II.F.2 Fundamentals of a Solar-Thermal Hydrogen Production Process Using a Metal-Oxide Based Thermochemical Water Splitting Cycle

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Objectives

- Research and develop a cost effective Mn_2O_3/MnO solar-thermal thermochemical cycle through theoretical and experimental investigations.
- Based on the above, develop a process flow diagram and carry out an economic analysis of the best process option.

Technical Barriers

This project addresses the following technical barriers from the High-Temperature Thermochemical, Solar-Driven Production of Hydrogen section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(U) High-Temperature Thermochemical Technology

(V) High-Temperature Robust Materials

(W) Concentrated Solar Energy Capital Cost

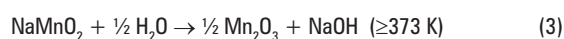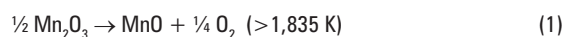(X) Coupling Concentrated Solar Energy and Thermochemical cycles

Technical Targets

Solar-Driven High-Temperature Thermochemical Hydrogen Production

This project is conducting fundamental studies of the manganese oxide-based thermochemical cycle. Insights gained from these studies will be applied toward solar-driven high-temperature hydrogen production that meets the following DOE 2012 targets:

TABLE 1. Solar-Driven High-Temperature Thermochemical Hydrogen Production

Characteristics	Units	2008 Target	2012 Target	2017 Target
Solar-Driven High-Temperature Thermochemical Cycle Hydrogen Cost	$/gge H_2	10.00	6.00	3.00
Heliostat Capital Cost (Installed Cost)	$/m^2	180	140	80
Process Energy Efficiency	%	25	30	>35

Accomplishments

- Demonstrated high conversions of Mn_2O_3 dissociation in an aerosol flow reactor (AFR).
- NaOH removal by vaporization was investigated.
- Explored carrying residual $NaMnO_2$ through the cycle.
- Testing in progress with mixed manganese oxides for more efficient NaOH recovery.

✧   ✧   ✧   ✧   ✧

Introduction

A three-step metal oxide cycle to produce renewable hydrogen has been proposed. This cycle employs manganese oxide and solar energy to produce hydrogen [1-3]:

$$\tfrac{1}{2}\,Mn_2O_3 \rightarrow MnO + \tfrac{1}{4}\,O_2 \quad (>1{,}835\ K) \tag{1}$$

$$MnO + NaOH \rightarrow \tfrac{1}{2}\,H_2 + NaMnO_2 \quad (900\ K) \tag{2}$$

$$NaMnO_2 + \tfrac{1}{2}\,H_2O \rightarrow \tfrac{1}{2}\,Mn_2O_3 + NaOH \quad (\geq 373\ K) \tag{3}$$

$$H_2O \rightarrow H_2 + \tfrac{1}{2}\,O_2 \tag{4}$$

The Mn_2O_3/MnO water splitting cycle is a three-step cycle and has advantages that make it an attractive water splitting cycle. First, Mn_2O_3 reduction occurs at low enough temperatures that feasible reactor materials of construction may be found. In addition, the somewhat lower temperatures (compared with other potential cycles) involved in this solar driven cycle allow for lower re-radiation losses, and in turn a higher reactor efficiency [2]. Second, an inert gas flow must be present in the metal oxide reduction of many high-temperature thermochemical cycles to thermodynamically carry out the reactions. However, the Mn_2O_3 reduction to MnO is thermodynamically favored even in the presence of air. This would eliminate the need to use inert gas to separate oxygen downstream of the reactor, which can significantly increase the overall process efficiency. Third, the phase separation of MnO from dissociated O_2 appears simple because MnO is a solid at the reaction temperature. Due to these advantages of the manganese oxide cycle it is suggested to further study the feasibility of this cycle [2,4,5].

Approach

The Mn_2O_3 dissociation and NaOH recovery step have been identified as the essential steps that must be investigated to make the cycle realistic. It is essential to understand the Mn_2O_3 dissociation step because the entire feasibility of the manganese oxide cycle is based on this reaction having a high overall conversion [2]. Specifically, the viability of the MnO and O_2 phase separation must be investigated to determine how much recombination might occur during the quench step [1,5,6]. For the past year, kinetic studies have been performed in an AFR, as it can handle a high throughput of powder, while allowing reaction conditions to be tightly controlled.

The step described by Reaction 3 has proven to be the most challenging of the three steps. Challenges arise from the reaction not going to completion and a difficult Mn_2O_3/NaOH separation. There have been many approaches in the past fiscal year to resolve the issues associated with this step and they include: (1) thermal separation of NaOH, (2) creation of mixed manganese oxides to improve the separation and (3) processing residual $NaMnO_2$ through the cycle.

Results

Experiments for the Mn_2O_3 dissociation were completed in the AFR. An oxygen monitor showed a significant increase when the reaction was initiated, which indicated that the reaction was occurring. Initial results showed conversions ranging between 56-75%. Analyzing the results indicated that the main effects (temperature and residence time) are statistically significant and that the binary effects are not. The

highest conversion was achieved with a combination of a high temperature and short residence time. A high temperature favors the forward reaction and the low residence time possibly stopped the reaction in the quench tube more rapidly, thus preventing oxygen recombination. Further verifying the results, X-ray diffraction (XRD) spectra (Figure 1) illustrated a strong MnO spectrum and a weak Mn_3O_4 spectrum. A dotted line helps illustrate that all of the peaks can be seen from the MnO standard and that only the major peaks from the Mn_3O_4 standard. The results from this study may be used in the DOE framework to help evaluate the efficiency of the cycle and for a plant simulation to put the cycle in context in an H2A cost estimate.

It has been proposed to vaporize NaOH to separate it from Mn_2O_3. A horizontal tube furnace was utilized to conduct experiments where the sample is pulled into the hot zone at the desired temperature. Results indicated that a significant amount of NaOH was not vaporized. In addition, a statistical analysis indicated that there were no significant effects. This indicated that within the ideal operating ranges selected for the factors that it is not possible to achieve a high vaporization rate of NaOH. For the vaporization to proceed at an ideal rate, a high temperature would be required. Likely problems with a higher temperature include reverse reaction to $NaMnO_2$ and partial reduction of Mn_2O_3 to Mn_3O_4. It was thus concluded that vaporization of NaOH is not a viable method to separate Mn_2O_3 and NaOH.

Use of mixed manganese oxides may potentially improve Mn_2O_3/NaOH separation. The investigation of mixed manganese oxides has been divided into three phases: (1) synthesis of $Mn_xFe_{1-x}O$ and $Mn_xZn_{1-x}O$, (2) verification of hydrogen production with the mixed oxides and (3) investigation of the mixed manganese oxide-NaOH separation efficiency. A sol-gel precipitation reaction in basic solution from metal salts is used to create a precipitate which is then calcined in N_2 to produce the mixed metal oxide. A successful synthesis
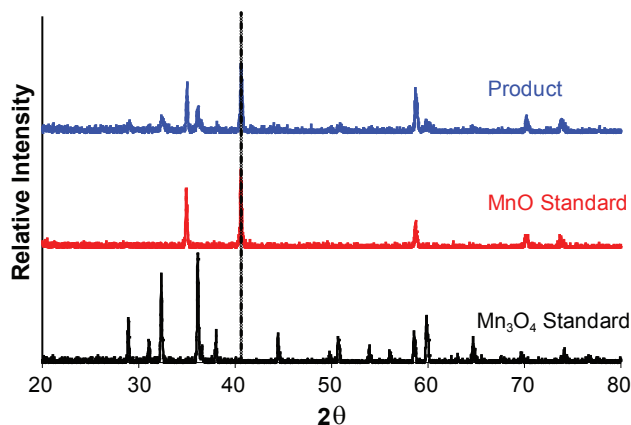

FIGURE 1. XRD Product Spectrum of Mn_2O_3 Dissociation Product

of a mixed manganese oxide with 5:1 manganese to zinc ratio has been done. Figure 2 is an XRD spectrum showing mixed manganese/zinc oxide. This mixed manganese oxide was then heated with NaOH and the H_2 generation step was demonstrated (Figure 3). With the hydrogen generation demonstrated, the NaOH separation with the mixed manganese oxide will be investigated in the next fiscal year. This result fits into the DOE framework by potentially improving the efficiency of the Mn_2O_3/MnO cycle.

Under reaction conditions, Reaction 3 will have approximately 10% residual $NaMnO_2$, thus processing the residual $NaMnO_2$ with Mn_2O_3 in the dissociation step is being explored. The reaction sequence is theorized in Equations 5 and 6:

$$2NaMnO_2 \rightarrow Na_2O + 2MnO + \tfrac{1}{2}O_2 \qquad (5)$$

$$Na_2O + H_2O \rightarrow 2NaOH \qquad (6)$$
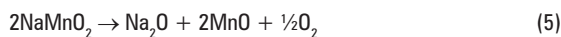
A proof-of-concept of Equation 5 was done in a thermal gravimetric analyzer (TGA) in conditions
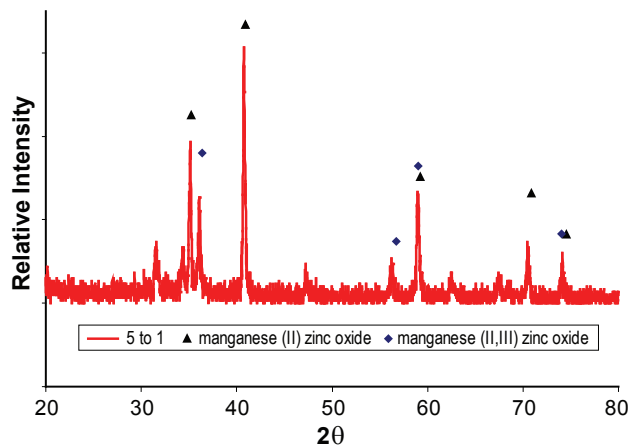

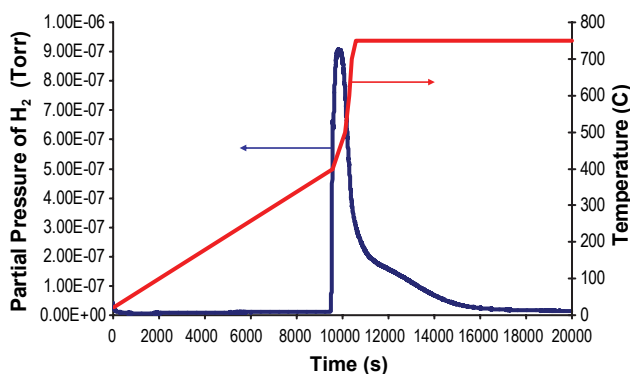**FIGURE 2.** XRD Spectrum of Synthesized Mixed Manganese Oxide

FIGURE 3. H_2 Generation from a Mixed Manganese Oxide and NaOH Reaction
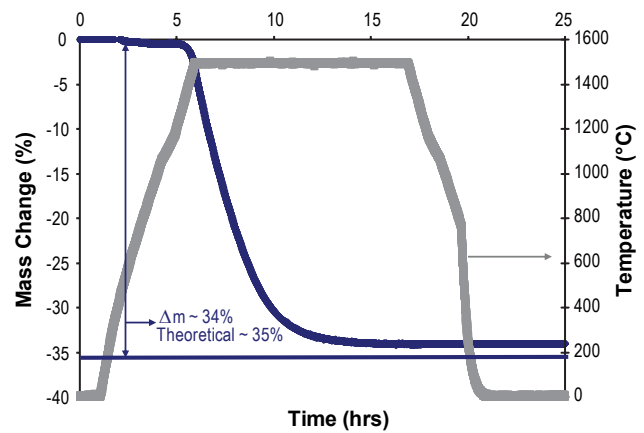

FIGURE 4. TGA Mass Trace Showing Near Theoretical Conversion

that Mn_2O_3 would dissociate. TGA results (Figure 4) showed that Reaction 5 will proceed to near theoretical conversion at 1,500°C. With Equation 5 proven to work, more research must be done to better understand processing the residual $NaMnO_2$. Specifically what form does the sodium take in Equation 5 and will the reaction kinetics become faster when diffusion resistances are negligible in an AFR? If it is demonstrated that residual $NaMnO_2$ can be processed with Mn_2O_3, then the efficiency of the manganese oxide cycle will likely increase.

Conclusions and Future Directions

Significant experimental progress has been made with the Mn_2O_3/MnO cycle:

- High conversions for Mn_2O_3 dissociation have been demonstrated.
- Potential solutions for NaOH recovery have been identified and investigations have begun.
- Studies on ways in to process non-reacted $NaMnO_2$ have been shown and more work is ongoing.

Future Work

- On sun testing of Mn_2O_3 dissociation.
    - Reactor design and construction.
    - Reactor materials testing.
- Continue work plans for NaOH recovery.
- Perform H2A analyses with experimental results.

FY 2007 Publications/Presentations

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