The Process of Carbon Monoxide Oxidation at

Magnetically Modified Electrodes –

CO Tolerance at Platinum Electrodes

Wayne L. Gellett and Johna Leddy*
University of Iowa
Department of Chemistry
Iowa City, IA 52242
johna-leddy@uiowa.edu

and

Kimia Bahram-ahi and Shelley D. Minteer
St. Louis University
Department of Chemistry
St. Louis, MO 63103

Electrolysis of carbon monoxide at platinum surfaces occurs through oxidation of adsorbed CO. Because adsorption of CO to platinum is highly favored, CO is oxidized at high overpotentials and current is set by the stripping of CO. Voltammetry reveals a CO stripping wave on Nafion coated platinum at ~500 mV vs SCE in aqueous Na_2SO_4 electrolyte.

Recent work has shown that incorporating magnetic microparticles into a Nafion layer on platinum dramatically alters the process of carbon monoxide oxidation. The magnetic microparticles are coated with a polymer to ensure chemical inertness and preclude chemical mediation by the magnetic material. Specific examples include the following observations.

- For neodymium iron boron (NdFeB) magnets under cyclic voltammetric conditions, CO is oxidized at -100 mV vs SCE, which is ~ 600 mV negative of the potential of oxidation absent the magnets.

- For NdFeB micromagnets and cyclic voltammetric sweep rates of 10 to 100 mV/s, CO oxidation on platinum is diffusion controlled. Absent magnets, the voltammetric response is characteristic of thin layer behavior, consistent with the rate controlled by kinetics, not mass transport.

- Under appropriate conditions, proton exchange membrane (PEM) fuel cells modified with magnetic microparticles and platinum catalyst exhibit substantially enhanced tolerance to a synthetic reformat of hydrogen containing 100 ppm of CO.

Thus, under magnetic modification, the diffusion limited oxidation of CO on platinum is possible.

The question arises as to the mechanism by which the magnets and their associated fields alter the voltammetric response from one of total kinetic control without magnets to one of diffusion limited oxidation with magnets.

Kinetic control occurs when a rate step is slow. If that step can be facilitated, then it may be possible to drive the reaction to the mass transport limit, provided that no other step in the reaction process becomes rate limiting instead. The magnetic field is facilitating the slow kinetic step in CO oxidation. Consider the following.

Electrons have two characteristics: charge and spin. While consideration of the charge is common in electrochemical studies, accounting for the spin is not. But, it is reasonable to anticipate the following:

★ *If the electron is transferred, the spin must also be transferred.*

Computer models of radical species yield charge and spin densities. The densities are calculated over the whole framework of the radical. In many cases, the spin and charge densities are located in different parts of the structure. If the spin and charge density are not localized, then the magnetic field can be effective in coupling the spin and charge and thereby facilitating the electron transfer reaction. Models will be presented that show the spin and charge densities are delocalized for adsorbates relevant to the oxidation of CO on platinum.

Both electrodes in solution and membrane electrode assemblies (MEAs) of PEM fuel cells are modified with polymer shrouded magnetic microparticles suspended in Nafion. Cyclic voltammetric data at magnetically modified electrodes demonstrates the facilitation of CO oxidation at platinum. The peak potential for CO oxidation shifts to more negative potentials as the maximum energy product of the magnetic material increases. Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy under voltammetric perturbation allows an in situ assessment of adsorbates on the platinum surface. For a magnetically modified, platinum containing layer on the ATR crystal, CO waves diminish and disappear as the potential is scanned through the peak potential. Past the peak potential, carbon dioxide absorbances are found. Data for CO tolerance in PEM fuel cells run on synthetic reformate will also be presented.