

Nuclear Magnetic Resonance at an Electrochemical Interface: EC-NMR

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Past development of nuclear magnetic resonance spectroscopy at electrochemical interfaces, i.e., EC-NMR, will briefly be reviewed. EC-NMR 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 the results of electrochemical measurements, enable access to chemical information on Fermi-level local density of states (E_F -LDOS) of both metal surfaces and adsorbates, together with new insights into surface diffusion of the adsorbate species. Such detailed information may not only test modern quantum theories of heterogeneous catalysis, but may also provide new guidelines for designing better catalysts, especially for the fuel cell use.

Following a triggering activity [1], and some previous work [2], several years of active research by three research groups: at Urbana-Champaign [1-14], Berkeley [15,16] and at Lausanne, Switzerland [3,17,18] have contributed to obtaining an enhanced understanding of several critical issues in electrochemical surface science with platinum (and also palladium [18]) nanoparticle electrodes in the metal NMR perspective. Specific accomplishments include:

1. Electrode potential dependent NMR spectra of ^{13}C -enriched adsorbates were measured [1] and interpreted [3,7]. (Previous work was done at an open circuit potential [2]).
2. First ^{195}Pt NMR spectra of platinum nanoparticle electrocatalysts were obtained [4,5,7]. The data provided access to E_F -LDOS values at clean Pt surfaces in relation to platinum-adsorbate bonding [7].
3. Detailed ^{195}Pt NMR layer-model analysis offered direct experimental evidence for the applicability of the Heine-Friedel invariance theorem to the electrochemical systems. A correlation was established between the adsorbate electronegativity and the degree of adsorbate influence on the electronic properties of platinum [10].
4. A two-band model was developed for ^{13}CO adsorbed on platinum and produced data on 5σ and $2\pi^*$ E_F -local densities of states at the carbon atom [9]. In parallel, infrared spectro-electrochemistry offered complementary qualitative information regarding the influence of electronic fields on the stretching frequency of a C-O bond in chemisorbed CO [8]. By coupling the two techniques, alteration in the bond strength measured by infrared spectroscopy was linked to the changes in the E_F -LDOS measured by EC-NMR. (Further work on this issue is in progress.)
5. ^{13}C EC-NMR of CO on Pt and on Pd [4,18] offered evidence that the electrode potential dependent Stark effect (the Stark slope) predominantly results from the

electronic contribution to the CO bonding to platinum [9].

6. Promotion of methanol oxidation electrocatalysis on platinum by ruthenium in the metal electronic perspective has recently been investigated, together with studies of CO surface diffusion on ruthenium "decorated" Pt surfaces [14].
7. Quantitative analysis of ^{13}C NMR spectra of gaseous ^{13}C -CO adsorbed on a Pt electrocatalyst in conjunction with voltammetry [17,18] enabled the identification of three distinct forms of adsorbate CO: a atop CO, a bridge-bound CO, and a reduced CO.

Many other interesting systems can now be investigated, including further studies in heterogeneous catalysis, anion adsorption, metal deposition, together with underpotential deposition. The field is now opened for a broader exploration, and the technique could serve to harness various fields such as electrochemistry, surface science, organometallic chemistry, nanoscience (clusters, nanoparticles) of catalytically attractive materials, and theory.

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