Modeling of Magnetic Enhancement of Homogeneous Electron Transfer Reactions

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Magnetic effects electron transfer rates have been found in a variety of electrochemical systems: energy storage (alkaline and nickel metal hydride batteries) and generation (dye sensitized solar cells and proton exchange membrane (PEM) fuel cells run on hydrogen, reformat, and alcohols), fuel production (H_2), fuel storage (hydrides), and magnetoelectrocatalysis for the hydrogen evolution reaction (HER), CO oxidation, and alcohol reduction. For these studies, magnetic microparticles are introduced onto or into the electrode. Micromagnets are either made chemically inert either by silane and polymer coatings or are inert under the experimental conditions.

Magnetic effects on electron transfer are most readily observed in systems where transport is slow or negligible. This includes electroactive species either embedded in a polymer matrix (e.g., Nafion®) or participates in a near solid state electron conduction process (e.g., in a battery electrode). Largest effects are found for adsorbates such as hydrogen, carbon monoxide, alcohols, and hydrides where transport does not limit electrochemical processes.

Fundamental studies of magnetic effects on electron transfer are undertaken for academically interesting redox probes such as $M(bpy)_3^{n+}$ that are studied at electrodes modified with Nafion films and composites of magnetic microparticles in Nafion. In Nafion, redox probes are so concentrated that the probes are separated by 0.1 nm. Measured diffusion coefficients reflect electron hopping, not physical motion. For adjacent positions A and B,

$$M(bpy)_3^{2+}{}_A + M(bpy)_3^{3+}{}_B \rightleftharpoons M(bpy)_3^{3+}{}_A + M(bpy)_3^{2+}{}_B \quad (1)$$

From Dahms Ruff models for electron conduction, measured diffusion coefficients yield the self exchange rate between the two charge states of the redox probe. Cyclic voltammetric peak currents increase several fold on introduction of micromagnets to the Nafion coating. This is ascribed to magnetically increased self exchange rates.
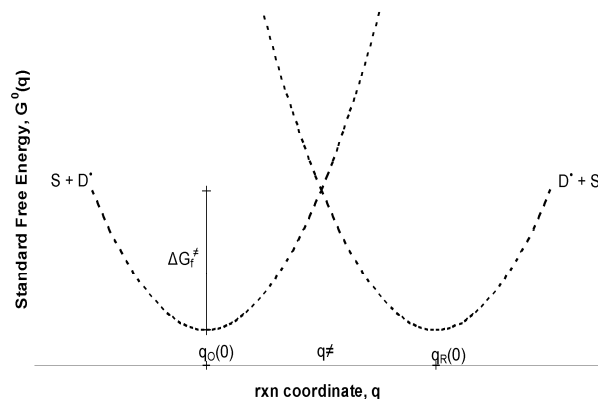

Figure 1: A simple Marcusian energy surface for a self exchange reaction between a singlet S and a double D. For example, $Ru(bpy)_3^{2+}$ is a singlet and $Ru(bpy)_3^{3+}$ a doublet. The energy of activation $\Delta G^{\neq}$ for the self exchange reaction is measured from the bottom of the reactant surface.

Self exchange rates for a variety of $M(bpy)_3^{n+}$ complexes are measured as a function of temperature. The observed large increases in current under magnetic modification are characterized under a first, simple Marcusian model for a self exchange reaction. The reaction coordinate diagram for a self exchange reaction between a singlet S and a doublet D is shown in Figure 1. Magnetic effects are introduced to the simple Marcusian model and applied to the data.

In the model, the Zeeman energy figures prominently. Measured rates are shown to vary with the magnetic fields of the microparticles and the magnetic properties of the redox couples involved in the self exchange reaction. Effects on enthalpy and entropy are considered.

[1] Heung Chan Lee, Ph.D. dissertation, University of Iowa, 2012.

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