Hydrogen Storage in Palladium: Magnetically Improved Interfacial Kinetics

Jessica Jewett Reed and Johna Leddy*

University of Iowa Department of Chemistry Iowa City, IA 52242 johna-leddy@uiowa.edu

More hydrogen can be stored as a hydrogen atom (H^*) absorbed in palladium than can be stored as compressed hydrogen (H_2) gas. The need to store hydrogen is driven by portable electrochemical energy systems, such as H_2 proton exchange membrane (PEM) fuel cells. Although efficiency of hydrogen fuel cells is high, transportation of hydrogen as fuel/energy storage media is one of the limitations to wide spread commercialization in portable applications. Despite the high storage capacity of hydrogen in metals like palladium, palladium hydrides are of limited use because the interfacial kinetics for hydrogen transfer across the solution | metal interface is slow and therefore a substantial energy tax.

The steps in hydride storage are:

- 1. Proton (H+) transports from solution to the electrolyte | Pd interface and adsorbs.
- 2. Proton then undergoes reduction to form surface adsorbed hydrogen atom (H[•])
- 3. Hydrogen radical H[•] crosses the solution metal interface and absorbs into the bulk Pd metal.

On the reverse process, H^{\bullet} desorbs from the bulk Pd metal and is adsorbed to the solution side of the electrolyte | metal interface and is oxidized to proton that then desorbs into solution.

In prior studies at the University of Iowa, introduction of magnetic microparticles to the surface of an electrode has been shown to increase rates of electron transfer. Effects are most pronounced in systems with slow transport and high concentrations. Notably large effects are observed for surface adsorbed species.

Because formation of Pd hydrides involves both adsorbates and radical H^{*}, hydride storage at Pd electrodes modified with magnetic microparticles was undertaken to good effect as shown in Figure 1. Here, electrodes are modified with a long chain alkyl ammonium salt (TMODA) embedded in Nafion[®]. Voltammograms for silane coated magnetite microparticles and glass microbeads embedded in TMODA-Nafion and TMODA-Nafion films are shown in the Figure.



Figure 1: Cyclic voltammograms recorded vs SCE at 50 mV/s are shown for 0.438 cm² Pd electrodes in 1.0 mM HNO₃ where electrodes are modified with TMODA modified Nafion (solid blue), TMODA-Nafion + silane coated magnetic microparticles (pink dots), or TMODA-Nafion + glass microbeads (black long dash). The kinetics are significantly faster with magnetic microparticles with reduced overpotentials on reduction to H^{*} and higher currents on oxidation.

The overpotential for hydride formation with magnetic microparticles is reduced several hundred millivolts and the current on oxidation is enhanced several fold. From other evaluations, the enhanced rates of absorption and desorption arise from impacts of the magnetic microparticles on interfacial kinetics.

Additional results and simple models that suggest the rates are enhanced more than several orders of magnitude will be discussed. Results are consistent with magnetic facilitation interfacial kinetics of hydrogen storage in palladium.

Data are drawn from reference [1].

References and Acknowledgments

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[1] Jessica Jewett Reed, M.S. Thesis, University of Iowa, 2012.