

Basis Science Research in Support of Fuel Cell Catalysis
and Technology

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reaction on such surfaces, will be discussed. Comments
will be made on obtaining images of the topography of
admetal decorated Pt nanoparticles, as compared with
single crystal surfaces, by high resolution STM and TEM.

The group specializes in producing fundamental scientific
information for further development of new and potent
fuel cell catalysts. Recent discoveries on the oxidation
reactions -- in relation to fuel cell anodes -- will be
reported. These are the following.

(1) We carry out experimental and theoretical
investigations of decomposition pathways of methanol on
low index Pt(hkl) (well-defined) and Pt(poly) electrodes.
Experimental data will be presented on: (i) electrode
potential dependence and (ii) surface structure effects
involved in the dual path (the latter for the first time) as
well as on: (iii) time distributions of the CO uptake vs.
other parallel pathways (advanced kinetics). A clear
discovery here is that the dual path and rate distributions
are highly sensitive to surface structure. Further
experiments involve the identification of reactive
intermediates as linked to the dual path on well-defined
surfaces by sum frequency generation and theory.
Exemplary questions are: can CO be a reactive
intermediate at low potentials, before stable CO is
activated to react to CO₂? Is COOH the reactive
intermediate at high potentials at all surface geometries?
Is there yet another stable intermediate(s)?

(2) We produce experimental EC-NMR data to
interrogate which type of Fermi level electrons, *d* or *s*,
relax platinum (¹⁹⁵Pt) spins in Pt nanoparticles. The
current understanding of NMR spectra of platinum
nanoparticles is that due to a considerable drop in the 5*d*-
like local density of states at the Fermi level, (E_F-LDOS),
between the bulk (at 1.138 G/kHz) and the surface (at
1.10 G/kHz) in a Pt nanoparticle, the surface Pt atoms
have higher resonance frequencies from those in the bulk
(Figure 2). This theory contradicts our Pt/Ru nanoparticle
NMR data that show an inverted trend, which will be
discussed.

(3) Fuel cell scientists tend to accept our recent data that
indicates that the reactivity of bimetallic surfaces as
catalysts for methanol oxidation is critically dependent on
the presence of specific defects on the surface, such as
edges of ruthenium on platinum. This is most likely true
on both model single crystal and nanoparticle surfaces; all
such surfaces display 2D compositional heterogeneity, or
a nanoisland morphology, and the nanoisland
distributions are insensitive to structural defects present
on the substrate surface. On such surfaces, the steady-
state oxidation of methanol occurs at acceptable (for fuel
cells) potentials only if surface CO is catalytically
removed as CO₂ at the Ru edge. However, there is a clear
dilemma here, in that CO stripping from ruthenium on
platinum occurs with a lower overpotential than at the
ruthenium edge. Previous attempts to resolve this
dilemma have been unsuccessful as CO surface diffusion
was brought to bear to explain the effect. Surface
motional issues will be discussed according to these lines.

(4) The STM imaging of Pt/Ru bimetallic single crystal
surfaces in alkaline media, as well as the CO stripping