

UNIVERSITY OF FLORIDA

Solar Thermal Power for Bulk Power and Distributed Generation

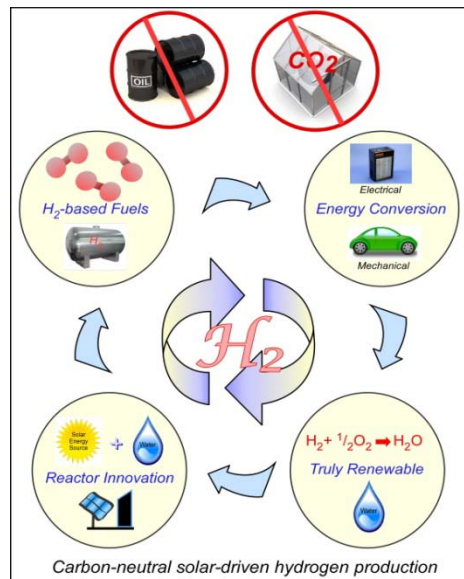
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Description: While there are many different approaches to hydrogen generation, the most attractive means is to split water molecules using solar energy. The current approach is to develop highly reactive metal oxide materials to produce intermediary 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 green house gas emissions, and establishment of a new power industry in Florida.

Budget: \$446,000

Universities: University of Florida



Progress Summary

Efforts to date have focused on two primary tasks, namely, construction of two laboratory-scale reactors for fundamental studies of the reactor processes and surface chemistry for hydrogen production. The first reactor is a monolithic configuration that was specifically designed and constructed to allow for fundamental measurements of surface kinetics during hydrogen production from reduced ferrous surfaces. This reactor is powered by resistance heating to enable precise temperature control. Real-time species measurements are made with on-line mass spectrometry using a heated gas capillary to sample directly from the reactor stream. The second reactor design is configured around the concept of a fluidized bed to achieve high efficiency with actual reactors. In a parallel effort, this reactor design was extended to magnetically-assisted fluidized bed configurations. As a laboratory system, this reactor will also be configured with resistance heating to allow precise control. Ultimately, we will move toward pilot-scale radiatively heated reactors using solar simulator lamps. However, for fundamental studies, the electrically heated reactors are most efficient and precise.

The current work has focused on the use of ferrous metals, primarily elemental iron as the reduced material. Upon exposure to water vapor under favorable temperatures (600-800 K), the iron is oxidized primarily to hematite and magnetite (as validated with Raman spectroscopy), generating hydrogen in the process. The goals of the above described facilities are to measure the fundamental reaction kinetics of the oxidation states, and to explore the final state of oxide, as well as gage process efficiency under highly dispersed powdered reactants. Assessment of oxidized states will be done through a combination of surface analysis tools, including micro-Raman spectroscopy for speciation, and depth analysis using a focused-ion beam (FIB) and SEM/EDS analysis, which will enable detailed

assessment as to the penetration of the oxide layer into the bulk iron substrate, as well as the stability of the oxide band.

At present, the monolithic reactor is now fully operational. All fabrication and acquisition of the necessary heating elements, reactor housing, process controllers, flow controllers, and gas-sampling interfaces have been completed, assembled and tested. The primary power is via a series of four high-temperature 400 W heater coils. These are formed around a concentric-tube annular flow reactor, designed to provide an isothermal reactor test section. During this period of performance, the system was fully tested, benchmarked and calibrated. Using the new monolithic reactor, a full series of iron oxidation studies for actual hydrogen production have been accomplished over a range of 600 to 750 K (reactor temperature), which has yielded reproducible kinetic production rates that vary from 0.00002 to 0.0002 ml/cm² s of hydrogen production. Complementary surface analysis tools have been used, including Raman spectroscopy and SEM/EDS on the reacted rods, to explore the oxide state.

At present, the fluidized bed reactor is complete and has undergone testing and has now been used for extensive experimental investigations under actual hydrogen production conditions. The reactor was constructed about a high-temperature tube furnace to provide uniform process heat. A reduced iron-oxide power was used for assessment of the reactor performance, including assessment of magnetically-assisted fluidization. On-line mass spectrometry was used to quantify hydrogen production over a range of conditions.

Additional efforts have focused on understanding of surface reaction processes and the relationships between surface properties and functionality, specifically on correlating catalyst properties with water splitting activity and thermal reduction, and clarifying mechanistic details of the surface reactions.

Finally, computational activities are focused on the fluidized bed, in which critical transport phenomena are being addressed with regard to scaling to larger processes or to solar-driven processes.

2010 Annual Report

Our project efforts to date have focused on direct hydrogen splitting from water in support of our overall mission to conceive, design, and develop advanced reactor technologies that utilize concentrated solar energy and highly reactive materials to produce low cost hydrogen. These activities directly align with the National Academy of Engineering Grand Challenge and published DOE strategic goals.

High temperature thermochemical production of hydrogen that uses concentrated solar radiation for process heat has been suggested as a candidate technology for renewable hydrogen. This process entails a two step approach where endothermic dissociation of a metal oxide is driven in a solar furnace. The liberated metal (or reduced metal oxide) is mixed with water vapor, and the resulting exothermic reaction liberates hydrogen molecules and re-oxidizes the metal. The metal oxide decomposition requires very high temperatures, on the order of 1500 C. The advantage of the two-step process is that the high-temperature separation of H₂ and O₂ is avoided and no explosive H₂ and O₂ mixtures are formed, since the H₂ and O₂ are formed in different steps. Current technological hurdles to achieving successful hydrogen production are the high operating temperatures needed to achieve reasonable reaction kinetics, cyclic stability of the reactive material, non-uniform transient heating, and recuperation of thermal energy lost through high temperature operation. In order to overcome these technological hurdles, our FESC team has specifically initiated a plan to revolutionize thermochemical reactor design through the development of magnetically fluidized bed reactors. There are many technological advantages to operating such a reactor including, very high reaction surface area to yield rapid kinetics at more moderate operating temperatures (<1000 K), more spatially uniform temperature distribution during transient heating, and substantial control over the fluidization characteristics of the bed using magnetic fields. For the reactor temperature operating regime, the most likely phase transition during the iron oxidation process is a

conversion of iron powder to magnetite. Both have excellent magnetic properties and are easily fluidized using electromagnets. Activities for the past year have focused extensively on experimental characterization of key process kinetics and on reactor design, with supporting modeling efforts and fundamental catalysis studies.

Fundamental Kinetics Study

During this period of performance, a laboratory scale reactor was fully designed, built and optimized to allow for steady state hydrogen production. All design constraints were met, which allow the reactor to operate at the full temperature range (600 to 800 K) along with accurately controlled flow rates (steam, carrier gas and inert gas) into the system. The data acquisition system has successfully been applied to the reactor using mass spectrometry, and all system calibration has been performed to enable quantitative analysis of experimental data.

The main focus during this reporting period was to begin to quantify the reaction kinetics for the oxidation reaction and to investigate the chemical phase that is produced from the reaction. Multiple experimental tests were done in the temperature range of 600 K to 750 K with repeatable reaction parameters. Flow rates of liquid water, nitrogen and argon were maintained at a constant rate for all the tests at 12.5 μ L/min, 100mL/min and 200mL/min, respectively. The reactive metal for all the tests was an elemental iron rod (99.5% purity) with an estimated surface area of 71 cm². Typical experimental runs lasted 3 hours, and operated at atmospheric pressure. After each test, the rod used during the experiment was cooled to room temperature and stored in inert gas (nitrogen) to await investigation of its chemical phase by means of Raman spectroscopy and surface electron microscopy (SEM), including focused ion beam (FIB) depth profiling and EDS elemental analysis. The experimental reactor is shown in Figure 1 below, noting the vertical orientation of the reactor vessel to eliminate creep of the monolith (i.e. iron rod) at high temperatures, which was observed in a preliminary, horizontal reactor orientation.



Figure 8: Image of the laboratory-scale reactor used to measure oxidation reaction kinetics under hydrogen production conditions. The capillary for on-line mass spectrometry is visible to the left.

The results from the kinetics testing are tabulated below in Table 1, in terms of average hydrogen production rates for the four temperatures investigated for each hour of operation and the total operation time. All data are quantified directly from the calibrated mass spectrometry data.

Table 2: Tabulated hydrogen production rates for reduced iron monolithic reactor studies.

Hydrogen Production (mL/cm ² min)				
Surface Temperature	Hour 1	Hour 2	Hour 3	Average
600 K	.00115	.00108	.00111	.00111
650 K	.00385	.00351	.00350	.00395
700 K	.00633	.00565	.00508	.00606
740 K	.01027	.00815	.00691	.00853

These results show that as temperature increases, the hydrogen production rate also increase, which is expected for kinetic-controlled surface reactions. However, the data also suggest that the surface reactions may be somewhat dependent upon diffusion, due to the decrease in production rate as time increases, especially at higher temperatures. Hence, the lower temperature (i.e. lower production rates) data support kinetic limited regime, while the higher temperature data suggest some diffusion effects as the oxide layer grows thicker, thereby limiting access to the iron surface. This data can also be used to calculate the average oxide layer linear production rate which are reported in Table 2. These numbers can be directly compared to the SEM results for oxide thickness in order to corroborate the *in situ* production data, as well as provide additional insight into the oxide state.

Raman spectroscopy was then used to determine what iron oxide has been produced from the water shift reaction in order to know where the reduction process will originate, as well as to help predict the thickness of the oxide layer. Such data is important to accurately model the oxidation/reduction cycle from a thermodynamic perspective. SEM analysis combined with EDS was used to further the investigation into oxide layer thickness and to test the homogeneity of the oxide layer, as reported below in Figure 5.

Table 3: Tabulated linear oxide layer growth rates, as magnetite.

Oxide Layer Growth Rate (nm/s)				
Surface Temperature	Hour 1	Hour 2	Hour 3	Average
600 K	.089	.083	.086	.086
650 K	.30	.27	.27	.31
700 K	.51	.44	.39	.47
740 K	.79	.63	.53	.66

The Raman spectroscopy analysis of the resultant oxide on the rods has shown a dominance of magnetite (Fe_3O_4) with a small presence of hematite (Fe_2O_3). Graphs of the Raman spectra for reference samples of both iron oxides, and of the iron rods following hydrogen production can be seen and compared below in Figures 3 and 4.

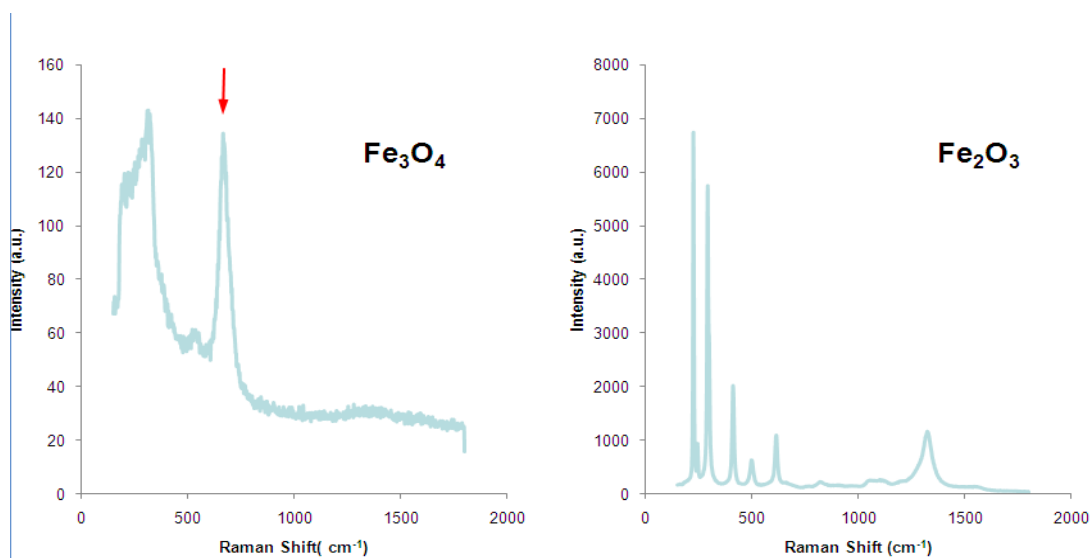


Figure 9: Raman Spectra for the reference, pure iron oxides magnetite and hematite.

From the data in Figure 4, it is apparent that the iron rod oxide spectra contain both Fe_3O_4 and Fe_2O_3 vibrational peaks. However, the overall Raman response of the hematite is significantly greater (order of magnitude) than the Raman response of Fe_3O_4 ; hence the Raman spectroscopy data suggest that the majority of the oxide layer is in fact Fe_3O_4 . Future work will seek to further quantify the Raman data.

SEM and EDS analysis were performed after section the oxidized rods for all four temperature conditions reported in Table 1. The analysis revealed very distinct oxide layers upon the iron substrates. Overall, the oxide layer thicknesses are consistent with the linear growth rates as reported in Table 2. For example, a linear growth rate of 0.4 nm/s (see Table 2) is expected to produce an oxide layer of about 4.3 microns after three hours. As observed in Figure 5, this thickness is in excellent agreement with the measured oxide layers per SEM analysis. The EDS analysis confirmed the presence of a distinct oxide layer, although future work will quantify the exact O/Fe ratios. Preliminary data revealed a slight gradient in the O/Fe ratio, which increased toward the outer surface. This is consistent with a greater presence of water at the outer surface, enabling a slightly greater overall oxidation state.

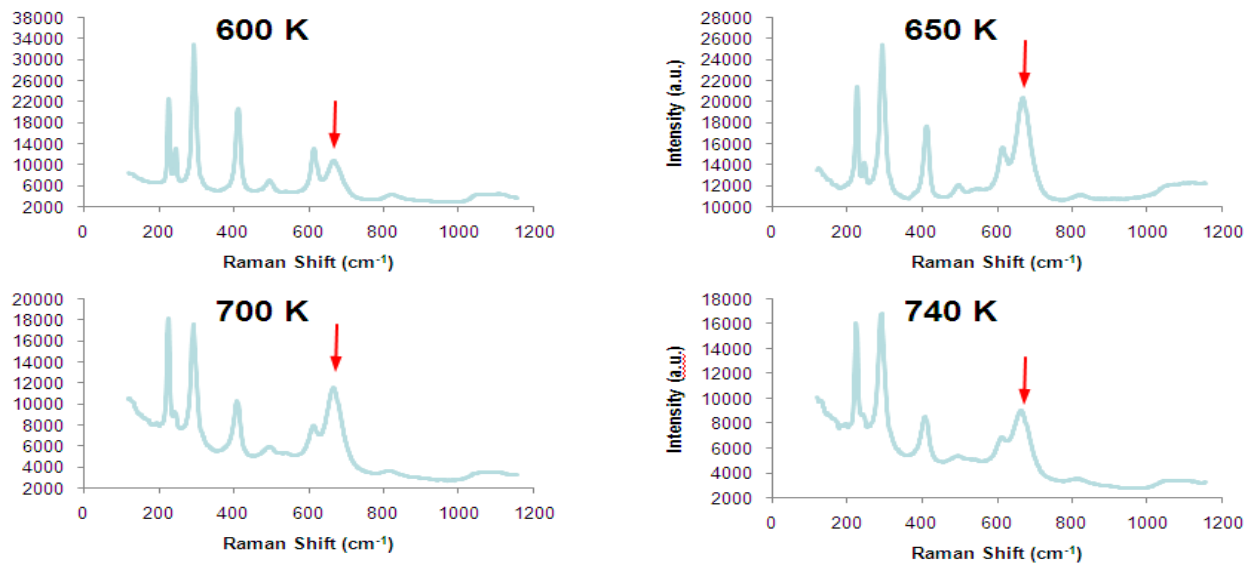


Figure 10: Raman spectra of the oxidized iron rods following hydrogen production. The red arrow indicates the prominent magnetite peak as labeled in Figure 3.

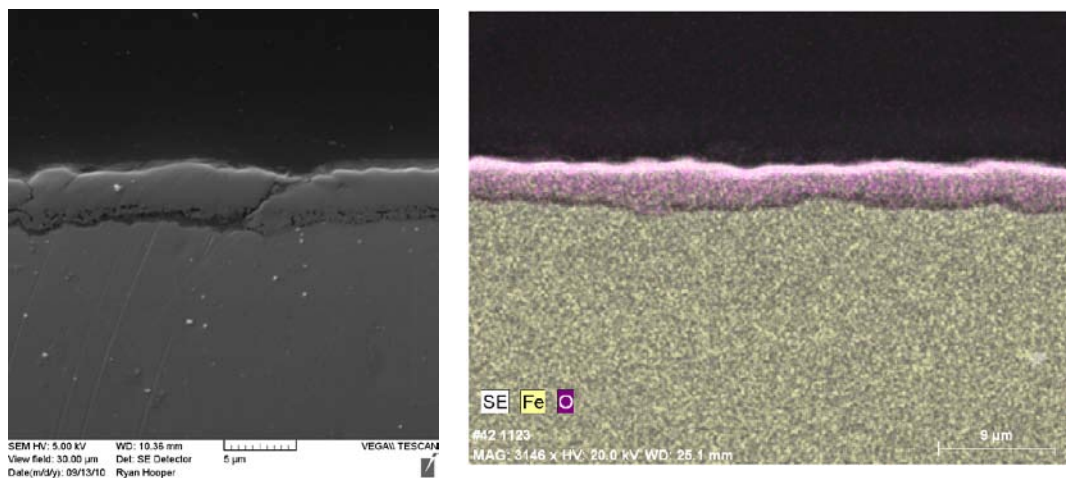


Figure 5: SEM (left) and SEM/EDS (right) images of the iron oxide layer after 3-hours.

Fluidized Reactor Study

A key overall goal this year was to investigate the effect of the magnetic field on the particles and use the magnetic property of particles to establish a robust reactor that can cycle through many oxidation and reduction cycles. Geometry properties of iron particles and the chemically active surface area were studied in detail, including the reduction of the active surface area of particles after sintering. A goal was to prevent or minimize the adverse effects of sintering on the hydrogen production looping process. Two novel ideas, referred to as “magnetically stabilized bed” and “particle coating with zirconia”, were studied for solving the sintering problem. Figure 6 shows the sintered iron particles at 850 C. It can be seen that iron particles are homogeneously aggregated to each other, where the resulting structure is like a chunk of iron. The homogeneous structure causes a dramatic reduction of active surface area and consequently the reaction rate. The apparent density of sintered particles is about 5.3 gr/cm^3 , while the void fraction of the formed structure decreases by 48% compared to that of the original powder.

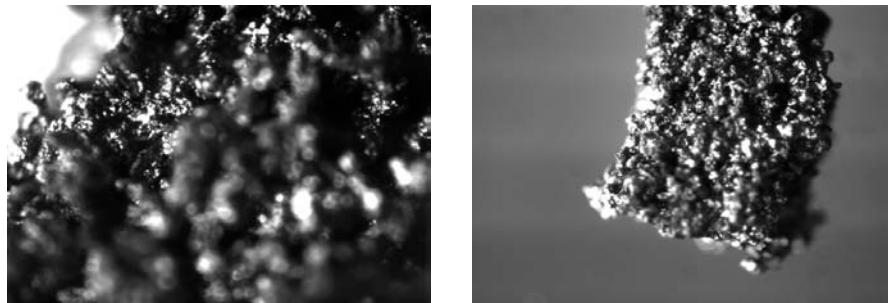


Figure 6: Sintered iron particles at 850 C.

The hydrogen yield for various conditions in the fluidized bed was evaluated. It is evident, as shown in Figure 7, that the hydrogen yield increased with increasing reactor temperature, even though sintering occurred at greater temperatures. Apparently, effects of reduced surface area via sintering are coupled to increased kinetic rates with temperature (see Table 1). The effect of the particle size on hydrogen yield is also illustrated in Figure 7; as the particle size increased the hydrogen yield decreased. This is a direct effect of the reduction of surface area with increasing particle size. This pattern can be clearly observed for the case of 550°C and 650°C. This pattern is not observed in the case of 750°C, accordingly, these cases will be reevaluated. Overall, continuing research will seek to further quantify the performance of the fluidized bed under various operating conditions, with a goal of optimizing hydrogen production.

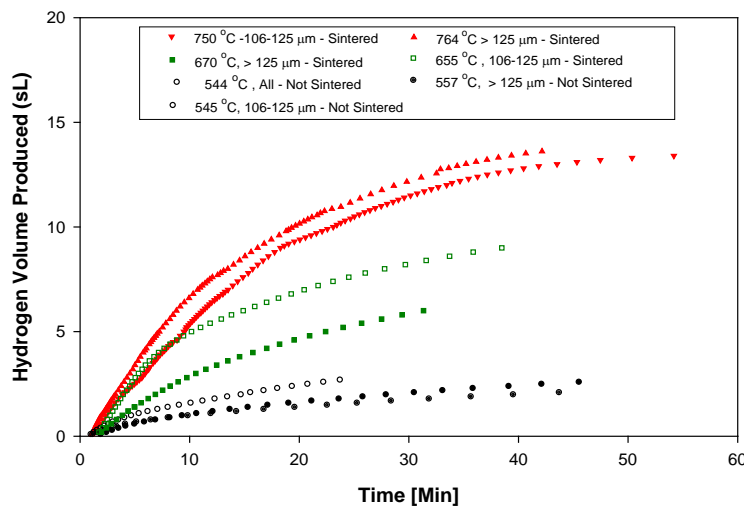


Figure 6: Produced Hydrogen volume for uncoated iron particles at various temperatures.

Fundamental Catalysis Work

The development of iron-based mixed-metal oxide catalysts for hydrogen production via water-splitting has focused on the thermal reduction step at high temperatures. The challenge with this step is to develop mixed metal oxides that can be reduced thermally without losing all their surface area. We have been investigating iron oxides supported on ZrO_2 and CeO_2 . These oxide supports have been chosen due to their oxygen mobility and thus potential to give up oxygen at a lower temperature. In addition to the pure ZrO_2 and CeO_2 , we also included CeO_2 - and Y_2O_3 -doped ZrO_2 to potentially improve temperature stability. Out of the supported iron oxides investigated, the $FeO_x/n-ZrO_2$ is shown to have the greatest weight loss at the lowest temperature and this catalyst also does not agglomerate into a hard disk after high temperature treatment.

Presentations:

1) FESC Summit in Orlando, Florida (October 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.

Additional manuscript are in the early stages of preparation covering the kinetics work and the surface analysis.

Additional activities:

July 26 and 27, David Hahn and Richard Stehle visited the Solar Energy Group at Sandia National Laboratories (Albuquerque, NM) to tour their solar facilities and discuss possible collaborative activities.