II.D Electrolytic Processes

II.D.1 Photoelectrochemical Systems for Hydrogen Production

Ken Varner, Scott Warren, J.A. Turner (Primary Contact)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401
(303) 275-4270, fax: (303) 275-3033, e-mail: john_turner@nrel.gov

DOE Technology Development Manager: Roxanne Danz
(202) 586-7260, fax: (202) 586-9811, e-mail: Roxanne.Danz@ee.doe.gov

Objectives

- Identify and characterize possible semiconductor materials that have appropriate bandgaps and are stable in aqueous solutions.
- Study multi-junction semiconductor systems for higher efficiency water splitting.
- Develop techniques for the preparation of transparent catalytic coatings and their application to semiconductor surfaces.
- Identify environmental factors (i.e., pH, ionic strength, solution composition, etc.) that affect the energetics of the semiconductor, the properties of the catalysts, and the stability of the semiconductor.
- Develop techniques for the energetic control of the semiconductor electrolyte interphase.

Approach

- Identify new semiconductor materials with bandgaps in the ideal range.
- Catalyze the surfaces and engineer the bandedges of the identified semiconductor materials as required.
- Determine if existing photovoltaic (PV) device structures could be easily modified to effect the direct splitting of water.

Accomplishments

- Work on the stability and efficiency characteristics of amorphous silicon structures for direct water splitting systems clearly showed that it is feasible to utilize amorphous silicon devices in direct contact with aqueous electrolytes without additional protective coatings.
- Work on the study of gallium indium nitride materials for water splitting showed that if the bandgap can be reduced, these materials have very promising bandedge energetics and stabilities.
- Studies of bandedge engineering of gallium indium phosphide (p-$GaInP_2$) have shown that the bandedges can be controlled within a small range of pHs.

Future Directions

- Continue to evaluate samples of new semiconducting materials with appropriate bandgaps.
- Continue to design and test additional multi-junction systems (CuGaInSSe, GaPN, and GaInN materials, and a-Si triple junction systems) for possible photoelectrochemical water splitting.

- Study the stability of semiconductor materials and coatings for protection against corrosion.
- Develop techniques for controlling the semiconductor energetics so that the bandedges are matched for water splitting, and identify factors that influence the catalysts of hydrogen and oxygen.

Introduction

The goal of this research is to develop a stable, cost-effective, photoelectrochemical (PEC)-based system that will split water upon illumination, producing hydrogen and oxygen directly, using sunlight as the only energy input. Past work has shown that PEC hydrogen producing devices can have an efficiency 30% higher than separated PV electrolysis devices, and analysis work has shown that the cost of PEC hydrogen can be lower than PVelectrolysis. For direct photoelectrochemical decomposition of water to occur, the following conditions must be met:

- The semiconductor system must generate sufficient voltage to split water.
- The energetic of the semiconductor must overlap those of the hydrogen and oxygen redox reactions.
- The semiconductor system must be stable in aqueous electrolytes.
- The charge transfer from the surface of the semiconductor must be fast enough to prevent corrosion and reduce energy losses due to overvoltage.

In developing PEC hydrogen systems that will meet these requirements, research efforts are focused in two areas: (1) chemical modification of the semiconductor electrode surface material to improve system energetics, and (2) evaluation of triple-junction amorphous silicon structures as low-cost thin-film water splitting systems.

Approach

Surface Modification of Semiconductor Material

Gallium indium phosphide (p-$GaInP_2$) is a semiconducting material that meets the bandgap energy criteria, but does not meet the bandedge overlap criteria required for PEC hydrogen production. This electrode also accumulates photogenerated charges at its surface, contributing to surface corrosion and bandedge migration away from the desired electrode energetics. In this research, p-$GaInP_2$ surfaces were modified by adsorption of metallated porphyrins and transition metals with the aim of moving bandedge energies and catalyzing interfacial charge transfer for PEC hydrogen generation.

Characterization of Triple-Junction Amorphous Silicon Systems

Low-cost solid state multi-junction systems, based on triple-junction amorphous silicon (a-Si) solar cells, have voltages sufficient for water splitting, and the cells can be tailored to produce voltages matched to the energetic requirements of the water splitting reaction. In this research, efforts focused on characterization of various a-Si triple junction samples. These samples underwent current-voltage tests, corrosion measurements, and metal-ion catalyst treatments. Because of the instability of a-Si in an aqueous environment, research efforts included evaluation of a surface coating of amorphous silicon carbide (a-SiC) to stabilize and protect the system. The a-SiC samples were tested for their effect on the overall efficiency of water splitting and their effectiveness in protecting the underlying semiconducting material from corrosion.

Results

Surface Modification of Semiconductor Material

After initial characterization of the p-$GaInP_2$ electrode material, seven different porphyrin treatments were evaluated for their ability to modify the surface of the p-$GaInP_2$ electrode. All of the porphyrins show a statistically significant shift in flat band potential, with the ruthenated porphyrins showing the greatest shift. The bandedges shifted into overlap conditions about 20% of the time with ruthenium octaethyl porphyrin carbonyl RuOEP CO. The variability observed in the flat band potential was attributed to the porphyrin application method and/or the age of the electrode, both of which affect the amount of porphyrin on the p-$GaInP_2$ surface.

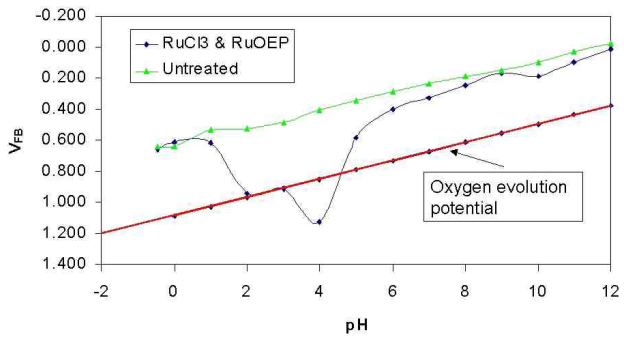

Figure 1. The effect of pH on the flat band potential of an untreated electrode and an electrode treated with both ruthenium chloride ($RuCl_3$) and RuOEP CO. Dip-coating an untreated electrode with $RuCl_3$ and then drop-evaporating RuOEP CO vastly improves charge catalysis properties up to a photocurrent of 1 mA/cm^2. Testing is in a 4 pH buffer. The most substantial shift in flat band potential occurs at pH 4, hence the testing at that pH.

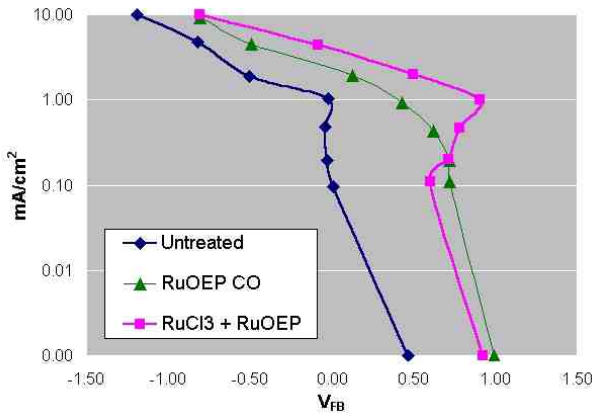

Figure 2. Charge transfer catalysis of various treatments. Testing performed in pH 4 buffer.

When combining the RuOEP CO with a transition metal, such as ruthenium or platinum, the bandedge shift increases up to 0.48 electron volts (eV) in the positive direction. These combination treatments allowed overlap of the water redox potentials to occur in the dark. The effect of pH on the flat band potential of an untreated electrode and

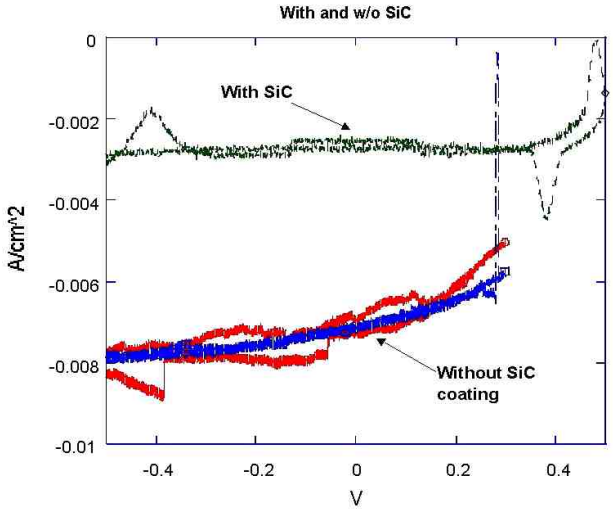

Figure 3. Comparison of the photocurrent for coated and uncoated samples in acid.

an electrode treated with RuOEP CO in combination with transition metals is shown in Figure 1. The largest shifts in flat band potential occurred at a pH of 4. Adding platinum or ruthenium to the porphyrin also significantly improves the charge transfer catalysis properties under light irradiation up to a photocurrent of 1 mA/cm^2, as shown in Figure 2. Despite the improved placement of bandedges, no significant change in the two-electrode current-voltage curve was perceptible. In addition, differences in open circuit cell potential between modified and unmodified systems were not statistically significant.

Characterization of Triple-Junction Amorphous Silicon Systems

In order to evaluate the effectiveness of a-SiC as a protective layer on a triple-junction a-Si device, triple-junction a-Si devices, both with and without a-SiC deposited on the surface, were exposed to chemically aggressive basic (1 molar [M] potassium hydroxide [KOH]) and acidic (1 M sulfuric acid) solutions. Current density measurements showed that the a-SiC coating provided some protection in the basic solution, but in acid, no noticeable difference occurred between the protected and non-protected samples. This suggests that a-SiC may not be necessary to protect the device, especially when the electrolyte solution is acidic.

However, as shown in Figure 3, in some cases, the a-SiC actually decreases the current density as compared to an unprotected sample. Because the a-SiC is deposited on the surface of the electrode, its physical and optical properties must be optimized to work with the a-Si triple junction it is designed to protect. Researchers determined that for a-SiC to be effective in this device without hindering the photocurrent, bandgaps in the 2.5 eV range and higher would be ideal. In addition to the light, electrons must also be able to move through the a-SiC to effect water splitting. Because it has a finite thickness, there will be some resistance associated with it. The resistance of a-SiC samples ranged from 0.8-1.0 ohm (Ù). At 15 milliamps per centimeters squared mA/cm^2 (typical photocurrent values), a 1 Ù resistance causes a 15 millivolts (mV) decrease in voltage, which would drop the current and corresponding hydrogen production by a factor of 2.5. Much additional work needs to be done to optimize this material before it can be used as a protective coating, including increasing the a-SiC's bandgap and decreasing the resistance, or possibly integrating the top cell in the device with a-Si and a-SiC.

Conclusions

- The surface of p-GaInP$_2$ can be modified by adsorption of metallated porphyrins and transition metals, resulting in improved energetics and catalysis for PEC water splitting.
- It is feasible to utilize amorphous silicon devices in direct contact with aqueous electrolytes without an additional protective coating.
- The combination of an optimized protective coating and an inherent underlying stability in the semiconductor material itself can lead to an extended lifetime in operation, because a breach in the protective layer would not be fatal to the device.
- Continued work with Energy Conversion Devices, Inc. to optimize the triple junction for increased efficiency and to tune the top layer for optimum stability is clearly indicated.

FY 2002 Publications/Presentations

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2. Aroutiounian, V.M., Arakelyan, V.M., Shahnazaryan, G.E., Stepanyan, G.M., Turner, J.A., and Khaselev, O. "Investigation of Ceramic Photoelectrodes Fe_2O_3<Ta> For Solar Energy Photoelectrochemical Converter," International Journal of Hydrogen Energy, 27, pp. 33-38 (January 2002).

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6. Fernández, A.M. and Turner, J.A. "Preparation and Photocharacterization of Cu-Sb-Se Films Prepared by Electrodeposition," submitted to Solar Energy Materials and Solar Cells.

7. The Energy Council's 2001 State Trends in Energy and the Environment, entitled "Long Term Research on Solar Production of Hydrogen", June 30, 2001.

8. American Chemical Society meeting in Chicago, IL entitled "Renewable Energy: Sustainable Energy for all Future Generations", August 26, 2001.

9. General Motors Corporation, entitled "Renewable Energy, Hydrogen, and Direct Water-Splitting Systems", September 17, 2001.

10. Chemistry Department of the Colorado School of Mines entitled "Photoelectrochemical Direct Water Splitting Systems", October 4, 2001.

11. North Carolina State University entitled "Photoelectrochemical Systems for Hydrogen Production via Direct Water Splitting", October 30, 2001.

12. Lecture on basic fuel cell technology and operation at the ICBO/SBCCI Conference in Greensboro, NC, November 1, 2001.

13. National Academy of Sciences/National Research Council Workshop on Carbon Management, entitled "Renewable Energy: Generation, Storage and Utilization", January 8, 2002.

14. The USDOE Hydrogen Program's first Quarterly Program Performance and Results Briefing, for upper DOE management entitled "Advances in Photoelectrochemical Hydrogen Production Technologies", February 20, 2002.

15. American Institute of Chemical Engineers' Spring meeting, in a session on climate change, entitled "The Renewable Energy and Hydrogen Infrastructure", March 12, 2002.

16. American Physical Society's Spring meeting, in a session on climate change, entitled "Renewable Energy: Energy Security and Sustainability", March 19, 2002.

II.D.2 Photoelectrochemical Hydrogen Production

Eric L. Miller (Primary Contact), Richard E. Rocheleau
Hawaii Natural Energy Institute, University of Hawaii, Manoa
1680 East-West Road, POST 116
Honolulu, HI 96822
(808) 988-5337, fax: (808) 956-2336, e-mail: ericm@hawaii.edu

DOE Technology Development Manager: Roxanne Danz
(202) 586-7260, fax: (202) 586-9811, e-mail: Roxanne.Danz@ee.doe.gov

Main Subcontractor: University of Toledo, Toledo, OH

Objectives

- To develop high efficiency, cost-effective photoelectrochemical processes for the production of hydrogen.
- To engineer stable multi-junction photoelectrodes based on low-cost materials [such as stainless steel (SS) foil, amorphous silicon/germanium (a-Si:Ge), copper-indium-gallium-diselenide (CIGS), iron oxide (Fe_2O_3), etc.] that match energy requirements for efficient hydrogen production.
- To design, fabricate and test optimized photoelectrodes suitable for eventual commercial-scale use.

Approach

- Develop multi-junction a-Si:Ge and CIGS photovoltaic structures incorporating additional catalyst and protective thin film layers for use as hydrogen photoelectrodes.
- Establish industry and university partners to accelerate development of advanced thin-film materials and devices for photoelectrode use.
- Upgrade in-house fabrication facilities for advanced materials and devices.
- Adapt integrated electronic/optical/electrochemical models for analysis of advanced a-Si:Ge and CIGS photoelectrode configurations, including "hybrid" devices combining solid-state and photoelectrochemical junctions.
- To design, fabricate and test prototype photoelectrode systems for efficiency and stability.

Accomplishments

- Maintained present and established new university and industrial partnerships for developing advanced a-Si:Ge and CIGS materials and devices.
- Upgraded University of Hawaii (UH) in-house a-Si:Ge and CIGS deposition systems.
- Demonstrated 12% efficiency in in-house fabricated CIGS solar cells (2" x 4").
- Established partnerships for development of Fe_2O_3, WO_3 and TiO_2 for use in hybrid photoelectrode designs.
- Adapted models for hybrid photoelectrode analysis.
- Performed initial modeling of hybrid photoelectrodes using published data for nano-structured Fe_2O_3, WO_3 and TiO_2 films.
- Selected Fe_2O_3 for initial hybrid photoelectrodes based on model results.
- Initiated program to develop Fe_2O_3 in-house, and with Duquesne University.

- Completed an evaluation of a-Si:Ge devices deposited on various metal-foil substrates for determining optimal yield (with the University of Toledo).
- Fabricated initial set of multi-junction a-Si:Ge devices for use in preliminary hybrid photoelectrode tests (with the University of Toledo).

Future Directions

- Complete fabrication and testing of initial hybrid photoelectrode prototypes.
- Identify materials and design issues needed for improving hybrid photoelectrode performance.
- Continue cooperative partnerships with research organizations to further develop optimized a-Si:Ge, CIGS, Fe_2O_3, WO_3 and TiO_2 materials.
- Design, fabricate and evaluate optimized multi-junction a-Si:Ge hybrid photoelectrodes.
- Design higher-efficiency hybrid photoelectrodes using advanced CIGS tandem configurations.

Introduction

In recent years under the sponsorship of the U.S. Department of Energy (DOE), the Thin Films Laboratory at the Hawaii Natural Energy Institute of the University of Hawaii (UH) has been developing high-efficiency, potentially low-cost, photoelectrochemical (PEC) systems to produce hydrogen directly from water using sunlight as the energy source. The main thrust of the PEC systems research at UH has been the development of integrated multi-junction photoelectrodes, comprising semiconductor, catalytic, and protective thinfilms deposited on inexpensive substrates (such as stainless steel), for solar hydrogen production [1].

Figure 1a shows sunlight shining on photoactive regions of a generic photoelectrode, producing electric current to drive the hydrogen and oxygen evolution reactions at opposite surfaces. In the conceptual design for a large-scale reactor shown in Figure 1b, arrays of photoelectrodes are arranged in tubular reactors, and electrolyte is circulated to extract the high-purity hydrogen and oxygen gases produced, which are separated using membranes (as shown in Figure 1c). In order to meet the DOE's goals, the photoelectrode system must be low-cost and must be capable of operating stably in corrosive aqueous electrolyte environments with solar-to-hydrogen (STH) conversion efficiencies greater than 10%.

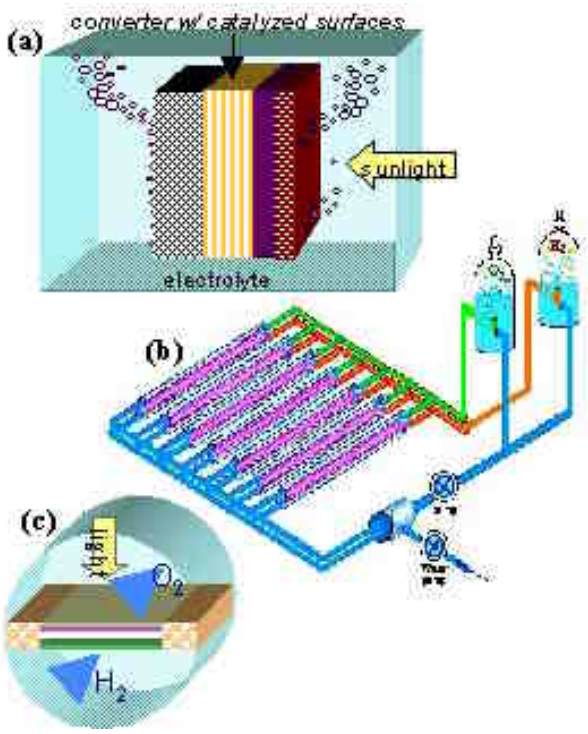


Figure 1. (a) Integrated planar photoelectrode for H_2 production; (b) Conceptual design of large-scale reactor; (c) Photoelectrode installed in collection tubes with separating membrane

Approach

Numerous approaches involving a variety of semiconductors have been explored for hydrogen photoelectrolysis since the early 1980s, but none

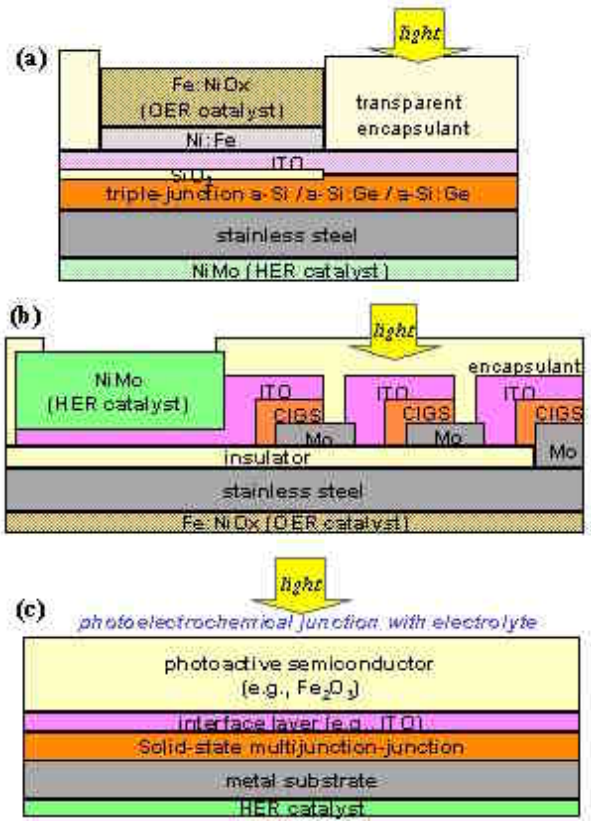


Figure 2. Encapsulated triple-junction photoelectrodes using (a) a-Si:Ge; (b) CIGS; and (c) basic structure of a hybrid solid-state/ photoelectrochemical photoelectrode

Note: HER = hydrogen evolution reaction
OER = oxygen evolution reaction

have successfully met both efficiency and stability goals. A photoelectrode design approach developed at UH incorporates multi-junction thin-film photoconvertors for high voltage along with thin-film catalyst and protective layers for stability. This research approach has relied on continued use of integrated models for photoelectrode design; establishment of industry and university partners with materials expertise and fabrication capabilities; and fabrication and evaluation of photoelectrode test structures for photoactivity and stability.

Examples of photoelectrode designs developed using this approach are shown in Figure 2, including (a) monolithically-stacked amorphous silicon/ germanium (a-Si:Ge), and (b) side-by-side stacked copper-indium-gallium-diselenide (CIGS) encapsulated triple-junction devices [2]. An important recent advance has been the design of a "hybrid" photoelectrode structure, shown in Figure 2c, combining solid-state multi-junctions with stable, photoactive semiconductor outer layers. Significant advantages of this hybrid design include elimination of lateral current collection, simplification of device geometry for ease of fabrication, and improved stability based on the thick, seamless outer oxide layer. Development of high performance hybrid photoelectrode structures using low-cost materials such as a-Si:Ge, CIGS and photoactive nano-structured iron oxide (Fe_2O_3) is currently the primary focus of our work.

Results

To date, significant progress has been made in the advancement of a-Si:Ge and CIGS materials and devices for use in photoelectrode applications, and in the initial development of hybrid photoelectrode designs. Important industry and academic partnerships have been established, in-house materials fabrication facilities have been significantly upgraded, and integrated models have been adapted for the design of prototype hybrid photoelectrode structures.

This past year, while maintaining close ties with the Institute for Energy Conversion (IEC) at the University of Delaware, who have recently reported progress in several key areas of CIGS research (including deposition of high-performance cells onto lightweight polyamide substrates [3]), and with the University of Toledo, who has reported photovoltaic efficiencies approaching 13% in multi-junction a-Si:Ge devices [4], we've also established a critical industry partnership with Daystar Technologies, whose principal scientist has reported record efficiencies approaching 19% in thin-film CIGS devices [5]. Another important new partnership established this year has been with Dr. Shahed Khan at Duquesne University, who has demonstrated nanostructured Fe_2O_3 films with good photoactivity deposited by spray pyrolysis [6], and who has been enthusiastic to participate in our hybrid photoelectrode research.

Partly with the help of our industry and university partners, we have successfully completed

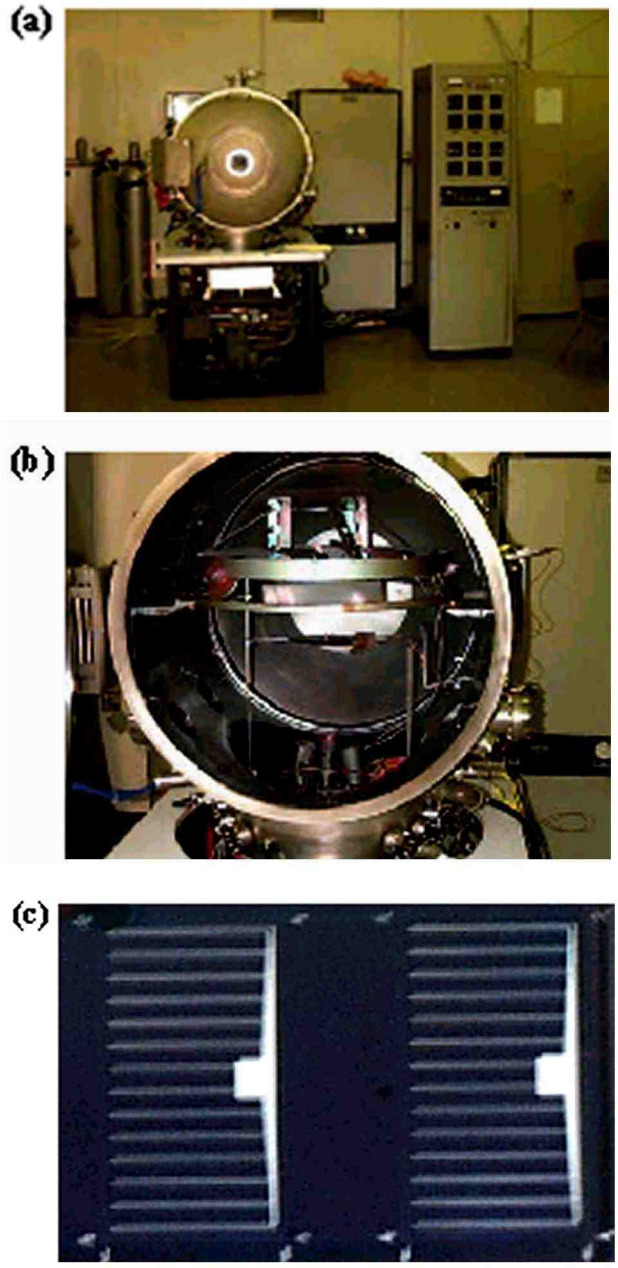


Figure 3. (a) CIGS deposition system at UH; (b) Interior view; (c) Completed CIGS PV device

important upgrades of our in-house materials fabrication equipment. The upgraded plasma-enhanced chemical vapor deposition (PECVD) system for a-Si:Ge films now includes a pulsed plasma generator for improved material properties. The upgraded CIGS system, pictured in Figures 3a and 3b, produces device-quality films over

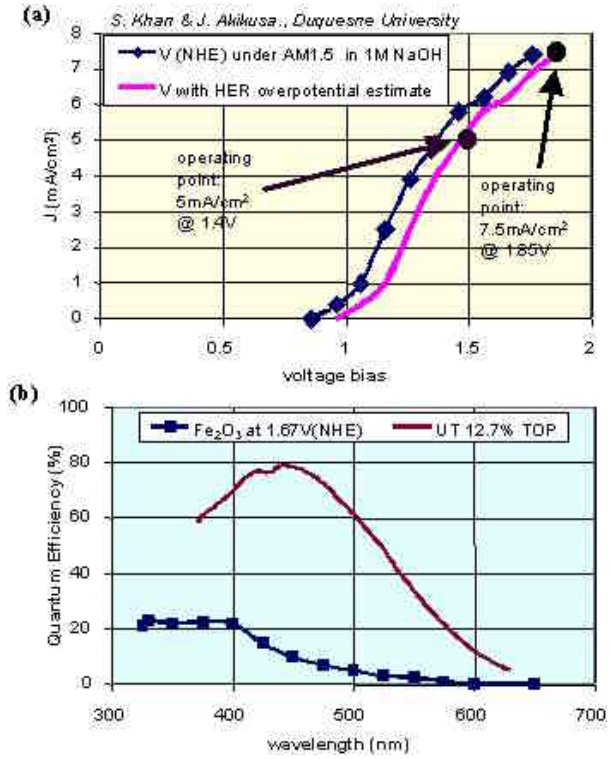
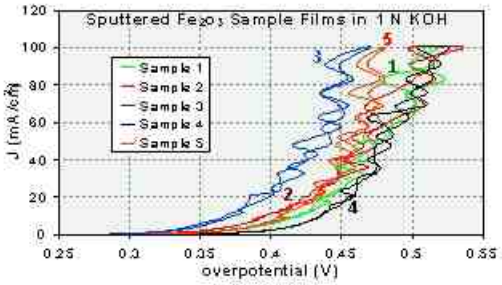


Figure 4. Hybrid design based on (a) Photocurrent response and (b) QE of nanostructured Fe_2O_3 films

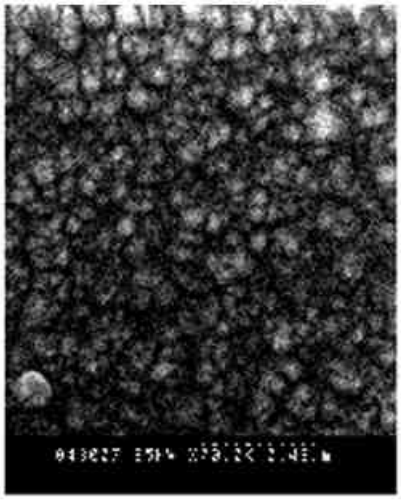
approximately a 4" x 4" area. A significant achievement has been the in-house fabrication of CIGS photovoltaic devices onto 2" x 4" metal foil substrates (completed device shown in Figure 3c) with efficiencies exceeding 12%.

Also this year, we adapted our integrated electronic/optical/electrochemical models for the analysis of hybrid photoelectrode systems. Hybrid modeling using published data for nano-structured Fe_2O_3, WO_3 and TiO_2 films was performed, and based on this analysis (which utilizes current-voltage and quantum-efficiency film characteristics, as shown in Figure 4 for iron oxide films), Fe_2O_3 was selected for the initial hybrid prototypes. As a result, we initiated an Fe_2O_3 film development program focusing on the spray-pyrolysis material fabricated at Duquesne University and on sputter-deposited material fabricated in-house at UH. Preliminary hydrogen-reaction activity and surface morphology



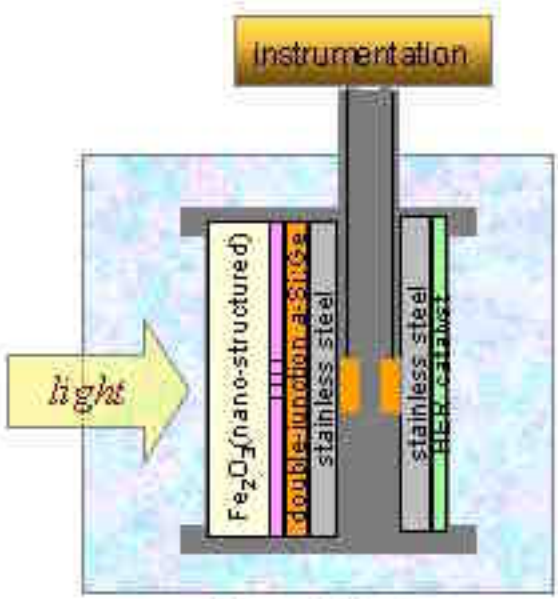
(a) hydrogen evolution activity in sputtered films

(b) sputtered film morphology



(c) pyrolysis film morphology

Figure 5. (a) OER overpotentials in sputtered Fe_2O_3; (b) scanning electron microscopy (SEM) of sputtered Fe_2O_3; (c) SEM of photoactive spray-deposited Fe_2O_3



(a) test jig design

(b) implementation

Figure 6. Photoelectrode testing jig for monitoring current under different biases: (a) Cross section of design; (b) Implementation with prototype hybrid photoelectrodes

data for various iron-oxide films is shown in Figure 5.

Efforts are currently underway to fabricate and test prototype a-Si:Ge/Fe_2O_3 hybrid devices. With the University of Toledo, we completed an evaluation of a-Si:Ge device yield on different metal-foil substrates, and a series of multi-junction devices

for use in hybrid photoelectrode experiments was deposited on the highest-yield foil. The test jig shown in Figure 6 was designed and fabricated to facilitate evaluation of hybrid photoelectrode performance.

Conclusions

With this year's work, we have continued our emphasis on developing high-performance multi-junction hydrogen photoelectrodes based on low cost semiconductor and catalyst films. Significant progress was made in the advancement of amorphous silicon/germanium and copper-indium-gallium-diselenide materials for solid-state photojunctions, and great strides were made in the research and development of the 'hybrid' photoelectrode concept, including important initial work on nanostructured wide-bandgap semiconductor films for the photoelectrochemical interface. As a result of preliminary research and modeling efforts, iron oxide was selected as the most promising material for incorporation into first prototype hybrid devices. Development efforts to optimize Fe_2O_3 films, to design a-Si:Ge tandems with the correct optical and electronic properties, and to fabricate and evaluate test-structures combing the materials are currently underway. The conceptual design for higher efficiency hybrid devices using novel tandem CIGS configurations (in place of the a-Si:Ge tandems) with Fe_2O_3 outer layers is also under development.

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FY 2002 Publications/Presentations

1. International Conference on Advanced Materials (ICAM 2001): Invited Lecture on Hybrid Photoelectrode Design.

2. "Design Considerations for a Hybrid Amorphous Silicon/Photoelectrochemical Multijunction Cell for Hydrogen Production" (in press: International Journal of Hydrogen Energy).

3. "Evaluation of RF-Sputtered Indium-Tin Oxide Films for Photoelectrochemical Applications" (submitted to the Journal of the Electrochemical Society).

Special Recognitions & Awards/Patents Issued

1. Patent Disclosure: "Hybrid Solid-State/ Electrochemical Photoelectrode for Hydrogen Production".

II.D.3 Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials

Eric W. McFarland (Primary Contact), Sung Hyeon Baeck, Kyoung-Shin Choi, Anna Ivanovskaya, Thomas F. Jaramillo
Department of Chemical Engineering
University of California, Santa Barbara, CA 93106-5080
(805) 893-4343, fax: (805) 893-4732, e-mail: mcfar@engineering.ucsb.edu

DOE Technology Development Manager: Roxanne Danz
(202) 586-7260, fax: (202) 586-9811, e-mail: Roxanne.Danz@ee.doe.gov

Main Subcontractor: University of California, Santa Barbara, CA

Objectives

- Design and construct a versatile automated system and methodologies for automated electrochemical synthesis of combinatorial libraries of mixed metal oxides
- Define electrosynthetic routes amenable to the automated electrochemical deposition system for synthesizing for doped and mixed metal
- Develop an automated high-throughput photoelectrochemical screening system
- Create and screen libraries of materials
- Complete the development of a chemo-optical detection system based on optical sensing of the reduction of tungsten oxide as a high-throughput screening system for monitoring hydrogen production
- Begin exploratory synthesis and screening of new metal-oxide systems and begin to examine composition-structure-function relationships
- Design and synthesize libraries of potential patterned metal oxides using diverse types of structure directing agents under a variety of deposition conditions

Approach

- Create synthesis and screening systems for rapid automated combinatorial synthesis of materials suitable for photoelectrochemical hydrogen production
- Develop chemical synthesis routes amenable to automated high-throughput experimentation
- Utilize the automated synthesis systems to create libraries of potential hydrogen photocatalysts
- Rapidly screen libraries for potential materials with high photoelectrocatalytic activity
- Synthesize in conventional manner selected materials for detailed analysis

Accomplishments

- Designed and built several prototype systems for electrosynthetic deposition of metal oxides, including both parallel and automated serial systems
- Developed direct cathodic routes to oxides of several metals including tungsten (W), nickel (Ni), niobium (Nb), titanium (Ti), Fe, copper (Cu), colbalt (Co), molybdenum (Mo), and zinc (Zn) by stabilization with several ligand types, and preliminary studies with libraries which have shown general trends

- Completed our chemo-optical high throughput screening system and demonstrated the first thin film results with zinc oxide (ZnO)
- Preliminary work on electrosynthesis of mesoporous tungsten trioxide (WO_3) and titanium dioxide (TiO_2) films from a peroxo-stabilized electrolyte using ionic surfactants has at last shown definitive evidence of highly structured materials (July 2002)
- From libraries of pulsed electrodeposited platinum (Pt) doped WO_3, whereby a new means of creating nanoparticles has been developed. The nanoparticles show high activity for methanol oxidation without the poisoning problems of Pt

Future Directions

- Explore the composition-function relationships of dopants in ZnO hosts
- Investigate metal oxide libraries for electrocatalytic hydrogen production and expand our high-throughput screening to include relative electrocatalytic overpotential as a routine screen
- Develop a high-throughput optical screening system to measure the effective bandgap of metal oxides in libraries
- Synthesize and screen model libraries optically for bandgap as a primary screen and create secondary libraries of compositions
- Investigate library designs for synthesis of semiconductor heterostructures utilizing two-photon absorption processes
- Continue and expand investigations of nanoporous materials with emphasis on the ZnO, WO_3 and TiO_2 hosts.

Introduction

The overall project objective is the development and application of combinatorial methods to discover an efficient, practical, and economically sensible material for photoelectrochemical production of hydrogen from water and sunlight. We will introduce a shift in the research paradigm from the present method of conventional serial chemical research to a combinatorial approach featuring a systematic and deliberate high-speed exploration of the composition-structure-property relationship of new metal-oxide based solid-state materials to discover new and useful energy producing materials as well as better understand the fundamental mechanisms and composition-structure functional relationships of these materials.

Approach

Our studies have focused on the development of automated chemical synthesis and screening systems, then on the preparation and analysis of diverse photoelectrochemical libraries of metal-oxides with semiconducting and other properties suitable for photoelectrocatalysis. Diversity has included: 1) variations in composition (by variable doping, electrochemical synthesis conditions, and surface redox catalysts) and 2) variations in structure (by deliberate and diverse ionic and non-ionic templating agents, synthesis conditions, and doping). The libraries are screened directly for hydrogen production using a two-dimensional chemo-optical sensor array.

Results

Specific Aim 1

Automated electrochemical synthesis routes are used to create libraries of mixed metal oxides, and we have designed and constructed the necessary apparatus and developed the detailed methodology to do so. Figure 1 schematically illustrates how our synthesis systems operate.

Combinatorial methods only make sense when very large numbers of different materials are made and screened quickly. Compositional diversity across a library is obtained by varying the

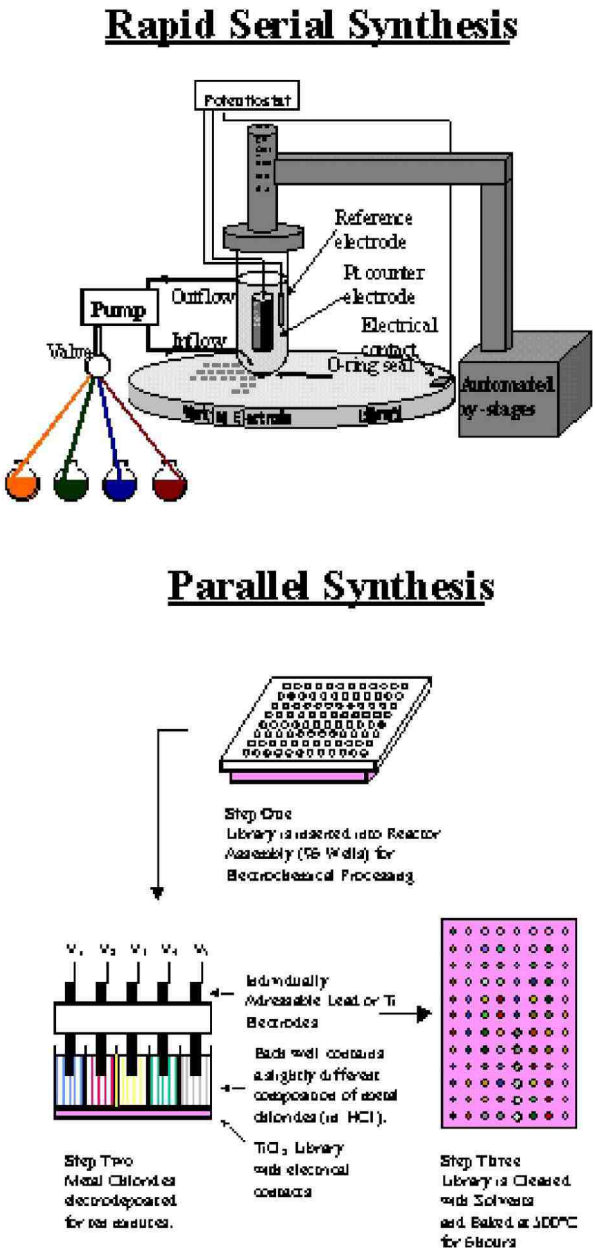

Figure 1. Schematic illustration of combinatorial synthesis by electrochemicaldeposition. The parallel approach is faster, but the rapid serial methodoffers greater control for each deposition.

electrochemical deposition conditions of time, voltage, current, surfactant additives and electrolyte. In the parallel system, the substrate (which is a common working electrode) has individual electrochemical cells isolated from each other by virtue of a perforated polypropylene block that is sealed to the substrate with an array of o-rings. This provides for different synthesis conditions at each library position; each cell constitutes an individual two-electrode system and is filled with a compositionally unique electrolyte. Clearly, synthesis speed is the advantage in a parallel scheme since all depositions occur simultaneously. In the rapid serial system, a complete three-electrode probe is scanned over the surface of the library substrate by an automated, computer-controlled set of x-y-z stages. The probe contains an o-ring at the bottom which forms a seal at the substrate. Electrolyte of choice flows into the cell by a computer-controlled pump, and a highly controlled deposition is conducted at each location by a potentiostat/ galvanostat. Several material systems have exhibited extraordinary sensitivity to deposition voltage.

Specific Aim 2

We have developed new electrochemical synthesis routes and extended existing ones to create routes amenable to our automated synthesis system for the generation of mixed metal oxides.

A number of metal hydroxides have been deposited by cathodic reduction. Metal oxides (WO_3, MoO3, TiO_2, ZnO, Fe_2O_3, Co_3O_4…) can be produced from the metal hydroxide by thermal annealing. In some cases, metal (Ni, Zn, Mn . . .) can be deposited by cathodic reduction and, after thermal annealing or electroanodization, a metal oxide can be obtained. We have also used electrochemical anodization for the synthesis of Al_2O_3 to roughen the surface and create a porous base material [13]. Our approach has been to stabilize the metal cations with ligands to allow for direct metal oxide deposition and the co-deposition of dopant cations. Several ligands we have used include hydrogen peroxide, citric acid, lactic acid, and acetic acid. WO_3, TiO_2, Nb_2O_5, and MoO_3 have been cathodically deposited from metal-peroxo solution. We have found that mixed metal oxides, such as WO_3-MoO_3, and WO_3-TiO_2 can be synthesized by mixing metal peroxo electrolytes. Pt or Ru doped tungsten oxide has been directly deposited under cathodic conditions in the presence of hydrogen peroxide, and diversity has been achieved by changing the concentration of the dopants in the electrolyte solution or by varying deposition potential. We have also stabilized the

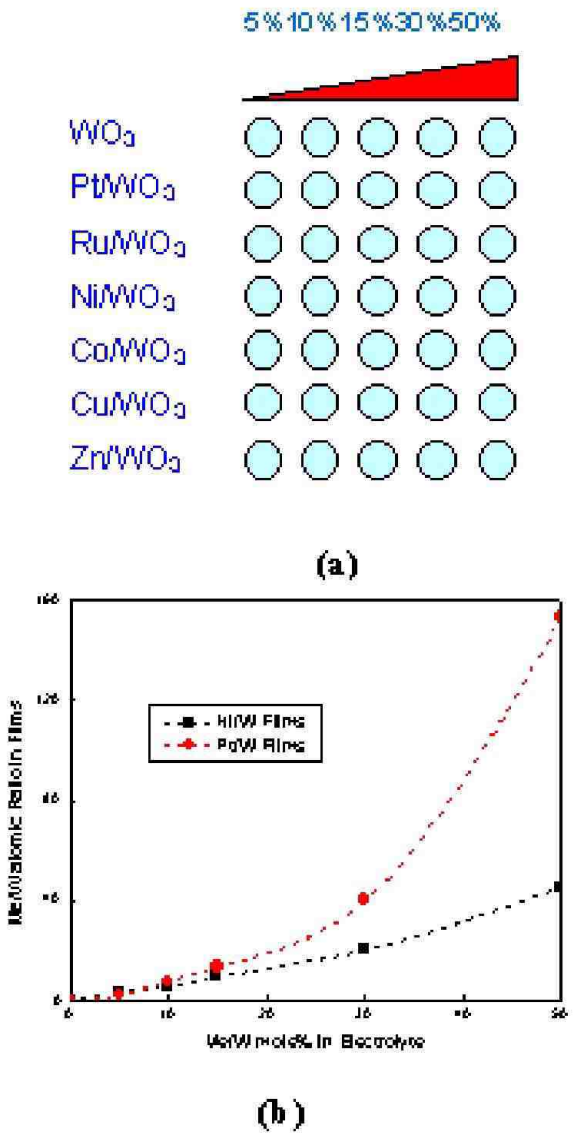

Figure. 2. Metal-doped WO_3 binary library. (a) Library design: variation indoping density is achieved by varying dopant concentration in theelectrolyte. (b) Relationship between dopant concentration in thedeposited film versus dopant concentration in the electrolyte.

metal cations in basic media using a complexing agent such as citric and lactic acid.

Specific Aim 3

We have developed two major systems for automated high-throughput photoelectrochemical screening designed to measure electrochemical and photoelectrochemical responses of combinatorially prepared photocatalyst libraries. The system in its electrochemical screening configuration allows for measuring cyclic voltammograms (I-V curves) and Mott-Schottky plots, which reveal flatband potential and sample dopant concentrations. The system is modular in nature - easy to set up for the experiment of interest by connecting the appropriate programmable source/measure devices: potentiostat, digital multimeter, data acquisition board, impedance analyzer and lock-in amplifier. This configuration allows for varying electrolytes for different samples by filling the wells of a perforated polypropylene block with a programmable pipette.

Specific Aim 4

We created a pair of libraries of WO_3 doped with different transition metals (at a variety of doping densities) with the aim of improving upon the photocatalytic activity of pure WO_3. The first library design is shown in Figure 2(a). The library incorporates Pt, Ru, Ni, Co, Cu, and Zn as dopants within polycrystalline WO_3. The materials were each co-deposited with WO_3 electrochemically from a mixture of 50 mM metal chloride solution and a W-peroxo solution. Altering the metal-chloride concentrations in the electrolyte, from 0% to 50% allowed for variation of doping concentrations within the deposited films. Figure 2(b) shows the relationship between doping density in the deposited film versus the concentration in the electrolyte for Pt and Ni as determined by Electron Dispersive X-Ray (EDX). Figure 3(a) illustrates the zero-bias photocurrent for the library members, and Figure 3(b) shows a cyclic voltammogram taken of the pure WO_3 film. We expect several photocurrent trends from this library. First of all, Ni has been shown to be an excellent absorber of visible light when doped into large band-gap oxide hosts, such as WO_3, so we expect an increase in photocurrent from that row. Similarly, we would expect better photocurrent from Pt and Ru dopants, since Pt is an excellent reduction catalyst and RuO_2 is a well-known oxidation catalyst. Figure 3(a) shows that, indeed, Ni doping increased photocurrent significantly compared to pure WO_3, with a maximum photocurrent achieved for 10% Ni. Pt and Ru dopants show a different trend. Seemingly, a greater doping concentration of either element decreases the photoactivity of WO_3.

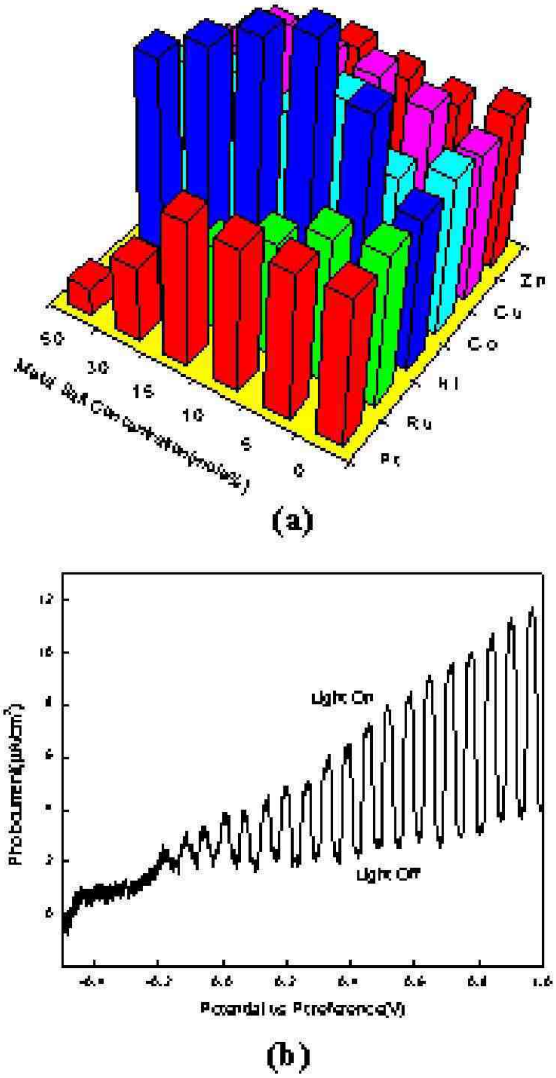

Figure 3. High-throughput photocurrent screening of the WO_3 library at zero bias.(a) Photocurrent trends in the library. (b) Cyclic voltammogram of pure WO_3 (0.2 cm^2) under chopped illumination from a 150 W Xe lamp (2.3 mW/cm^2).

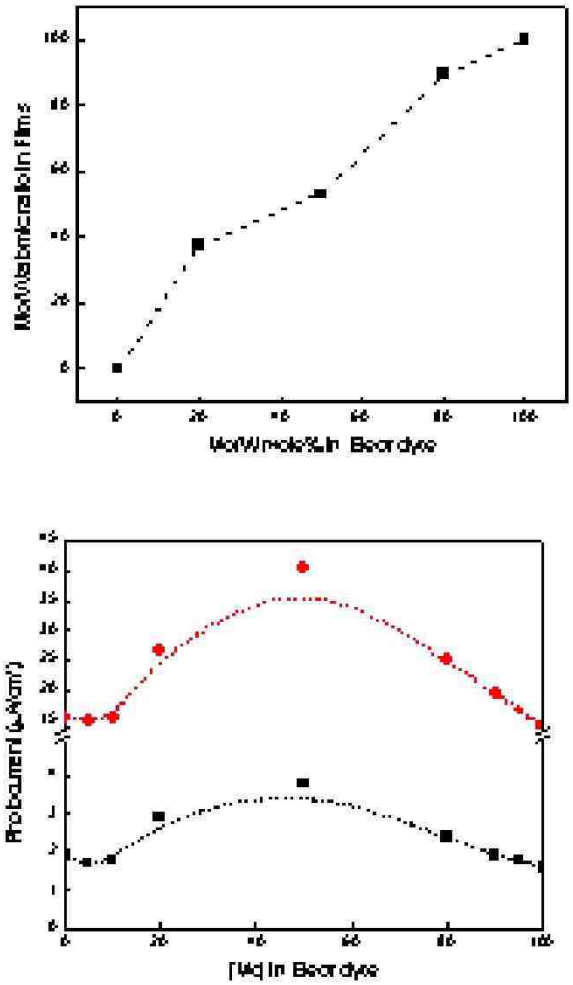

Figure 4. (a) EDS measured atomic ratio of Mo to W in films as a function of Mo concentration in electrolyte. (b) Photocurrents in 0.1 M sodium acetatesolution at zero bias(=)and 1 V bias(<) for WO_3-MoO_3 mixed oxides as a function of Mo concentration in electrolyte.

Specific Aim 5

We have engineered a high-throughput screening system for monitoring H_2 production based on a chemo-optical H_2 sensor [14-16]. This colorimetric sensor utilizes a Pd/WO_3 bilayer, whereby molecular H_2 dissociates on the Pd surface and diffuses as atomic hydrogen to reduce WO_3 to a tungsten bronze, H_yWO_{3-x}. The reduced tungsten oxide is photometrically distinct from WO_3 due to a decreased index of refraction. The reduction is reversible and the sensor can be regenerated in O_2. Details are presented in our published papers.

Specific Aim 6

A library consisting of a 45-member (5 x 9 array) WO_3-MoO_3 mixed binary oxide library, with diversity achieved by variations in deposition voltage and Mo concentration in the electrolyte was synthesized. The concentration of Mo was varied

from 0 to 100 mol% and all films were deposited for 10 minutes. After deposition, the library was calcined at 450°C for 4 hours in air.

The film compositions were determined by EDX for fifth row (prepared from 50% W- 50% Mo mixture) and fourth column (electrodeposited at -1.0 V). As expected, with increasing concentration of molybdenum in solution, the atomic fraction of molybdenum in the film increased (Figure 4(a)). However, the atomic ratio was independent of deposition voltage (-0.2 ~ -1.5 V, not shown). A trend in photoresponse as a function of molybdenum concentration in electrolyte was clearly observed. Figure 4(b) shows photocurrent at 0 and +1 V bias for the WO_3-MoO_3 mixed oxide. The photoresponse increased and reached a maximum when 50% Mo and 50% W concentration in electrolyte was used, and then decreased as concentration of Mo in electrolyte increased. In the cases where MoO_3 concentration was below 10% or above 90%, there is no enhancement of photoactivity compared to either pure WO_3 or pure MoO_3. Interestingly, in the range of 20 ~ 80% MoO_3, an increase of photoactivity was observed.

Nano-particulate tungsten oxide films were also synthesized by pulsed electrodeposition in libraries. Particle sizes between 45 ~ 330 nm were achieved by varying pulse duration from 5 ms to 500 ms. Films prepared by continuous electrodeposition had an average particle size of approximately 375 nm. As the pulse time decreased, particle size decreased as well. For a 5 msec pulsed deposition, the average particle size was approximately 45 nm. We checked the particle size with respect to deposition time (30 sec to 30 min, that is 3,000 to 180,000 pulses) and found that particle size was independent of total number of pulses; the total number of pulses seemed to affect only film thickness and not the final particle size.

We discovered that metal oxides (WO_3, MoO_3, TiO_2, Nb_2O_5) can be synthesized from peroxo-stabilized solution onto Cu foil by electroless deposition. The deposition rate was found to be strongly dependent on temperature, electrolyte concentration, and deposition time. As-synthesized films were amorphous and showed weak p-type photocurrent due to the formation of Cu_2O on the surface of Cu foil. After calcination at 450°C, metal oxide films were found to be crystalline. A 27-member (3 x 9 array) WO_3-MoO_3 mixed oxide library was prepared by electroless deposition on Cu foil, with diversity achieved by variations in deposition time and Mo concentration in electrolyte.

Specific Aim 7

In addition to our effort of finding better performance photocatalysts by tuning the composition of the films, we have been developing a general method for the production of high surface area nanostructured films by utilizing electrochemically driven self-assembly of surfactants at solid-liquid interfaces. We combined potential-controlled surface assembly with an electrodeposition process to fabricate nanostructured films. We have successfully electrodeposited mesoporous platinum and zinc oxide films by controlling deposition potentials and electrolyte compositions. The nanostructures of these films have been confirmed by transmission electron microscopy (TEM). The hexagonal structure of the Pt films, with the pores perpendicular to the substrate and the lamellar structure of ZnO, with the normal direction of the layers parallel to the substrate, are expected to allow facile access of the guest molecules and analytes to the pores and interlayers. The electrocatalytic properties of mesoporous Pt films, towards methanol oxidation were measured in order to confirm the increased effective surface areas and to evaluate a potentially important application of these films (i.e. direct methanol fuel cell applications).

Conclusions

Our work during the first 9 months of this project has focused on the development of combinatorial methods to rapidly synthesize and high-throughput screen mixed metal oxides, and on using these systems to begin to investigate new materials for photocatalytic hydrogen production. We have designed and constructed much of the combinatorial infrastructure (automated parallel and rapid serial synthesis and screening systems), and we have developed synthesis routes (based on electrochemistry) amenable to our combinatorial instruments. Rapid synthesis and functional

screening of mixed metal oxides of W, Cu, Ti, and Fe hosts has been demonstrated, and new electrosynthetic routes to W-Mo-oxide and nanoporous WO_3 have been developed. Recent data from $W_x(Mo,Ni,Pt)_yO_z$, $Cu_x(Zn_yNi_y)O_z$ and $Fe_x(Ti)_yO_z$ show (reserved) promise as improved materials.

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FY 2002 Publications/Presentations

1. S.H. Baeck, T.F. Jaramillo, C. Brandli, and E. McFarland, "Combinatorial Electrochemical Synthesis and Characterization of Tungsten-based Mixed Metal Oxides", J. Combi. Chemistry, (accepted and in press 2002).

2. S.H. Baeck, T.F. Jaramillo, G.D. Stucky, and E. McFarland, "Controlled Electrodeposition of Nanoparticulate Tungsten Oxide", Nano Letters, (accepted and in press 2002).

3. S.H. Baeck and E.W. McFarland, "Combinatorial Electrochemical Synthesis and Characterization of Tungsten-Molybdenum Mixed Oxides", Korean.J.Chem.Eng., (accepted and in Press 2002).

4. S.H. Baeck, T.F. Jaramillo, and E. McFarland, "Influence of Composition and Morphology on Photo and Electrocatalytic Activity of Electrodeposited Pt/WO_3", 224th National ACS Conference Proceedings, Boston, MA (2002).

5. Invited Seminar October 2001 "Combinatorial Methods of New Materials Discovery For Photocatalytic Hydrogen Production: A Long Way to a Million Million Watts", Department of Nuclear Engineering, MIT.

6. Invited Talk November 2001 "Combinatorial Electrosynthesis and Photoelectrocatalytic Screening of New Materials for Hydrogen Photosynthesis", AICHE Annual Meeting, Reno, Nevada.

II.D.4 Combinatorial Discovery of Photocatalysts for Hydrogen Production

Brent MacQueen (Primary Contact), Al Hirschon, Ted Mill, Mike Coggiola
SRI International
333 Ravenswood Ave
Menlo Park, CA 94025
(650) 859-5286, fax: (650) 859-4321, e-mail: brent.macqueen@sri.com

DOE Technology Development Manager: Roxanne Danz
(202) 586-7260, fax: (202) 586-9811, e-mail: Roxanne.Danz@ee.doe.gov

Objectives

- Develop a high throughput system for evaluating photocatalytic materials for hydrogen production
- Develop a methodology to produce a database of photocatalytic materials
- Discover new photoactive materials capable of producing hydrogen using solar radiation

Approach

- Construct automated high throughput testing equipment to evaluate physical properties and measure solar hydrogen production of photoelectrochemical systems
- Evaluate the effectiveness of nanosized materials for hydrogen generation from water using visible light
- Develop database useful for all researchers

Accomplishments

- Built and calibrated a light source for use as a solar simulator
- Built and tested a 4-cell reactor with pressure transducers for measuring hydrogen production from photocatalysts
- Modified and programmed a Gilson sampler for pressure transducer activated automated analysis of hydrogen production
- Synthesized and screened semiconductor materials, including nanosized titanium dioxide (TiO_2) materials, for water splitting using visible light
- Designed and constructing a 25-cell combinatorial reactor for screening photocatalysts for hydrogen production

Future Directions

- Develop a prototype multi-cell reactor for high throughput evaluation of the electrochemistry of photocatalytic materials
- Optimize the high throughput tools for discovery of water splitting catalysts
- Evaluate new nanoparticle materials synthesized as candidate photocatalysts
- Design and synthesize new materials which can produce hydrogen using visible light based on experimental results

Introduction

The conversion of the dominant energy source from one that is petroleum-based to one based on hydrogen will have a profound effect on the reduction of greenhouse gases being emitted by current technologies. Furthermore, if the hydrogen is generated from a non-carbon containing feedstock, such as water, using an energy source that is not carbon-based, such as solar radiation, the reduction in emitted gases will be enhanced even further. The key hurdle to overcome the obstacles to such a technology, photolytic generation of hydrogen from water, is a materials related issue and can be solved by the discovery of materials with the appropriate energetics and stability upon solar irradiation. A key aspect of this project is that it incorporates a nanoparticulate semiconductor producer, NanoGram, with a research institute, SRI International, with the required capabilities to be successful in this very important endeavor. The combination of NanoGram's synthetic process, which is scalable to Kg/hour quantities, with SRI's high throughput screening capabilities has the potential to make breakthrough discoveries with respect to the photolytic generation of hydrogen from water.

The goal of this effort is to develop more efficient ways to discover photocatalysts for the economical and environmentally sound production of hydrogen by splitting water with sunlight. SRI is developing combinatorial tools to identify new semiconductor compositions, surface modification(s), and experimental conditions that lead to efficient hydrogen production with visible light. Our specific objective in Year 1 of this effort has been to develop and validate a combinatorial workstation that can be used to rapidly screen an array of materials in terms of electrochemical properties and photocatalysis. To that end we have constructed a combinatorial system consisting of a simulated sunlight source, a multi-cell reactor with pressure and sampling capabilities and a programmed sample handler.

Approach

We are using a combinatorial approach to discover new photocatalytic materials, which can generate hydrogen using visible light. By first constructing combinatorial tools to quickly screen for effective photocatalysts, we can then investigate new materials as photocatalysts, including nanoparticulate semiconductors prepared by NanoGram, Corp., with whom we are collaborating on this project. Our approach is divided into three tasks as follows:

In Task 1 we are developing tools for combinatorial evaluation of the photoelectrochemical properties of semiconductors relevant to photogeneration of hydrogen. The objective of Task 1 is to develop plug and play components that will allow the rapid screening to find photocatalysts that generate hydrogen efficiently with visible light.

The goal of Task 2 is to synthesize photocatalysts for combinatorial screening for rapid hydrogen generation. We plan to use a rational design for materials synthesis that leverages the particle fabrication capabilities of our partner in this project, NanoGram, Corp, with SRI's chemistry and engineering capabilities. Systems level investigation will include modified commercial materials as well as new materials such as nanophase powders produced by NanoGram with various particle sizes, phases, and dopant levels using their proprietary synthetic process.

The goals of Task 3 are to identify photocatalysts that merit further investigation as evidenced by the combinatorial screen results and to begin a systematic evaluation of the materials identified in Task 2 using the tools developed in Task 1.

Results

We have modified a 1 kW Oriel xenon light source to provide an 8 inch illuminated circle with light between 300 and 1,000 nm to simulate sunlight for our prototype device. We have measured the light intensity distribution in the circle so that we can correct for effects of non-uniformity in the light field on the performance of photocatalysts.

We have developed two modular designs for the combinatorial screening of photocatalysts. One design focuses on hydrogen production from particles suspended in water and the other measures the electrochemical properties of monolithic (solid) substrates. The latter design provides a more detailed

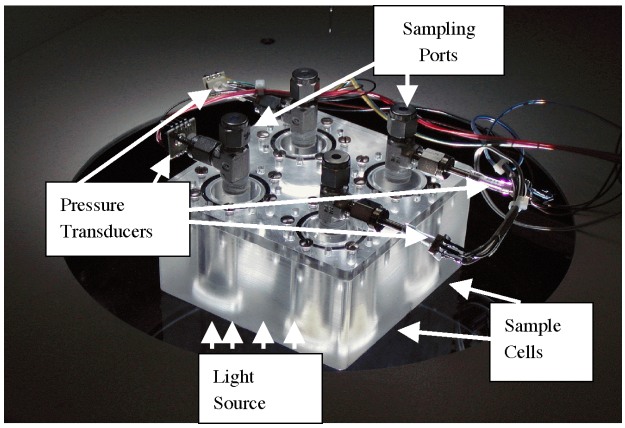

Figure 1. 4-cell Prototype of Photolysis Product Analysis Module

Figure 2. Gilson Autosampler and 4-cell Analysis Module

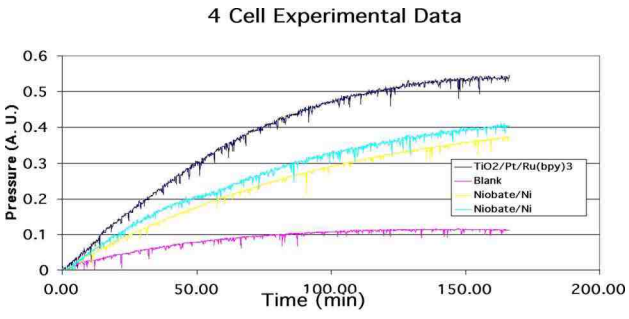

Figure 3. Pressure Transducer Output from 4-cell Module

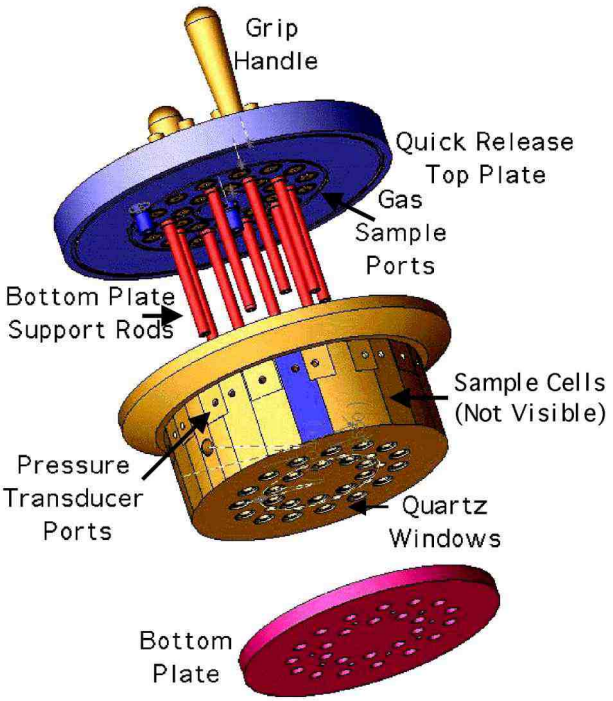

Figure 4. Design of 25-cell Analysis Module Currently Under Construction

analysis of the physical properties of the photocatalysts as a result of electrical (ohmic) contact to the measuring system, while the former design allows for rapid screening of particle dispersions to find active catalysts to be investigated in detail.

A 4-cell prototype of the particle suspension analysis design has been constructed (Figure 1). Individual cells are illuminated from the bottom, and each cell has a septum port and a micropressure transducer to detect evolution of gaseous products (i.e. H_2/O_2). A Gilson X-Y sampler (Figure 2) was programmed for autosampling based on the response of the micropressure transducers. The sampler injects the gas into a gas analyzer to determine how much hydrogen and oxygen were formed from any catalyst. Figure 3 shows typical data obtained during the course of a photolysis experiment. We are building a larger prototype with 25 cells, which has advantages in ease of assembly suitable for combinatorial use. The design of this multi-cell reactor is illustrated in Figure 4. A three-electrode system will be used for

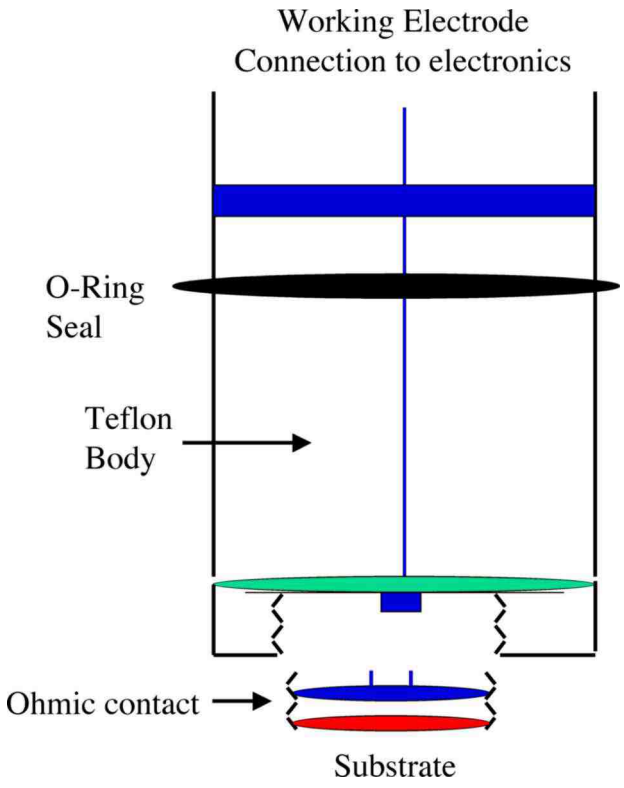

Figure 5. Design of Electrode Assembly Used for Electrochemical Analysis Module

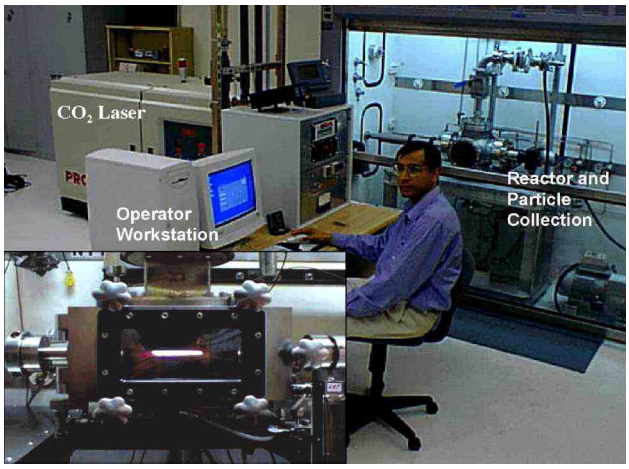

Figure 6. NanoGram Synthesis Workstation with Insert ShowingLaser Pyrolysis Reaction Zone

electrochemical measurements on monolithic materials. This module is attached to a common top that can be inserted onto the cell system designed for the particulate analysis (Figure 5). Thus, electrochemical properties of active semiconductor catalysts can be measured by switching the top plate of the analysis module.

The particle synthesis is progressing with the use of NanoGram's proprietary laser pyrolysis nanoparticulate synthesis technology (Figure 6).

Conclusions

We have made a great deal of progress in assembling the components necessary to conduct high throughput screening of materials for photocatalytic generation of hydrogen from water. This includes building a solar simulator, assembling and modifying the sample collection and sample analysis equipment, and designing, constructing analysis cells. When completed our equipment will allow us to facilitate the discovery of new photocatalysts able to produce hydrogen using solar radiation.

Special Recognitions & Awards/Patents Issued

Invention disclosure on quick release top plate design in progress.

II.D.5 Low Cost, High Efficiency Reversible Fuel Cell Systems

Christopher Milliken (Primary Contact), Dr. Robert Ruhl
Technology Management, Inc.
9718 Lake Shore Blvd.
Cleveland, OH 44108
(440) 995-9500, fax: (440) 720-4527, e-mail: milliken@stratos.net

DOE Technology Development Manager: Sigmund Gronich
(202) 586-1623, fax: (202) 586-5860, e-mail: Sigmund.Gronich@ee.doe.gov

Main Subcontractor: Technology Management, Inc., Cleveland, OH

Objectives

- Improve performance of reversible stacks (capable of operating in both fuel cell and electrolysis modes) by reducing area specific resistance, rate of degradation, and seal leakage.
- Demonstrate an integrated fuel cell hot subassembly opeating with a stack of about 50 reversible type cells operating on natural gas.
- Evaluate the economic impact of the reversible solid oxide fuel cell /solid oxide electrolyzer system and consider applications where a competitive advantage may be achieved.

Approach

- Evaluate alternate materials and geometric factors to reduce cell resistance.
- Reduce operating temperature to improve life and performance.
- Design and fabricate an integrated test station capable of testing reversible stacks (nominally 50 cells).

Accomplishments

- Optimized cell geometry by modeling the stack and system.
- Designed, fabricated, and evaluated performance of reversible stack over a range of temperatures and operating conditions.
- Demonstrated stable operation for >1200 hours in small reversible stacks at acceptable efficiency.
- Completed preliminary economic analysis and identified applications where reversible electolyzer/fuel cell systems may have a competitive advantage.

Future Directions

- Design, fabricate, and commission an integrated test system.
- Scale up fabrication to produce 50 cell stacks using standardized processes.
- Complete evaluation of alternate materials for improved life and performance.

Introduction

The Technology Management, Inc. (TMI) reversible (fuel cell - electrolyzer) system employs a high temperature solid-oxide based electrochemical process to produce either electricity from common hydrocarbon fuels (e.g., natural gas, propane, and bio-derived fuel) or hydrogen from supplied electricity. In electrolyzer mode, the reversible system uses electricity and thermal energy to convert pure water into fuel (hydrogen and oxygen). TMI's reversible system uses the waste thermal energy produced during electricity generation mode to achieve high system efficiency during electrolysis

mode, ultimately lowering product life cycle costs for the combined system. To further increase system efficiency, TMI has implemented a 'passive' (cell) system design which reduces the number and complexity of the balance of plant components.

During the current phase of the program, TMI has demonstrated reversible cells and stacks which met many of the performance targets including reversible efficiency and life. Several conditions were evaluated to understand the sensitivity of performance on operating variables such as temperature and current density. The highest reversible efficiency ($DC_{Volts\text{-}Out}$ / $DC_{Voltage\text{-}In}$) measured was 90.8% at 925°C and 50 mA/cm^2. A five cell stack was operated at < 2% / 1000 hours voltage degradation in fuel cell mode for over 1200 hours. Data from this work was used to expand economic and engineering studies completed earlier. An outcome of this was the concept for a system capable of delivering 5000 pounds per square inch (psi) pure hydrogen (e.g., needed for vehicle uses) in addition to electric power and recovered usable heat. The proposed systems would be configured in redundant modules to ensure high reliability and could be sized for either residential or commercial applications (including "power parks") being fed by electric power (renewable or low-cost grid) and/or fuel (fossil or biomass-derived).

Approach

Reversible stacks goals require negligible gas leakage rates, low polarization voltages, stable microstructures, and reproducible fabrication techniques to meet the goals. Low gas leakage rates have been demonstrated in limited tests that will continue. The DOE has suggested an alternate sealing technology that may be applicable if it can be adapted.[i] Low polarization voltages will be sought by optimizing the electrode microstructure and by continuing to improve the separator interface. Microstructure stability will be addressed through materials and processing improvements. Reproducible fabrication will be achieved through the following: enhanced inspection techniques, data analysis, and mechanized production methods. Finally, the design of the hot subassembly will be based on proven engineering designs developed by TMI over the past 10 years.

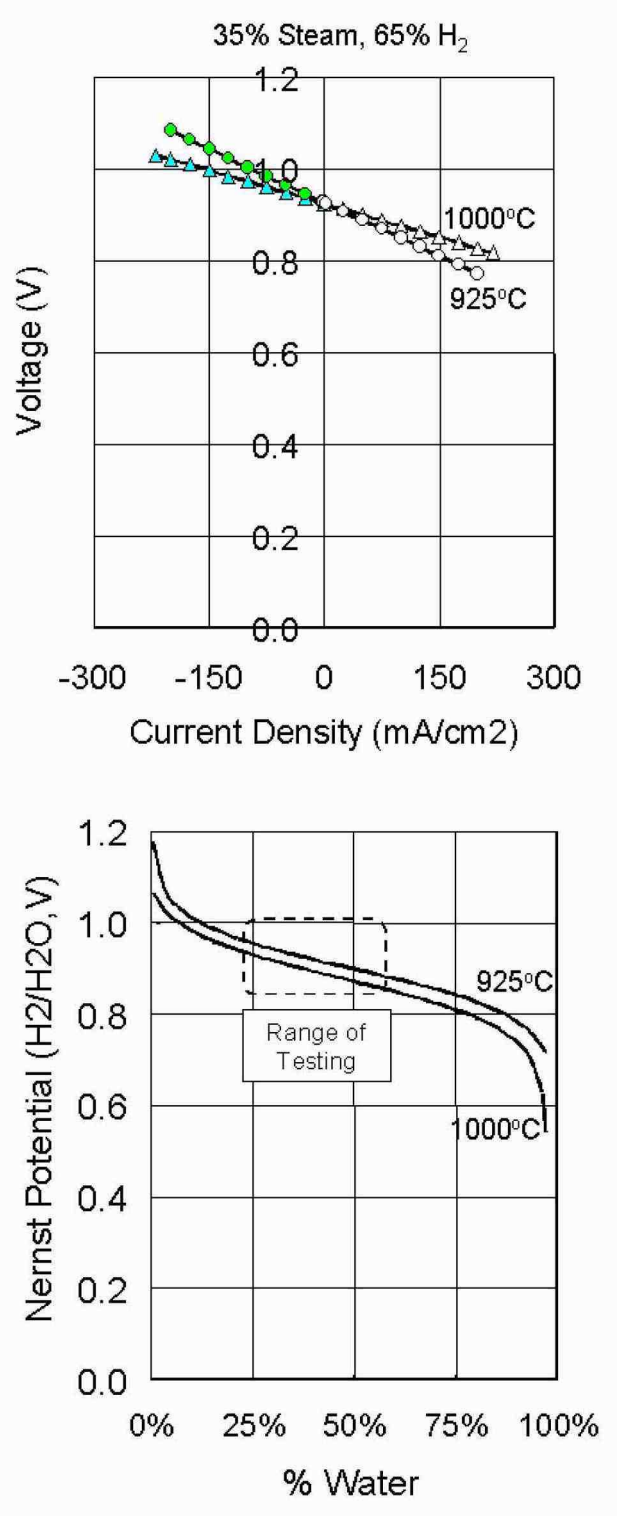

Figure 1. Reversible Testing of Cells

Results

Cell Component Development

The goal of the cell testing task was to validate the passive mode of operation and characterize performance. Temperature and gas phase concentration gradients are of particular interest because the processes are driven by gaseous diffusion.

Evolutionary improvements and modifications were made to existing TMI materials specifications, fabrication methods, and cell dimensions to accommodate this design. Minor modifications of standard TMI fabrication procedures were sufficient to produce thicker fuel + oxygen electrodes. Larger diameter, thicker seals were made using methods from internally funded programs. Fifty-percent thinner electrolytes were procured and used in some of the trials.

Figure 1 shows data from cells operated with a 65% hydrogen/35% steam mixture at two different temperatures. Operation was primarily in electrolysis mode with daily intervals in fuel cell mode. The mixture choice of fuel composition corresponds to the approximate midpoint in oxygen potential in a complete system as shown in the second part (b) of the figure. Characterization at extreme conditions was not considered during this phase.

The lack of offsets or slope changes near zero current indicates that no significant activation polarization exists in these cells (in marked contrast to proton exchange membrane [PEM] cells). The plot also shows that practical electrolysis current densities (100-200 mA/cm^2) required electrolysis voltages under 1.1 Volts --- far lower than PEM electrolyzers (which typically operate near 1.9 Volts) -- thus enabling higher electrolysis efficiencies when using TMI's solid oxide cells. Trends were consistent for similar materials and construction. The most likely sources of variability were fabrication quality and processing parameters. Because of the short program duration, fabrication condition optimization could not be explored. Finding an optimal set of fabrication conditions is essential for reproducible results.

Reversible cell efficiency is the ratio of fuel cell to electrolysis voltage at the same cell current and hydrogen/steam feed. It is a measure of the maximum possible energy storage efficiency for a reversible system using the cell (system efficiencies will be lower than cell efficiencies). The highest reversible cell efficiency observed was 90.8% (at 925°C and 50 mA/cm^2).

Engineering Studies

A modular system design producing both electricity and hydrogen was studied in the context of several assumptions. In this concept, AC power could be produced for local needs with possible sale of surplus power to the grid. High pressure (e.g., 5000 psi) pure hydrogen could also be produced for later use in vehicles after temporary storage in adjacent tanks. Hot water would be produced as a useful byproduct when operating from natural gas fuel augmented by renewable electricity where applicable. The exhaust would be extremely clean, and CO_2 emissions would be minimized during operation due to the high efficiency of the system.

Individual module sizes considered ranged from 1 to 30 kW. For each kilowatt of capacity, a module could either produce up to 1.0 AC kilowatt or up to 12.1 standard cubic feet per hour (scfh) of hydrogen (enough to power fuel cell cars for 21,200 miles per year) or a combination of electricity and hydrogen. The fuel cell subsystem would operate at atmospheric pressure, and the electrolysis subsystem would operate up to 5000 psi. Batteries could provide high power when needed for load-following, and surges would only require a small energy storage capacity. Mechanical auxiliary devices include a high-pressure water pump and compact heat exchangers. Complete systems assembled from two or more identical modules would have the added benefits of redundancy and ease of service. In multiples, overall system capacities could range from an individual residence to large vehicle filling stations or "power parks". Energy storage capacity can be supplanted by producing hydrogen at steady-state for later use in vehicles, thereby eliminating "round trips" and increasing overall efficiency.

For some special applications, an electrolyzer-only module could be sufficient, operating on DC

input power plus water and delivering high pressure pure hydrogen. Such a module would have much lower installed cost than the above but the same DC to hydrogen efficiency given in Table 1.

Table 1. Projected Efficiencies for Several Systems

Operating Mode	Electrical Efficiency at 60% Output	Electrical Efficiency at 100% Output	Energy Efficiengy
Renewable DC to AC	96%	96%	
Natural Gas to AC	72%	65%	97%
Renewable DC to Hydrogen	95%	95%	
Natural Gas to Hydrogen	83%	75%	97%

Conclusions

The project has met or exceeded all technical objectives (as revised by DOE Hydrogen Program management) on budget and on time. Experimental results have been promising. The economic / engineering studies indicate the potential for reversible systems to set new standards of performance, achieving lower cost of H_2 production, lower pollution levels, and potentially serving as an enabling technology for hydrogen fuel cells. At the system level, a demonstration reactor of sufficient size to demonstrate technology proof-of-concept will be designed, built, and operated. The design of the hot subassembly will be advanced based upon engineering designs developed by TMI over the past 10 years and will include the understandings from the work presented above and learning from advanced stack development.

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FY 2002 Publications/Presentations

1. Hydrogen/Fuel Cells for Transportation/Fuels for Fuel Cells, DOE 2002 Annual Meeting, Denver Colorado, May 6-10, 2002.

II.D.6 High-Efficiency Steam Electrolyzer

Ai-Quoc Pham (Primary Contact), Ervin See, David Lenz and Robert Glass
Lawrence Livermore National Laboratory
P.O. Box 808, L-350
Livermore, CA 94551
(925) 423-339, fax: (925) 422-6892, e-mail: pham2@llnl.gov

DOE Technology Development Manager: Sigmund Gronich
(202) 586-1623, fax: (202) 586-5860, e-mail: Sigmund.Gronich@ee.doe.gov

Objectives

- Develop a novel steam electrolysis approach for highly efficient hydrogen production.
- Demonstrate the concept of using natural gas as anode depolarizer to reduce the electrical energy consumption.
- Develop the materials, processes and engineering designs for the natural-gas-assisted steam electrolyzer (NGASE).
- Build and demonstrate prototype electrolyzers.

Approach

- Investigate the depolarizing effect of natural gas using disk type samples.
- Evaluate new materials for the electrolyzer anode and cathode.
- Study the effect of microstructure on electrode performance.
- Develop low cost electrolyzer tube fabrication processes.
- Develop ceramic-to-metal seal for easy gas manifolding.
- Design tubular electrolyzer stack for high-pressure operation.
- Build and test several electrolyzer prototypes.

Accomplishments

- Demonstrated feasibility of using methane to reduce the electrical energy consumption in high-temperature steam electrolyzer.
- Developed high performance anode and cathode.
- Developed a low-cost but highly reliable thin-film coating technique.
- Explored various tube fabrication techniques, including cold isostatic pressing and low-pressure injection molding.
- Demonstrated a metal-to-ceramic seal that withstands 150 psi pressure differential.
- Built the first electrolyzer stack capable of producing 700 sccm hydrogen.

Future Directions

- Develop better tube-to-tube series connections for high voltage, low current operation.
- Study the long-term stability of the electrodes.
- Design and build 1 and 3 kW electrolyzer stacks.
- Work with our industrial partner to do system integration.

Introduction

Currently, most hydrogen demand is met by hydrogen production from fossil fuels, i.e., by steam reforming of natural gas and by coal-gasification. It is unlikely that the same approach can be used for producing and delivering hydrogen for a hydrogen-based transportation system because of the absence of an adequate hydrogen distribution infrastructure. Hydrogen produced on-site would be much more attractive and would require less costly initial investments. Unfortunately, distributed hydrogen production using small-scale conventional steam reforming is not a viable option because of the high cost and low efficiency of the reactors at small scales. More interesting approaches, such as auto-thermal reforming, micro-channel steam reforming, as well as partial oxidation processes, are currently being pursued. However, these approaches are fairly complex, involving several additional steps, such as high-temperature shift, low-temperature shift, and preferential oxidation or hydrogen gas separation.

Hydrogen can be produced from water using the simple electrolysis reaction. Because of the modularity of the electrolyzer, electrolysis can be done at large central plants, at a refueling station, or even at home. However, water electrolysis has not had a significant commercial impact because of the high electrical energy consumption and the resulting high cost. Furthermore, using the grid electricity that is produced by burning coal and natural gas will result in high greenhouse gas emissions, which would defeat the purpose of the hydrogen program.

In the near-term, fossil fuels will still be a major source for hydrogen production. The challenge is to make the production efficient and suitable for a distributed generation scenario. The purpose of this project is to develop a system that has the simplicity of conventional electrolysis while being compatible with the existing fuel infrastructure and having high efficiency with respect to primary energy, and thus having low greenhouse gas emissions.

Approach

Our approach to decrease the electrical energy input requirements for electrolysis is to use natural gas as an anode depolarizer. This approach essentially replaces one unit of electricity by one equivalent energy unit of natural gas at one-fourth the cost. There are two possible modes of operation. In the total oxidation mode, i.e. when methane is just used to reduce the electrochemical potential difference across the two sides of the electrolyzer membrane, the system does not require any gas separation and has the potential to produce pure hydrogen at high pressures. In the partial oxidation mode, methane is converted to hydrogen and carbon monoxide, which is subsequently converted to hydrogen via the water-gas shift reaction. We choose to focus our current efforts on the development of a system operating in the total oxidation mode because of its simplicity. Using an appropriate system design, it is possible to electrochemically compress hydrogen in-situ, thus eliminating the need for an expensive hydrogen compressor.

Results

We have demonstrated the proof-of-concept of the NGASE approach using single cells. A voltage reduction of 1 V was observed when methane was used in the anode side. The electricity consumption was estimated to be about one order of magnitude lower than in conventional electrolyzers. Using thin film and novel catalyst materials, we subsequently demonstrated very high performance, up to 1 A/cm^2 at only 0.5 V at 700°C. At 900°C, cell current density was as high as 2.4 A/cm^2. For electrolyzer stack development, we selected the tubular approach since tubular structures have good mechanical integrity (relative to planar designs) while enabling operation at high pressure differentials.

During FY02, we continued to improve the tube performance by improving the tube microstructure. Figure 1 shows the current-voltage characteristics for various electrolyzer tubes as compared to disk data.

We have evaluated several ceramic tube fabrication techniques. The cold isostatic approach turned out to be inadequate for the present purpose because of the difficulties to incorporate sufficient porosity in the structure. A low pressure injection molding technique was successfully developed to fabricate green tubes with lengths up to sixteen inches (Figure 2).

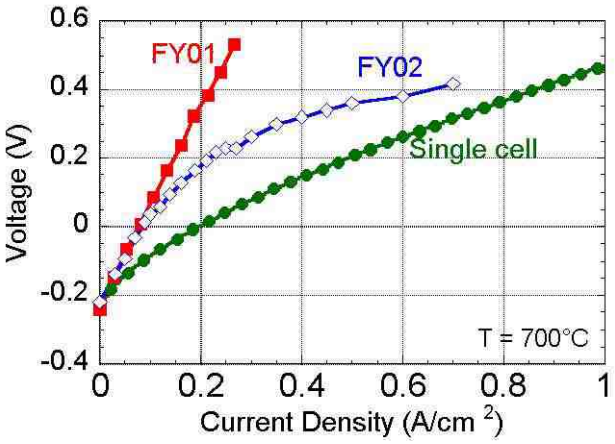

Figure 1. Current-Voltage Curves of Various Electrolyzer Tubes and of Single Disk

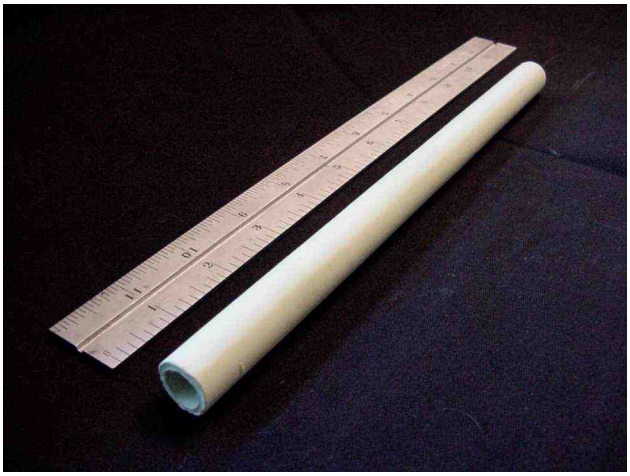

Figure 2. An Injection-Molded Electrolyzer Tube

Figure 3. Metal-to-Ceramic Seal

Figure 4. A 4-tube Electrolyzer Stack Prototype

Although the tubular design reduces significantly the issues typically encountered with sealing, there is still a need to seal the two ends of the tubes in order to avoid potential CO contamination and to enable operation with a pressure differential across the tube. We successfully developed a metal-to-ceramic seal that is leak-free up to 150 psi pressure differential (Figure 3).

Four electrolyzer tubes were assembled in parallel to form a prototype stack (Figure 4). When operated at 750°C, the stack produces 700 sccm hydrogen standard temperature and pressure. The stack performance was somewhat lower than what was expected from single tube results. The difference could come from the resistive loss in the cables because of very high current in the stack. This observation suggests that a series design with lower current and higher voltage is more desirable. A new stack design is being developed.

Conclusions

The electricity required for steam electrolysis can be reduced significantly if natural gas is used as anode depolarizer. The efficiency of the NGASE was estimated to be between 60 to 75%, depending on the current density. That number is significantly higher than the typical 40% efficiency for conventional electrolysis using average grid electricity.

We have demonstrated the concept and have developed the materials and initial system design. The development of the first electrolyzer stack prototype indicated that a number of issues remain to be improved. Most important of all are the long-term stability and the electrical connection between tubes.

FY 2002 Publications/Presentations

1. DOE Annual Program Review for 2002, May 8, 2002, Denver, CO

II.D.7 Enabling Science for Advanced Ceramic Membrane Electrolyzers

Fernando Garzon (Primary Contact), Rangachary Mukundan, and Eric Brosha
Los Alamos National Laboratory
MS D429, MST-11 Group
Los Alamos, New Mexico, 87545
(505) 667-6643, fax: (505) 665-4292, e-mail: garzon@lanl.gov

DOE Technology Development Manager: Sigmund Gronich
(202) 586-1623, fax: (202) 586-5860, e-mail: Sigmund.Gronich@ee.doe.gov

Main Subcontractor: Los Alamos National Laboratory, Los Alamos, New Mexico

Objectives

- Evaluate proton-conducting ceramic membranes for use in electrolyzers.
- Fabricate dense ceramics of cerates and zirconates and measure the bulk hydrogen conductivity using AC impedance spectroscopy and DC conductivity measurements; demonstrate water electrolysis using these materials.
- Synthesize electrode materials for electrolysis and characterize their polarization behavior using electrochemical methods.

Approach

- Synthesize cerate and zirconate proton-conducting oxides from the component oxides.
- Evaluate the structure and composition of the cerate and zirconate ceramics using X-ray diffraction and X-ray fluorescence techniques.
- Characterize the bulk hydrogen conductivity of the sintered proton-conducting ceramics using AC impedance spectroscopy and DC conductivity measurements.
- Obtain tubes of the proton-conducting ceramics and apply electrodes to these proton-conducting tubes.
- Design an experimental setup to demonstrate water electrolysis and hydrogen generation.
- Optimize electrode materials for electrolysis and characterize their polarization behavior using electrochemical methods.

Accomplishments

- Synthesized $SrCe_{0.95}Yb_{0.05}O_{3-x}$ and $SrZr_{0.9}Y_{0.1}O_{3-x}$ proton-conducting oxides.
- Confirmed the orthorhombic crystal structure of the proton-conducting oxides using X-ray diffraction. The lattice parameters of the proton-conducting oxides were also measured.
- The composition of the oxides was verified using X-ray fluorescence.
- Dense sintered proton-conducting ceramics were prepared, and their electrical conductivity was characterized using AC impedance spectroscopy and DC conductivity measurements.
- Tubes of the proton-conducting ceramic $SrCe_{0.95}Yb_{0.05}O_{3-x}$ were obtained from TYK Ceramics, and platinum electrodes were applied to the inner and outer sides of these tubes.
- An experimental setup to demonstrate water electrolysis and hydrogen generation has been designed by modifying a furnace to fit the electrolyzer tubes and by using an HP 5890 Series II chromatograph to analyze the evolved gases.

Future Directions

- The hydrogen evolution from the $SrCe_{0.95}Yb_{0.05}O_{3-x}$ tubes will be characterized under various conditions of temperature, water vapor and oxygen partial pressure.
- The polarization due to the platinum electrodes will be evaluated using AC impedance techniques.
- Alternative oxide electrodes to replace the platinum electrode will be prepared and evaluated.

Introduction

Efficient and economical electrolysis of water to hydrogen and oxygen gases is of great importance to renewable hydrogen energy programs. Combined fuel cell/electrolyzer systems offer the potential for efficient energy storage and conversion. Unfortunately, low-cost and low-maintenance electrolyzer technologies are not commercially available. Current alkaline and polymer membrane based electrolysis systems suffer from the following disadvantages:

- The hydrogen product gas is saturated with water vapor; the gas must be dried before the hydrogen can be stored in a hydride bed.
- Both technologies require high loadings of precious metal catalysts to reduce the overpotential losses.
- Neither technology is amenable to high-pressure operation. It is very difficult to pressurize wet alkaline electrolyte cells. Polymer membrane cells allow high crossover rates of gases across the membranes at elevated pressures.
- Long-term stability and contamination is a problem with both alkaline and polymer membrane electrolysis electrolytes. Alkaline electrolytes adsorb carbon dioxide readily and form carbonates. Polymer membrane systems must use very pure de-ionized water or they will accumulate cations that displace protons and increase the cell resistance over time.

A promising alternative to liquid and polymer membrane electrolytes is a proton conducting ceramic solid electrolyte technology. These materials offer a number of potential advantages over current systems:

- The ceramic electrolyzers are solid-state devices with no polymer or liquid electrolyte to contaminate, and they are well suited to operate at elevated pressures.
- The devices should operate with steam without expensive cation removal/carbon dioxide pretreatment.
- The ceramic cells operate at temperatures from 450-800°C and thus at a lower thermodynamic potential than the low-temperature systems.
- The elevated operating temperatures enable the use of non-precious metal electrodes, and electrode reaction kinetics may also be faster at these elevated temperatures.
- Temperatures in this range are directly compatible with solar furnace operating temperatures, offering potentially attractive integrated hybrid electrical/hydrogen generation systems.

Finally, this technology is intrinsically different from the other solid-state technology using zirconia-based oxygen ion electrolyzers in that the transported (separated) species is hydrogen rather than oxygen. The zirconia oxide ion systems produce a wet hydrogen product stream. The proton conducting ceramic electrolyte does not suffer from this disadvantage and produces a dry hydrogen stream with no further purification needed. The electrolysis of water vapor on oxygen ion and proton conducting ceramics is illustrated in Figure 1. We propose to demonstrate the feasibility of water electrolysis using solid-state electrochemical cells based on proton ion conducting solid electrolytes.

Approach

The principal goal of this project is to demonstrate electrolysis technology using ceramic electrochemical cells based on solid oxide proton conductors. Los Alamos National Laboratory (LANL) has experience in solid-state bulk and thin

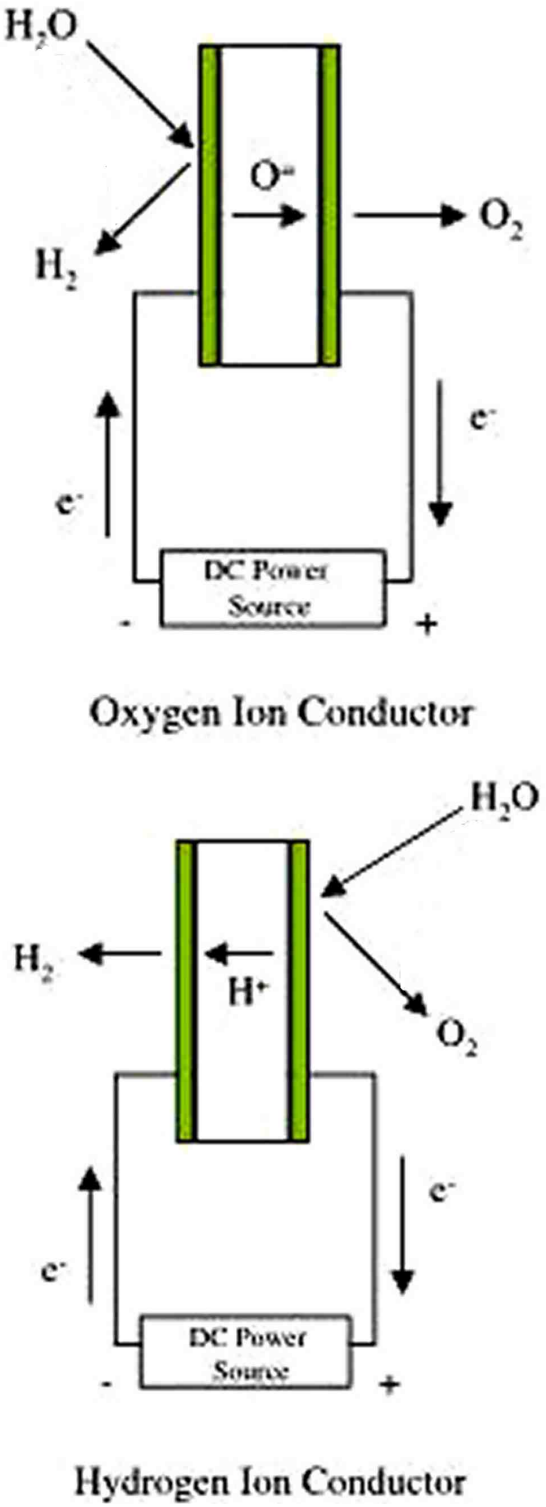

Figure 1. Schematic Illustration of Water Electrolysis on an Oxygen Ion Conducting Electrolyte (top) and a Hydrogen Ion Conducting Electrolyte (bottom).

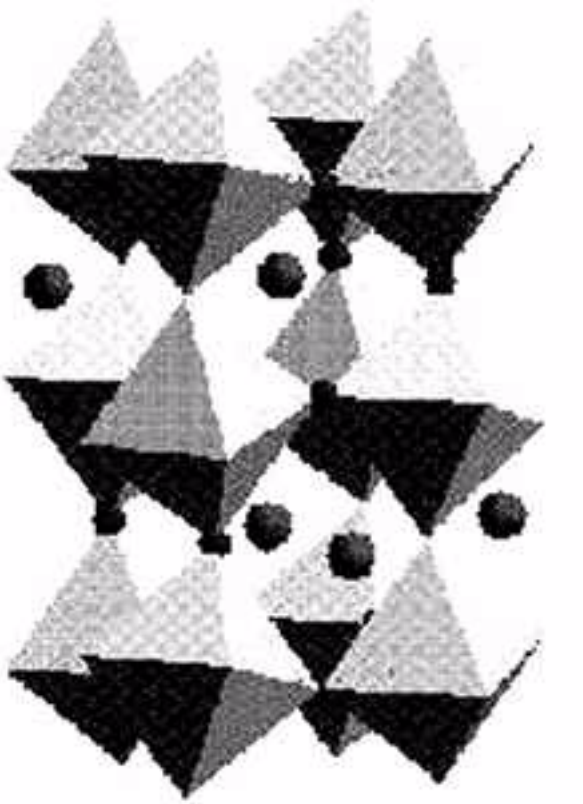

Figure 2. Polyhedral representation of the $(Sr,Ba)(Zr,Ce)(B)^{3+}O_{3-y}$ perovskites where $(B)^{3+}$ designates a trivalent substituted cation. The (Sr,Ba) occupy the A site; $(Zr,Ce)(B)^{3+}$ occupy the B center positions of the octahedrally coordinated oxygen.

film materials synthesis and characterization capability. We will synthesize and characterize electrolyte and electrode materials and fabricate test cell apparatus. Characterization methods available in the Electronic and Electrochemical Materials and Devices Group include X-ray diffraction, thermo gravimetric analysis, energy dispersive X-ray analysis, scanning electron microscopy and AC impedance and DC cyclic voltammetry electrochemical methods.

Recently, a number of perovskite structure ceramic proton separation membranes have been developed and reported by Iwahara et. al. [1]. These materials exhibit good stability, high ionic transport rates for protons and also operate in the 600-900°C temperature range which is optimal for insitu

catalysis reactions. The materials are also of great value for high temperature fuel cell technologies, isotope separation systems, sensor applications and heterogeneous catalysis [2,3].

The proton conducting materials are rare earth cerate and zirconate ABO_3 formula oxides, e.g. (Sr,Ba) (Zr,Ce)$(B)^{3+}O_{3-y}$, where $(B)^{3+}$ is a three valent yttium or lanthanide cation. The crystal structures of all of these materials are typically orthorhombic distortions of the cubic perovskite structure due to a tilt of the oxygen coordinated octahedra as illustrated in Figure 2. The perovskite materials contain oxygen ion vacancies introduced by the $(B)^{3+}$ substituting for four valent zirconium or cerium. Exposing these materials to steam at elevated temperatures causes water to hydrolyze and fill the vacancies with oxygen and two mobile protons.

Since these first reports, Iwahara and other investigators have studied the conductivities (both ionic and electronic), conduction mechanism, deuterium isotope effect, and thermodynamic stability of these materials. The motivation for most of this work derives from the desire to utilize these materials for high temperature, hydrogen-fueled solid oxide fuel cells. In a reverse operation mode, if metal or metal oxide electrodes are deposited onto a dense pellet of this material and heated to temperature T, the application of an electric potential to the electrodes will cause a hydrogen partial pressure difference across the pellet according to the Nernst equation:

$$\Delta V = \frac{RT}{zF} \ln \frac{P'_{H2}}{P_{H2}}$$

where F is Faraday's constant and z is the number of electrons transferred upon oxidation and reduction. For example, at 500°C the application of 1.5 V would produce a hydrogen partial pressure difference across a pellet on the order of 1020. These differences in hydrogen activity are high enough to decompose water at elevated temperatures.

The Sr and Ba-doped cerate electrolytes exhibit the highest proton conductivities; however, recent reports question the thermodynamic stabilities of the Ba compounds at intermediate temperatures and in the presence of high partial pressures of CO_2 and H_2O. It is unclear whether this will present a problem for electrolysis applications; therefore, we will evaluate the thermodynamic stability of these materials and study the stability of potential substitute candidates.

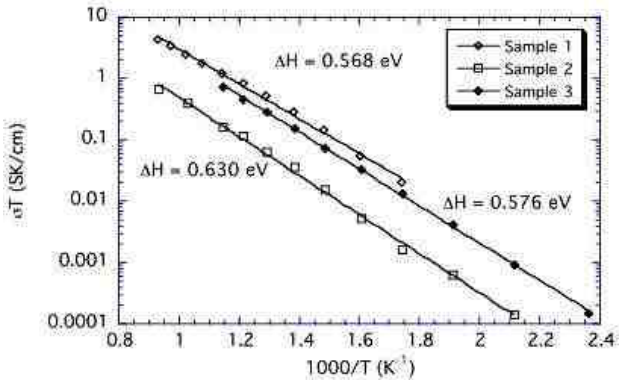

Figure 3. The Conductivities of Three $Sr_{0.95}Yb_{0.05}CeO_{3-x}$ Ceramic Samples Produced Using Differing Ceramic Processing Methods

Results

Consequently, we are in the startup phase of our program. Our first task was to identify candidate perovskite oxide materials with high protonic conductivities. We have identified ytterbium doped strontium cerate and yttrium doped strontium zirconate materials as possible electrolyte materials. Barium cerate perovskites exhibit higher protonic conductivity, but the reactivity with carbon dioxide would require pretreatment of the steam.

We have designed and assembled a high temperature AC impedance system for measurement of protonic conductivities. Our measurements of candidate ceramic protonic conductivities indicate that the electrolyte resistance in thin membrane form should not impose a large internal resistance (IR) loss on the electrolysis cell. However, ceramics processing also plays an important role in determining the conductivities of these materials. Figure 3 displays the conductivities of three $Sr_{0.95}Yb_{0.05}CeO_{3-x}$ samples made using differing starting powders and sintering schedules.

Figure 4. Ceramic Electrolyte Tube of $SrCe_{0.95}Yb_{0.05}O_{2.975}$ Custom Fabricated for LANL by TYK Corporation

We have identified and contracted a ceramics supplier, TYK Corporation, to fabricate electrolyte tubes for prototype electrolyzer research studies. The supplier has successfully manufactured and delivered closed end electrolyzer membrane tubes to LANL. The composition of the tubes is $SrCe_{0.95}Yb_{0.05}O_{2.975}$, and the tubes are 200 mm in length with an inner diameter of 12 mm and an outer diameter of 15 mm. Although the membrane thickness of 1.5mm could lead to significant IR losses (20-30 Ω cm^2 specific resistance), these tubes are ideally suited for the evaluation of these proton-conducting membranes as electrolyzers. Figure 4 is a photograph of a recently manufactured electrolyzer tube.

Platinum electrodes have been painted on an electrolyzer tube, and an experimental setup has been designed and built to evaluate the hydrogen permeation. The electrolyzer tube is placed in a modified Lindberg/BlueM furnace, and the gases are fed into an HP 5890 Series II gas chromatograph for analysis.

Conclusions

- $Sr_{0.95}Yb_{0.05}CeO_{3-x}$ has been selected as the first protonic conductor to be evaluated as an electrolyzer membrane.
- The conductivity of the ceramics reveals that thin films (<100 μm) of this material should be suitable for the manufacture of a practical electrolyzer.
- Tubes of the $Sr_{0.95}Yb_{0.05}CeO_{3-x}$ ceramic have been obtained and will be evaluated with the experimental setup that has been designed and built.

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II.D.8 Hydrogen Production Through Electrolysis

Robert J. Friedland (Primary Contact), A. John Speranza
Proton Energy Systems, Inc.
10 Technology Drive
Wallingford, CT 06492
(203) 678-2000, fax: (203) 949-8078, e-mail: rob.friedland@protonenergy.com

DOE Technology Development Manager: Sigmund Gronich
(202) 586-1623, fax: (202) 586-5860, e-mail: Sigmund.Gronich@ee.doe.gov

Objectives

- Reduce the cost of proton exchange membrane (PEM) electrolysis to levels of $1250/kW for 10,000 standard cubic feet per day (scfd) at production levels of 10,000 units per year.
- Reduce the cost of smaller units (1,000 scfd) of $2500/kW in production volumes of 10,000 units per year.
- Evolve the use of PEM electrolysis as an energy storage device to enable renewable energy technology as a sustainable source of electricity.

Approach

- Validate the design and cost reductions for the hydrogen oxygen generator (HOGEN®) 40 generator control board and advance that design into the more complicated controls of the HOGEN® 380 hydrogen generator.
- Design a cell stack compression scheme that reduces the material and labor cost associated with the manufacture of the cell stack.
- Investigate low cost power conversion options for use across the line of hydrogen generators.
- Test a renewables interface to a HOGEN® 40 generator and collect data to understand how the system interacts with the renewable (photovoltaic- or wind-powered) device.

Accomplishments

- Completed the validation of the HOGEN® 40 generator control board and the design specification for the HOGEN® 380 hydrogen generator control board. Savings of at least $3,500 of material and 40 hours of labor were removed from the HOGEN® 40 generator.
- Reduced the number of parts in the cell stack compression from 1344 to 15, assembly time from 75 minutes to 5 minutes, and overall volume by over 30%.
- Determined that a non-isolated power converter with minimal energy storage can get to between $.033-$.05/watt for the generators.
- Developed a 5 kW converter for photovoltaic (PV) and wind systems and tested the converter at Northern Power Systems.

Future Directions

- Validate the design of the control board for the HOGEN® 380 generator.
- Analyze additional power electronics options for the HOGEN® 380 generator.
- Conduct additional testing using a PV array coupled to a HOGEN® 40 generator.

Introduction

Proton's goal is to drive the cost of PEM electrolysis to levels of $1250 per kilowatt for 10,000 scfd and $2500 per kilowatt for 1,000 scfd of hydrogen gas output. Both of these costs assume a manufacturing volume of 10,000 units per year, and the cost per kilowatt is based on electrical power into the electrolyzer. In addition, this project will evolve the use of PEM electrolysis as an energy storage device to enable renewable energy technology as a sustainable energy source.

For this past fiscal year, Proton has focused on several aspects associated with these cost reduction efforts. First, all of the previous cost reductions on the HOGEN® 40 generator (see Figure 1) needed to be fully validated by testing to show they would meet the technical requirements of the product and support the customer and market requirements. Second, the control board on the HOGEN® 40 was to be advanced into the HOGEN® 380 generator product (see Figure 2). Third, investigation work was to be conducted on power supply options for the HOGEN® 380 generator based on some of the work on the HOGEN® 40 generator, but advanced to incorporate the higher power levels required on the larger units. Fourth, cell stack cost reduction activities on compression hardware was to be advanced and cost traded with traditional spring washer approaches. Finally, data was to be collected on renewable power inputs using power conditioning equipment developed by the project.

Approach

The HOGEN® 40 generator was chosen as the model for cost reduction for two reasons. First, the smaller size of the HOGEN® 40 generator made cost reduction activities and hardware purchases less costly, and thus enabled a larger scope of effort and impact on return. Second, advances are scalable. In other words, improvements and cost reductions made on the HOGEN® 40 generator can be scaled to the larger HOGEN® 380 generators with less financial and project related risk. The specifics of this approach were outlined in the Technical Paper submitted for that year's annual review[2].

Figure 1. HOGEN® 40 Hydrogen Generator

Figure 2. HOGEN® 380 Hydrogen Generator

The cost reduction effort targeted the electrical controls and mechanical systems that were common across the range of hydrogen generators and would need to be used for future products involving renewable energy technologies. The control board design and development done in this project yielded significant reductions in both material and labor costs. In addition, mechanical system

Figure 3. Current Cell Stack Compression Configuration

Figure 4. Improved Cell Stack Compression Configuration

simplifications, plumbing and fitting reductions and part substitutions also played a large role in the cost reduction effort for both labor and material. These modifications coupled with new technology developments like a power interface for renewable energy input successfully moved the HOGEN® 40 generator product towards renewable energy utility. By the end of FY2001 many of these design improvements and cost reductions had been developed but not fully validated[3].

Results

Cell Stack Compression

This task was to study the cost and performance differences of changing the methodology of compressing the electrolysis cell stack from a large number of spring washers (see Figure 3) to a fewer number of larger spring washers (see Figure 4). This change has yielded some impressive results. Changing to the large diameter spring reduces the assembly time of the washers from 75 minutes to 5 minutes, and reduces the parts count from 1344 pieces to 15. From a manufacturing standpoint, these are very impressive reductions that also have a tremendous impact on quality and consistency of assembly. Each of the smaller springs needs to be oriented in a certain way and with a certain ordering configuration on each rod. This complicated assembly is prone to mistakes that cause rework and could possibly jeopardize the sealing integrity of the cell stack.

Control System Cost Reduction

The HOGEN® 40 generator control board design represents a significant cost reduction to the overall electrolyzer control system. The material cost for the control system has been reduced from over $3,500 to less than $300 with a 40 hours to one hour reduction in labor (see Figures 5 and 6). This year's effort was focused on validating the design changes that were made to cost reduce the electrolyzer control system

in order to insure that the integrity and reliability of the product was not compromised. The control board was developed beyond the prototype stage and underwent extensive design validation testing prior to production release. Validation of the control board included Highly Accelerated Life Testing (HALT), which exposed the board to environmental extremes in order to identify hardware limitations. The results of the HALT testing were fed back into the design process to further enhance the robustness of the control board design. Validation testing also included agency safety/EMC testing and equivalent certifications for Underwriters Laboratory, CSA, and CE. The control board also underwent operational testing to insure that the electrolyzer operated within design specifications through all modes of operation.

The cost reduction efforts on the HOGEN® 380 generator control system have resulted in a greater than 90% control system cost reduction. The fact that the HOGEN® 380 generator control board was developed off of the HOGEN® 40 generator control board design and was able to maintain the same basic architecture and function has resulted in a much more dramatic hardware cost reduction. The current HOGEN® 380 generator control system costs in excess of $10,000. The projected cost of the production control board in modest volumes is less than $500. The validated HOGEN® 40 generator control board was used as the base platform for the HOGEN® 380 generator control board.

The HOGEN® 380 generator control board specification was drafted and a prototype board was delivered for functional testing early this year. The prototype board was then incorporated into an electrolyzer system to verify the design and test the basic functionality of the cost-reduced system. Basic design verification testing was completed, and the board design was modified to incorporate the changes that resulted from the verification testing. The beta board will be delivered this year and undergo extensive validation testing

HOGEN® 380 Generator Fluid Management Cost Reduction

Following the same strategy as was used on the control board development, a tremendous amount of cost reduction has been realized on the HOGEN® 380 generator fluids system with a minimal amount of reengineering. The components that were developed for the HOGEN® 40 generator were used as the platform for further cost reductions on the HOGEN® 380 generator. The development efforts on gas drying for the HOGEN® 380 generator have resulted in a low-cost pressure swing absorption dryer that can be manufactured in low quantities for under $4,000 compared to the previous design that was

Figure 5. Current Discreet Electrical Component Layout

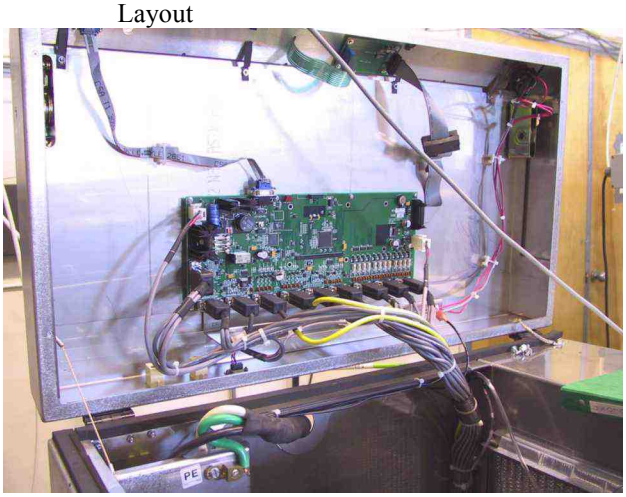

Figure 6. New Control Board Design

over $8,000. In higher volumes the cost of this dryer will be well under $2,000.

Power Conversion Cost Reduction

One of the first efforts that needed to occur, for the power conversion cost reduction to be successful, was a cell stack electrical characterization study. This task helped to understand the electrolysis cell stack as a power load.

Utility Grid Converter

With the cell stack characterization complete, a feasibility study and paper design based on a power electronics cost reduction effort for the HOGEN® 40 hydrogen generator was conducted. It was concluded that the high cost of power conversion of these units is due mainly to two factors: buying an "off-the-shelf" design that is not optimized for the electrolysis application and providing galvanic isolation to the electrolysis cell. The study concluded that a non-isolated power converter with minimal energy storage has the potential to achieve $.033/watt for the HOGEN® 40 generator and $.05/watt for the HOGEN® 380 generator.

Based on the initial results of the feasibility study, the design and development of a cost reduced power electronics package appears feasible. The path to the lowest cost for power electronics is in a design that is optimized for the electrolysis process, and the best approach to accomplish this is to develop the design "In House" or in cooperation/collaboration with a third party.

Presently, the HOGEN® 40 generator power electronics costs $0.30/watt and delivers DC power at an average efficiency of 85%. The feasibility study identifies a design path with the ability to reduce the cost of power electronics to less than $0.10/watt and an average efficiency of 94%.

Renewable Energy Interface Converter

Sustainable Energy Technologies (SET) was contracted to develop an interface converter with the capability to accept a power input from a photovoltaic or wind source. SET delivered two 5 kW photovoltaic interface converters that were tested by Northern Power Systems in Waitsfield, Vermont and found to meet the basic specifications of the design. SET also delivered an interface converter that was capable of accepting a wind turbine input, but due to the inability to interface directly to a wind turbine the converter was never tested beyond the basic power test. One of the PV converters has been delivered to the Illinois Institute of Technology for integration into a renewable energy system utilizing one of Proton's HOGEN® 40 hydrogen generators.

Conclusions

A sustainable energy system utilizing renewable energy technology must have the fundamental capability of storing excess renewable energy when it is available so it can be utilized on demand. Renewable energy technology is inherently intermittent based on the fundamental fact that the wind does not always blow and the sun does not always shine. Electrolyzer technology has great promise for helping to bridge the gap and make electricity available twenty-four hours a day, seven days a week. Proton's hydrogen generators also follow the load extremely well and can respond virtually instantaneously to fluctuations in power levels from the renewable energy device. However, the cost challenges associated with electrolysis must be overcome. This project has made tangible progress on reducing cost through various design initiatives and bringing those designs forward into products

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II.C Fossil-Based

II.C.1 Production of Hydrogen by Superadiabatic Decomposition of Hydrogen Sulfide

Francis S. Lau (Primary Contact), Rachid B. Slimane, Remon J. Dihu, and Mark Khinkis
Gas Technology Institute
1700 S. Mt. Prospect Rd., Des Plaines, Illinois 60018
(847) 768-0592, fax: (847) 768-0600, e-mail: francis.lau@gastechnology.org

Jacques Bingue, Alexei Saveliev, Alexander Fridman, and Lawrence Kennedy
University of Illinois at Chicago, Chicago, IL

DOE Technology Development Manager: Peter Devlin
(202) 586-4905, fax: (202) 586-9811, e-mail: Peter.Devlin@ee.doe.gov

Main Subcontractor: University of Illinois at Chicago, Chicago, IL

Objectives

- Demonstrate the feasibility of the superadiabatic partial oxidation concept as a basis for developing an innovative process for production of economically viable quantities of hydrogen through the thermal, noncatalytic decomposition of hydrogen sulfide (H_2S) in H_2S-rich waste streams into hydrogen and elemental sulfur, without the input of additional energy (and no additional carbon dioxide [CO_2] emissions).
- Outline a research and development strategy leading to the demonstration of an integrated process at an industrial site.

Approach

- Develop a numerical model for the superadiabatic H_2S decomposition reactor.
- Design, construct, and operate a bench-scale reactor system to demonstrate technical feasibility of the superadiabatic partial oxidation concept.
- Evaluate process economics and markets.
- Conduct thermodynamic and kinetic modeling studies to evaluate agreement between modeling predictions and experimental data, and to extend model applicability to conditions not tested experimentally.

Accomplishments

- Identified key process variables and optimum operating conditions, and developed reactor design guidelines.
- Prepared a design package for a bench-scale testing system.
- Performed preliminary confirmation of technical viability of the concept.
- Designed and constructed a state-of-the-art superadiabatic H_2S decomposition reactor system to carry out a rigorous demonstration of the technical feasibility of the superadiabatic decomposition approach.