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Instrumental Design and Prospects for NMR-Electrochemistry

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Summary

We describe the design, construction and operation of two types of nuclear magnetic resonance (NMR) sample probes for use in electrocatalysis/surface NMR studies. The first is an NMR-electrochemical cell, which permits observation of NMR signals of surface adsorbed species under external potential control. This cell also permits conventional voltammograms to be recorded from the actual NMR sample. The second or "mini-cell" has a long, thin sample region and better sensitivity than the NMRE cell, but is not capable of voltammetry. Spectra have been obtained for ^{13}CO, $^{13}CN^-$ and $C^{15}N^-$ adsorbed on polycrystalline platinum black, as a function of applied potential, demonstrating the feasibility of multinuclear NMR studies at electrified interfaces.

1. INTRODUCTION

The use of spectroscopic techniques to investigate the structures of and reactions at the solid-liquid interface in electrochemical systems is an area of rapid progress [1]. However, because many conventional surface techniques are difficult to apply in these systems directly, there is a growing need to develop new approaches to structure determination, especially in systems of potential technological importance such as fuel cells. Nuclear magnetic resonance (NMR) spectroscopy, which has a long history in solid-gas interfacial studies, is one technique which can, in principle, give substantial amounts of information about the solid-liquid interface, and previously some preliminary results were reported [2,3], showing feasibility.

The strengths of NMR lie in the detailed types of information which can be derived. These include structural and motional information with regards to the adsorbate being studied, e.g., what is the adsorbate [4]? Is there any motion such as diffusion or internal motion? Furthermore, in the case of adsorbates on metals, information regarding the electronic environment can also be obtained from the Korringa relation [5], which in suitable situations can be related to densities of states at the Fermi level. Thus, the use of NMR to study adsorbates at the electrochemical solid-liquid interface represents a logical and systematic progression in the

investigation of adsorbates on heterogeneous catalysts. The study of CO, adsorbed from the gas phase (solid/gas interface), on supported catalysts has received considerable attention previously [6,7], and the methodologies in this area, at least from the NMR perspective, should be directly transferable to the solid-liquid interface. To illustrate this, such information has already been determined for electrochemically prepared *sealed* samples [8], where from T_1 data, it has been determined that the type of adsorbate derived from the electrodecomposition of methanol on polycrystalline (PC) platinum occupies a single adsorption site, regardless of the decomposition potential or surface coverage.

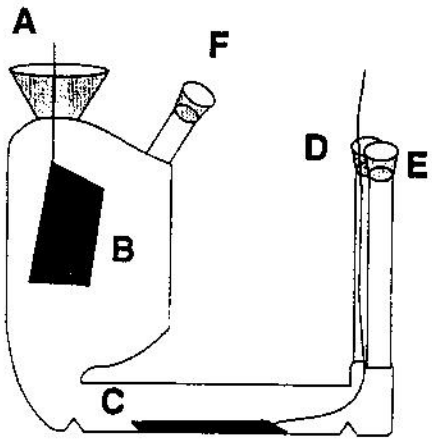
In this paper, we present recent work on the development of the NMR-electrochemical (NMRE) cells for the study of electrode adsorbates as a function of applied potential. A number of novel design features permit the routine and reliable detection of adsorbed species, such as ^{13}CO (ex MeOH) and CN^- on fuel cell grade platinum black. Much higher sensitivity than previously reported is possible with our new instrumentation, which permits the recording of NMR frequency shifts as a function of applied potential. While previous work from this laboratory demonstrated the feasibility of these techniques, it was limited in results and applicability in that the previous designs could only *maintain* the potential of the adsorbate during the NMR measurements, and sample preparation was accomplished in a separate cell suitable for the rigors of cyclic voltammetry. This restricted application to adsorbates which could withstand being transferred from a preparation cell into the NMRE cell. The older versions of the NMRE cell also suffered from poor sensitivity and required $>10^5$ transients for modest signal to noise ratio spectra. Finally, the old designs suffered from joints and Teflon stoppers that were positioned below the electrolyte level, and often leaked, thus placing time constraints on spectral measurements, preventing the lengthy and elaborate NMR experiments required for detailed structure/dynamics characterization from being performed. The new cells permit routine operation as a function of applied potential, and forms the basis for an even higher field (600 MHz, 14 Tesla) system under construction.

2. INSTRUMENTATION

2.1 The NMRE Cell.

Our recent improvements in instrumentation are centered around the new NMRE cell (**Figure 1**). This cell has been designed to allow for sample preparation and signal acquisition to occur

without interruption of circuit continuity, since it is now possible to prepare samples within the probe, then immediately begin NMR measurements. The large electrolyte reservoir, which houses the counter and reference electrodes, provides ample electrolyte for complex and lengthy measurements to be made, without solvent evaporation. The location of the PC platinum black powder is within the long sample region of the NMRE cell (**Figure 1A**). The sample cell is wrapped with a copper wire (NMR coil) which serves for both excitation and signal acquisition (**Figure 1B**). The NMRE cell incorporates the ability to exchange the electrolyte without removing the probe containing the NMRE cell from the magnet. When directly connected to a potentiostat, use of the NMRE cell requires electronic filtering of the electrochemical leads entering the probehead, in order to eliminate environmental radiofrequency pickup which would otherwise be introduced (See section 2.3).



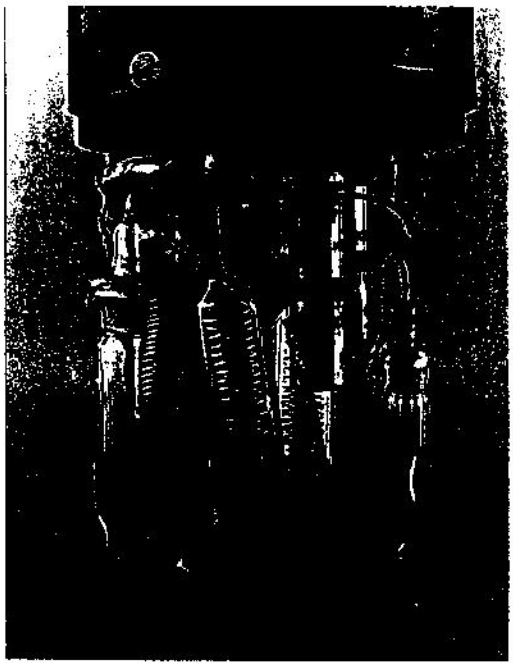
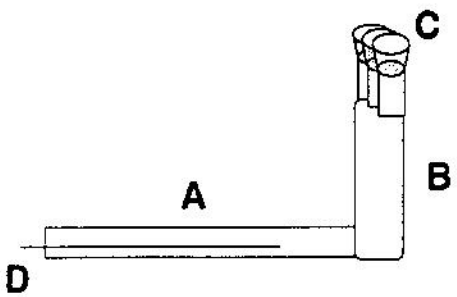


Figure 1. A: Diagram of NMRE cell. A: The counter electrode, encased in a 14/20 male joint. B: Upper electrolyte reservoir. C: Sample chamber for Pt-black. D: Working electrode lead connected to Pt gauze in sample chamber. E: Vacuum/waste Luer connection. F: Reference electrode Luer connection. **B:** Photograph of the assembled NMRE probehead.

2.2. The Mini Cell.

The second type of cell we have used for our studies of species adsorbed onto platinum black is the "mini-cell" [9]. The mini-cell has higher sensitivity over the NMRE cell due to an enhanced filling of the rf coil. The trade off is that the mini cell cannot be used directly in sample preparation, since it is difficult to obtain a voltammogram with this configuration. This limits its use to adsorbates that can withstand transfer from a more conventional "powder" electrochemical cell. The mini-cell has been used with and without electrochemical-lead filtering during signal averaging. We found that it was unnecessary to use rf filters for carbon-13 NMR signal acquisition from enriched sodium cyanide ($^{13}CN^-$) adsorbed onto PC platinum black, but for less sensitive nuclei such as nitrogen-containing adsorbates ($C^{15}N^-$), rf filtering is essential. Clearly, more complex features such as skin depth, rf penetration and sample granularity also affect sensitivity, the main point being that even in a "harsh" environment, external rf pickup can be greatly reduced even with electrodes being in direct contact with the NMR sample during data acquisition.



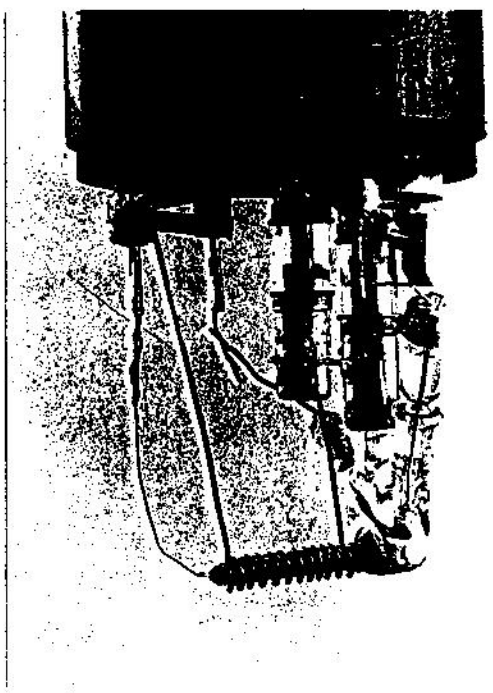


Figure 2. A: Diagram of the mini cell. A: Sample chamber. B: Electrolyte reservoir. C: Ports for counter and reference electrodes. D: Platinum wire for contact with the platinum black sample. **B:** Photo of mini-cell probehead set for nitrogen-15 NMR data acquisition.

2.3. The NMR Probes.

Both the NMRE cell and the mini-cell require a custom built probe (**Figure 3**) in order to be loaded into the NMR spectrometer. The probe is designed for an 8.45 Tesla (360 MHz) wide bore (89 mm) superconducting magnet, and is loaded into the top of the magnet with the center of the sample positioned at the magnetic center. The electrochemical leads are connected to 0.141 inch diameter semi-rigid coax, which are part of the probe, by BNC connectors. The semi-rigid coax runs the length of the probe and enters into the probehead where the NMRE cell/mini-cell is located. LC low pass filters are installed at this point (**Figure 1B** and **Figure 4**). These filters serve the dual purpose of minimizing the introduction of environmental noise, which can be transmitted through the electrochemical leads, plus they also act as rf chokes in the reverse direction, preventing the leakage of high power excitation pulses out into the potentiostat. The optimal arrangement of the LC circuit is determined experimentally, and can be done on a bench top with an oscilloscope and a frequency sweeper. Care must be taken to insure that the filter's inductor is not self resonant at the Larmor frequency of the nuclei under investigation, or tuning problems arise due to multiple resonances in the probes' LC circuit. In the case of carbon-13 NMR at 8.45 T, the inductors are tuned to resonate at around 150 MHz. This prevents multiple tuning resonances at 90 MHz, yet provides sufficient impedance to block the rf power from shunting out of the electrochemical leads.

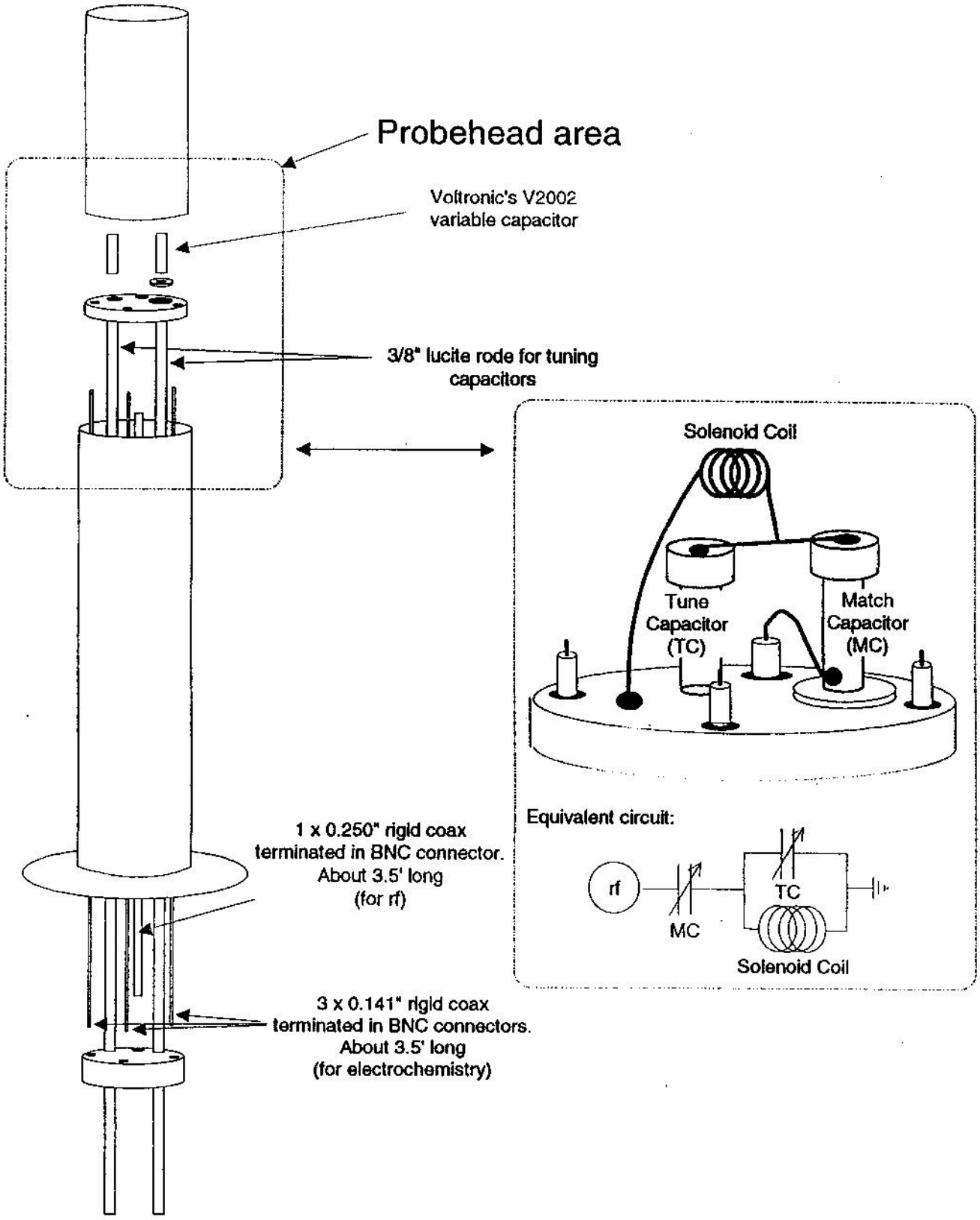


Figure 3. Schematics of the NMRE probe and circuitry. The probes' casing and cap are made of brass. All the internal pieces are made of copper.

2.4. The NMR Spectrometer.

The techniques and equipment necessary for solid-liquid interface surface adsorbate NMR signal acquisition are those typically used in solid state NMR at the solid-gas interface. The frequency domain linewidths of typical ^{13}C or ^{15}N signals (^{13}CO, ^{13}CN, $C^{15}N$) on platinum at 8.45 Tesla signal are between ~20 and 30 kHz (full width at half maximum), requiring fast digitization for faithful reproduction of the rapidly decaying signal in the time domain (~1 to 5 μsec dwell times). At present, we are using the following equipment: for digitization, a Nicolet Explorer IIIA fast digitizer; for pulse control and data acquisition and transformation, a Nicolet 1280 computer system. The magnet is a wide bore (89 mm) Oxford superconducting magnet. The 90° pulse width used for $^{13}CO/Pt$ (NMRE cell) is 10 μsec, for ^{13}C of cyanide (mini cell) it was 3.5 μsec, and 7.5 μsec for ^{15}N of cyanide (mini cell). Signal acquisition is accomplished by applying a Hahn spin-echo sequence followed by a signal acquisition period: [$\pi/2$-τ_0-π-τ_1-acquire] - where $\tau_1 < \tau_0$ so that acquisition begins before the echo maximum. Typical values for τ_0 are in the range of 25 - 40 μsec. The precise echo maximum is located prior to Fourier transformation.

The fact that the echo decays very rapidly in the time domain leads to a problem common in solid state NMR work: the appearance of a "pulse feedthru". This artifact results from the recovery of the receiver circuits and a ring down of the transmitter and probe circuits after the high-power excitation pulses. To reduce this problem a pulse sequence used to eliminate "ringdown" in quadrupolar echo NMR was employed [10]. In this sequence, the phase of the $\pi/2$ and the π pulses of the Hahn-echo sequence are varied such that the artifacts add destructively and are essentially eliminated.

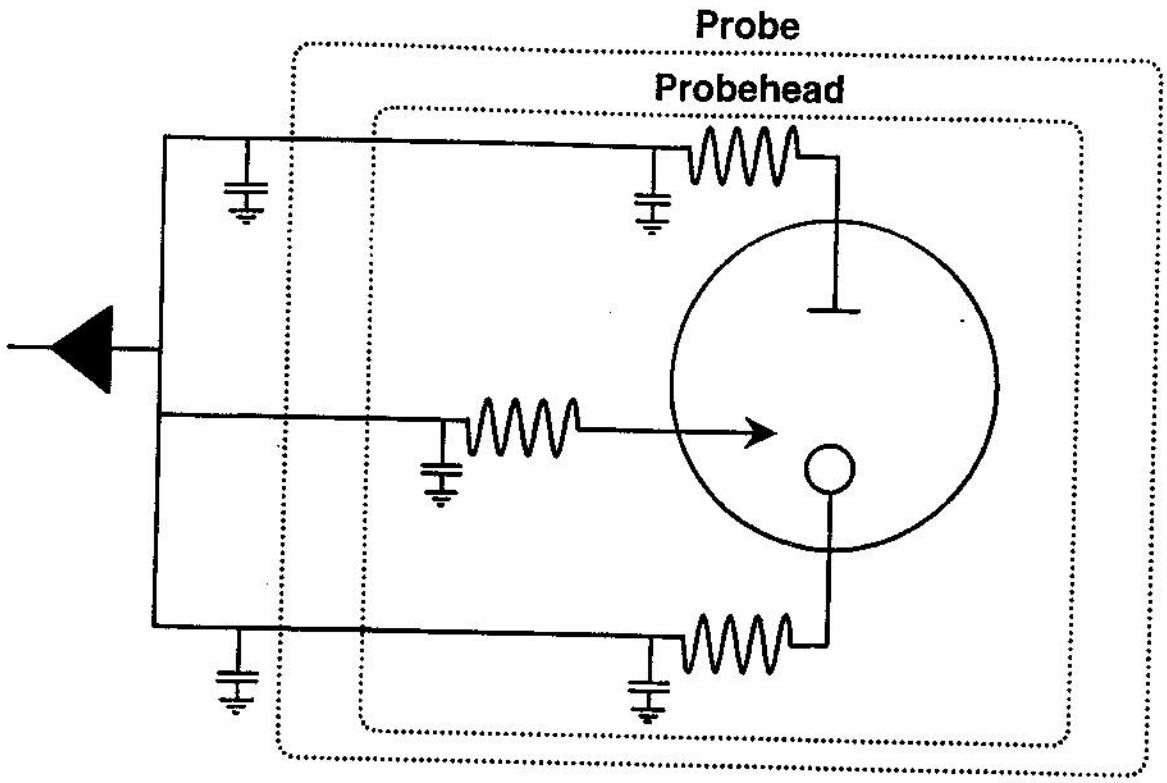


Figure 4. Schematic of the lowpass filters used to enhance signal-to-noise ratio and prevent excitation power from shunting out the electrochemical leads. **Table 1** lists the configuration of the tuning elements

Table 1: Configuration of filter elements.

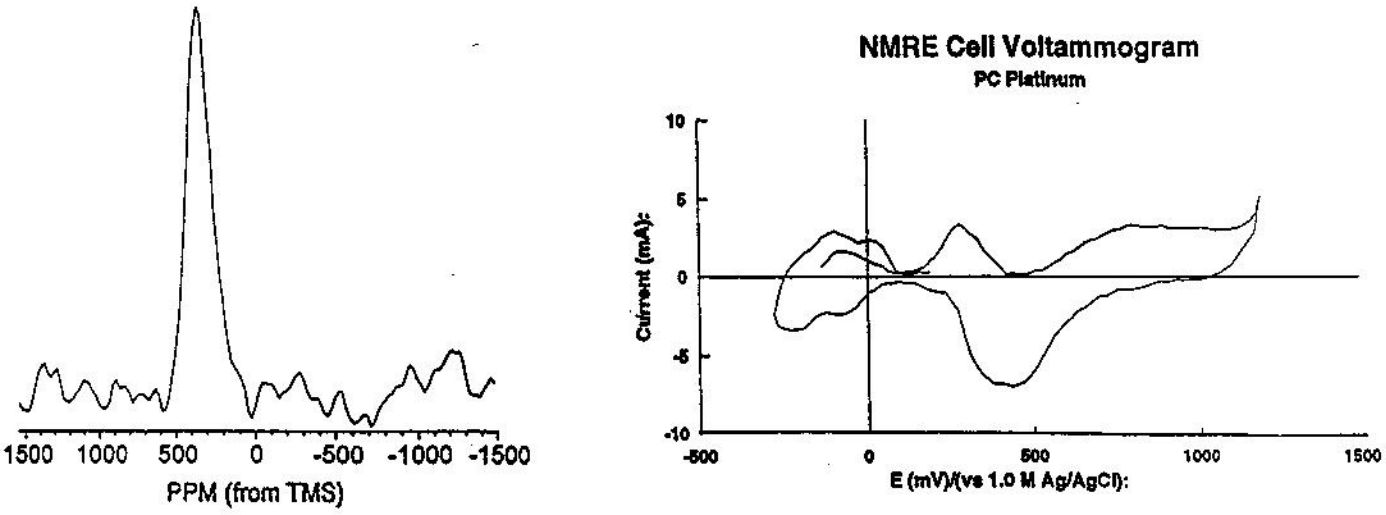
	^{13}CO (90 MHz)				$C^{15}N$ (36 MHz)			
	Probehead		Probe Input		Probehead		Probe Input	
Electrode:	L(μH):	C(pF):	L(μH):	C(pF):	L(μH):	C(pF):	L(μH):	C(pF):
Working	1.1	680	-	-	8.0	680	-	300
Reference	1.1	680	-	-	11	-	-	-
Counter	1.1	680	-	-	3.5	680	-	330

3. EXPERIMENTAL RESULTS

A typical spectrum of ^{13}CO derived from the decomposition of ^{13}C enriched methanol on PC platinum black is shown in **Figure 5A.** **Figure 5B** shows the first electrochemical cycle after methanol decomposition, followed by rinsing, without circuit interruption. The voltammogram

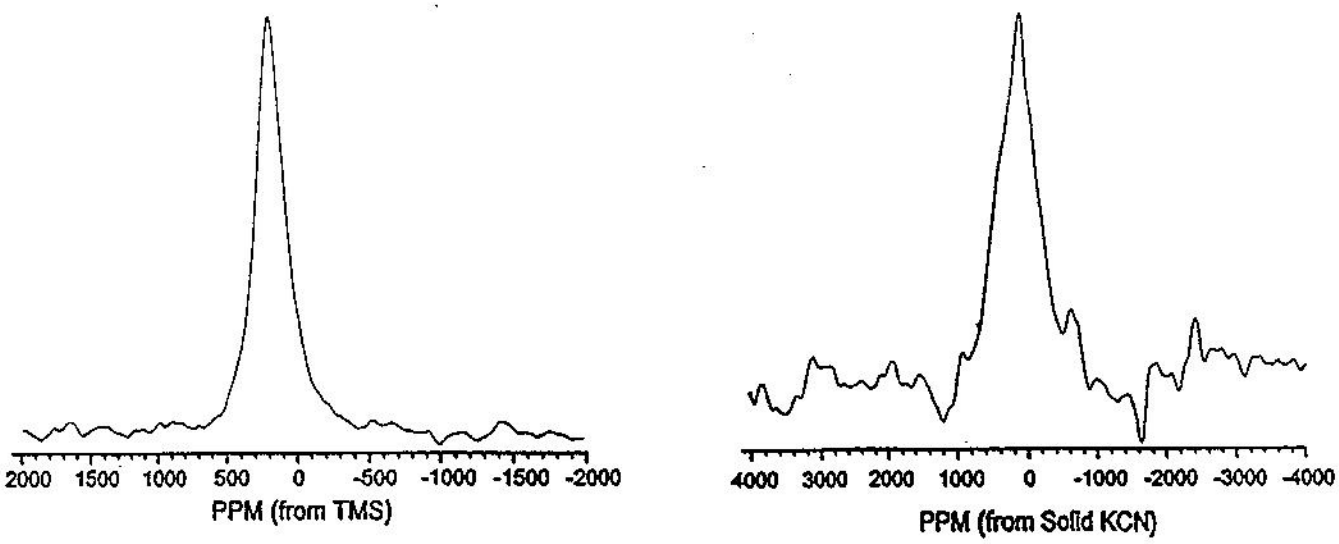
is used to determine surface coverage from the CO → CO_2 oxidation peak at around 400 mV (versus a Ag/AgCl reference electrode, in 1.0 M NaCl). Typical mini-cell NMR spectra for carbon-13 and nitrogen-15 labeled CN^- on platinum black are shown in **Figure 6.**

Using the NMRE cell, the potential dependence of the frequency shift for CO and CN on platinum black are currently being investigated. Data such as these will then be used as a basis for modeling how chemical shifts and electronic structure may be influenced by an applied electric field.



(A) (B)

Figure 5. (A) A typical ^{13}CO-Pt-black spectrum with a 0.0 V applied potential at 8.45 Tesla, 13200 transients, S/N ratio = 14.0:1. (B) CV after NMR measurements, taken at 0.1 mV/sec (see Text).



(A) (B)

Figure 6. (A) A spectrum of ^{13}CN-Pt-black in the mini-cell, 3000 transients, S/N ratio = 36.2:1. (B) A spectrum of C^{15}N-Pt-black in the mini-cell, 20000 transients, S/N = 9.4:1.

4. CONCLUSIONS

The results we have presented above show that quite high sensitivity ^{13}C and ^{15}N NMR spectra of species adsorbed at a solid-liquid interface can now be obtained. The ability to prepare samples, record cyclic voltammograms, and to obtain surface NMR spectra under potential control opens up new avenues for NMR at the solid-liquid interface in general, and at electrified interfaces in particular. The signal-to-noise ratios obtained at 8.45 Tesla enable initial studies of T_1 and T_2, and as we note below, will be greatly facilitated in the future via higher-field operation.

5. FUTURE RESEARCH

Studies using the present NMRE cell designs are practical for many types of adsorbates containing magnetically active nuclei such as ^{1}H, ^{2}H, ^{13}C, ^{15}N, ^{17}O, ^{103}Rh, ^{195}Pt, etc. Plans are under way in this laboratory for studies of the static and dynamic structure of CO on binary and

ternary alloys (e.g., ruthenium/platinum/tin) in methanol for fuel cell applications. Such alloys display enhanced resistance to CO poisoning, and the nature of this resistance is appropriate for NMR investigation. For example, Pt-CO bonding information such as Pt-C connectivities, CO orientation and clustering, are accessible by T_1, T_2, isotope dilution, and related techniques. In fact, essentially all of the techniques used in the past 20 years to study the solid-gas interface should now be applicable to NMR-electrochemistry, with the added bonus of potential control.

Work in this area is, of course, not limited to using Pt-black as the electrocatalyst. Virtually any electroactive catalyst, such as gold, rhodium, or palladium, which can be prepared with a particle size small enough to provide the necessary surface area and rf penetration, can be investigated.

6. ACKNOWLEDGMENTS

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7. REFERENCES

[1] Electrochemical Interfaces - Modern Techniques for In-situ Interface Characterization, Ed. H. D. Abruña, VCH, New York, 1991.

[2] P. J. Slezak, A, Wieckowski, J. Electroanal. Chem. 339, 401 (1992).

[3] P. J. Slezak, A. Wieckowski, J. Magn. Reson. 102, 166 (1993).

[4] W. Kolodziejski, J. Klinowski, in *NMR Techniques in Catalysis*; Bell, A. T.; Pines, A., Eds.; Marcel Dekker: New York, New York, 1994; p 3.

[5] Korringa, J. Physica 16, 601 (1950).

[6] J. P. Ansermet, C. P. Slichter, J. H. Sinfelt, Progress in NMR Spectroscopy, 22, 401 (1990).

[7] T. M. Duncan, J. Phys. Chem. 16(1), 125 (1987).

[8] J. Day, P. A. Vuissoz, E. Oldfield, A. Wieckowski, J-Ph. Ansermet, Manuscript in preparation.

[9] K. Franaszczuk, J. Wu, J-Ph. Ansermet, J. Day, B. Montez, E. Oldfield, A. Wieckowski, J. Chem. Soc., Faraday Trans. I, submitted.

[10] A. C. Kunwar, G. L. Turner, E. Oldfield, J. Magn. Reson. 69, 124 (1986).