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Quarterly Progress Report

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Project Title: Solar Thermo-Chem for H_2 (STCH)

Project Period: July 1, 2010 through Sept. 30, 2010
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Principle Investigator:

Nathan Siegel, (505) 284-2033, npsiege@sandia.gov

Other Key National Lab Researchers:

Tony McDaniel, (925) 294-1440, amcdani@sandia.gov
Ivan Ermanoski, (505) 284-0740, iermano@sandia.gov
Greg Kolb, (505) 844-1887, gjkolb@sandia.gov

Sub-Contractors Funded through AOP Task:
Industrial Partners:

DOE Managers: Sara Dillich, Eric Miller

Project Objective:

The overall objective of this work is to continue the development of hydrogen producing thermochemical cycles based on non-volatile metal oxides with the ultimate goal of demonstrating the continuous production of hydrogen in a solar powered reactor. We have two parallel technical R&D efforts. The first targets the identification and characterization of reactant materials while the second is focused on the development of solar reactor concepts, associated hardware, and system analysis.

Background:

Water splitting via two-step, non-volatile metal oxide cycles has been shown to a potentially efficient pathway to producing hydrogen with solar energy. Past efforts have focused on reactions based on the chemistry of iron oxide using materials broadly characterized as "ferrites". These materials have been shown to have relatively good thermodynamic performance, but insufficient kinetics in cases where high reactive surface area cannot be maintained. In addition, volatility of the active materials at temperatures in excess of 1400^{o}C is problematic. Cerium oxide has recently been investigated at Sandia National Laboratories as part of an internally funded effort to

produced carbon monoxide from carbon dioxide. It is also able to produce hydrogen via a two step water splitting cycle that is analogous to that used for the ferrite materials. Relative to iron oxide, pure cerium oxide does not perform as well thermodynamically, but the reaction kinetics during water splitting are considerably faster. In addition, volatility is not as great of a concern with cerium oxide-based materials.

We are currently developing and characterizing reactive materials based on cerium oxide. There is reason to believe that combining cerium oxide with other materials such as zirconium oxide may boost thermodynamic performance. However, this has been shown to come at the expense of kinetic performance. Therefore, we are also developing a solar reactor concept that uses a particulate reactive material. We believe that the increase in surface area achieved with a particulate system may offset the reduction in reaction rate that is incurred when cerium oxide is mixed with other compounds.

In FY10 we have focused on completing the conceptual design and high level performance analysis for our particulate reactor concept and identifying the areas where additional technical work is needed. We have also purchased equipment to enable a more realistic characterization of the reactive materials under development. In particular, we will soon have the capability to rapidly cycle prospective materials thermally and chemically in a manner that closely represents the operating environment in a solar reactor. In addition, we will also be able to closely monitor reaction products with much more accuracy that we have been able to achieve with on-sun test equipment at our solar furnace facility. This will allow us to quantify reaction rates for both the thermal reduction and re-oxidation reactions and identify rate limiting processes.

As we move forward we will identify and characterize one or more prospective reactive materials and incorporate them in a small scale on-sun prototype reactor to be evaluated using our solar furnace facility. We also plan to develop system level models with ASPEN and other tools that will enable the estimation of performance for a larger scale system as well as future economic analyses.

A relatively small fraction of our efforts are dedicated to performing H2A analyses on cycles developed by the group and to participating in the IEA Task 25 working group. The Task 25 work program is divided into 4 subtasks:
A) technical review of the different HTPs, B) comparative analysis of the HTPs, C) definition of a HTP project to be deployed within the next 10 years to demonstrate industrial feasibility and to validate techno-economic evaluations, D) development of communication tools. The task was initially a 3-year project, approved by the ExCo in May 2007. But in December 2009 an extension period of 1 year was approved in order to fulfil the Task objectives.

Status:

Task 1: Cerium Oxide Materials for Two-Step Water Splitting

As mentioned above, this task has two main thrusts, materials development and reactor development. Here follows a summary of the status of both:

Materials Development – Two concepts are being pursued to modify the thermochemical reduction/oxidation (redox) behavior of ferrite and ceria non-volatile oxide materials under consideration for CSP hydrogen production. For ferrites, stabilizing thin films on high surface area supports is paramount to maintaining sufficiently fast kinetics. For ceria, decreasing the temperature required for thermal reduction is key.

In Q4FY10, Sandia hosted a graduate student (Darwin Arifin) from Al Weimer's group at the University of Colorado for several months during this reporting period. Mr. Arifin prepared multiple samples of ALD ferrite and cobalt ferrite coated onto various ceramic fiber supports, as well as platinum on ceria. The fibers were commercial grade CeO_2, ZrO_2, and Y_2O_3-stabilized ZrO_2 with a mean core diameter between 1-10 micrometers. The coated and uncoated fibers were analyzed by electron microscopy (SEM/EDS and TEM), x-ray photoelectron spectroscopy (XPS), and surface Raman both before and after redox cycling. Water splitting chemistry was evaluated for both chemically and thermally reduced samples in the stagnation flow reactor at Sandia. In summary:

- The ALD process for coating these particular fiber samples was not optimal as evidenced by surface Raman and XPS. Measurements revealed the coating was not conformal nor as thick as desired. Another attempt to improve the ALD film quality of ferrite on fibers and/or similar supports will be conducted in FY11.
- A method for chemically reducing these samples using mixtures of H_2 and/or CO in CO_2 was developed in order to evaluate the intrinsic kinetic properties of these fibers before exposure to high thermal reduction temperatures. The focus of this activity was to demonstrate an equivalent extent of reduction (for both ferrite and ceria) at temperatures much lower than 1500 °C. This was achieved.
- Platinum coating CeO_2 did not significantly improve the peak production rate or total amount of H_2 produced for water splitting at oxidation temperatures between 600-700 °C.
- Extensive analysis of the thermally reduced, uncoated CeO_2 fiber indicate good structurally stability with little change in morphology at temperatures as high as 1450 °C, as well as fast water splitting kinetics and H_2 capacity as expected of a non-stoichiometric metal oxide.
- Preliminary analysis of thermally reduced ferrite-coated ceramic fibers indicate severe morphological changes occur to fibers upon heating to temperatures in excess of 1300 °C. It is possible for the case of ceria that FeO induces compound formation at the ferrite/CeO_2 interface which enhances sintering. The ZrO_2 and YSZ fibers were expected to degrade more readily at these temperatures than the CeO_2 fiber.
- Preliminary analysis of the water oxidation kinetics for the coated fibers indicates that ALD treatment reduces the peak H_2 production rate and also the total amount of evolved H_2 when compare to uncoated CeO_2. This observation may be due in part to a poor quality ALD coating. In addition, morphological changes in the coated fibers degraded the ALD coating to an extent where the iron oxide likely dissolved into the fiber.

In Q1FY11, work will shift towards investigating ceria and modified forms of ceria with the intent of evaluating the extent to which the thermal reduction temperature can be reduced while maintaining sufficient oxygen non-stoichiometry for CSP hydrogen production.

Reactor Development –
A concept for a particle based thermochemical reactor suitable for two-step water splitting has been developed. In support of this effort we've completed the following tasks:

- high level conversion efficiency calculations for various operating conditions (temperature, pressure, heat recovery) of a 2-step reactor for H2 production via water splitting have been completed
- theoretical evaluation of several methods for oxide particle transport with emphasis on oxide throughput and heat recovery efficiencies
- calculations regarding scaling reactor concepts from table-top demonstration, ~1kW, to power tower (>1MW)
- experimental compatibility evaluation of construction materials and cerium oxide at highest expected operation temperatures
- Preliminary optical design and analysis of the central receiver platform is underway.
- System design and analysis capability is being brought online

Task 2: H2A Analysis

We did not participate in H2A activities in Q4FY10

Task 3: IEA Task 25 interaction

The 6th official meeting of the group occurred on September 16th and 17th in Helsinki, Finland. The meeting gathered 8 participants coming from 6 different countries. In addition to the introducing round table, 3 presentations were made concerning 1) the new strategy at CEA (French Atomic Energy Commission), 2) the status of the techno-economic evaluation of 13 hydrogen-generation processes by the Task 25 group (ENEA, Italy), and 3) Outotec commercial interest. The highlights of each are summarized below.

CEA predicts that low-temperature alkaline electrolysis (AE) powered by nuclear reactors will produce the lowest-cost CO2-free hydrogen in the near term. However, with a cost of ~3 Euro/kg, this is still not competitive with the CO2-generating methane-reforming method at 1.6 Euro/kg. CO2 must be taxed for electrolysis to be economically preferred. Of the high temperature processes, CEA predicts that high-temperature electrolysis (HTE) will be the first high-temperature CO2-free process that will be implemented in France since costs are predicted to be 3.6 Euro/kg. The thermochemical cycles of interest to CEA are sulfur hybrid (SHy) and copper chloride (CuCl). CEA is no longer interested in sulfur iodine (SI) due to poor economics (~12 Euro/kg by their assessment). The CEA strategy calls for implementation of a high-temperature electrolysis demo after 2020. They will keep abreast of SHy and CuCl progress being made throughout the world but currently do not have a significant budget devoted to their R&D.

The IEA group performed a multi-criteria evaluation of 13 hydrogen generation processes of interest to STCH and other international organizations. The 7 criteria used to judge the cycles were 1) economic competitiveness, 2) maturity, 3) efficiency, 4) process resource availability, 5) maximum process temperature, 6) environmental threat, and 7) complexity. The first results tend to identify AE, HTE, SHy, and CuCl as the preferred cycles for both nuclear and solar applications. The first results were documented in a report prepared by CEA [1]. The report was condensed into a journal article that was recently accepted for publication within the *International Journal of Multicriteria Decision Making.*

Outotec is a large ore-processing technology provider that is headquartered in Finland. More than 3000 professionals deploy technology throughout the world. Because most ores are sulfur based, they have much experience with sulfuric acid and SO2 because it is separated from the ore. Outotec thus has a natural interest in the SHy cycle. At the meeting they proposed using an open-loop SO2 electrolyzer at a mine head to produce hydrogen. Their initial economic evaluation suggests that CO-free hydrogen could be produced for ~1 Euro/kg, a price that is less than methane reforming. Greg Kolb suggested that Outotec might team with Savannah River to pursue this proposed project. Outotec also developed the HSC software that STCH used to screen thermochemical cycles. On the 2nd day of the meeting at Helsinki Technology University, the Task 25 group was given an in depth briefing on the capabilities of HSC 7.0.

The final Task 25 meeting will occur in the Spring of 2011. The meeting location will likely be in Europe. A possible follow-on task was discussed. The group thought that a new task devoted to electrolyzer technology and issues might be of interest to many countries, since all 4 preferred hydrogen-generation processes (AE, HTE, SHy, and CuCl) all contain electrolyzers. This idea will be floated at the next IEA ExCo meeting.

Plans for Next Quarter and Key Issues:

Materials Development:

In Q4FY10 we also embarked on modifying the stagnation flow reactor at Sandia, CA to incorporate a laser diode heater. The contract was awarded to Apollo Instruments of Irvine, CA. They provide laser diode heating solutions to industry. A 500 CW fiber-coupled infrared diode laser (800-1000 nm) and custom optical head were ordered and we expect delivery early in Q1FY11. With this added capability it is anticipated that we can achieve sample heating rates in excess of 1000 °C per minute, which closely matches the rapid heating rates experienced by reactive materials in CSP applications. The optical head was designed to produce a photon flux *greater* than 500 W cm^{-2} at the sample surface (which is essentially 5000 suns). It is our intent to characterize proposed reactive materials using the well-instrumented stagnation flow reactor as a more controlled environment than the solar receiver, while still achieving comparable operational conditions.

Reactor Development:

In general, the key challenges in developing this reactor concept are:

- Achieving a sufficient degree of internal heat recovery (recuperation)
- Demonstrating high optical efficiency
- Determining the best method for conveying particles vertically
- Minimizing the impact of pumping losses

The following activities are planned for next quarter:

- Continue to refine models and reactor designs.
- Select one or more particle conveyors/heat exchangers for construction and preliminary experimental evaluation.
- Complete the optical analysis of a baseline central receiver system using beam down optics and the particle reactor

Patents:

Publications / Presentations:

1. "A multicriteria methodology for assessing high temperature hydrogen production processes – first results," CEA Report RT/10-009, August 25, 2010.