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FINAL REPORT

MODULAR SYSTEM FOR HYDROGEN GENERATION AND OXYGEN RECOVERY

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Executive Summary

In response to DOE's Solicitation for Grant Applications DE-PS36-03GO93007, "Hydrogen Production and Delivery Research," SRI International (SRI) proposed to conduct work under Technical Topic Area 5, Advanced Electrolysis Systems; Sub-Topic 5B, High-Temperature Steam Electrolysis.

We proposed to develop a prototype of a modular industrial system for low-cost generation of H_2 (<\$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 .

The process is expected to be at least 10 times more energy-efficient than low-temperature electrolysis and will generate H_2 at a cost of approximately \$1–\$1.5/kg. The operating economics of the system can be made even more attractive by deploying it at locations where waste heat is available; using waste heat would reduce the electricity required for heating the system. Two critical targets must be achieved: an H_2 production cost below \$2/kg, and scalable design of the pilot H_2 generation system.

The project deliverables would be (1) a pilot electrolysis system for H_2 generation, (2) an economic analysis, (3) a market analysis, and (4) recommendations and technical documentation for field deployment.

DOE was able to provide only 200K out of 1.8M (or about 10% of awarded budget), so project was stopped abruptly.

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Introduction

Technical Approach

The State of the Art of the Proposed Technology and Competing Technologies

High-temperature electrolysis of steam is known to be at least 2 times more energy-efficient for H_2 generation than low-temperature electrolysis. An additional, at least fivefold, increase in efficiency can be achieved by reducing electrolyzer voltage using an anodic depolarizer. The cost of H_2 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 [SOFC] and/or solar). The proposed system's modular design will allow scaling up and customization to meet a variety of site-specific requirements.

SRI International (SRI) proposed to develop a prototype of the modular industrial system for the generation of H_2 from steam with anodic depolarization. Water (steam) will be decomposed electrochemically into H_2 and O_2 on the cathode side. Oxygen will be ionized on the cathode side, and oxygen ions will migrate through an oxygen-ion-conductive electrolyte consisting of yttria-stabilized zirconia (YSZ, the candidate electrolyte assumed in this proposal) leaving H_2 on the cathode side. The anodic process will be depolarized by a mixture of CO and CO_2 . 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-oxide electrolyte. Using laboratory prototypes, the authors have proved this approach to be electrochemically feasible. System integration problems, including stability of the electrochemical cells and of structural materials, have been solved. Technical approaches to optimize the gas distribution system and the overall design of the high-temperature electrolyzers have been developed. The results have been successfully implemented in design and construction of industrial prototypes such as electrolyzers, converters, and SOFC generators [1-6].

Competing technologies either (1) use high-temperature electrolysis without depolarization of the anodic process, or (2) suggest using natural gas as the anodic depolarizer [7]. Electricity consumption by competing technologies in the first group will always be at least 5 times higher than that for the proposed technology and, accordingly, the cost of generated H_2 will be higher. The proposed system's advantages over the second group of competing technologies result from the use of CO instead of natural gas. Using CO as a depolarizer offers the following additional benefits: (1) reduction of greenhouse emissions by internal regeneration of CO_2 to produce CO and O_2 , (2) the possibility of generating depolarizer gas internally within a closed recirculation loop, thereby eliminating the need for a constant supply of the gas, and (3) the generation of ultrapure O_2 , as a by-product, which has high value for technical and medical needs and whose sale will further reduce H_2 production costs. Overall efficiency

can be further improved by minimizing losses in the electrochemical modules and implementation of different gas flow and electrical connection schemes.

Electrolyzer for H₂ Generation from Steam with CO as the Anodic Depolarizer

Generating H₂ by conversion of CO in a steam atmosphere essentially consists of high-temperature electrolysis of water with the anodic process depolarized by a mixture of CO and CO₂. The electrochemical cell in this case is:

The cathodic reaction is:

The anodic reaction is:

The total reaction essentially uses steam to convert the CO:

In this case, gas mixtures on the cathode side (H₂ + H₂O) and on the anode side (CO + CO₂) will be reliably separated by the solid-oxide electrolyte (YSZ is assumed). Because reaction (4) shifts to the right at temperatures below 823°C for thermodynamic reasons, electricity consumption will be reduced to a minimum below that temperature. Gas streams on the cathode side and anode side will be forced to flow in opposite directions, thereby further improving the electrolyzer's energy efficiency. As noted, we believe a reasonable choice for the solid-oxide electrolyte in the high-temperature electrolyzer is YSZ (defined for the purposes of this proposal as 0.9 ZrO₂ + 0.1 Y₂O₃). The thin film deposition process developed at IHTE allows deposition of the electrolyte and interface layers with thicknesses ranging from a few microns to a few hundred microns. Selection of materials for the electrodes is less obvious and will require experimentation during the proposed work.

Technical Feasibility of the Concept

The electromotive force of the electrolyzer with the opposite direction of the gas mixtures (H₂ + H₂O) and (CO + CO₂), and for equal volumetric consumption of CO and H₂O, can be estimated from

$$E = E_{H_2/H_2O}^0 - E_{CO/CO_2}^0, \quad (7)$$

where E^0 depends on corresponding equilibrium constants and temperature:

$$E_{H_2/H_2O}^0 (mV) = 1290 + 0.292T(K), \quad (8)$$

$$E_{CO/CO_2}^0 (mV) = 1458 + 0.447T(K) \quad (9)$$

Preliminary calculations indicate that E is very low in this case (< 0.05 V at 1000°C). The potential drop observed across the electrochemical cell with YSZ electrolyte with a thickness of 0.05–0.25 mm, a Ni anode and cathode, and a current density of 0.5–1 A/cm² did not exceed 0.2–0.3 V in the temperature range of interest. Under these conditions, the energy consumption will be on the order of 5–6 kWh/kg H₂. These estimates confirm the attractiveness of the proposed process for H₂ generation. Experience in developing

high-temperature electrolyzer systems indicates that energy consumption may be 20–40% higher, resulting in 6–8 kWh/kg H₂. Our experience [1-6] and the estimates of others [7] indicate that energy efficiency in the 60–70% range can be expected (if efficiency is estimated with respect to primary energy consumption), and in the 75–90% range if estimated with respect to total energy into the electrolyzer (which more closely corresponds to the proposed approach when electrolysis is combined with local or distributed electricity generation).

The cost of electricity to generate 1 kg H₂ under these conditions will be approximately \$0.46–\$0.75, assuming an electricity cost of \$0.07/kWh. The cost of electricity is expected to be the major component (in the 50% range) of the plant gate cost of H₂, which provides confidence that the target cost of \$2/kg H₂ will not be exceeded. Our estimates indicate that the expected plant gate cost is in the \$1-1.50/kg H₂ range.

Test System

Each test cell consist of a single tubular closed end electrolyzer element (Figure 1), separated anode and cathode space, internal gas distribution system, voltage connectors, and additional terminals for DC measurements or AC impedance spectroscopy (Figure 2). 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.

The experimental system (Figure 3) will include (1) gas distribution, (2) heating, (3) power supply, (4) process control, and (5) a data acquisition system. The heating system will consist of tubular furnaces for parallel testing of the electrolyzer cells at temperatures up to 1200°C. The gas distribution system will be configured to supply steam, collect H₂, recirculate CO₂ and CO, and collect O₂. The power supply system will maintain variable voltage along the electrolyzer cells. The process control system will maintain the desired concentration of gases on the anode and cathode sides of the test cells. The cells will be equipped with gas sensors and additional electrodes to monitor performance along the cell working area. The data acquisition system will collect and store data on process parameters (e.g., temperature, total electrical energy input for electrolysis, voltage distribution in the test cells, H₂ output).

Figure 1. Electrolyzer element

Figure 2. Electrolyzer test system.

Figure 3. Experimental system

Assembly of the high-temperature electrolyzer cells.

To minimize polarization losses, we explored 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., CeO_2) was deposited.

A set of 21 flat electrolyzer cells (Figure 4) was prepared at SRI. Cells consist of porous anode, gas tight electrolyte, and porous cathode (Figure 5). Thickness of the electrolyte is approximately 20 microns (Figure 6). These cells were used in parametric experiments to select candidate anode, cathode, electrolyte, and interface layer materials, including composition and morphology.

A set of 4 full scale tubular electrolyzer cells (Figure 7) was prepared (2 by NexTech Materials and 2 by IEP, Russia). Cells of this type were intended for optimization of electrolyzer operating regimes and for endurance tests.

We used 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 sectioned ring samples from single elements.

Fabricated button cells using premixed NiO/YSZ manufactured by Nextech. Cells were tested in H_2 with 2% steam on anode and cathode. Cell resistance of 100's of $\Omega\text{-cm}^2$ was measured. Electron microscope images show poor porosity, limiting gas flow.

We designed new tape cast slip recipe (Ni cermet #2) with higher porosity. Some problems with delamination during firing solved by adjusting initial heating (reduced rate to $0.5^\circ\text{C}/\text{min}$ to 400°C). Measured open porosity of as-fired ceramic using water infiltration: 45% porosity. Reduced under H_2 and measured impedance under 2% steam. At 750°C ohmic impedance $0.2\Omega\text{-cm}^2$, DC impedance $6\Omega\text{-cm}^2$.

Sealed cells were tested with controlled steam on cathode, tested with 50% steam on cathode, pure H_2 on anode. Open circuit voltage 0.12-0.13V was measured. Impedance data were collected at 750°C : $0.15\text{—}5.1\Omega\text{-cm}^2$.

Cells with Pt paste and Au wire current collector have been performed to determine if Silver current collector is interfering with performance. DC impedance of $8\Omega\text{-cm}^2$ was measured.

Repeated test with new recipe 2 cell, silver current collector, symmetrical H_2 /steam have been performed. At 750°C : 0.5 to $4.7\Omega\text{-cm}^2$ was measured.

Consulting with IEP, decided to modify NiO/YSZ ratio and particle size in tape cast slip was started. Eventually, we prepared 3 new recipes with 60,65,70 wt % NiO, using Alfa NiO powder. Sintered at 1400°C , reduced under H_2 at 750°C .

Table 1. Optimization of weight composition

60 wt %	$>20\text{M}\Omega$
65 wt %	$0.06\Omega\text{-cm}$
70 wt %	$0.03\Omega\text{-cm}$

Figure 4. Top view of the flat electrolyzer element (diameter 1.1 cm) for parametric experiments to select candidate materials

Figure 5. Side view of the flat electrolyzer element

Figure 6. Cross section of the flat electrolyzer element consisting of Ni/YSZ anode, YSZ thin film electrolyte and Ni/YSZ anode

Figure 7. Tubular electrolyzer element: diameter 1 cm, length 15 cm

Thermodynamic analysis

Thermodynamic analysis of the high temperature electrolysis with anodic depolarization by CO was completed. Additional option to reduce electrolysis voltage has been discovered: non-stoichiometric operation (Figure 8).

Target key parameter of the electrolyzer cell (cell resistance) was defined. In order to operate at 0.2-0.3V under electrolysis current $0.5\text{--}1.0\text{ A/cm}^2$, cell resistance (ASR) should be in $0.25\text{--}0.60\text{ ohm-cm}^2$ (Figure 9). Published data on ASR measured for similar systems are in the $0.1\text{--}1.0\text{ ohm-cm}^2$, which confirms that our target ASR is realistic.

Figure 8. Theoretical voltage of electrolyzer with anodic depolarization by CO operating in stoichiometric (reagent ratio on the anode and cathode side =1) and non-stoichiometric regimes

Figure 9. Voltage of electrolysis as a function of electrolyzer cell resistance for electrolysis current densities 0.5 and 1 A/cm^2 . Target voltage range is $0.2\text{--}0.3\text{ V}$ defines target cell resistance range $0.25\text{--}0.7\text{ ohm-cm}^2$.

Cost Analysis

Cost of hydrogen was estimated for two scenarios: high operating and maintenance cost (Figure 10) and lower operating and maintenance cost (Figure 11). Target cost of hydrogen may be met under both scenarios if target cell parameters (ASR, endurance) and electrolyzer parameters (operating voltage is 0.2-0.3V and operating current density is 0.5-1.0 A/cm²) will be achieved.

Figure 10. Estimated cost of hydrogen for the case of high capital and operating costs (fraction of electricity cost is 20%, fraction of capital and operating cost 80%)

Figure 11. Estimated cost of hydrogen for the case of lower capital and operating costs (fraction of electricity cost is 50%, fraction of capital and operating cost 50%)

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