

Energy Frontiers Focus Topic

Room: 211B - Session EN+AS+EM+SE+SS-TuM

Photocatalysis

Moderator: Jason Baxter, Drexel University, Manjula Nandasiri, Pacific Northwest National Laboratory

8:00am **EN+AS+EM+SE+SS-TuM1 Ultra-dense Hydrogen and Low Energy Nuclear Reactions, Sveinn Olafsson**, Science Institute, Physics department University of Iceland, *L. Holmlid*, University of Gothenburg, Sweden

For over the last 25 years the science of cold fusion/LENR has been researched around the world with slow pace of progress. Modest quantity of excess heat and signatures of nuclear transmutation and helium production have been confirmed in experiments and theoretical work has resulted in a flora of possible theoretical scenarios. [1-2]

Here we present energy production in several stages of surface processes that result first in the formation of Rydberg matter of Hydrogen [3] that can later condense in a new ultra-dense Hydrogen phase with 2.3 pm short bond distances. This phase is nuclear active showing break-even fusion reaction [7] under 100mW laser pulsing and slow spontaneous fusion occurring without laser pulsing[4,5,6]. The experimental work in around 30 publications is briefly reviewed and latest experimental results presented and discussed.

In that work high-energy particles are detected from the spontaneous processes using scintillation and other similar detectors. Both spontaneous line-spectra and a spontaneous broad energy distribution similar to a beta-decay distribution are observed indicating detection of particles such as muons. The broad distribution is concluded to be due to nuclear particles, giving straight-line Kurie-like plots. They are observed even at a distance of 3 m in air and have a total rate of 10^7 - 10^{10} s⁻¹. In the talk the link of these observation to Low energy nuclear reactions (LENR) or so called cold fusion will be discussed experimentally and theoretically.

1. The science of low energy nuclear reaction.

Storms E. World Scientific Publishing Company; **2007**.

2. The explanation of low energy nuclear reaction.

Storms E. Ienergy Press; **2014**.

3. Review paper: Experimental Studies and Observations of Clusters of Rydberg Matter and Its Extreme Forms Leif Holmlid. *J Clust Sci* (**2012**) 23:5-34

4. Spontaneous ejection of high-energy particles from ultra-dense deuterium D(0)

Leif Holmlid and Sveinn Ólafsson

Volume 40, Issue 33, 7 September **2015**, Pages 10559-10567

5. Charged particle energy spectra from laser-induced processes: nuclear fusion in ultra-dense deuterium D(0) Leif Holmlid and Sveinn Ólafsson submitted **2015**.

6. Muon detection studied by pulse-height energy analysis: Novel converter arrangements

Leif Holmlid and Sveinn Ólafsson. *Rev. Sci. Instrum.* 86, 083306 (**2015**);

7. Heat generation above break-even from laser-induced fusion in ultra-dense deuterium

Leif Holmlid. *AIP Advances* 5, 087129 (**2015**);

8:20am **EN+AS+EM+SE+SS-TuM2 Optical and Surface Properties of Semiconductor Nanowires for Solar Fuels, Eleonora Frau, J. Vukajlovic, A. Dalmau-Mallorquí, A. Fonctuberta i Morral, E. Alarcon Llado**, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Semiconductor nanowires (NWs) are filamentary crystals with new properties from their bulk counterparts. Their large versatility makes them excellent candidates as building blocks for contributing to solving the energy problem in the near future. In this work, we will assess two main properties of semiconductor NWs that have an impact to solar energy conversion.

First, it is known that light is strongly absorbed by NW arrays since light resonances give rise to effective absorption cross-sections that are much larger than the geometrical ones. Optical resonances depend on NW geometry and dielectric environment, and can result into absorption effective diameters up to 25 times larger than the geometrical for certain wavelengths. We have used finite-difference time-domain (FDTD)

electromagnetic simulations to understand and design NW-based sunlight scavengers. For instance, a GaAs NW array that is only covering 3% of the surface can generate more photocurrent than a planar film, considering a 30% reflectivity (see figure1). Also that thanks to optical resonances, an indirect-bandgap material such as Si is capable of absorbing most of the light within a 2um long NW array that only covers 7% of the device surface.

On the other hand, it is also known that surface states and traps detriment device performances. However, in case where solar energy is directly converted into fuel (such as hydrogen) in a photoelectrochemical (PEC) cell, the large surface-to-volume ratio of NW forests is an important asset. Since the electrochemical reactions happen at the semiconductor surface, NWs enable the use of low-cost catalysts (e.g. MoSx) even though they exhibit lower performances than noble metals (e.g. Pt). In order to assess the effects of nanostructuring photo-electrodes for solar fuel generation, we have studied photo-cathodes based on Silicon nanopillar structures. The photo-cathodes were fabricated by using a top-down approach and their diameters range from ~200 to 900nm and lengths ~2um. We observe that reducing the size of the nanostructure, increases the overpotential, and thus the overall efficiency (see figure 2). By coating the surface with thin TiO₂ layers, the performance is improved in terms of overpotential and fill factor. We explain these findings by using an electrico-kinetic model of the semiconductor-water junction. We find that the TiO₂ layers actually act as a hole blocking layer, preventing recombination.

8:40am **EN+AS+EM+SE+SS-TuM3 Engineering Surfaces and Interfaces for Photoelectrochemical (PEC) Water-Splitting, Thomas Jaramillo, J.D. Benck, Stanford University, J. Kibsgaard, SLAC National Accelerator Laboratory, T.R. Hellstern, C.J. Hahn, P. Chakthranont, R. Britto, K.D. Fong, Stanford University** **INVITED**

The talk will focus on engineering surfaces and interfaces for solar photoelectrochemical (PEC) water-splitting for the direct, renewable production of H₂. In particular, this talk begin by describing research efforts to develop H₂ evolution catalysts that are active, stable, and comprised of only earth-abundant elements, including transition metal sulphides, phosphides, and phosphosulfides.¹⁻³ Next, we will describe recent efforts to integrate these catalysts onto semiconductor surfaces to provide corrosion protection as well as enhanced interfacial catalysis for PEC water-splitting.⁴ This talk will focus on the need for high turnover frequency (TOF) catalysts, which ultimately enable the greatest flexibility in designing optimum interfaces for high performance devices.

[1] J. Kibsgaard, T.F. Jaramillo, F. Besenbacher, "Building an appropriate active site motif into a hydrogen evolution catalyst with thiomolybdate [Mo₃S₁₃]²⁻ clusters," *Nature Chemistry*, **6** (2014) 248.

[2] J.D. Benck, T.R. Hellstern, J. Kibsgaard, P. Chakthranont, T.F. Jaramillo, "Catalyzing the Hydrogen Evolution Reaction (HER) with Molybdenum Sulfide Nanomaterials," *ACS Catalysis*, **4** (2014) 3957.

[3] J. Kibsgaard and T.F. Jaramillo, "Molybdenum Phosphosulfide: An Active, Acid-Stable Earth-Abundant Catalyst for the Hydrogen Evolution Reaction," *Angewandte Chemie*, **53** (2014) 14433.

[4] J.D. Benck, S.C. Lee, K.D. Fong, J. Kibsgaard, R. Sinclair, T.F. Jaramillo, "Designing active and stable silicon photocathodes for solar hydrogen production using molybdenum sulfide nanomaterials," *Advanced Energy Materials*, **4** (2014) 1400739.

9:20am **EN+AS+EM+SE+SS-TuM5 Bulk and Surface Effects of Incorporating Titanium Into Hematite Thin Films to Improve Photoelectrochemical Water Splitting, Anthony Abel, A.M. Patel, Drexel University, I.G. Torregrosa, Utrecht University, Netherlands, B. Opananont, J.B. Baxter, Drexel University**

Hematite (α -Fe₂O₃) has emerged as a promising photoanode material for photoelectrochemical (PEC) water splitting due to its chemical stability, earth-abundance, low cost, and suitable band gap for both water splitting and visible light absorption. However, poor charge separation due to low hole mobility and high recombination rate, and sluggish oxygen evolution reaction kinetics have limited its potential as an economical water-splitting catalyst. Here, we investigate titanium incorporation into hematite photoanodes and provide insight into the role of Ti⁴⁺ in improving PEC performance. Planar hematite thin films (~45 nm thick) were deposited by successive ionic layer adsorption and reaction (SILAR) of FeOOH on an FTO/glass substrate and subsequent annealing to induce phase transition to α -Fe₂O₃, and titanium was incorporated up to 10% Ti/(Ti+Fe) by either modification of the SILAR solution (SM: α -Fe₂O₃) or solid-state diffusion (SSD: α -Fe₂O₃) during the annealing process. PEC measurements revealed substantial improvements in both charge separation efficiency and hole injection into the electrolyte, increasing photocurrent from nearly zero to

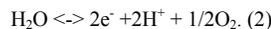
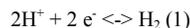
~0.6 mAc^m-² under 1-sun irradiation at 1.23 V_{RHE}. Mott-Schottky analysis indicated a 100 mV cathodic shift in the flat band potential upon doping with Ti⁴⁺ regardless of fabrication method, but a 100-fold increase in carrier density only in SM:α-Fe₂O₃ films, resulting in a high 20 % separation efficiency at 1.23 V_{RHE} with optimized 5 % Ti/(Ti+Fe) in the modified SILAR solution. Electrochemical impedance spectroscopy showed a 4x increase in the surface state capacitance peak near the water oxidation onset potential, possibly due to reduced Fermi level pinning as a result of more efficient hole injection into the electrolyte. More importantly, doping with titanium resulted in a 100-fold decrease in the charge transfer resistance from surface states to the electrolyte, revealing the strong influence of Ti⁴⁺ on interfacial kinetics. Further surface modification with an ultrathin FeOOH surface passivation layer raised the plateau photocurrent to ~0.8 mAc^m-² at 1.23 V_{RHE}, representing a 3x improvement over previous reports of SILAR-deposited hematite films and comparable with record performance for planar hematite deposited using high vacuum synthesis techniques.

9:40am **EN+AS+EM+SE+SS-TuM6 Iron Oxide Nanoparticle Growth on Highly Oriented Pyrolytic Graphite (HOPG) and Photocatalytic Properties of Pt on Iron Oxide.** *Jayde Kwon, J.C. Hemminger*, University of California, Irvine

Highly oriented pyrolytic graphite (HOPG) is an ideal substrate to study the fundamental growth mechanism of iron oxide independent from substrate effects. Platinum on iron oxide is a model heterogeneous catalyst with importance to biotechnology and solar cell applications. Selective growth of iron oxide nanoparticle (NP) either on step edges of HOPG or oxygen plasma treated HOPG by physical vapor deposition (PVD) will be presented. The successful selective iron oxide NP growth was validated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The development of the NP array system is highly significant in that it can provide an ideal template for theoretical calculations for fundamental metal growth studies. Pt nanoparticles were subsequently deposited on the iron oxide nanoparticles using a selective photodeposition technique. The application of these nano-systems (Pt nanoparticles on iron oxide nanoparticles) towards photocatalysis of methylene blue will be presented. Although iron oxide is a promising semiconductor photocatalyst, it suffers from a short hole diffusion length, low electrical conductivity and a high rate of electron hole recombination. However, this bimetallic system using platinum deposited on iron oxide overcomes these barriers. A novel method was developed using small quantities of Pt on iron oxide to significantly enhance methylene blue decomposition. This system is also being explored as a catalytic model for water-gas shift reactions.

11:00am **EN+AS+EM+SE+SS-TuM10 Interface Design for Efficient and Stable Photoelectrochemical Water Splitting.** *Joel Ager*, Lawrence Berkeley National Laboratory **INVITED**

Solar photoelectrochemical (PEC) water splitting is potential future carbon-neutral energy source which could dramatically change the landscape of global energy generation and storage. The half reactions for water splitting are as follows:



The free energy change for the overall reaction, $\text{H}_2\text{O} \leftrightarrow \text{H}_2 + 1/2\text{O}_2$ corresponds to 1.23 eV per electron transferred; however, typically >1.5 V is required to overcome kinetic limitations, particularly for the O₂ evolution reaction. The most commonly used approach for integrated solar water splitting employs photocathodes (H₂ or hydrocarbon producing) and photoanodes (O₂ producing) linked in a tandem geometry [1].

The interface challenges required to demonstrate a practical system which is both efficient and stable under operation are substantial and severe. In addition to constructing interfaces, either solid-solid or solid liquid, which achieve the desired photovoltaic charge separation, the surfaces of these photoelectrodes can be a failure point under sustained operation due to corrosion. We have found that the use of nanoscale conformal oxide layers can greatly reduce corrosion rates. Moreover, it is possible to achieve both high performance and lifetime by the use of protection layers which are also tuned for selective carrier contact.

Examples of such a strategy will be shown for photocathodes [2-5] and for photoanodes [5]. Recent work on p-type transparent oxides (p-TCOs) used as selective hole contacts for photoanodes will be emphasized. For example, it will be shown that using NiCo₂O₄ as the p-TCO and n-type Si as a prototypical light absorber, a rectifying heterojunction capable of light driven water oxidation can be created. By placing the charge separating junction in the Si using a np⁺ structure and by incorporating a highly active Ni-Fe oxygen evolution catalyst, efficient light-driven water oxidation can be achieved. The generality of the p-TCO protection approach is

demonstrated by multi-hour, stable, water oxidation with n-InP/p-NiCo₂O₄ heterojunction photoanodes.

Acknowledgements. This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993.

References.

1. J. W. Ager *et al.*, *Energy Environ. Sci.* (2015). DOI:10.1039/C5EE00457H
2. M. H. Lee *et al.*, *Ang. Chemie Int. Edition* **51** 10760 (2012).
2. Y. Lin *et al.*, *Nano Letters* **13** 5615 11 (2013)
3. Y. Lin *et al.*, *J. Phys. Chem. C* **119**, 2308 (2015).
4. J. Yang *et al.*, *J. Amer. Chem. Soc.* **136** 6191 (2014).

11:40am **EN+AS+EM+SE+SS-TuM12 Buried, Hetero, and p-i-electrolyte III-V Photoelectrochemical Junctions with Significantly Enhanced Photocurrent Onset Potentials.** *James Young, H. Doscher, J. Turner, T. Deutsch*, National Renewable Energy Laboratory

To approach the maximum achievable solar-to-hydrogen (STH) conversion efficiencies with photoelectrochemical (PEC) devices, it is necessary to employ the lowest possible band gap (E_g) absorbers that can still provide sufficient voltage to drive water splitting at high rates (1.7-1.8 V for 25% STH). The record 12.4% STH was achieved by a GaInP₂/GaAs PEC/photovoltaic (PV) tandem device while an all solid state GaInP₂/GaAs PV/PV tandem produces an open-circuit voltage that approaches 2.4 V. Since GaAs (E_g = 1.4 eV) is the current-limiting junction in these devices, it can be substituted by InGaAs with E_g = 1.0 eV to reach 25% STH. The current-for-voltage tradeoff of using lower-E_g absorbers moves toward the constraint of insufficient voltage for spontaneous water splitting. To address this approaching constraint, we investigate several alternative device structures at the III-V/electrolyte interface that show photocurrent onset potential enhancements of a few hundred mV. We will present band diagram calculations and electrochemical measurements to discuss the voltage performance of these structures.

12:00pm **EN+AS+EM+SE+SS-TuM13 X-ray Absorption Studies on the Li-S Battery Cathode Side.** *Yifan Ye*, University of Science and Technology of China, *A. Kawase*, Lawrence Berkeley National Laboratory, *H.X. Ju*, University of Science and Technology of China, *E. Cairns*, Lawrence Berkeley National Laboratory, *J.-H. Guo*, Lawrence Berkeley Lab, University of California, Berkeley, *J.F. Zhu*, University of Science and Technology of China

As increasing global energy consumption in the coming days, sustainable, clean energy technologies are highly desirable. The high theoretical specific capacity of 1675 mA·h/g for elemental S has prompted intense effort to study the Lithium-Sulfur batteries. With the application of cetyltrimethyl ammonium bromide (CTAB), modified sulfur-graphene oxide (S-GO) nano-composite based Li/S batteries exhibited a very high initial discharge capacity of 1440 mA·h/g of sulfur at 0.2C with excellent rate capability of up to 6C for discharge and 3C for charge while still maintaining high specific capacity. And the batteries demonstrated cycling performance up to 1500 cycles with extremely low decay rate of 0.039% per cycle. With the introduction of CTAB, the performance of the GO-S based Li-S battery has been improved significantly, thus it is important to figure out the role of CTAB played in the system. During the synthesis process of the cathode materials, S and Na₂S were used as the precursors, the ratio of S/Na₂S is crucial to the components of the precursors. Moreover, the sequence of mixing GO/CTAB solution with precursor solution is a key point to effective cathode synthesis procedure. Understanding these information helps to optimize the methodology for the controllable synthesis of desired cathode material that can be used to fabricate an efficiency and well-performed Li/S battery. S K-edge X-ray absorption spectroscopy (XAS) is applied to study the chemical species evolution during the GO-S-CTAB cathode material synthesis. The influences on the cathode materials related to the battery performance are monitored by S K-edge XAS. The research revealed the interaction between CTAB and GO, S, Na₂S and Na₂S_x. It indicated that CTAB can physical adsorbed on Na₂S_x molecules by bonding with the terminal S atoms of Na₂S_x chains, and this kind of bonding can convert to chemical C-S bonding with heating treatment. Thus the interaction of CTAB with GO, formed C-S between CTAB and S and interaction of GO and S provided a tight tri-layer structure which can immobilize the S particles on GO sheet and finally enhanced the battery performance. The information from this work proved the importance of Na₂S:S ratio, CTAB/GO adding procedure in the fabrication process, and we can easily apply XAS to optimize these recipe. And moreover, this work proved strong evidence that XAS tools can be used to do the initial characterization on the battery performance before real cycling procedure.

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