Magnetically Enhanced Hydrogen Evolution Reaction (HER) on Non-Catalytic Electrodes

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Hydrogen is an excellent energy carrier that finds use in fuel cells. Low temperature proton exchange membrane (PEM) fuel cells display greatest efficiency with H_2 fuel. High purity hydrogen provides better efficiencies than reformats. In PEM fuel cells run reformat, trace CO poisons noble metal catalysts in the anode and cathode. To remove CO from reformat, CO is oxidized to CO_2 by preferential oxidation (PROX) reactors before reformat is introduced to the anode and by air bleeds into the reformate stream as the fuel is introduced to the anode. High purity hydrogen is produced commercially by steam reforming of natural gas. Electrolysis of water can generate high purity hydrogen, but is limited by poor oxygen evolution kinetics and the use of noble metal electrodes such as platinum.

Here, H_2 evolution efficiency at non-catalytic electrodes is increased by introduction of micromagnets on electrode surfaces. Magnetic fields at non-catalytic electrode surfaces facilitate heterogeneous electron transfer kinetics for the hydrogen evolution reaction, HER.

$$H^+_{ads} + e \rightleftharpoons H^{\bullet}_{ads} \quad (1)$$
$$2H^{\bullet}_{ads} \rightleftharpoons H_{2,ads} \quad (2)$$

The improved kinetics are manifest as significant decreases in the overpotential for hydrogen evolution. Magnetic fields are thought to impact electron transfer events through the spin (e.g., $H^{\bullet}$ and/or e). Consider that electrons have properties of charge and spin. To transfer an electron, spin and charge must both transfer. Magnetic fields introduced by micromagnets on the electrode surface may couple to the spin of the radical and/or electron to facilitate spin transfer at non-catalytic electrodes.

Three electrode materials are considered: platinum, glassy carbon, and p-Si under illumination. Electrodes are modified with a composite of magnetic microparticles in the cation exchange polymer, Nafion®. The magnetic microparticles are magnetite Fe_3O_4 shrouded in a silane coating so as to render the particles chemically inert. Electrodes are examined in simple electrolytes such as 0.1 M HNO_3.

Results are compared for unmodified electrodes, Nafion films on electrodes, and magnetic composites on electrodes. Results are summarized as follows for Pt, glassy carbon, and irradiated p-Si.

Pt: Platinum is an effective electrocatalyst for H_2 generation. Addition of magnetic microparticles little impacts the onset potential and current at a given potential for the HER.

Glassy Carbon (GC): Glassy carbon is a poor electrode for hydrogen evolution. On modification with magnetic composites, the overpotential for the onset of H_2 evolution decreases. At any potential where HER occurs, current is higher under magnetic modification. The onset of H_2 evolution occurs at more positive potentials as the strength of the magnetic field of the microparticles increases. Observed potential shifts are a few tenths of volts.

p-Si under 20 mW/cm^2 Illumination: This system illustrates improved kinetics for H_2 evolution under conditions of photoelectrosynthesis. Without modification, p-Si is an extremely poor electrode for the HER even under illumination. Introduction of a Nafion film decreases the overpotential for H_2 evolution. Introduction of a magnetic composite further decreases the overpotential for the HER. For three crystal faces and under illumination, the overpotential is decreased half a volt as compared to unmodified p-Si.

Hydrogen evolution efficiency of the two non-catalytic electrodes, GC and p-Si is markedly improved by introduction of chemically inert, magnetite particles onto the electrode surface. For the already catalytically efficient Pt electrode, magnetic modification has little impact on the HER. Introduction of magnetic fields and gradients to the surface of non-catalytic electrodes can improve the efficiency of the HER.

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[1] Heung Chan Lee, Ph.D. Dissertation, University of Iowa, 2011.

[2] Johna Leddy and Heung Chan Lee, "Magnetically Modified Semiconductor Electrodes for Photovoltaics, Photoelectrosynthesis, and Photocatalysis," Published U.S. Patent Application 20110214997 A1.

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