

Monday Afternoon, October 20, 2008

Energy Science and Technology Focus Topic

Room: 203 - Session EN+SE+NS+SS-MoA

Hydrogen Storage

Moderator: J.F. Herbst, General Motors R&D Center, E.

Ronnebro, Sandia National Laboratories

2:00pm **EN+SE+NS+SS-MoA1 Hydrogen Storage for Automotive Vehicles: Methods and Materials, J.F. Herbst**, General Motors R&D Center

Fuel cells operating on hydrogen are a strong potential alternative to internal combustion engines relying on fossil fuels for a variety of reasons. If a hydrogen fuel cell transportation future is to be realized, however, several major hurdles must be overcome, among them a light, compact, robust, and cost-effective system for storing hydrogen on a vehicle. High pressure compressed gas is a viable option, but its implementation at the commercial scale raises serious manufacturing and cost challenges. A similar statement applies to cryogenic liquid storage, for which dormancy is an additional issue. There is justifiable optimism that new materials may offer significant improvement of the prospects for two other options: (1) hybrid approaches combining compressed gas and a high surface area physisorption medium at 77K, and (2) reversible storage near ambient conditions. Progress on the broad materials front as well as recent research at GM R&D will be discussed.

2:20pm **EN+SE+NS+SS-MoA2 Response of Ultra-Thin Palladium Films to Hydrogen Exposure Studied by Low Energy Electron Microscopy and Diffraction, B. Santos**, Universidad Autonoma de Madrid, Spain, *J.I. Cerda, J. de la Figuera*, CSIC, Spain, *K.F. McCarty*, Sandia National Laboratories, *J.M. Puerta*, CSIC, Spain

The ability of Palladium to store hydrogen is well known. Nevertheless surface science studies of the exposure of Pd(111) samples to hydrogen have found only a dense hydrogen layer between the last palladium-palladium layers, with additional hydrogen going into the bulk as a solid solution.^{1,2} On Pd films a few atomic layers thick on a substrate which does not accept substantial quantities of hydrogen such as Ru, it should be possible to saturate completely the Pd film, and thus study the formation of PdH hydride with surface science techniques. In particular, as there is a substantial lattice mismatch between Pd and the beta-PdH hydride, the incorporation of H in Pd-interstitial places should induce a significant expansion of the Pd layers. Although H itself is basically invisible to low energy electron diffraction, the change of the Pd-Pd distances should be easily resolvable by LEED.³ In this work, we present a low energy electron microscopy study of the hydrogen exposure of thin films of Pd on Ru(0001) and W(110). We characterize and study the growth and structure of Pd thin films. LEEM is a useful technique to monitor and control the growth of thin films in real space. Furthermore, a LEEM microscope can be used to acquire selected area diffraction (SAD-LEED) to determine the structure of such film.⁴ Our experiments reveals that Pd films 2 to 6 ML thick on Ru(0001) follow the fcc sequence with the Ru in-plane lattice spacing, and present a corresponding expansion in the out-of-plane lattice spacing. Thicker films on Ru(0001) relax to a bulk-like Pd in-plane spacing. Both thick films on Ru(0001) or W(110) show a slight expansion of the last interlayer spacing, in line with reported studies on the surface of bulk Pd. We follow the dosing of atomic H on the Pd films by means of real-time LEED IV curves acquired by LEEM. We have found preliminary indications that room and low temperature exposure produce a significant expansion in the interlayer distance for a 4 ML thick film. But this expansion is smaller than the one expected for a full PdH beta-hydride formation.

¹G.E. Gdowski, T.E. Felner and R.H. Stulen Surf. Sci. 181, L147, (1987)

²Sampyo Hong and Talat S. Rahman Phys. Rev. B 75, 155405 2007

³T. E. Felner, Eric C. Sowa, and M. A. Van Hove, Phys. Rev. B 40 num. 2, 891-899, (1989)

⁴J. de la Figuera, et al, Surf. Sci. 600, L105 (2006)

2:40pm **EN+SE+NS+SS-MoA3 Destabilized Magnesium-based Alloy Thin Films as Model Systems for Hydrogen Storage, D. Mitlin, J. Haagsma, C. Ophus, C.T. Harrower**, University of Alberta and NRC National Institute for Nanotechnology, Canada, *M. Saoudi, H. Fritzsche*, National Research Council Canada, SIMS, Canadian Neutron Beam Centre, Chalk River Laboratories **INVITED**

The key for achieving 100 °C - range hydrogen sorption is to have favorable thermodynamics, i.e. a hydrogen binding energy near 30 kJ/mol. Metallic magnesium possesses sufficient gravimetric and volumetric sorption capacity, but has unfavorable thermodynamics (-77 kJ/mol α -MgH₂

formation energy) and poor kinetics. In this presentation I will discuss our general methodology for tuning the hydrogen sorption thermodynamics of magnesium, through alloy design. We use a thin films approach to create a range of destabilized magnesium-based alloys and of accompanying catalytic layers. Thin films make for ideal "model" systems that may be used for accurately and rapidly screening a variety of matrix and catalyst formulations. Because of the small diffusion distances, films also allow for better separation of system thermodynamics from the kinetics. The synthesized films were tested volumetrically through multiple adsorption-desorption cycles. The microstructures were characterized by neutron reflectometry and x-ray diffraction. We show that alloying magnesium with light elements that have weak hydrogen interaction, such as aluminum, is a very effective method for lowering the sorption temperature to near ambient. At certain compositions, the addition of aluminum promotes the high-pressure γ -MgH₂ phase at the expense of the equilibrium α -MgH₂. At other compositions, the sorbed microstructure is a composite of α -MgH₂ intermixed with α -AlH₃. We also demonstrate that there is critical temperature above which the palladium catalyst caps are not stable, reacting with the underlying material and losing their efficacy. Additionally, there will be a discussion of the processing and sorption kinetics of MgH₂ - metal catalyst - carbon nanotube (CNT) powder composites, and of direct TEM characterization of milled MgH₂.

3:20pm **EN+SE+NS+SS-MoA5 Thermodynamics and Kinetics of Hydrogen Storage in Metallic Nanoparticles Studied by Surface Plasmon Resonance Spectroscopy and Quartz Crystal Microbalance Techniques, C. Langhammer, I. Zoric**, Chalmers University of Technology, Sweden, *S.T. Kelly, B.M. Clemens*, Stanford University, *B. Kasemo*, Chalmers University of Technology, Sweden

Nanosized metallic particles may have advantageous hydrogen storage properties compared to the corresponding bulk material both in terms of sorption/desorption kinetics and in terms of storage capacity. In order to understand the physical principles behind the influence of nanosizing on hydrogen uptake/release properties, we have developed a novel localized surface plasmon resonance (LSPR) based optical hydrogen sensing scheme for nanoparticle storage systems. As model experiments we carried out measurements of the phase diagram and thermodynamic properties for supported Pd nanodisks, ranging in size from 30 nm to 300 nm. By monitoring the shift of the LSPR extinction peak upon hydrogen uptake/release as a function of hydrogen pressure, at different temperatures, we have mapped out a series of pressure-concentration (p-C) isotherm for a range of particle sizes. These optical studies are complemented by gravimetric studies using a quartz crystal microbalance (QCM). In the latter case the corresponding p-C isotherms were obtained by monitoring the frequency shifts when the Pd nanodisks were prepared on the QCM electrode and exposed to hydrogen environment at different temperatures. We have used Van't Hoff plots (log of the isotherm plateau pressure, in the two-phase region, versus inverse plateau temperature), to obtain the enthalpy and entropy for hydride formation in Pd nanodisks of different sizes. Furthermore, we have used Sievert's plots in the low hydrogen concentration limit (α -phase) to extract enthalpies and entropies of hydrogen dissolution. An excellent agreement was obtained for the corresponding thermodynamic variables obtained from LSPR sensing data and QCM data. Similarities and differences to the corresponding thermodynamic variables for bulk systems are discussed. In addition, we have carried out corresponding measurements with Mg nanoparticles "capped" with few nanometers of Pd to facilitate H₂ dissociation. The "capping" with a Pd layer circumvents the bottleneck associated with low dissociative sticking of hydrogen on Mg. Double plateau isotherms were obtained indicating initial onset of the mixed phase formation at low hydrogen pressure in Mg nanoparticle followed by a corresponding two phase onset in the Pd cap at higher pressure, characteristic for Pd nanoparticles at a given temperature. In addition, we also present the QCM and LSPR based studies of hydrogen uptake/release kinetics at different temperatures.

4:00pm **EN+SE+NS+SS-MoA7 Atomistic Mechanisms of Reversible Hydrogen Storage in Complex Metal Hydrides, P. Sutter**, Brookhaven National Laboratory **INVITED**

The storage of hydrogen in a lightweight, high-capacity medium with fast charge/discharge kinetics has been recognized as one of the primary challenges in achieving the transition to a hydrogen-based economy. Hydrogen-rich compounds, such as complex metal hydrides, offer potentially high storage capacities but the solid-state hydrogen storage reactions in these materials generally proceed slowly and in many instances are not reversible, i.e., re-hydrogenation of the depleted products cannot be realized by controlling temperature and hydrogen pressure alone. The use of

doping to achieve reversibility and fast reaction kinetics has been demonstrated successfully for a particular complex metal hydride, sodium alanate (NaAlH_4). Here we discuss our recent efforts on identifying the atomic-scale effects of such doping by microscopy and spectroscopy experiments on well-defined model systems (e.g., single crystal surfaces), closely linked to ab-initio theory and simulations. A comprehensive understanding of important microscopic reaction mechanisms allows deriving general guidelines for the use of dopants or catalysts to accelerate hydrogen storage reactions in alanates, and possibly in a broader class of solid-state storage materials.

4:40pm **EN+SE+NS+SS-MoA9 Microwave Irradiation for the Reversible Desorption of Hydrogen from Sodium Aluminum Hydride, T.A. Dobbins**, Louisiana Tech University and Grambling State University, R. Krishnan, Louisiana Tech University

Materials such as complex metal hydrides and hydrogen adsorbents have been the primary focus of the on-board hydrogen storage research program. Complex metal hydrides offer great potential in making it into the transportation industry due their reliable on-board reversibility. These materials can perform very well even after multiple dehydrogenation-hydrogenation cycles. Conventional heating mechanisms have been used to desorb hydrogen from complex metal hydrides. However, conventional heating processes involve high energy penalties (because the energy invested to heat the complex metal hydride is equal to or greater than the energy generated by a fuel cell using the desorbed hydrogen). This research is aimed at establishing the use of microwave irradiation to desorb hydrogen from sodium aluminum hydride (NaAlH_4). Microwave heating is known to be more energy efficient than conventional heating. However, microwave fields are also known to drive order to disorder reactions in the hydrides, thus resulting in amorphous desorption products. This work reports a method to use microwave irradiation to desorb hydrogen from NaAlH_4 via the reversible desorption pathway. This is the first report of using microwaves to drive a dehydrogenation reaction with the same pathway as driven by conventional heating processes. The method established in this research makes use of the energy efficiency of microwave irradiation and can be extended to other hydride systems for future research.

Funding for this project was provided by the Department of Energy, Office of Basic Energy Sciences (Contract No.: DE-FG02-05ER46246).

5:00pm **EN+SE+NS+SS-MoA10 Alane Formation on Al(100) and Ti-doped Al(100), I.S. Chopra, J.-F. Veyan, Y.J. Chabal**, University of Texas at Dallas, S. Chaudhuri, Washington State University

Complex metal hydrides, such as NaAlH_4 , are candidates for hydrogen storage as they can reversibly release and recapture hydrogen. Alane Clusters (Al_xH_y) are believed to be the mass transport intermediate in the hydrogen storage reactions involved in hydrogen uptake and release. Understanding the surface chemistry behind the formation and evolution of alane clusters is therefore important to lower the temperatures needed for these processes. Since doping metallic Al is critical for H_2 dissociation, we have undertaken a comprehensive study of H interaction with Al(100) and Ti-doped Al(100) surfaces to better understand the atomic scale mechanisms underlying this reversible hydrogen storage behavior. The results have been compared with similar study performed earlier on the Al(111) and Ti doped Al(111) surface. In-situ infrared absorption spectroscopy had previously shown¹ that the nature of alanes (size, bonding configuration) formed on Al(111) depends on both H exposure and sample temperature. At low temperatures ($\sim 90\text{K}$), small alanes such as AlH_3 and Al_2H_6 are predominant. At higher temperatures ($\sim 250\text{K}$), larger alanes are formed. The study of alane formation on the Al(100) surface as a function of H exposures and substrate temperatures make it possible to explore the dependence of the alane formation on the crystal orientation. The effect of Ti doping is also explored as a function of both Ti concentration and H_2 pressures. Our first-principles calculations indicate that Ti atoms should occupy hollow sites of the (100) unit cell. We are therefore using LEED to test whether this site is indeed the most favorable and IR spectroscopy to explore whether Ti in that site does dissociate H_2 . On Al(111), no dissociation was observed for H_2 pressure up to 10^{-6} Torr. We are therefore exploring dissociation up to 10^{-4} Torr on Al(100). Finally, we are using TPD to probe the nature of desorbed species from both Al(100) and Ti-doped Al(100) surfaces.

¹ Santanu Chaudhuri, Sylvie Rangan, Jean-Francois Veyan, James T. Muckerman, Yves J. Chabal, J. Am. Chem. Soc. (submitted).

5:20pm **EN+SE+NS+SS-MoA11 Infrared Spectroscopy Studies of Hydrogen Interaction in Metal Organic Frameworks, N. Nijem, J.-F. Veyan**, University of Texas at Dallas, J. Li, Rutgers University, Y.J. Chabal, University of Texas at Dallas

Hydrogen storage is one of the most challenging problems in hydrogen-based energy technology. One of the goals of hydrogen storage is the ability to store a high volumetric density of hydrogen at room temperature. As a

result, studies exploring hydrogen interaction in storage materials are important to facilitate further development of materials. Metal-organic Frameworks are promising candidates for hydrogen storage because their high surface area and porosity facilitate high hydrogen physisorption on specific sites of the structures. This work explores the incorporation of hydrogen into the structure using infrared (IR) absorption spectroscopy. IR spectroscopy can distinguish possible H_2 binding sites based on the perturbation of the internal H_2 stretch mode. The measurements are performed at room temperature on three different types of MOF structures, two of which have the general formula $[\text{M}(\text{bdc})(\text{ted})_{0.5}]\cdot 2\text{DMF}\cdot 0.2\text{H}_2\text{O}$, differing in the metal core M (Ni and Zn). These two compounds are isostructural and crystallize in the tetragonal phase (space group P4/ncc), they construct a 3D porous structures with relatively large pore size ($\sim 7\text{-}8\text{\AA}$, pore volume ($\sim 0.63\text{-}0.84$ cc/g) and BET surface area ($\sim 1500\text{-}1900$ m²/g). Another type of MOF is the $[\text{Ni}_3(\text{HCOO})_6]\cdot \text{DMF}$ structure which crystallizes in space group P21/c and features a 1D open channels with smaller pore diameters ($\sim 5\text{-}6$ Å). Preliminary results show perturbation of the H_2 gas vibrational modes leading to a ~ 30 cm⁻¹ shift of the ortho- and para- peaks of the unperturbed H_2 . This perturbation is due to the interaction of the hydrogen with the MOF and can be seen as evidence of the hydrogen adsorbed onto specific sites of the MOF. Although the data are taken for high pressure H_2 gas at room temperature, the shift is consistent with previous observation of Bordiga et al.¹ performed at very low pressures and temperatures. The intensities of the perturbed ortho- and para- H_2 peaks have a linear dependence with pressure, indicating that the perturbation of the H_2 with the MOF lattice is dominant, i.e. $\text{H}_2\text{-H}_2$ interactions are much less important than in the pure H_2 gas.

¹ S. Bordiga, J. G. Vitillo, G. Ricchiardi, et al., Interaction of hydrogen with MOF-5 Journal of Physical Chemistry B 109, 18237 (2005).

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