## UNIVERSITY OF FLORIDA

### *Solar Thermal Power for Bulk Power and Distributed Generation*

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**Students:** Richard Stehle (PhD); Michael Bobek (PhD); Kyle Allen (PhD); Justin Dodson (PhD), Like Li (PhD)

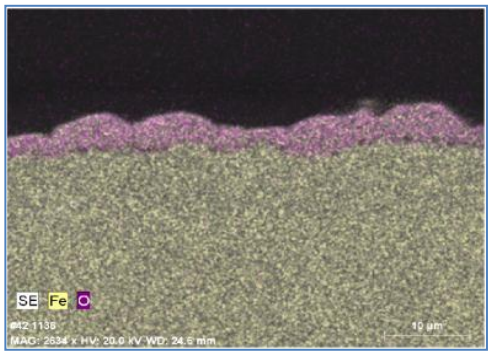
**Description:** While there are many different approaches to hydrogen generation, the most attractive means is to split water molecules using solar energy. The current approach is to develop highly reactive metal oxide materials to produce intermediary reactions that result in the splitting of water to produce hydrogen at moderate temperatures (<1000 K). It is envisioned that the metal oxide reactors will ultimately be mounted within a solar concentrating reactor, and irradiated via heliostats. This Task is structured toward the overall goals of solar-driven, thermochemical hydrogen production, with associated efforts toward the enabling surface science, catalysis, particle science, material synthesis, nano-structures, multiscale-multiphase physics modeling, and process simulation that will enable the realization of solar hydrogen-based fuels to power the transportation economy. Successful efforts as targeted in this project are a critical step toward increased renewable-resource based fuels and energy, reduction of GHG emissions, and establishment of a new power industry in Florida.

**Budget:** $446,400
**Universities:** University of Florida

## Progress Summary

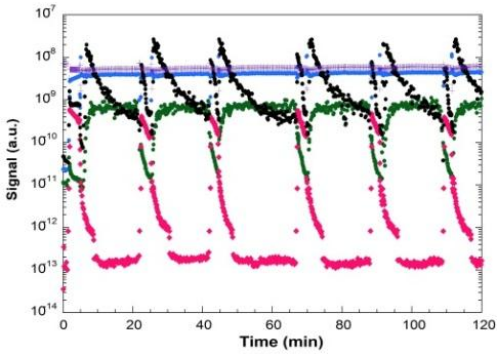
Research continues to focus on highly reactive metal oxide materials to produce intermediary reactions that result in the splitting of water to produce hydrogen at moderate temperatures (<1000 K). This year we have quantified the fundamental reaction kinetics using our laboratory reactor, and extensively studied the oxidation-reduction cycles that are necessary for practical reactors with high efficiency. In parallel, activities have progressed toward reactor scale-up and modeling using a fluidized bed design, and efforts have advanced to identify novel new nano-particulate catalysts. For example, a nano-particle zirconia (n-$ZrO_2$) support was identified as a promising catalyst for two-step water-splitting reaction that does not readily agglomerate, thus the surface area of this catalyst is larger and the potential for $H_2$ production remains high. Successful efforts, as targeted in this project, are a critical step toward increased renewable-resource based fuels and energy, reduction of greenhouse gas emissions, and establishment of a new power industry in Florida.

A temperature range of 600 to 750 K was investigated as the temperature for the water-splitting process because of the thermodynamic favorability of the reaction in this range. Under excess reactant conditions, it is concluded that resulting oxide thickness presents only a negligible barrier to diffusion of the water reactants when compared to the kinetic rates, allowing accurate calculation of the effective hydrogen production kinetic rate coefficient, as well as the Arrhenius pre-exponential factor and the overall activation energy (49 kJ/mol). Of significant importance in any practical reactor, which remains an important practical goal, is the exact nature of the oxide layers formed during water splitting. Extensive Raman spectroscopy and energy dispersive spectroscopy (EDS) were used to verify the presence of magnetite ($Fe_3O_4$) as the primary oxide. Furthermore, depth profiling was



Magnetite oxide layer formed during water splitting at a reactor temperature of 650 K.

performed to examine the local O/Fe atomic ratio through the matrix. A slight gradient was observed, with diminished oxidation moving away from the outer surface, suggesting minor diffusion effects as the reaction progresses. Finally, knowledge of the oxide states and kinetic growth rates enables calculation of an effective linear growth rate, which ranged from about 6 to 45 nm/min over reaction temperatures from 600 to 750 K, respectively.




Reactor output showing real-time $H_2$ production and reactor oxide regeneration over 6 cycles.

A final area of critical importance for practical hydrogen production is the ability to cycle between oxidation (hydrogen production) and reduction (reactor regeneration). Preliminary experiments were performed to cycle between these two reactor conditions. As shown in the adjacent plot, repeatable cycling between these two processes was achieved, which shows premise for operating a scaled-up production system. Future efforts will focus on several remaining critical questions, including efficient and repeatable reactor cycling, kinetics and mechanics of surface oxides under oxidation/reduction, and fluidization for efficient scale-up of hydrogen production.

**Presentations:**

1) FESC Summit in Orlando, Florida (September 28, 2010). Oral presentation by Richard Stehle. Co-authors: D.W. Hahn and M. Bobek. Fundamental oxidation reaction kinetics for the steam-iron process in a solar thermal reactor.

**Papers:**

L. Li, R. Mei, J.F. Klausner, D.W. Hahn, Heat transfer between colliding surfaces and particles, ASME/JSME 8th Thermal Engineering Joint Conference, ATJEC2010, March 13-17, 2011.

R.C. Stehle, M.M. Bobek, R. Hooper, D.W. Hahn, Oxidation Reaction Kinetics for the Steam-Iron Process in Support of a Solar Thermal Reactor, to be submitted in May 2011 to *International Journal of Hydrogen Energy*.

**Grants Awarded**

Title: Novel magnetically fluidized bed reactor development for the looping process: Coal to hydrogen production R&D.
Agency: US DOE
Investigators: J. Klausner (PI), D.W. Hahn (co-PI), R. Mei (co-PI), and J. Petrasch (co-PI).
Period of performance: 9/30/2009 to 9/30/2011.
Funding: $1.25M

**Proposals**

Title: Sunlight to Fuel: A global sustainable energy future.
Agency: NSF Science and Technology Center
Investigators: J. Klausner (PI). Co-PIs: D.W. Hahn, R. Mei, J. Petrasch, N. Sullivan, H. Cheng, K. Schanze, J. Weaver, H. Weaver, P. Dickrell at UF. Additional partnering institutions: Univ. of Minnesota, Cal Tech, ETH-Zurich, Johns-Hopkins, University of Illinois, and University of Colorado.
Period of performance: 5 years
Funding: TBD
Status: Passed internal UF review and currently preparing pre-proposal for NSF.