PURDUE UNIVERSITY
Discovery Park Energy Center

HYDROGEN

SYMPOSIUM 2008

April 24-25, 2008

Stewart Center, Purdue University, West Lafayette, Indiana

www.purdue.edu/dp/energy/centers/hydrogen.php

EA/EOU

HYDROGEN SYMPOSIUM 2008

We are delighted to have you join us in West Lafayette for the 3rd Hydrogen Symposium sponsored by Purdue's Energy Center. We cannot escape hydrogen as a future fuel. What will be the source of future hydrogen supplies? How will it be stored and transported? And what technologies and materials will be developed for its utilization? These are the questions science and engineering must address in the near future to allow energy security and independence.

In this year's symposium we are very fortunate to have an outstanding lineup of speakers who are working at the leading edge of research in exactly these issues, storage, catalysis, materials for fuel cells, production, and delivery. We look forward to a stimulating two days that will result in forging future collaborations and advancing the frontiers of science and engineering in hydrogen research.

Most Sincerely,

Mahdi Abu-Omar, Chair

Timothée Pourpoint, Co-Chair

SYMPOSIUM COMMITTEE

SYMPOSIUM CHAIR

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HERBERT C. BROWN AWARD FOR INNOVATIONS IN HYDROGEN RESEARCH

The Herbert C. Brown Award for Innovations in Hydrogen Research award is a $5,000 cash award made to an individual in recognition of outstanding contributions in hydrogen research and for advancing energy issues around the globe.

The Herbert C. Brown award is named after the late Purdue Chemistry professor and 1979 Nobel Prize recipient. Dr. Brown shared with Georg Wittig (Germany) the Nobel Prize "for their development of the use of boron- and phosphorus-containing compounds, respectively, into important reagents in organic synthesis."

2007 INAUGURAL RECIPIENT

Dr. Borislav Bogdanovic, Max-Planck-Institut für Kohlenforschung

Dr. Borislav Bogdanovic was honored for his innovation in hydrogen storage research for over two decades. His research spanned the fields of chemistry and materials science and laid the foundation for development of new devices. Dr. Bodanovic is most recognized for his breakthrough discovery of low temperature reversible hydrogen storage in sodium alanate with titanium dopants in the late 1990s. His education includes studies in chemistry at Belgrade from 1953-59 and Ph.D. work at the Max-Planck-Institut für Kohlenforschung (Mulheim) from 1960-62. Throughout 1974-1997, Dr. Bodanovic taught at various universities in Italy, France, and Germany, and he served as the head of the Catalysis Research Group in the MPI (Mülheim) from 1974 to1999. After retirement, he has continued to work as a consultant in the MPI in the area of hydrogen storage.

2008 RECIPIENT

The 2008 recipient will be announced at the 2008 Hydrogen Symposium Awards Banquet held on Thursday, April 24th.

AGENDA

Thursday, April 24, 2008

STEWART CENTER, ROOM 314

7:15–8:00 AM	Registration (STEW 314) & Continental Breakfast (STEW 310)
8:00–8:05 AM	Symposium Welcome **Symposium Chair: Mahdi Abu-Omar**
8:05–8:20 AM	Overview of Purdue's Energy Center at Discovery Park & Hydrogen Activities **Dr. Jay Gore,** *Director*
8:20–8:25 AM	**SESSION I: STORAGE** **Session Chair: Daniel Raftery,** *Purdue University*
8:25–9:10 AM	**KEYNOTE: Computational Approaches to the Prediction of Molecular Properties for Chemical Hydrogen Storage** **David Dixon,** *University of Alabama*
9:10– 9:35 AM	Solid State Chemical Hydrogen in NHxBHx Materials **Tom Autrey,** *Pacific Northwest National Laboratory*
9:35–10:00 AM	An Overview of U.S. DOE Hydrogen Program R&D Activities in Hydrogen Storage Materials **John Kopasz,** *Argonne National Laboratory*
10:00–10:25 AM	Break–STEW 310
10:25–11:10 AM	**KEYNOTE: Materials Aspect of Hydrogen Storage for Transportation Applications** **Gholam-Abbas Nazri,** *General Motors Research & Development Center*
11:10–11:35 AM	Chemical Hydrogen Storage Research at Los Alamos National Laboratory **John Gordon,** *Los Alamos National Laboratory*
11:35 - 12:00 PM	Hydrogen Storage Activities in the DOE Metal Hydride Center of Excellence **Ewa Ronnebro,** *Sandia National Laboratory*
12:00–1:15 PM	**Luncheon–East & West Faculty Lounges, Purdue Memorial Union**

AGENDA

Thursday, April 24, 2008 (continued)

STEWART CENTER, ROOM 314

1:30 - 1:35 PM	**SESSION II: CATALYSIS & FUEL CELL RESEARCH** **Session Chair: Fabio Ribeiro,** *Purdue University*
1:35–2:20 PM	**KEYNOTE: An Energy-Based Approach to the Development of Molecular Catalysts for H2 Oxidation and Production** **Daniel DuBois,** *Pacific Northwest National Laboratory*
2:20–2:45 PM	U.S. Fuel Cell Bus Evaluation **Leslie Eudy,** *National Renewable Energy Laboratory*
2:45–3:10 PM	Fundamental Studies of Model Electrocatalysts for Fuel-Cell Cathodes **Hoydoo You,** *Argonne National Laboratory*
3:10–3:40 PM	Break–STEW 310
3:40–4:05 PM	Non-Precious Metal Catalysts for PEM Fuel Cell **Radoslav Atanasoski,** *3M*
4:05–4:30 PM	Electrode Materials For Solid Oxide Fuel Cells **Scott Barnett,** *Northwestern University*
4:45–5:00 PM	Bus Transport from Stewart Center to Ross-Ade Stadium
5:00–6:30 PM	Reception and Poster Session–Buchanan Room, Ross-Ade Stadium
6:30–9:00 PM	Dinner and H.C. Brown Award Banquet–Buchanan Room, Ross-Ade Stadium
9:00–9:15 PM	Bus Transport from Ross-Ade Stadium to Purdue Memorial Union

AGENDA

Friday, April 25, 2008

STEWART CENTER, ROOM. 314

7:15–7:55 AM	Continental Breakfast and Coffee (STEW 314)
7:55–8:00 AM	Opening Remarks **Symposium Chair: Mahdi Abu-Omar**
8:00–8:05 AM	**SESSION I: MATERIALS FOR FUEL CELLS** **Session Chair: Kyoung-Shin Choi,** *Purdue University*
8:05–8:50 AM	**KEYNOTE: Low Temperature Functionalization of Small Molecules and Applications to Energy Storage** **Roy Periana,** *Scripps Research Institute-Florida*
8:50–9:15 AM	Novel Proton Conductive Membranes Derived from 1,3-Cyclohexadiene **Jimmy Mays,** *University of Tennessee*
9:15–9:40 AM	New High Temperature Polymer Electrolyte Membranes: Influence of the Chemical Structure on Their Properties **Morton Litt,** *Case Western Reserve University*
9:40–10:05 AM	The Nanostructure of Nafion from Small-Angle Scattering and NMR Analysis **Klaus Schmidt-Rohr,** *Iowa State University*
10:05–10:30 PM	Materials Issues for Photoelectochemical Water Splitting: Chalcopyrite Thin-Films and III-V Nitrides **John Turner,** *National Renewable Energy Laboratory*
10:30–10:45 AM	Break–STEW 314
10:45–10:50 AM	**SESSION II: PRODUCTION & DELIVERY** **Session Chair: Steve Son,** *Purdue University*
10:50–11:15 AM	Hydrogen Production from Bio-derived Liquids **Yong Wang,** *Pacific Northwest National Laboratory*
11:15–11:40 AM	Hydrogen Supply Options Including the Development of an On-Site Hydrogen Production System for Vehicle Fueling Stations **Tim Aaron,** *Praxair, Inc.*
11:40–12:05 PM	Multi-Layered Polymer and Polymer/Metal Materials for Large- and Small-Scale Hydrogen Delivery **James Blencoe,** *Hydrogen Discoveries, Inc.*
12:05–1:30 PM	Boxed Lunch Option for Lab Tour Participants (please register)
1:30–4:00 PM	**Scheduled Lab Tours–Meet Bus Outside Purdue Memorial Union**
1:30–2:30 PM	Maurice J. Zucrow Laboratories
3:00–4:00 PM	Birck Nanotechnology Center

SESSION I

STORAGE

KEYNOTE

Computational Approaches to the Prediction of Molecular Properties for Chemical Hydrogen Storage

David A. Dixon, Department of Chemistry, The University of Alabama, Shelby Hall, Box 870336, Tuscaloosa, AL 35487-0336

ABSTRACT

With the confluence of advances in theory, algorithms, software, and high performance computer architectures, it is now possible to calculate reliably the thermodynamics of compounds of most elements in the Periodic Table at a level of accuracy only dreamed of 15 years ago. New correlation-consistent basis sets, coupled with effective core potentials in some cases, are available for all main group elements and the transition metals. Calculations at the CCSD(T) level with extrapolation to the complete basis set asymptotic limit are now possible for most elements. We will review the basic science drivers for energy needs and the role of high performance computing as well as issues in the calculations and then describe applications to chemical hydrogen storage. Chemical hydrogen storage is an alternative approach which eliminates issues such as high pressure and low temperature, as hydrogen is stored in a compound and delivered via a chemical reaction. Because of their high weight percent capacity for storing hydrogen, boron-nitrogen compounds are good candidates for achieving DOE's goals for on-board transportation systems. We have used high level electronic structure calculations to predict the heats of formation and heats of reaction for the hydrogen release from cyclic and acyclic B-N compounds. Our studies also include the thermodynamics and kinetics for hydrogen elimination from BH_3NH_3 (with and without Lewis acid catalysts) and from other boron-nitrogen compounds. In addition, results on predicting reaction pathways for hydrogen regeneration will be described. This work has been extended to alane chemistry and organic hydrogen storage applications will be described as well.

Solid State Chemical Hydrogen in NHxBHx Materials

Tom Autrey, Pacific Northwest National Laboratory

ABSTRACT

The NHxBHx class of materials may be classified as complex hydrides and/or a chemical hydrogen storage materials. Chemical hydrogen storage materials are of great interest for on-board hydrogen storage because they are capable of providing large quantities of hydrogen with rapid kinetics at moderate temperatures. Nevertheless, by definition the hydrogen must be 'resorbed' back into the spent material by chemical pathways, off-board the vehicle. Some Chemical Hydrogen Storage materials may have been unfairly categorized as *irreversible hydrides*. The connotations associated with this classification may be unjust given the recent efforts demonstrating chemical pathways to regenerate ammonia borane from the spent materials and perhaps the term irreversible chemical hydride is inappropriate. Our group has been working on developing an in-depth understanding of the chemical and physical properties of amine borane materials for solid state on-board hydrogen storage. These materials, (NHxBHx) provide both high gravimetric and volumetric densities of hydrogen. Hydrogen is released at low temperatures through a series of moderate exothermic reactions. In this work we present experimental studies designed to elucidate more details about the potential mechanism for H_2 formation from NHxBHx compounds in the solid state and in solution. Battelle operates PNNL for DOE.

An Overview of U.S. DOE Hydrogen Program R&D Activities in Hydrogen Storage Materials

Sunita Satyapal, Grace Ordaz, Carole Read, Monterey Gardiner; U.S. Department of Energy

John Kopasz, Argonne National Laboratory

ABSTRACT

Commercially viable on-board storage of hydrogen for hydrogen-fueled vehicles is a technical challenge that requires significant breakthroughs in materials development. An overview of key research development programs for hydrogen storage being carried out through the U.S. Department of Energy's National Hydrogen Storage Project will be presented. Issues associated with hydrogen storage in materials, including metal hydrides, sorbents and chemical hydrides, will be presented and the current status of hydrogen storage systems will be discussed. Important recent research avenues and results will be highlighted.

KEYNOTE

Materials Aspect of Hydrogen Storage for Transportation Applications

Gholam-Abbas Nazri, General Motors Research & Development Center, Energy Storage Systems, Warren, Michigan

ABSTRACT

The inevitable global equilibration along with rising standard of living and growing worldwide population demand a dramatic increase in energy consumption within the next decades. The grand scientific challenge of many nations is to find a long-term solution for a secure, diversified, and clean energy source also in combination with a more logical and conservative use of current resources. Hydrogen storage for transportation applications is an essential component of the new energy strategy. Hydrogen storage in a condensed solid form is a potential candidate to replace the traditional gas tanks. Among various solid sate hydrogen storage materials, the high-pressure hydrogen storage alloys are the most promising ones, as they operate in a temperature range suitable for transportation applications. However, successful transfer and integration of this technology from laboratory environment into future vehicles requires improvement in performance, safety, and lower cost.

In this presentation, the strategy to meet the requirements of hydrogen storage for transportation will be discussed. Correlation between structure – composition – hydrogen sorption capacity will be explored, and optimization of hydrogen sorption capacity and equilibrium pressure plateau of intermetallic alloys will be discussed. Challenges and opportunities for material designers and engineers with a focus on engineering of high-pressure alloys will be described.

Chemical Hydrogen Storage Research at Los Alamos National Laboratory

John Gordon, Los Alamos National Laboratory

ABSTRACT

Transformation of our current fossil fuel based transportation infrastructure to one that uses hydrogen (H_2) could address numerous public health and energy security issues. For successful implementation of a H_2 based economy, storage of H_2 is a vital component. Los Alamos National Laboratory (LANL) is a partner within the Department of Energy's (DOE) Chemical Hydrogen Storage Center of Excellence (CHS CoE). The Center focuses on a variety of chemical candidates that are capable of storing H_2 in materials that have higher hydrogen densities than compressed or liquefied hydrogen as well as undergoing H_2 release in a controlled fashion for fuel cell (or other) use.

Ammonia borane (AB, H_3NBH_3), a stable colorless solid, has attracted much attention due to its large H_2 capacity (19.6 wt %). LANL is exploring various methodologies for both release of hydrogen from AB and regeneration of AB from BNH_x spent fuel. Some recent progress in these areas will be discussed.

Hydrogen Storage Activities in the DOE Metal Hydride Center of Excellence

Ewa Rönnebro, Sandia National Laboratory

ABSTRACT

The DOE Metal Hydride Center of Excellence is researching, developing and validating reversible on-board metal hydride storage materials and systems that meet the 2010 DOE system targets for hydrogen storage, with a credible path forward for meeting the 2015 DOE storage targets. Sandia National Laboratories is leading this effort involving 19 partners from National Labs, Universities and Industries. We are focusing on a variety of different materials, such as destabilized systems, borohydrides, amides and regeneration of alane. This presentation will give you an overall view on how we are approaching the technical targets and how theorists and experimentalists are working together on addressing the critical issues on how to improve kinetics, thermodynamics and reversibility. Our progress will be exemplified with high-lights from the past year's research.

SESSION II

CATALYSIS & FUEL CELL RESEARCH

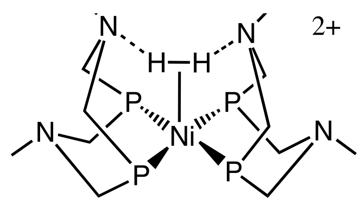
KEYNOTE

An Energy-Based Approach to the Development of Molecular Catalysts for H_2 Oxidation and Production

Daniel DuBois, Pacific Northwest National Laboratory

ABSTRACT

Both the first and second coordination spheres play important roles in the activation of H_2 by hydrogenase enzymes. Our research focuses on determining those features that control the energetics of elementary steps involved in the catalytic oxidation or production of H_2. For example, what parameters are responsible for controlling the hydride acceptor ability of the metal site during the heterolytic activation of H_2, and what are the roles of pendant bases in transferring protons from the metal to solution during the catalytic oxidation? It has been found that the hydride acceptor abilities of $[M(diphophine)_2]^{2+}$ complexes (M = Ni, Pd, Pt) are controlled by factors such as the electron-donating ability and steric bulk of substituents as well as the chelate bite angle imposed by the backbone of the diphosphine ligand. This information can be used to design Ni complexes containing diphosphine ligands with pendant N bases that catalyze the electrochemical oxidation and production of H_2.



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The pendant bases in the second coordination sphere of a variety of metal complexes of Fe, Co, and Ni have been shown to play an important role in the H_2 activation and proton transfer in these complexes. In particular, the presence and precise positioning of the pendant bases have been shown to be important in the catalytic activity of both Co and Ni complexes as shown in structure 1 for Ni. The study of Fe complexes have provided evidence that the structure of the metal complex also plays an important role in the rate of proton transfer between the metal and the pendant base of the diphophine ligand. For example, rapid proton/hydride exchange between the protonated pendant base occurs for *trans*-$[Fe(PNHP)(dmpm)(H)(CH_3CN)]^{2+}$ but not for *cis*-$[Fe(PNHP)_2(H)(CH_3CN)]^{3+}$ (where PNHP is $[Et_2PCH_2N(Me)(H)CH_2PEt_2]^+$ and dmpm is $Me_2PCH_2PMe_2$). Our results demonstrate the importance of both the first and second coordination spheres of metal complexes in the catalytic oxidation and production of H_2 using simple mononuclear model complexes.

REFERENCES

Wilson, A. D.; Shoemaker, R. K.; Meidaner, A.; Muckerman, J. T.; Rakowski DuBois, M.; DuBois, D. L. *Proceedings of the National Academy of Sciences,* 2007, 104, 6951-6956.

Jacobsen, G. M.; Shoemaker, R. K.; McNevin, M. J.; Rakowski DuBois, M.; DuBois, D. L. *Organometallics* 2007, 26, 5003-5009.

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U.S. Fuel Cell Bus Evaluation

Leslie Eudy, National Renewable Energy Laboratory

ABSTRACT

The National Renewable Energy Laboratory (NREL) conducts evaluations of fuel cell transit buses for the U.S. Department of Energy's (DOE) Hydrogen, Fuel Cells & Infrastructure Technologies Program. NREL works with transit agencies, manufacturers, fuel providers, and the industry to validate hydrogen and fuel cell vehicles in heavy-duty applications. The data collected and analyzed are used to verify performance targets and assess technology readiness. Using an established protocol, NREL provides comprehensive, unbiased results on the performance, operation, and costs of the buses in comparison to those of conventional-technology buses used in the same type of services. Transit fleets demonstrating this technology have shown fuel economy improvements of nearly two times that of conventional buses. This presentation provides an update of the progress and accomplishments of three transit agencies demonstrating a total of five fuel cell buses including AC Transit in Oakland, California; SunLine Transit Agency in Thousand Palms, California; and CTTransit in Hartford, Connecticut. These agencies are currently operating hybrid fuel cell buses developed by UTC Power, ISE Corporation, and Van Hool. Through the end of September, 2007, these five fuel cell buses had accumulated more than 110,000 miles in service with a fuel economy ranging between five and eight miles per kilogram. The presentation provides descriptions of the technology, operating performance, maintenance, cost, and overall experience with the buses. Specific data results will be presented on fuel economy, mileage accumulation, availability, reliability, and operational costs.

Fundamental Studies of Model Electrocatalysts for Fuel-Cell Cathodes

Hoydoo You, Argonne National Laboratory, hyou@anl.gov

ABSTRACT

Model electrocatalysts, one-dimensional (1d) and two-dimensional (2d) nanoparticle arrays, and single crystal surfaces were studied for their oxygen reduction reaction (ORR) and dissolution reaction. 1) The ORR activities of 1d and 2d model catalysts are found to be higher than expected from their geometry where oxy-species of reaction intermediates cross over between adjacent facets in nanometer proximities. Density-functional theory are used to theoretically model the equilibrium shapes and electrocatalytic activities. The dissolution reactions were found sensitive to the crystallographic orientations and nanostructures although the overall dissolution rates increase with electrochemical potential as expected. Studies of some nanoparticle electrocatalysts and comparison to the model electrocatalysts will also be presented.

*Supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under DOE Contract No. DE-AC02-06CH11357

Non-Precious Metal Catalysts for PEM Fuel Cell

Radoslav Atanasoski, 3M

Radoslav Atanasoski and Thomas E. Wood,
3M Fuel Cell Program and Corporate Research Materials Laboratory, St. Paul, Minnesota 55144 (USA),
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ABSTRACT

The cost of platinum is one of the major obstacles in the commercialization of PEM (proton exchange membrane) fuel cells. Non-precious metal catalysts as an inexpensive alternative to platinum have been viewed as the only long-term solution to the problem.

After a brief introduction of the topic of non-precious metal-oxygen reduction catalysts and a review of the most important progress during the last ten years, we will present our work in this area. We will focus on fundamental aspects of the catalyst characterization, the specific activity and durability, and correlate those with the real fuel cell performance.

In the development of the non-precious metal catalysts, we have adopted three strategic directions. One is based on vacuum processes [1], a second is focused on synthesis of nanoparticles finely dispersed on carbon substrate, and the third approach seeks to develop active sites through metal-assisted polymerization of nitrogen-containing, aromatic molecules [2]. Due to vast area open for new catalysts systems outside the platinum group metals, our effort was enhanced by a high throughput experimental approach [3]. In order to identify the nature of the active centers, intensive physicochemical characterization of the new catalytic materials was carried out, the results of which were followed by an ab initio modelling effort [4].

REFERENCES

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2. T. E. Wood, Z. Tan, A. K. Schmoeckel, D. G. O'Neill, R. Atanasoski, *J. Power Sources* (available on-line)

2. E. B. Easton, A. Bonakdarpour and J. R. Dahn, *Electrochem. Solid State Lett.*, 9, A463, 2006.

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*This work was supported by the U.S. Department of Energy (DOE), Cooperative Agreement No. DOE-FC36-03GO13106. DOE support does not constitute an endorsement by DOE of the views expressed in this presentation.

Electrode Materials for Solid Oxide Fuel Cells

Scott A. Barnett, Department of Materials Science and Engineering, Northwestern University, Evanston, IL

ABSTRACT

This talk will describe recent solid oxide fuel cell (SOFC) research at Northwestern University and Functional Coating Technology LLC, focusing on nano-scale electrode materials. A new type of oxide anode material, where solid-state precipitation produces nano-scale metal (Ru or Ni) clusters on the oxide surfaces, will be described. Infiltration of cathode materials to produce nano-scale mixed oxide conductors will also be discussed. The use of focused ion beam – scanning electron microscopy for three-dimensional reconstruction of electrode microstructure will be discussed. Finally, the use of SOFCs for efficient conversion of natural gas into electricity and hydrogen will be described.

SESSION I

MATERIALS FOR FUEL CELLS

KEYNOTE

Low Temperature Functionalization of Small Molecules and Applications to Energy Storage

Roy Periana, Scripps Research Institute-Florida

ABSTRACT

Today, with fossil fuels reaching new record prices and escalating concerns about Global Warming from man-made carbon dioxide emissions, it is imperative that we consider: A) Alternatives to petroleum and B) New hydrocarbon conversion technologies that are substantially more efficient as well as less expensive. Methane from abundant, under-utilized Natural Gas is an ideal alternative to petroleum if low cost technology could be developed to selectively generate products such as methanol or electricity. In general, substantial improvements could be made to hydrocarbon conversion technologies for the production of power, fuels and materials if low cost processes could be developed that convert parent hydrocarbons directly to these products at high selectivities and lower temperatures. Key to developing such next generation technologies will be the development of new generations of catalysts that facilitate the conversion of parent hydrocarbons to the corresponding alcohols (CH to CO bonds) at low temperatures while maintain high reaction rates and selectivities. Progress toward the development on these next generations of hydrocarbon hydroxylation catalysts that are based on the CH Activation reaction will be presented. The CH Activation reaction is a facile, selective reaction that proceeds without the involvement of free-radicals to convert parent hydrocarbon C-H bonds to M-C bonds. Combining the CH activation reaction with new reactions that convert M-C bonds to C-O bonds provides a basis for the rational development of the next generation of selective hydrocarbon oxidation catalysts that operate at low temperatures. Strategies and progress in overcoming the issues reported for the best Hydroxylation catalysts developed to date will be discussed. An important longer term benefit of such new catalysts is the possibility to develop carbon-neutral technologies that uses energy from light or other non-carbon-based sources to efficiently convert the C-O bonds in CO_2 to useful hydrocarbons (the microscopic reverse of CH to CO bonds) that can be utilized as feed-stocks by the petrochemical industry.

Novel Proton Conductive Membranes Derived from 1,3-Cyclohexadiene

Jimmy Mays, Department of Chemistry, University of Tennessee, Knoxville, TN 37996
Center for Nanophase Materials Sciences and Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, jimmymays@utk.edu

ABSTRACT

Poly(1,3-cyclohexadiene) (PCHD) is of interest as an alternative polymer electrolyte membrane (PEM) material due to its ring-like structure, which imparts superior mechanical and thermal properties, and due to the fact that PCHD can readily be incorporated into a range of homopolymer and copolymer structures. Furthermore, PCHD can be aromatized, sulfonated, or fluorinated, allowing for tuning of key performance properties such as conductivity, hydrophilicity, permeability, morphology, thermal stability, crystallinity, and cost. The basic building block, 1,3-cyclohexadiene, is a hydrocarbon monomer that could be inexpensively produced on a commercial scale.

The chemistry, characterization, and properties of PCHD-based membranes will be described. Some of these materials have been shown to exhibit superior proton conductivity to Nafion when tested under identical conditions. These membranes have excellent thermal and dimensional stability. The novel strategy used to prepare these membranes is conducive to their large scale production.

New High Temperature Polymer Electrolyte Membranes: Influence of the Chemical Structure on Their Properties

Morton Litt*, Junwon Kang and Sergio Granados, Case Western Reserve University, 10900 Euclid Ave., Cleveland OH 44106-7202

ABSTRACT

We have been working on rigid-rod liquid crystalline polyelectrolytes for many years. There is one great advantage in using such materials as polyelectrolytes. Because all molecules are linear rigid rods, they lie parallel. If a small mole fraction of a comonomer that has a large cross-sectional area is inserted, it increases the distance between molecules over their whole length. Most of the molecule is still the polyelectrolyte with a smaller cross-sectional area, so the increase in chain spacing between the molecules generates pores that are lined with acid groups. Water is held tightly in the pores because of capillary attraction and H-bonding; the structure can shrink only by high energy bending of the molecules. We call this "frozen in free volume."

This was exemplified for poly(phenylene sulfonic acid) with ~25 mol% grafted di-t-butyl phenol groups. The film swelled 25% at 100% RH, only in the film thickness direction, and retained high conductivity at low humidity.

We are now studying poly(phenylene disulfonic acid). Water absorption as a function of relative humidity was characterized by WAXD, DSC and weight and volume measurements: the results imply that a large amount of water is held very strongly. The acid groups are so crowded that even the homopolymer shows frozen in free volume, about equivalent to 4 waters per sulfonic acid. This is reflected in its remarkably high conductivity values at low humidity. Conductivity at 15% RH is 10 mS/cm at 25^{o}C, rising to ~100 mS/cm at 75^{o}C. However, the homopolymer is water soluble. We are working on making copolymers.

The Nanostructure of Nafion from Small-Angle Scattering and NMR Analysis

Klaus Schmidt-Rohr, Iowa State University, Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa

ABSTRACT

We have investigated the long contentious nanometer-scale structure of the Nafion ionomer used in proton exchange membranes of H_2/O_2 fuel cells. Using a recently introduced algorithm, we have quantitatively simulated previously published small-angle scattering data of hydrated Nafion. The characteristic "ionomer peak" arises from long, parallel but otherwise randomly packed water channels surrounded by the partially hydrophilic sidebranches, forming inverted-micelle cylinders. The channels are stabilized by the considerable rigidity of the Nafion backbones, detected by NMR. At 20 vol% water, the water channels have diameters between 1.8 and 3.5 nm, with a 2.4-nm average. Nafion crystallites (~10 vol%), which form physical crosslinks crucial for the mechanical properties of Nafion films, are elongated and parallel to the water channels, with cross sections of $\sim(5\ nm)^2$. Simulations for a dozen other models of Nafion, including Gierke's cluster and the polymer-bundle model, do not match the scattering data. The new model is the first without constrictions of ~ 1.2 nm diameter; it can explain important features of Nafion, including fast diffusion of water and protons through Nafion and its persistence at low temperatures.

Materials Issues for Photoelectochemical Water Splitting: Chalcopyrite Thin-Films and III-V Nitrides

John Turner, National Renewable Energy Laboratory, Golden, CO USA 80401, jturner@nrel.gov

ABSTRACT

The direct photoelectrochemical (PEC) splitting of water is a one-step process for the production of H_2 using solar irradiation; water is split directly upon illumination. This direct conversion system utilizes the process where an illuminated semiconductor material immersed in aqueous solution is used to decompose water directly. Light is absorbed in the semiconductor and water is split at the semiconductor surface. The key is to match the light-harvesting properties of the semiconductor with a catalyst that can efficiently collect the energy and direct it towards the water splitting reaction. The simplest PEC based direct water splitting system would consist of an illuminated single gap semiconductor having a bandgap greater than 1.6 electron volts coupled to a surface catalyst immersed in an aqueous solution.

To date, no semiconducting material has been discovered that simultaneously meets all the criteria required for economical hydrogen production via light-driven direct water splitting. Whilst considerable work has been directed at metal oxides due to their expected stability, little thought has been given to the requirement that these PEC devices must have the same fundamental internal quantum efficiency as the commercial high efficiency PV devices. Chalcopyrite materials in the family of Cu(In,Ga)(SSe) are known to have high PV conversion efficiencies and can be made with low-cost thin film approaches, making them appealing candidates for PEC water splitting. $CuGaSe_2$, with an energy gap close to 1.7eV, is at the lower end of the desired band gap range for water splitting materials but nonetheless of interest. The III-V nitride materials have shown excellent stability as evidenced by corrosion analysis; however, they show a significant decrease in overall conversion efficiency as compared to other non-nitride III-Vs.

This report will summarize our efforts on these materials and their application to tandem cells for photoelectrochemical water splitting. Issues relating to metal oxides will also be discussed.

SESSION II

PRODUCTION & DELIVERY

Hydrogen Production from Bio-derived Liquids

Yong Wang, Pacific Northwest National Laboratory

ABSTRACT

Biomass is available from variety of sources that are highly diverse. These sources include animal waste, municipal solid waste, forest residue, and agricultural residue. Three main components of biomass include hexose oligmers, pentose oligmers, and polymeric phenolics. Biomass derived feedstocks are highly oxygenated compounds that have a high degree of functionality and low thermal stability. The challenge is how to economically convert the biomass resources into hydrogen that can either be used as an integral part of future biorefinery or for distributed fuel cell applications. Both biological and thermochemical transformation technologies are currently being developed in converting biomass to hydrogen. Thermochemical transformation includes gasification followed by water gas shift, fast pyrolysis followed by steam reforming, deconstruction of ligonocellulosic biomass followed by the reforming of monomers, or reforming of bio-ethanol or glycerol, a bio-diesel by-product. In this talk, the current status, challenges, and future research directions using thermochemcial transformation technologies will be discussed.

Hydrogen Supply Options Including the Development of an On-Site Hydrogen Production System for Vehicle Fueling Stations

Tim Aaron, Praxair, Inc.

ABSTRACT

This presentation includes an analysis of hydrogen fueling station criteria, including delivery and production options as well as an overview of issues related to on-board hydrogen storage. The presentation details the development of an on-site hydrogen supply system based on steam methane reforming (SMR) that could easily be added to a typical fueling station. The presentation will show that opportunities exist for a significant reduction in fueling station hydrogen cost by introducing advanced design technologies, such as Design for Manufacturing and Assembly (DFMA), to the development of hydrogen production systems. Praxair, in cooperation with the U.S. Department of Energy (DOE), is developing a small SMR-based system using this approach. An overview of the impact of this effort on the overall cost for small on-site hydrogen production including comparisons with gasoline will be presented.

Multi-Layered Polymer and Polymer/Metal Materials for Large- and Small-Scale Hydrogen Delivery

James G. Blencoe, Simon L. Marshall, and Michael T. Naney, Hydrogen Discoveries, Inc., 1133-C Oak Ridge Turnpike, #116, Oak Ridge, TN 37830

ABSTRACT

Large amounts of time, effort, and money have been spent investigating the practical feasibility of using carbon steels as materials of construction for pipeline delivery of high-pressure (500-3000 psi) hydrogen gas. Most of the gaseous hydrogen produced today is transferred short distances through relatively small-diameter pipes at pressures of just a few hundred psi. For this purpose, pipes made of carbon steel are perfectly adequate. However, at internal gas pressures above ~500 psi, carbon-steel pipes are susceptible to hydrogen embrittlement, which is typically manifested by surface cracking, crack propagation, decreases in tensile strength, loss of pipeline ductility, and reduced burst-pressure rating. This degradation can lead to premature failure of one or more segments of a pipeline, resulting in leakage of gas—or in extreme circumstances, bursting of a pipe.

It has been suggested recently that many of the cost, weight, welding and joining, repair, and safety issues associated with hydrogen transfer through carbon-steel pipes can be resolved by switching to multi-layered, fiber-reinforced polymer (FRP) pipes. To have sufficient mechanical strength and hydrogen-containment capability, a FRP pipeline segment would probably consist of an inner, low-permeability, barrier tube that transmits the high-pressure hydrogen gas, a protective layer placed over the barrier tube, an interface layer placed over the protective layer, multiple glass- and/or carbon-fiber composite layers, an outer barrier layer, and an outer protective layer. The issues and challenges for adapting existing FRP pipeline technologies to hydrogen service at pressures above ~500 psi are: evaluating polymeric materials for hydrogen containment, compatibility, and prolonged pressure-cycling; identifying methods for profitable manufacture of pipes with inside diameters >4 inches; weighing the options for on-site pipeline fabrication, joining, and repair; determining the availability of sensor technologies for measuring gas temperature, pressure, and flow rate in real time; and writing the necessary codes and standards to meet the requirements of local, state, and federal regulatory agencies.

Thus, it is significant that scientists at Hydrogen Discoveries, Inc. have invented new methods for—first, reducing the diffusive flux of hydrogen gas through the walls of multi-layered polymer and polymer/metal pipes, and second, recovering any hydrogen that leaks from places where those pipes terminate. The techniques involve: (i) use of one or more layers of homogeneous or laminated polymeric material, solid metal(s), and/or liquid(s), to create multiple equilibrium *and kinetic* barriers to hydrogen diffusion; (ii) in special circumstances, physical separation of gaseous hydrogen from one or more static or flowing liquid interlayers; and (iii) using sealed covers connected to small-diameter tubes to recover hydrogen emanating from pipe connections. These technologies have numerous practical applications in transmitting and distributing pressurized hydrogen gas through pipes, pipelines, tubes, and hoses of various lengths, internal diameters, and wall thicknesses.

Rigorous theoretical modeling of hydrogen diffusion through multi-layered, polymer/metal tubes and pipes indicates that one or more thin layers of aluminum (Al), copper (Cu), or stainless steel will be particularly effective in decreasing overall hydrogen flux. Therefore, three-layer polymer (e.g., HDPE)/metal(Al, Cu, stainless steel)/polymer structures, with inner and outer layers of polymer protecting the thin metal interlayer from chemical attack and mechanical abrasion, are of particular interest in designing multi-layered FRP pipes, tubes, and hoses for hydrogen service.

POSTER

ABSTRACTS

POSTERS

Presentation Title: Ammonia Borane Slurry Hydrolysis

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Dr. Yuan Zheng, Assistant Research Professor, Purdue University Department of Mechanical Engineering
Dr. Jay Gore Reilly Professor of Engineering, Director of the Energy Center Purdue University

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ABSTRACT

Ammonia borane (AB), NH_3BH_3, has received much attention as a potential on-board hydrogen carrier for vehicles. AB is soluble in water up to 26%, and when reacted with water releases three moles of H_2 for every initial mole of AB. However, even at the saturation limit the solution cannot meet the 2010 target of 6 wt% H_2 set by the U.S. Department of Energy (DOE). This has motivated the present work where the maximum gravimetric H_2 density of the AB-water reaction is explored.

Experiments were performed using AB-water slurries, mixtures of AB and water above 26 wt% AB, with the objective of reducing the water needed for the reaction towards the stoichiometric minimum. The result of this series of tests indicates that AB slurry hydrolysis can meet the DOE's 2010 gravimetric H_2 density target. A density of 7.5 wt% H_2 was calculated based on data from a slurry mixture with a ratio of 2.37:1 moles water to mol AB.

It has also been observed that in addition to producing H_2, AB hydrolysis liberates approximately 7% of the initial NH_3 from a 25 wt% AB solution. If NH_3 were reformed to produce additional H_2, a hybrid AB-slurry hydrolysis and ammonia cracking system may be able to meet the 2015 DOE goal of 9 wt% H_2.

POSTERS

Presentation Title: Chemical Kinetic Parameter Estimation for Ammonia Borane Hydrolysis

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ABSTRACT

Onboard hydrogen storage is an enabling factor in the development of fuel cell powered passenger cars. Ammonia borane (AB) hydrolysis is one of the potential approaches for onboard hydrogen storage. In this study, kinetics of catalyzed ammonia borane hydrolysis using ruthenium-supported-on-carbon has been measured. For reacting flows, chemical kinetics determines the rates of heat generation and species production or consumption in the overall energy and mass balances respectively. Kinetic measurements under isothermal conditions provide critical data for the design of hydrolysis reactors. It is, however, not always possible to eliminate the effects of internal diffusion in a heterogeneous chemical reaction. In such cases, the reaction efficiency ( ), which depends on the effective liquid phase diffusivity (*Deff*) in the catalyst medium, should be determined. Determination of intrinsic kinetic parameters using apparent reaction data is, thus, a challenge.

In this study, the change in AB concentration (*C*AB) with reaction time (*t*) has been directly measured. It was observed that the AB hydrolysis reaction had orders between zero and one in a temperature range of 26oC to 55oC. A unified Langmuir-Hinshelwood model has been adopted to describe the reaction kinetics. The intrinsic kinetic parameters (*A, Ea, _Hads, K0*) as well as *Deff* need to be estimated by inverse analysis of the measured *C*AB vs. *t* data. Conventionally, kinetic parameters are determined using linear fitting. Sometimes, however, it is impossible to converge to a unique value by using the linear fitting approach as there are several values providing regression coefficients greater than 0.99. In this study, the multiple-variable inverse problem has been solved using a non-linear fitting algorithm based on Powell's conjugate-gradient error minimization. This algorithm minimizes errors without using derivatives. As a result, the uncertainties in the kinetic parameter estimation have been significantly reduced by the new approach.

POSTERS

Presentation Title: Development of a Photoelectrode based on a 3-Dimensionally Architectured p-CdTe/n-TiO_2 Heterojunction

Author(s) and Affiliation(s): Jason A. Seabold,[1] Karthik Shankar,[2] Rudeger H.T. Wilke,[2] Maggie Paulose,[2] Oomman K. Varghese,[2] Craig A. Grimes,[2] and Kyoung-Shin Choi[1]*

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ABSTRACT

Cadmium telluride is one of the more promising materials for the development of thin film photovoltaic (PV) cells for the conversion of light into electrical energy. CdTe has a bandgap of 1.45eV, which is an optimal match to the solar spectrum, and because of its high absorption coefficient, only a small layer of CdTe is required to efficiently absorb solar photons. To date, almost all CdTe-based solar cells have been constructed based on planar n-CdS/p- CdTe junctions. Because the energy converted by a solar cell directly depends on the size of its p-n junction area, utilizing a 3-dimensionally architectured junction will enhance the junction area and increase cell performance.

This presentation details the creation of a 3-dimensional interpenetrating p-n junction composed of p-CdTe and n-TiO_2. This is accomplished by filling an array of TiO_2 nanotubes with CdTe via a novel electrodeposition technique. Electrochemical synthesis of the nanotubes and subsequent filling with CdTe will be discussed, as well as the characterization of their photoelectrochemical properties.

POSTERS

Presentation Title: Economically Viable Process for Producing Hydrogen On-Demand

Author(s) and Affiliation(s): Charles R. Allen, Go Choi, Jong-hyeok Jeon, Jerry M. Woodall, Jerry T. Ziebarth, Robert Kramer

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ABSTRACT

Two major problems with using hydrogen as an energy source are the high cost and lack of safe transportation. Our group has been studying ways to generate hydrogen meeting both of these challenges. We have discovered that we can split water into hydrogen, heat and alumina on demand. We have varied the composition of aluminum alloys, and recently have found that we can split water on demand using solid alloys of 95 wt% aluminum (Al), and 5 wt% of a gallium-indium-tin alloy (Ga-In-Sn). This is both a technological breakthrough and an economic viability breakthrough since the more expensive Ga-In-Sn component is in small proportion. Since pure alumina can be reduced for about $0.30/lb, and the 5% component can reclaimed at about $0.0625/lb, we can show this technology is capable of delivering hydrogen energy at $0.15/kWh, and total energy of $0.08/kWh. Furthermore, the alloy itself is safer than any other hydrogen energy technologies. We have also created a pressure tank that will be used in our hydrogen powered vehicle prototype.

POSTERS

Presentation Title: Energy efficiency comparison between electric and hydrogen fuel cell vehicles

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ABSTRACT

This paper compares the energy efficiency between all electric vehicles (EVs) and hydrogen fuel cell vehicles (HFCVs). The expected future performances of the two types of vehicles are carefully evaluated based on the following assumptions: 1) electricity from renewable sources (such as solar and wind) is used for EV charging and for hydrogen production, 2) a driving range of about 300 miles is envisioned between EV charges and 3) hydrogen infrastructure is available in due time. The results show that EVs are about 100% more energy efficient than the HFCV counter part. The implication of the preliminary results is that EVs may be a better choice for the future transportation to address energy security and environmental problems.

POSTERS

Presentation Title: Enhancement of the Photoelectrochemical Properties of Electrochemically Grown Dendritic Cuprous Oxide Films

Author(s) and Affiliation(s): Colleen M. McShane, Matthew James Siegfried and Kyoung-Shin Choi; Chemistry, Purdue University, West Lafayette, Indiana

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ABSTRACT

Cuprous oxide is an affordable, non-toxic material useful for solar energy conversion (E_g = 2eV). Stabilizing dendritic growth (i.e. diffusion-limited growth) of cuprous oxide can be highly advantageous because it allows for facile surface coverage and an increase in surface reactivity and surface area. In this presentation, we report electrochemical conditions that allow for the dendritic growth of cuprous oxide. Typically, dendritic growth via electrodeposition can be stabilized when a high overpotential is applied to increase the deposition rate above the diffusion rate. This creates a depletion layer around the growing surface and the growth becomes limited by diffusion, allowing branching growth to occur. However, dendritic growth of Cu_2O has not been easily achieved because the application of higher overpotentials often results in the co-deposition of Cu metal. In addition, the pH drop accompanying the production of Cu_2O ($2Cu^{2+} + H_2O + 2e^-$ $Cu_2O + 2H^+$) promotes the development of well faceted surfaces preventing dendritic growth. Conditions to avoid this problem and produce pure dendritic cuprous oxide films will be discussed in this presentation. Finally, the effect of dendritic morphology on photo-electrochemical properties will be presented.

POSTERS

Presentation Title: Heat Transfer Characterization of Metal Organic Frameworks for Cryo-adsorption of Hydrogen Gas

Author(s) and Affiliation(s): Casey L. Porta (Ph.D. Candidate), Timothée L. Pourpoint, Dr. Timothy S. Fisher

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ABSTRACT

Solid-state hydrogen storage in Metal Organic Framework (MOF) materials offers the possibility of significant efficiency benefits as compared to other hydrogen storage options. Key issues with developing a successful MOF-based storage system include sufficiently rapid fill and release rates as well as thermal management during fill operations at liquid nitrogen temperatures.

In the present research, the hydrogen adsorption characteristics of various MOF materials are studied both theoretically and experimentally. General MOF characteristics including structure, density, and heat of adsorption are presented and implemented in a numerical model developed to facilitate the design of a representative test article.

The system being developed at the Hydrogen Systems Lab must include temperature control from ambient to cryogenic conditions for both the jacket surrounding the test article and the hydrogen gas fed into the test article. Presented here is the structure of a detailed heat and mass transfer analysis of the test article required to determine the size and shape of the test article, reduce wall boundary effects, and optimize the capacity of the pressure vessel's temperature conditioning system. The analysis includes a reacting porous media model assuming two-dimensional fluid flow and heat transfer in the MOF bed.

POSTERS

Presentation Title: Homoleptic Transition Metal Hydrides and New Approaches to Hydrogen Storage

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ABSTRACT

In the synthesis of hydrogen storage materials, the current frontier is to produce materials with nanoscopic control. One chief challenge is to utilize molecular precursors and convert them into solid state structures with that desired purpose. Conventional routes of laser abalation/matrix deposition chemistry, high-temperature chemistry, and aqueous solution chemistry need to be diversified with softer routes. This poster describes such a new route that produces potentially bare metal atoms in solution that coalesce to form particles down to the nanoscale and that will be much more efficient in reactions with hydrogen at or near room temperature and pressure. The thermodynamics of the Kubas-type complexes would have an ideal binding energy (10-40 kJ/mol) that would permit reversible hydrogen storage at near ambient conditions. Kubas hydrides, e.g. $[MH_x(H_2)_y]$ ($y \geq 2$; M = first row TM) species, would appear to meet DOE targets.

As a first step to reaching the above goal we have shown that nanoscopic iron results from the known species, $[FeH_6][MgX(THF)_2]_4$ (X = Cl & Br), via solution comproportionation with Fe(II). The expansion of the desired chemistry to other first row metals is supported by the preparation of $[CoH_6][MgX(THF)_2]_3$, for which we show evidence. Our homoleptic species and Lester Andrew's complex, $[WH_4(H_2)_4]$, prepared in hydrogen matrix encompass analogous cyano complexes.

POSTERS

Presentation Title: Hydrogen from Silicon Hydrides: a Catalytic Dehydrocoupling Approach

Author(s) and Affiliation(s): Guodong Du, Erin Smith and Mahdi M. Abu-Omar
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ABSTRACT

Extensive efforts have been dedicated to the area of hydrogen source and storage in moving toward a hydrogen-based economy. In many occasions, however, the products after hydrogen release are difficult and expensive to recycle. Now we present an alternative approach based on dehydrogenation of silicon hydrides, in which the resulting polysilanes can be converted back to silicon hydrides under mild conditions. The current emphasis is to evaluate various transition metal catalysts, primarily zirconium and nickel based complexes, in catalytic dehydrocoupling of primary and secondary silanes, and to investigate the kinetics and mechanism of these reactions in the context of hydrogen production.

POSTERS

Presentation Title: Modeling of Forced Ignition and Combustion in Stratified Hydrogen Mixtures

Author(s) and Affiliation(s): Rebecca Owston, Mechanical Engineering Graduate Program, Purdue University

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ABSTRACT

In hydrogen direct-injection spark-ignition (DISI) engines the spatial and temporal ignition event is fixed by the spark plug placement and timing. In order to provide stable combustion the fuel-air mixture at the spark location has to be controlled in order to prevent misfire. Two-dimensional direct numerical simulations of a forced-ignition event in an initially quiescent mixing layer of hydrogen and air have been carried out at atmospheric pressure using detailed chemistry and mixture-averaged diffusion coefficients. Overall, this study primarily investigates the effect of initial spark placement within the flammability limits of hydrogen-air. Displacement and stabilization speeds of the propagating flame fronts have been computed along isocontours of water vapor representing 10% and 25% of the downstream equilibrium concentration. Following the period of spark energy-addition the flame kernel is observed to bifurcate into twin triple flame structures that subsequently propagate towards opposite sides of the domain along the stoichiometric line. The point of maximum heat release was found to remain on the lean side after the transient spark interlude. For all cases of successful ignition, transient spark effects are observed to dissipate within 0.2 milliseconds.

POSTERS

Presentation Title: Novel noncatalytic methods to release hydrogen from boron compounds for fuel cell applications

Author(s) and Affiliation(s): Moiz Diwan, Evgeny Shafirovich, Arvind Varma, School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907-2100

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ABSTRACT:

A widespread use of hydrogen fuel cells is limited by the lack of availability of a practical, high density fuel source. Among various alternatives, chemical methods of hydrogen storage provide high specific energy at relatively easy storage conditions. Sodium borohydride (SBH) and ammonia borane (AB) are considered to be promising hydrogen storage materials as they contain 10.8 and 19.6 wt% hydrogen, respectively. Thermolysis, catalytic hydrolysis and heat generated by additional reactive mixtures are usually employed, but these methods have disadvantages that decrease the efficiency of hydrogen storage systems. We have proposed new approaches to release H_2 which do not require any catalyst and produce high H_2 yield and environmentally benign byproducts. One such approach involves the use of SBH or AB with gelled water and magnesium or nanoaluminum. Due to the highly exothermic metal-water reaction, such mixtures, upon ignition, exhibit self-sustained propagation of combustion wave with simultaneous release of H_2 from the boron compounds and water. For AB, we have also studied combustion in a separated AB – metal/water system. The other approach involves external heating of aqueous AB solutions under modest inert gas pressure. The research program involves various experimental methods (e.g., digital video recording, mass spectrometry, XRD, NMR and isotopic labeling), as well as mathematical modeling.

POSTERS

Presentation Title: Nitrogen-Doped and Carbon-Doped In_2O_3 Films for Photoelectrochemical Hydrogen Production

Author(s) and Affiliation(s): Karla Reyes-Gil, Yanping Sun, Carl Murphy, Enrique Reyes-Garcia and Daniel Raftery Purdue University, Chemistry Department.

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ABSTRACT

The photoelectrochemical production of hydrogen from water using solar energy has drawn considerable attention due to the importance of using hydrogen as a clean and renewable source. Wide band-gap semiconductors are the most promising materials due to their good stability and catalytic activity, but their poor visible light absorption represents a major problem. We recently reported work on a new visible-light absorbing photocatalyst, N-doped In_2O_3, which shows promise as an efficient material. N-doped In_2O_3 material reduces band gap, and we observe that N can either substitute for oxygen in the lattice or be present in interstitial sites depending of the N-source used. Recent EPR and XPS results indicate that a paramagnetic N-species is the origin of the photoelectrochemical activity. In addition to N-doped In_2O_3, a new visible-light photocatalyst, C-doped In_2O_3, was prepared by spray pyrolysis. XPS and ^{13}C SSNMR showed the presence of various carbonate-type species. Compared to the undoped In_2O_3, C-doped In_2O_3 materials show an obvious absorption in the 350-500 nm range and exhibit significantly higher photoelectrochemical activity for water splitting, with observed photocurrent densities as high as 1 mA/cm^2. These results provide very useful information towards understanding the structure and enhanced properties of these new materials.

POSTERS

Presentation Title: Parameters Affecting Design of Heat Exchanger for Storage of Hydrogen Using High Pressure Metal Hydrides

Author(s) and Affiliation(s): Milan K. Visaria, Timothée Pourpoint, Issam Mudawar

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ABSTRACT

Many metals and alloys react reversibly with hydrogen to form metal hydrides thus storing hydrogen. Recent advancements in development of metal hydrides have made them one of the most promising modes of hydrogen storage for automobiles. However, most current metal hydrides have low thermal conductivity and low gravimetric/volumetric densities. Also, the process of hydriding (charging) metal hydride releases large amounts of heat. Thus, thermal management becomes one of the major challenges in the development of successful and efficient on-board hydrogen storage system. Hydriding is a kinetics driven, self-limiting process and quick removal of heat is important for fast refueling. As a result, one of the important aspects of hydrogen storage is efficient design of heat exchanger. The heat exchanger must efficiently remove heat from the metal hydride during hydriding while allowing for hydrogen to be stored with high volumetric efficiency.

A number of parameters like the pocket width, fin size, metal hydride properties, contact resistance, coolant flow rates, etc. influence the heat exchanger design. A computational model was developed to predict the effects of these parameters on heat exchanger performance. The results from the model are compared with those obtained experimentally thus providing an essential tool for further development and optimization of hydrogen storage systems compatible with automotive requirements.

POSTERS

Presentation Title: Search for a Better Water Gas Shift Catalyst for the Production of Hydrogen

Author(s) and Affiliation(s): Luis Bollmann, Joshua L. Ratts, W. Damion Williams, Jorge Pazmino, Jeffrey T. Miller, W. Nicholas Delgass, Fabio H. Ribeiro, School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907-2100, [1]BP Research Center, E-1F, 150 W. Warrenville Rd., Naperville, IL 60563

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ABSTRACT

The water-gas shift reaction (WGSR) is a key step for the production of hydrogen by hydrocarbon reforming. Our goal is to formulate a catalyst for the WGSR that has the high turnover rate (TOR) of the commercial Cu-based system and the capability to recover from operational upsets, which is typical of noble metal systems. The search for a better WGS catalyst is based on the Discovery Informatics approach, which requires the identification of key chemical descriptors and in depth kinetic analysis of the catalysts. Using a library of over 200 catalysts, the effects of support, promoters, particle size and alloying was studied for the WGSR. Our results indicate a strong effect of the support on rates. With the non-interacting supports CeO_2, TiO_2, and ZrO_2, the TOR on Pt catalysts was about 10 times higher than on the most common SiO_2 and Al_2O_3 supports. The addition of Mo, Fe, and Zn promoters to Pd and Pt catalysts supported on alumina increased the TOR by a factor of up to 100. However, the TOR for the promoted catalysts was never higher than the rates on the pure metals on the non-interacting supports.

POSTERS

Presentation Title: Simplified Model for Thermochemical Hydrogen Production via Sulfur Iodine and Hybrid Sulfur Cycle

Author(s) and Affiliation(s): Nicholas R. Brown, Shripad T. Revankar, Seungmin Oh, Cheikou Kane

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ABSTRACT

This poster presents a transient control volume modeling scheme for both the sulfur iodine (SI) and Westinghouse hybrid sulfur (HyS) thermochemical cycles, two potentially important candidates for the large scale production of hydrogen. In this study, transient control volume models of the SI and HyS cycles are presented, along with a methodology for coupling these models to codes which describe the transient behavior of a high temperature nuclear reactor. The transient SI and HyS cycle models presented here are based on a previous model with the addition of pressure change in the reaction chambers. This pressure variation capability is obtained using the ideal gas law which is differentiated with respect to time. The HyS model is based on a time-dependent application of the Nernst equation. Investigation of the new pressure assumption yield a peak pressure rate of change of 5.877 kPa/s for a temperature driven transient test matrix and 2.993 kPa/s for a mass flow rate driven transient test matrix. These high rates of pressure change suggest that an accurate model of the SI and/or HyS cycle must include some method of accounting for pressure variation. The HyS model suggests that the hydrogen production rate is directly proportional to the SO_2 production rate.

POSTERS

Presentation Title: Simultaneous Water Vapor Concentration and Temperature Measurements in Unsteady Hydrogen Flames

Author(s) and Affiliation(s): David Blunck, Sumit Basu, Yuan Zheng, Jay Gore

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ABSTRACT

Techniques applicable to visualization and scalar measurements in large-scale hydrogen fires are highly desired, but lacking. In this research, planar thermal images of a buoyancy-driven unsteady laminar hydrogen/air flame and line images of a thin filament stretched across this flame were obtained using an infrared (IR) camera at a sampling frequency of 348 Hz. A pulsing frequency of 11 Hz was measured. Transient line measurements of temperature (*T*) and water vapor mole fraction (X_{H2O}) have been achieved using inverse radiation calculations. Instantaneous X_{H2O} and *T* distributions during a flame-vortex interaction cycle were obtained with temporal and spatial resolutions of 3 ms and 1.7 mm respectively. The instantaneous distributions of X_{H2O} and *T* were affected by preferential diffusion and flame stretching and compression. Vortices caused more scalar fluctuations outside the flame surface than inside. The present X_{H2O} and *T* measurements are consistent with previous laser diagnostics based measurements and with detailed chemistry based simulations of similar flames. Based on this, the present thermal imaging based technique can be extended to large-scale hydrogen fires.

POSTERS

Presentation Title: Thermal Management in the Measurement of Metal Hydride Kinetics

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ABSTRACT

Many metal hydride nanopowders are currently being investigated as a potential hydrogen storage media. The kinetic properties of hydrogen absorption in a metal hydride of interest are largely unknown. This study will use a combination of novel and well-established techniques to experimentally determine these properties. Since these measurements must be taken at isothermal conditions and the metal hydride absorption reaction is highly exothermal, specific thermal considerations must be made in these measurements.

Typical instruments available for kinetics measurements suspend the samples in a small chamber, effectively thermally isolating them from the cooling or heating system designed to control sample temperature. The design used herein will eliminate that convective resistance layer, thereby increasing the amount of heat that can be rapidly diffused out of the sample. An additional barrier to heat diffusion from the sample is the relatively high contact resistance between the nanopowder and the sample chamber wall. Increasing the powder-solid contact area and using a mechanical press to pack the powder in the chamber are two methods that may be used to decrease the resistance in this apparatus. Additionally, an active temperature control system will be used to maintain "quasi-isothermal" conditions in the metal hydride during measurements.

POSTERS

Presentation Title: Transient Plane Source Method for Thermal Property Measurement of Metal Hydrides

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ABSTRACT

Metal hydrides are promising hydrogen storage materials with potential for practical use in a passenger car. To be a viable hydrogen storage option, heat transfer must be well understood and accounted for. As such, the thermal properties of the metal hydride are measured and compiled to assess heat transfer behavior of the material. These properties include thermal conductivity, specific heat, and thermal diffusivity.

The transient plane source (TPS) method was selected especially due to a high level of versatility, including customization for high pressure hydrogen environments. To perform this measurement, a TPS 2500S thermal property analyzer by the Hot Disk Company was employed. To understand the measurement and analysis process of the TPS method, two different sample materials were evaluated at ambient conditions. These samples included a stainless steel pellet and an inactivated (non-pyrophoric) metal hydride pellet. Thermal conductivity and thermal diffusivity of these samples were measured using the TPS method. The thermal property measurements are compared to the data available in the literature (stainless steel) and the data obtained using laser flash method (metal hydride). The improvements needed for the TPS method are discussed in detail.

POSTERS

Presentation Title: Use of carbon-free Hydrogen to produce biofuels

Author(s) and Affiliation(s): Navneet R. Singh, Fabio H. Ribeiro, W. Nicholas Delgass and Rakesh Agrawal
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ABSTRACT

To overcome the concerns of energy security, peak oil, current high crude oil prices, and global warming, we proposed a hybrid hydrogen-carbon (H_2CAR) process for sustainable supply of liquid fuel. Biomass is primarily treated as a source of carbon atoms and hydrogen derived from carbon-free energy sources is used to supply hydrogen atoms and energy required for this gasification followed by Fischer-Tropsch based process. Novel feature of this process is recycle of CO_2 produced during entire process to the gasifier and its subsequent conversion to liquid fuel using hydrogen from carbon-free energy resulting in 3 times higher liquid fuel production than conventional process. The most important consequence of H_2CAR process is that it can supply entire need for US transportation sector using 1.366 billion ton biomass available sustainably in US with slight changes in agricultural and forestry practices whereas Billion ton biomass study estimates that this quantity is sufficient to meet 30% of US transportation need using conventional approaches. As any mixture of biomass can be gasified, this process promotes diversity in biomass growth and it has been shown in literature that diversity of crops enhances biomass yield by 180%. Three times higher liquid fuel yield ensures that land area required is decreased by a factor of 3. Lesser land area and hence, less biomass requirement implies less fertilizers, pesticide application and less water requirement to support a given plant capacity. For more details, see Agrawal et al., 2007, PNAS, 104 (12), 4828-4833. http://www.pnas.org/cgi/content/full/104/12/4828

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The Energy Center gratefully acknowledges the support of Quantachrome Instruments in sponsoring the printing of our 2008 program.

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