

**Studies of Electrochemical Interfaces by the Use of  
EC-NMR (The D. C. Grahame Award lecture.)**

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EC-NMR, the technique developed at Urbana-Champaign in the early 1990s [1], permits detailed electronic-level studies of solid/liquid electrochemical interfaces under potentiostatic control in the presence of electrolyte. The uniqueness of this technique is its sensitivity to chemical and electronic structure, both long-range and local, and the relative ease in providing spectroscopic signatures specific to surface motions. Those features, when combined with results of electrochemical measurements, enable access to chemical information on Fermi-level local density of states (Ef-LDOS) of both metal surfaces and adsorbates, together with new insights into surface diffusion of adsorbate species. However, in this presentation, we will investigate nanostructured platinum electrodes, clean and covered by ruthenium via the spontaneous deposition method, by using EC-NMR and cyclic voltammetry (CV). Surfaces were covered by CO (<sup>13</sup>C enriched) adsorbate, as the probe of surface properties, either from methanol or CO saturated solutions. The CV and EC-NMR results give evidence for two types of adsorbed CO on essentially pure Pt and on the Pt/Ru islands. CO molecules on the primarily Pt domains behave much like CO on pure Pt, there being little effect of Ru on the Knight shift or on Korringa relaxation. Major alteration of the surface CO behavior however is observed on the Ru islands. We will show that in addition to the “bi-functional” mechanism of the CO oxidation, there exist major cooperative electronic and surface dynamic contributions to the oxidation process. We will conclude that adding ruthenium to the platinum catalyst reduces Ef-LDOS, weakens the Pt-CO bonding, activates water on the surface, and increases the rate of CO surface diffusion on the Ru part of the Pt/Ru surface. Also, discussion of the following topics will be presented: (i) <sup>195</sup>Pt-metal NMR; (ii) Fermi level local densities of states in studies of nanoparticle systems, and (iii) studies of correlations between infrared and EC-NMR data. The combined EC-NMR/electrochemistry approach thus provides new insights into electrochemical surface science of the nanoparticle surface, and helps develop better understanding of critical issues in heterogeneous electrocatalysis [1-5].

Typical references:

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3. P.-A. Vuissoz, J.-Ph. Ansermet, A. Wieckowski, *Phys. Rev. Lett.*, 83, 2457 (1999). “Probing by NMR the Effect of Surface Charges on the Chemisorption Bond”.
4. Y. Y. Tong, H. S. Kim, P. K. Babu, P. Waszczuk, A. Wieckowski, E. Oldfield, “An NMR Investigation of CO

Tolerance in a Pt/Ru Fuel Cell Catalyst”, *J. Am. Chem. Soc.*, 124, 468, 2002.

5. P. K. Babu, Y. Y. Tong, H. S. Kim and A. Wieckowski, *J. Electroanal. Chem.*, 524/525, 157-167 (2002), “Nanostructured electrode surfaces studied by electrochemical NMR”.