The Impact of Magnetic Fields on the Oxidation of Carbon Monoxide at Platinum Electrodes

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Magnetic materials find use in various electrochemical technologies. The use of these materials is increasing as effects of magnetic fields on transport and kinetics are investigated. Effects of magnetic fields on chemical systems arise through the dynamics of transport and kinetics. In kinetics, magnetic fields can facilitate rates and open new reaction pathways [1-6]. For example, rates of reactions between organic radicals were substantially enhanced (approaching 10 fold) when a reaction occurred between the poles of a laboratory magnet as compared to reaction in its absence [6]. Effects arise through spin polarization.

Here, magnetic fields are shown to dramatically alter the oxidation pathway of carbon monoxide at a platinum electrode. When the oxidation of carbon monoxide is studied at a platinum electrode modified with magnetic particles and compared to results for a similarly prepared platinum electrode absent the magnetic particles, two observations are made.

- The oxidation of carbon monoxide occurs at 600 mV lower overpotential.

- Carbon monoxide oxidation is diffusion controlled on a cyclic voltammetric time scale.

In these experiments, platinum electrodes are modified with a suspension of Nafion and microparticles. The microparticles are silane coated with one of four core materials: glass (nonmagnetic) beads, magnetite (Fe_3O_4), samarium cobalt (Sm_2Co_7), and neodymium iron boron (NdFeB). Electrodes are placed in a hollow cylindrical magnet while the casting solvent evaporates. Once dried, the external magnet is removed and all four electrodes are placed in a 0.1 M Na_2SO_4 solution. The solution is purged with carbon monoxide. Then, the electrode is polarized at –0.55 V vs. SCE for 600 s. Cyclic voltammograms are then recorded.

Cyclic voltammograms recorded at 100 mV/s are shown in the Figure. For the electrode modified with glass microparticles, the voltammogram exhibits the characteristic CO stripping wave at 500 mV vs. SCE. For the magnetic microparticles, the CO stripping wave is diminished and a new oxidation wave grows in at lower potentials. For the new wave, the peak potential shifts to more negative potentials as the maximum energy product (roughly, the magnetic strength) increases. The peak potential shift is linear with maximum energy product. For the strongest magnetic material (NdFeB), the peak is at ~-150 mV, approximately 650 mV lower overpotential than for the platinum electrode modified with the glass microparticles. A scan rate study for the NdFeB sample shows that the peak height is linearly related to the square root of the scan rate, consistent with the diffusion controlled oxidation of carbon monoxide. The diffusion coefficient found for CO in the Nafion matrix is consistent with values found for oxygen and hydrogen. Results of a spectroscopic investigation of CO adsorption at magnetically modified surfaces will also be presented.

Magnetic fields are thought to couple the spin and the electron to facilitate electron transfer and enhance the rate of CO oxidation. Such facilitated CO oxidation has been shown to increase the CO tolerance of H_2/O_2 PEM fuel cells [7].

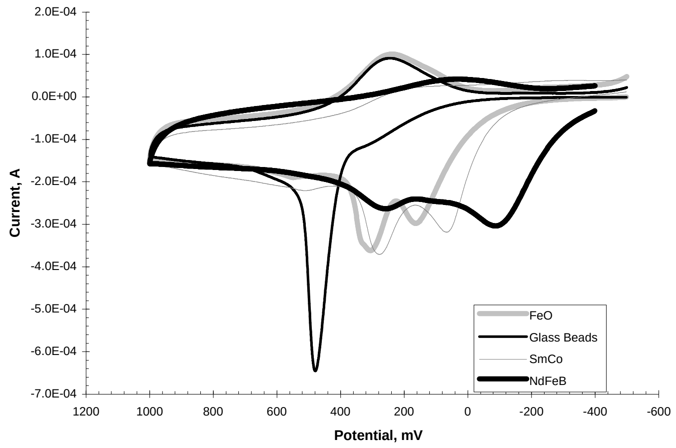

Figure 1: Cyclic voltammograms recorded at 100 mV/s for carbon monoxide in 0.1 M sodium sulfate at platinum electrodes modified with Nafion and microparticles of glass, magnetite, samarium cobalt, or neodymium iron boron.

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