

IV.H.9 Modular System for Hydrogen Generation and Oxygen Recovery

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SRI Consulting-Business Intelligence, Menlo Park, CA

Institute of Electro-Physics, Ekaterinburg, Russia

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Projected End Date: March 29, 2009

Objectives

- Develop a prototype of a modular industrial system for low-cost generation of H₂ (<\$2/kg) by steam electrolysis with anodic depolarization by CO

Technical Barriers

This project addresses the following technical barriers (listed in the order of the degree addressed) from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- K. Electricity Costs
- H. System Efficiency
- G. Capital Cost
- J. Renewable Integration

Technical Targets

Two critical targets must be achieved: H₂ production cost below \$2/kg and scalable design of the pilot H₂ generation system. The following technical barriers are envisioned:

- Performance and stability of the electrolyzer cell materials during long-term operation with multiple on/off and heat-up/cool-down cycles, including:
 - The ability of the electrolyte to retain an acceptable conductivity of the oxygen ions
 - The negative impact from interdiffusion of the electrolyte and electrode materials

- Polarization-related losses on the electrodes
The key target parameters to achieve are electrolysis voltage not exceeding 0.2–0.3 V (while maintaining a current density of 0.5-1 A/cm²) and stability of the electrolyzer within 1–3% during several thousand of hours of operation.
- Stability of the structural materials, including sealants and supporting structures in the gas distribution system.
- Optimal geometry and heat transfer of the gas distribution system.
- Electrical connections of the individual cells in the electrolyzer stack to minimize energy consumption and maximize H₂ output and purity.
- Stack design to allow pilot system scalability to meet the target H₂ production rate.

Approach

- Develop a single electrolyzer element with minimized energy consumption and sufficient endurance.
- Develop an electrolyzer stack of 4x4 elements, which allows scalability of multi-stack electrolyzers without technological complexities and negative impact on overall efficiency.
- Develop and build a multi-stack pilot electrolyzer system.
- Refine the design of the pilot system on the basis of long-term performance and endurance tests as well as an economic analysis conducted throughout the project to gauge industry's specific needs.
- Develop recommendations for field deployment, accompanied by economic analysis.

Accomplishments

Task 1.1 Design and assembly of the electrolyzer test system

- Design of the electrolyzer test system completed on April 24, 2005. Milestone 1 was met.
- Assembly test system planned start date – mid June, 2005. Planned completion date – mid July, 2005. Completion of system assembly was delayed because as of July 19, 2005 no DOE funding was received.

Future Directions

- *Selection of the candidate electrode, interface, and electrolyte materials.*
To minimize polarization losses, we will explore metal and metal-ceramic materials for the electrodes activated by candidate catalysts. To prevent diffusion of the electrolyte and electrode materials, antidiffusion interface layers (e.g., CeO₂) will be deposited. If YSZ (the candidate electrolyte) displays insufficient stability and deterioration of oxygen ion conductivity with time, we will explore more complex rare-earth-doped electrolytes.
- *Assembly of the high-temperature electrolyzer cells.*
We will prepare a set of test cells made of candidate materials. Each test cell will consist of a single electrolyzer element, separated anode and cathode space, internal gas distribution system, voltage connectors, and additional terminals for DC measurements or AC impedance spectroscopy. The test cell will represent a prototype of the 4x4 stack and allow for simultaneous testing of the materials of single elements and structural materials, including sealants.
- *Pre-examination of the electrode/electrolyte interfaces for candidate materials.*
We will use scanning electron microscopy (SEM) to examine cross sections of the electrolyzer and converter elements before and after the long-term tests. To conduct examinations before the tests, we will section ring samples from single elements. SEM images of the surface and cross section will be obtained, and composition analysis (using energy dispersive X-ray analysis, [EDX]) of the distribution of major

elements across the electrolyte and electrodes will be conducted. Structural analysis will be performed using X-ray diffraction.

- *Endurance and performance testing of the candidate electrolyzer and converter elements.*
Several electrolyzer and converter elements made of candidate materials will be tested in parallel. To do so, we will use a proven arrangement of the heating system and test cells [1], which will allow easy replacement of the tested elements and connection of the gas streams and electrodes. The tests will vary from 100 to 1,000 h in length. Tests will include multiple on/off and heat-up/cool-down cycles. Basic information on process parameters (e.g., temperature, electrical energy input for electrolysis, test cells voltage distribution, H₂ and O₂ output) will be monitored. We will periodically measure AC impedance to monitor the behavior of the major electrochemical parameters of the electrodes and electrolyte, and the performance of the tested elements. Test results will provide guidance on any modifications needed for the electrolyte, electrodes, and interface layers materials.
- *Post examination of the electrode/electrolyte interfaces for candidate materials.*
Post examination will be performed to obtain information on composition changes in the electrolyzer elements after endurance tests. For these examinations, we will section ring samples from the tested elements and employ the same SEM, EDX, and X-ray diffraction techniques used in the pre-examination. Post examination results will also provide guidance on modifying the electrolyte, electrodes, and interface layers materials.
- *Performance estimate of the candidate materials for the electrolyzer cells.*
We will rank all tested elements made of the candidate materials according to: (1) cell resistance before and after the tests (which directly affect the required electrolysis voltage), and (2) performance of the cells with time.
- *Selection of the best performing materials for a single-stack electrolyzer.*
We will select up to three candidate designs of the electrolyzer elements to make stacks of elements. Preliminary selection of the candidate structural materials, such as sealants, will also be made using the Phase 1 endurance test results.
- *Economic analysis, including performance/cost-value factor analysis of the electrolyzer cells.*
An economic analysis will be conducted at the end of Phase 1 using performance data for a single cell electrolyzer to estimate the production cost for a modular electrolyzer producing 1,000 kg/d H₂. The cost analysis will incorporate energy efficiency analyses and optimizations conducted during Phase 1. We will also evaluate potential cost reduction from: (a) use of low-cost waste heat available from nearby power plants, petroleum refineries, or other large process facilities, and (b) use of CO₂ to generate CO and recover ultra-pure O₂ by-product; and we will compare the proposed technology and competitive technologies (one of which uses natural gas as a depolarizer). An advisory panel, composed of industry representatives with an interest in the technology's development and deployment, will advise us to ensure that the process developed is compatible with industrial practice and market needs.

Introduction

High-temperature electrolysis of steam is known to be at least two times more energy-efficient for H₂ generation than low-temperature electrolysis. An additional, at least five fold, decrease in electricity consumption can be achieved by reducing electrolyzer voltage using an anodic depolarizer. The cost of H₂ generation will be further reduced if the high-temperature electrolyzer is deployed next to a source of waste heat and distributed power

generation unit (solid-oxide fuel cell and/or solar). The proposed system's modular design will allow scaling up and customization to meet a variety of site-specific requirements.

Approach

We will develop a prototype of a modular industrial system for low-cost generation of H₂ (<\$2/kg) by steam electrolysis with anodic depolarization by CO. Water will be decomposed

electrochemically into H_2 and O_2 on the cathode side of a high-temperature electrolyzer. Oxygen ions will migrate through an oxygen-ion-conductive solid oxide electrolyte. Gas mixtures on the cathode side ($H_2 + H_2O$) and on the anode side ($CO + CO_2$) will be reliably separated by the solid electrolyte. Depolarization of the anodic process will decrease the electrolysis voltage, and thus the electricity required for H_2 generation and the cost of produced H_2 .

Results

An experimental system for hydrogen generation by high-temperature electrolysis of water with anodic depolarization by CO (Figure 1) was designed and it is under construction at SRI.

FY 2005 Publications/Presentations

1. Presentation at the DOE Project Review Meeting May 2005

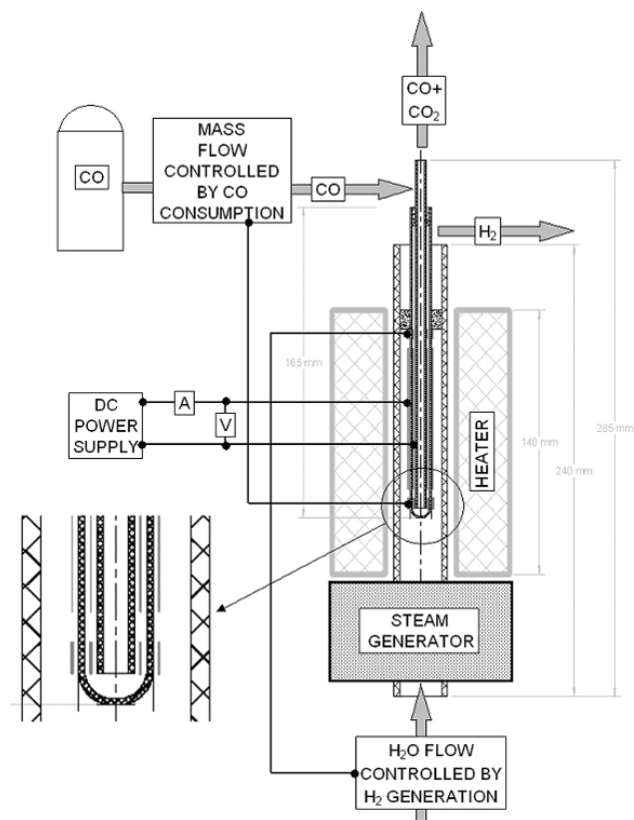


Figure 1. Experimental System for Hydrogen Production by High-Temperature Electrolysis of Water with Anodic Depolarization by CO