
II.J.3 Hydrogen Production and Fuel Cell Research*

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Technical Targets

This project is conducting experimental studies of UT-3 thermochemical cycle and its improvement in the cyclic performance for hydrogen production. On the basis of these studies, thermodynamic analysis of the cycle will be conducted to evaluate economical feasibility.

- Process energy efficiency: 40%

Approach

- Evaluation of characteristics of calcium and iron oxide solid reactant to improve their formulation.
- Chemical kinetic studies to evaluate and improve the solid reactant's cyclic life, reaction rates and conversion using lab-scale apparatus.
- Experiments on the feasibility of UT-3 thermochemical cycle for hydrogen production.
- Fabrication and evaluation of porous CaO and Fe_3O_4 reactants which have an enduring structure and favorable characteristics in cyclic transformations between oxide and bromide forms.

Accomplishments

- An attempt was made to increase the calcium oxide content through repetitive impregnation steps and resulted in higher calcium oxide contents in the samples.
- Cyclic performance of the samples with various calcium oxide contents was examined for the first cycle.
- Thermal efficiency of the UT-3 process was evaluated considering inert materials, heat recovery and incomplete conversion.
- In order to determine feasible heat recovery in the process, pinch analysis was employed in this thermodynamic analysis.

Conclusions

Calcium oxide fabric samples with higher calcium oxide contents were fabricated and evaluated for the first cycle. The hydrolysis rate was retarded with increasing the calcium oxide contents. Practical process efficiency was determined using the experimental results and theoretical thermodynamic analysis. It was found that the effect of heat recovery and inert materials cannot be disregarded in the calculation of thermal efficiency of the cycle. To increase the efficiency, heat recovery must be used and the use of the inert materials should be minimized.

Task 1. Thermochemical Hydrogen Production

Objectives

- Investigate UT-3 thermochemical cycle and conduct kinetic studies.
- Improve stability and performance of solid reactants for cyclic gas-solid reactions.
- Lower hydrogen production cost by increasing hydrogen yield with an improved pellet formulation.
- Reduce operating cost by lowering the reactor operating temperatures.

Technical Barriers

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

(U) High Temperature Thermochemical Technology

Task 2. Hydrogen Production from Biomass

Objectives

Improve the hydrogen production process of conventional biomass gasification and reduce capital cost by combining steps. In the present approach, the aim is to combine the two step shift and pressure swing adsorption separation into a single step by integrating biomass steam gasification, CO₂ removal and hydrogen separation. The project also aims to improve the total hydrogen yield and overall process efficiency.

Technical Barriers

This project addresses the following technical barriers from the Biomass Gasification/Pyrolysis Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(T) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology

Technical Targets

Our research aims to enhance the hydrogen yield of conventional biomass steam gasification by using simple inexpensive sorbents such as calcium oxide. The sorbent absorbs one of the co-products of gasification (namely CO₂) and thereby shifts the equilibrium in favor of additional hydrogen. Theoretical simulations and experimental studies have shown a substantial improvement in hydrogen yield. The insights gained from these studies will be applied towards further experimental investigation and regeneration of spent sorbent. The following DOE 2010 energy efficiency and hydrogen production cost are targeted:

- Energy Efficiency¹: 50%;
- Plant gate cost²: \$1.75/gge H₂

¹Efficiency defined as energy of hydrogen out of the process (lower heating value of hydrogen) divided sum of energies into the process (lower heating value of feedstock and all other energies needed).

²gge: gasoline gallon equivalent.

Approach

Biomass feedstock common to Florida such as pine mulch was steam gasified in a batch type reactor. The effects of temperature and presence of sorbent (calcium oxide) and form of sorbent (powder vs pellets) on the hydrogen yield were experimentally investigated. The initial experimental studies have shown a significant improvement in hydrogen and overall gas yield in presence of sorbents. In order to enhance cyclic

performance of the sorbents, a simple and effective immobilization technique of the calcium oxide sorbent in fibrous ceramic mat as a substrate was developed and the cyclic performance was evaluated.

Accomplishments

- Two calcium oxide absorbent samples using different materials of fabric, alumina and yttria, were fabricated for the severe calcination condition.
- The cyclic carbonation-calcination experiments of the two samples were conducted under the severe calcination condition, with 20% CO₂ at 850°C.
- Dolomite on alumina fabric was used in the preparation of the absorbent sample.
- Two samples were prepared of dolomite applied to alumina fabric and yttria fabric.
- The two samples were then analyzed using the thermogravimetric analysis.

Results

The use of dolomite is being investigated in this study as previous researchers have discovered that the inert magnesium oxide in dolomite contributes to stabilizing the structure of the solid sorbent in the multi-cycle carbonation-calcination process. One issue that arises as a result of using calcium oxide to capture carbon dioxide is that, at first the carbonation cycle is very fast as the carbon dioxide molecules are captured by the surface calcium oxide converting the calcium oxide into calcium carbonate. As the reaction proceeds it becomes difficult and takes longer for the carbon dioxide to get to the available interior calcium oxide in the structure. Since, magnesium carbonate has a lower decomposition temperature than calcium carbonate it improves access for the carbon dioxide molecules to react with the interior calcium oxide molecules available.

Initial data collected showed that dolomite was comparable to the calcium oxide in the capture of carbon dioxide. However, to make an accurate comparison to determine the efficiency and conversion ability of each compound further experimentation is required at the same conditions for each compound. Figure 1 shows the dolomite sample on the alumina fabric during a four hour carbonation/calcination cyclic run.

Conclusions

- Dolomite is being investigated to determine if the University of South Florida sorbent preparation method will increase the carbon dioxide capture capability and capacity.
- Carbon dioxide can be captured by dolomite type material using the inexpensive preparation method developed by the University of South Florida.

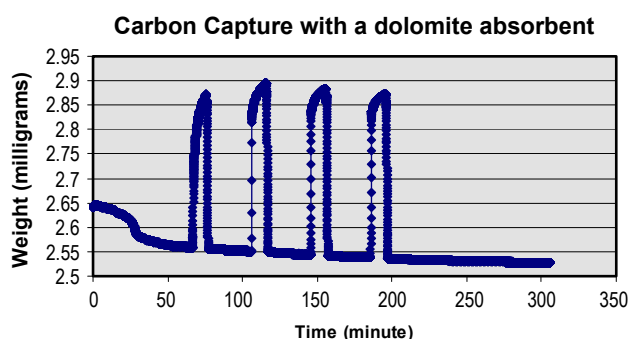


FIGURE 1. Cyclic Carbonation and Calcinations of Dolomite on Alumina Fabric

Task 3. Photoelectrochemical Hydrogen Production

Objectives

Overall

- To produce H_2 in the \$0.70–2.00/kg range
- Photocatalyst efficiency (sunlight to H_2) = 14%
- Photocatalyst cost (\$70/m²)
- Membrane cost (\$50/m²)
- Develop catalytic thin films that can function with a photoelectrochemical device

Current

- To develop tandem solar cells to meet the above efficiency and cost objectives.
- Current emphasis is on development of the p-window contact for CdSe in the CdSe/Si(CIGS) tandem structure.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability

Approach

- Device Structures
 - CdSe/Si – intermediate term, hybrid.
 - CdSe/CIGS – long-term, thin-film, low-cost.
- Key Technology Limitation
 - High efficiency, transparent p-window/CdSe/n-window device.

- The p-window is limiting performance because of low voltage open circuit.
- Current Focus
 - Development of ZnSe and ZnTeSe as p-windows.
 - Improving doping efficiency to increase voltage open circuit by use of ion source implantation of nitrogen.

Accomplishments

- Ion source implantation of N interferes with stoichiometry control in $ZnSe_xTe_{1-x}$:N p-window contacts except at low Te levels.
- Use of ZnTe/ZnSe:N superlattice structures allows better control at higher Te levels.

Summary and Future Work

- Significant improvement in window p-layer doping has been accomplished.
- Concomitant improvement in voltage open circuit has been realized.
- Additional techniques will be pursued to further improve doping and voltage open circuit:
 - Direct doping of $ZnSe_xTe_{1-x}$ p-window contacts with Cu.
 - Co-doping of $ZnSe_xTe_{1-x}$ p-window contacts.

Task 4. Photocatalytic Hydrogen Production

Objectives

Optimize mechanochemical treatment parameters (duration of ball-milling treatment, temperature and duration of post annealing).

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (AP) Materials Efficiency
- (AQ) Materials Quality
- (AR) Efficiency

Technical Targets

Design and synthesis of photocatalytic materials that meet the following DOE 2010 Photoelectrochemical Hydrogen Production targets:

- Chemical conversion process efficiency >10%
- Durability, >1,000 hrs

Approach

(i) Photocatalytic efficiency of modified TiO_2 based on the photodegradation kinetics of methyl orange.
 (ii) Correlation of photocatalytic properties with optical, bonding, structural and microstructural characteristics. Attempts were made to improve the photocatalytic behavior of TiO_2 by doping with various concentrations of Zn (0, 1.3, 2.2, 3.1, 4.0 and 4.9) in the sol-gel process.

Accomplishments

- Modified by ball-milling TiO_2 catalyst having improved efficiency.
- Optimized duration and temperature of thermochemical method for N-doping of TiO_2 .

Results

Figure 2 shows the dependence of initial rate of methyl orange degradation on the TiO_2 catalyst thermochemical treatment duration at two different temperature treatments, namely, 625°C and 550°C.

The most effective decomposition of methyl orange was observed with the thermochemical treatment temperature of 625°C and the treatment duration from 2 to 3 hours. The optimized thermochemically treated photocatalyst is at least four times more efficient than the untreated samples.

Conclusions

- Attempts were made to improve the photocatalytic behavior of TiO_2 by doping with various

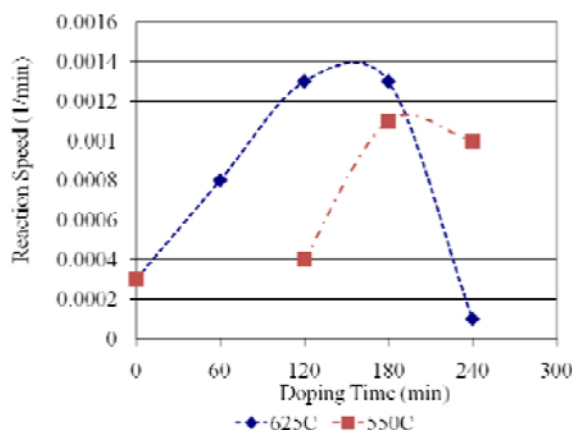


FIGURE 2. Dependence of initial rate of methyl orange degradation on the TiO_2 catalysts treated thermo-chemically at 625°C and 550°C.

concentrations of Zn (0, 1.3, 2.2, 3.1, 4.0 and 4.9) in the sol-gel process.

- There is no significant change in the photocatalytic efficiency for TiO_2 -Xwt% Zn at two different calcination temperatures (500 and 600°C).
- The reason for this may be due to the large crystallite sizes and the lower surface area of these initial samples.

Task 5. Development of High Performance, Low Cost PEM Electrolytes

Objectives

- Decrease cost per unit power for proton electrolyte membranes (PEMs).
- Improve long-term chemical stability of fuel cell PEM electrolytes operating at $\leq 120^\circ\text{C}$.
- Maintain or improve high protonic conductivity of PEM electrolytes.
- Minimize water content necessary to support high conductivity under stated conditions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is performing chemical modifications of polyether ether ether ketone polymer (PEEK), converting it into a PEM electrolyte. Insights gained from these studies will be applied toward the design and synthesis of PEMs that meet the following DOE 2010 technical targets targets:

- Operating temperature: 120°C
- Conductivity at operating temperature: 0.1 S/cm
- Room temperature conductivity: 0.07 S/cm
- Inlet water vapor partial pressure: 25 kPa
- Cost: \$20/m²
- Durability: 2,000 h at $>80^\circ\text{C}$

Accomplishments

- Successfully prepared via cross-linking chemistry a membrane based on highly sulfonated (water soluble)

sulfonated poly(ether ether ketone) (SPEEK), with an equivalent weight of 534 g/equivalent weight (EW).

- Developed a synthetic approach for fabricating a proton exchange membrane made from the fluorosulfonic acid of PEEK. The procedure begins with bromination of the bis-acetamide derivative of 2,5-diaminobenzotrifluoride. Have successfully performed the amidization, the monobromination, and the sulfatodehalogenation of the starting material.
- Developed multiple characterization methods for monitoring peroxide attack.

Conclusion

Water uptake is an important attribute of all membrane electrolytes, as it is related to mechanical strength, creep, and dimensional stability. Thus some means of controlling water uptake by a hydrophilic sulfonic acid polymer is desirable. This is particularly important for SPEEK, which at high degrees of sulfonation (i.e., low EW) has demonstrated substantial water uptake, on order of 10's of water molecules per sulfonic acid unit. We have attempted to control water uptake in SPEEK membranes by performing cross-linking reactions on the finished polymer. Water-soluble SPEEK (85% degree of sulfonation, or 418 g/EW), benzene dimethanol, and various transition metal chloride catalysts were cast together to form a membrane that was heated at 200°C for 10 min. The resulting insoluble membrane was shown to have conductivity comparable to an uncross-linked SPEEK membrane over a range of relative humidities.

Task 6. PEM Fuel Cell Freeze Degradation

Objectives

- Quantify a PEM fuel cell's power degradation resulting from subzero climate exposure.
- Develop a performance map for the membrane following the subzero temperature storage of the cell.
- Determine the effectiveness of industry accepted mitigation schemes at the Departments of Energy's operational limits.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost

Technical Targets

The goal of this research is to determine the amount of performance degradation experienced by a PEM fuel cell after being exposed to several freeze/thaw cycles at various subzero temperatures and humidification levels.

- Determination of critical membrane conditions in order minimize the subzero storage degradation.

Approach

Several membrane electrode assemblies with similar pore size, platinum content, and fabrication technique were subjected to freeze/thaw cycles at varying temperatures and levels of humidity. After each cycle was conducted a complete power profile was developed for each membrane. The profile was compared to the base line power profiles obtained before the first freeze/thaw cycle to obtain the inherent power loss.

Accomplishments

- Determined that current commercial fuel cell technology has progressed to meet the Department of Energy's goal of survivability to -40 degrees Celsius.
- Identified that the duration of subzero storage has a very strong influence on the amount of degradation experienced by the cell.

Conclusions

It can be seen from the results that the duration of the freeze/thaw cycle has the greatest effect on the internal ice formation and therefore the performance degradation exhibited by the membrane. The other operational parameters still may have a significant effect, but it is clear the internal ice takes a significant amount of time to form within the cell. This ability to delay or inhibit the ice formation is probably a result of the polytetrafluoroethylene coating applied to the gas diffusion layer of the membrane electrode assembly.

Patents Issued

1. Yogi Goswami, Man Su Lee, Nikhil Kothurkar and Elias K. Stefanakos, "Carbon Dioxide Sequestration", submitted as a US provisional patent, #61/013,844, USF Ref. No. 07B109PR, Dec.14, 2007.
2. Kislov, N., Schmidt, M., Kothurkar, N., Stefanakos, E., and Goswami, Y. "Method and Process for Producing Titanium Dioxide Exhibiting an Improved Photocatalytic Activity. Submitted on January 26, 2007 USF Ref. No.: 07A014PR (Provisional Patent).

FY 2009 Publications/Presentations

1. Man Su Lee, Yogi Goswami and Elias K. Stefanakos, "Immobilization of calcium oxide solid reactant on a yttria fabric and thermodynamic analysis of UT-3 thermochemical hydrogen production cycle", Accepted for the publication in International Journal of Hydrogen Energy.
2. Madhukar R. Mahishi, M. S. Sadrameli, Sanjay Vijayaraghavan and Yogi Goswami, "A Novel Approach to Enhance the Hydrogen Yield of Biomass Gasification Using CO₂ Sorbent", J. Eng. Gas Turbines Power January 2008 Volume 130, Issue 1.
3. Man Su Lee, Yogi Goswami, Nikhil Kothurkar and Elias K. Stefanakos, "Immobilization of calcium oxide absorbent on a fibrous alumina mat for high temperature carbon dioxide capture", ASME Energy Sustainability 2008.
4. J. Gass, H. Srikanth, H.; N. Kislov, S.S. Srinivasan, Y. Emirov, Magnetization and magnetocaloric effect in ball-milled zinc ferrite powder, *Journal of Applied Physics* (2008), 103(7, Pt. 2), 07B309/1-07B309/3.
5. N. Kislov, S.S. Srinivasan, Yu. Emirov, E.K. Stefanakos, Optical absorption red and blue shifts in ZnFe₂O₄ nanoparticles, *Materials Science and Engineering B*, 2008, DOI: 10.1016/j.mseb.2008.10.032, In Press.