region (1.100−1.140 G/kHz) for the oxide-supported systems studied previously.[25] Thus, the electrochemically cleaned surfaces in the electrolyte solution appear to have much larger RKKY J couplings than seen for either supported

platinum particles, platinum alloys, or polymer-protected clean, supported Pt particle surfaces. But how reliable are these conclusions?

Since there are several adjustable parameters which need to be fitted by using eq 1, we tested the hypothesis that J might actually be 4.2 kHz in the electrochemical environment, by constraining $J/2\pi = 4.2$ kHz, while allowing the other five parameters to vary freely (Table 1). As can be seen in Figure 2A, the beat in the echo decay cannot be reproduced using this constrained fit, and as shown in Figure 2B, the residuals between the constrained and unconstrained fits are clearly much larger in the case of the constrained fit (Figure 2B and Table 1). The rms errors for the Pt/Vul and Pt/PVP systems (Table 1) are ~1.2−1.3%, while in the case of the contained fit the rms error doubles, to 2.5%.

The very different results found between Pt/Vul and Pt/PVP strongly support the notion that the "clean" surface Pt atoms in the electrochemical environment experience major changes in electronic structure when compared to conventional "gas-phase" systems. By constraining $J/2\pi = 4.2$ kHz, the rms of the fit becomes much worse (see Table 1), and in addition, it also gives an unreasonably short T_{2j} and cannot describe the oscillatory features of the experimental data. The large enhancement of the RKKY J coupling indicates a major enhancement of s-like E_f-LDOS.[24,26] Furthermore, preliminary results in a D_2O-exchanged electrolyte (data not shown) strongly suggest that protons in H_2O do not play an important role in shortening T_2, which may also be explained by the enhancement of s-like E_f-LDOS. We also find for a sample having an average particle size of 8.8 nm, that the bulklike peak appears exactly at the conventional position of 1.138 G/kHz, which is not the case for the current sample. For smaller particles, the enhancement of s-like E_f-LDOS at the surface can be seen by most of the Pt atoms in a particle and results in the downfield shift of the bulklike peak observed in Figure 1B. The reason for this enhancement is probably related to the lowering of the electrode surface potential (by ca. 1−1.5 V) in the electrolyte versus that found in vacuo,[27,28] since lowering the surface potential will lower the work function value, ϕ, and enhance the E_f-LDOS at the electrode surface, when immersed in the electrolyte.[29]

In summary, the results we have reported above are of interest for two main reasons. First, they represent the first observation of ^{195}Pt NMR of electrochemically cleaned graphite-supported platinum electrodes under electrolyte solution conditions. This is of importance for future studies of real-world fuel cell catalysts. Second, at the more fundamental level, we observe a major enhancement of s-like E_f-LDOS at the electrode surface under wet conditions, as indicated by the increase in RKKY coupling and a low-field shift of the surface peak, consistent with a lowering of the surface potential in the electrolyte versus in vacuo. The way is therefore now open to study, using NMR techniques, both adsorbates *and* electrode surfaces at electrified interfaces, including the effects of external potential control.[4]

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