II.E.1 High-Capacity, High-Pressure Electrolysis with Renewable Power Sources

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Objectives

- Achieve a 15x increase in the gas production rate of a single high-pressure hydrogen production cell over the current standard Avālence cell.
- Demonstrate the high-pressure cell composite wrap which results in significant weight reduction.
- Build and test a 1/10th scale pilot plant.
- Create fabrication-ready drawings for a full-scale plant (300 kg/day, 750 kW).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Generation by Water Electrolysis section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(G) Capital Costs
(H) System Efficiency
(J) Renewable Electricity Generation Integration

Technical Targets

TABLE 1. DOE Technical Targets: Distributed Water Electrolysis Hydrogen Production

Characteristics	Units	2012 Target	2017 Target
Hydrogen Cost	$/gge	3.70	<3.00
Electrolyzer Capital Cost	$/gge $/kW	0.70 400	0.30 125
Electrolyzer Energy Efficiency	% (LHV)	69	74

gge = gasoline gallon equivalent; LHV = lower heating value

Distributed Water Electrolysis Hydrogen Production

In this project Avālence is developing an enlarged version of its present electrolyzer design that will have 15x the capacity of the current single tubular cell. To achieve this, the diameter of the current Avālence design individual tubular cell is being enlarged to enable an innovative cell core design: multiple coaxially arranged cylindrical electrodes, nested in a uni-polar configuration. This design is the core of a distributed water electrolysis hydrogen production system that will meet the following DOE 2017 targets:

- Hydrogen Cost: $3.00/gge
- Electrolyzer energy efficiency: 74 kWh/kg

Accomplishments

- Identified and tested formable sheet membrane material. (Figure 1)
- Successfully demonstrated membrane tube forming and seam joining. (Figure 2)
- Identified vendor and ordered 6,500 psi capable electrical isolation hoses.
- Completed design of single-cell test article and test apparatus.
- Demonstrated 6,500 psi production on small capacity cells.
- Began construction of the test cells to test the recirculation approach to enable 6,500 psi operation. (See Figure 3).
- Initial testing of 6,500 psi operation on the existing small-scale units has been completed demonstrating long-term operating potential of the core technology at very high pressure. Avālence completed the initial round of testing to evaluate the present cell design operation at 6,250 psi with the entire array of

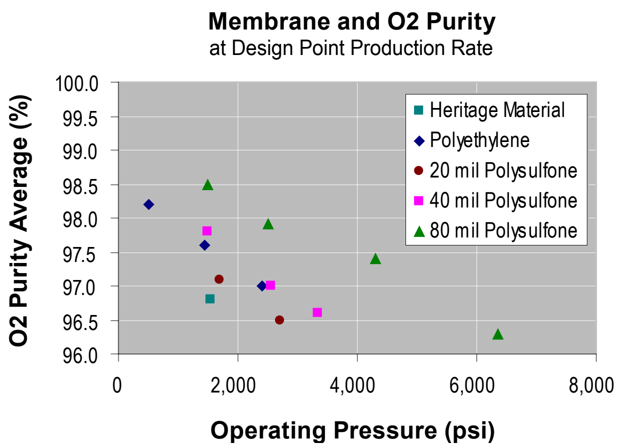

FIGURE 1. Demonstrated 6,500 psi Operation, Membrane and Oxygen Purity

FIGURE 2. Demonstrated Membrane Sealing

separation membranes available at this time. Eighty millimeter thick polysulfone membrane material achieved acceptable oxygen side purities (<4% H_2) when operating in excess of 6,000 psi. Avālence will continue to examine other operating approaches to obtain greater margin between the O_2 side purity and the explosive limit.

- Avālence has begun to build the cells necessary to test the circulation loop operation. These cells have separate electrical isolation hoses at both the top and the bottom of the cell to allow separate circulation of the oxygen and hydrogen side electrolyte without forcing cross flow through or under the separation membrane.

Introduction

Avālence has existing technology that is globally unique in its ability to deliver hydrogen directly at storage-ready pressures of 2,500 and 6,500 psi without a separate compressor. Using an alkaline electrolyte process, the Avālence Hydrofiller systems integrate the production and compression processes by operating the electrolytic cells at the desired delivery pressure. The systems can interface directly with renewable electricity supplies and have been shown in previous work (DOE Small Business Innovation Research project completed in April 2005) that the electrolyzer operates through the full range of voltages output from the connected photovoltaic array without using any power conditioning equipment. These characteristics result in a renewable hydrogen production and delivery system that is significantly more efficient and reliable, and substantially less expensive than existing commercially available electrolyzer and compressor system sets. The smaller scale Hydrofillers are based on a single cathode/anode tubular cell design with production capability of about 0.1 kg/day per cell. A revolutionary design approach to this high-pressure cell core is needed for an order-of-magnitude capacity scale up of the individual electrolyzer modules.

Approach

In this project, an enlarged version of the current Avālence design is being developed that will have at least 15x the capacity of the present single tubular cell. To achieve this, the diameter of the individual tubular cell will be substantially increased in order to enable an innovative cell core design – multiple coaxially arranged cylindrical electrodes, nested in a uni-polar configuration – enabling up to 1½ kg/day of production per individual cell. To accomplish this diameter increase with a practical pressure boundary while operating at either 2,500 or 6,500 psi, Avālence has partnered with a composite cylinder manufacturer, HyPerComp Engineering Inc. They will develop a custom designed containment vessel/cathode using their composite technology expertise that will allow an increase in the diameter of the individual electrolysis cell, enable operation at 2,500 psi and above, and reduce the cell weight and cost relative to conventional metal containment (similar to what is seen today with composite storage tanks used on vehicles). Ninety-six of these high-capacity cells will now produce a single unit (module) with a production capacity of 150 kg/day.

To complete this development process, Avālence is proposing to build a quarter-scale pilot plant to be composed of 20 cells that will replicate the full plant design and operation, but minimize the cost to DOE for this technology demonstration. The pilot plant will be sent to the National Renewable Energy Labortory

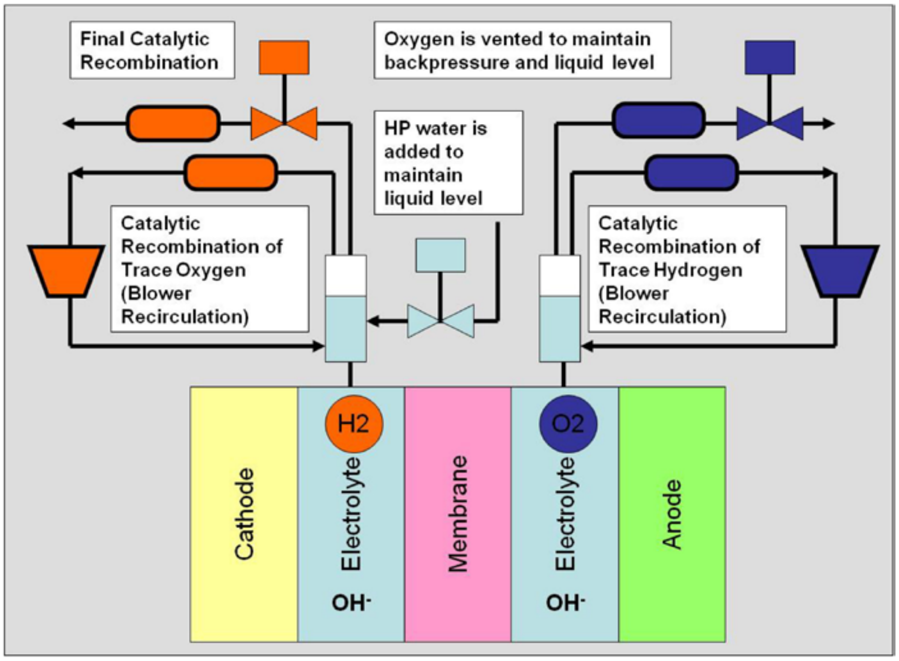

FIGURE 3. Long-Term 6,500 Psi Operating Approach 1, Recirculation/Diffusion with Purified Gas

for verification testing over the last three months of this nominal 30 month project. The final result of the project will be a commercially operating 30 kg/day pilot plant integrated with a wind turbine and/or photovoltaic array, and delivering hydrogen gas at pressure directly to storage cylinders. Operation of this plant and extensive testing of this and earlier development versions throughout the course of the project will thoroughly document the performance and operation of the technology. This combination of an operating pilot plant and substantial performance and operating data will position the technology for commercialization.

Results

In order to minimize project risk, a decision was made to demonstrate 6,500 psi operation in existing Avālence technology prior to and as a step towards designing and building the large cell prototype. A number of findings resulted from this action. While it was shown that as expected, that the basic electrochemistry work, some issues arose need to be addressed going forward.

- It was found that that the 80 mm membrane created a larger voltage drop between the anode and cathode and therefore resulted in decreased efficiency. Table 2 lists the energy requirement per kg of hydrogen produced for both the 40 and 80 mm membrane tests.

TABLE 2. Membrane versus Electrolysis Energy Use

Polysulfone Membrane Thickness	Energy Used in Electrolysis
40 mm	62 kWh/kg
80 mm	67 kWh/kg

- At high pressure, all leak paths also become more of an issue. As a result:
  - Pipe threads had to be removed from the cell design.
  - Multiple attempts were made before finalizing the design of the Parker dielectric hoses.
  - Internal cell seals have been redesigned on the head of legacy cells; and the new design concept is being used on the large cell.
- In achieving the goal of 6,500 psi operation, it was found that the present standard cell design requires periodic depressurization and electrolyte mixing to maintain cell performance and gas purity over the long term. Gas bubbles being formed are very small (almost invisible) and the velocity of bubbles is low, causing masking of the electrodes. As a result, high-pressure operation, which results in reduced buoyancy and smaller bubbles makes gravity based sweeping problematic at higher (design point) rates. A further issue is that since velocity is lower, dwell time in cells increases. This by itself can impact impurity, because there is more time to react with any electrolyte contaminants and greater time for any side electrolysis reactions (hoses) to accumulate

impurity. Also, since diffusion is either steady or increasing with pressure, the additional dwell time amplifies any impurity as a result of diffusion. To address all of these issues, it is proposed that a different, constant recirculation approach may eliminate the depressurization cycle need and therefore increase production availability, oxygen side purity, and production efficiency. The electrolyte will be circulated to cool the system and to sweep the electrodes of gas bubbles to maintain gas production rates (current density). Additional components required for recirculation such as pumps and blowers actually simplify other parts of the system such as passive level control, water addition, and cell-to-cell electrolyte balancing, which become essentially automatic (see Figure 3).

TABLE 3. Composite Shell Design

Specification for Composite Overwrapped Pressure Vessel for Electrolysis Cell			
Design Number	A	B	(units)
Service Pressure	2500	6500	(psig)
Minimum Burst Pressure	5625	14625	(psig)
Target Average Burst Pressure	8000	20000	(psig)
Overall Length	57	57	(in)
Liner Material	316L	316L	(in)
Liner OD	8.25	8.25	(in)
Liner Sidewall Thickness	0.12	0.31	(in)
Pressure Vessel ID	8.01	7.63	(in)
Liner Dome Config.	Isontensoid		-
Port Configuration	External Threads		-
Required Port OD	4.625	4.625	(in)
Fiber Overwrap Material	Carbon Fiber		-
Resin	Epoxy		-
Carbon Composite Hoop Thickness	0.086	0.258	(in)
Carbon Composite Helical Thickness	0.11	0.33	(in)
Carbon Composite High Angle Helical Thickness	0.038	0.114	(in)
Overall Carbon Composite Thickness	0.234	0.702	(in)
Pressure Vessel OD	8.718	9.654	(in)

Other findings include:

- Electrical isolation hoses need to be eliminated in order to mover the Y-axis intercept on purity to above 99% (see Figure 1).
- Structural issues can be addressed using a conventional design of an overwrap to the metallic inner pressure vessel (see Table 3).
- Gas production rates are achievable as long as masking does not block electrode surface.
- High surface area cathode treatment can be employed to increase production rate.

Conclusions

- Avālence has shown that the biggest challenge of 6,500 psi with no compressor can be met.
- A robust large cell design is complete, ready to build/test.
- The technology is valid:
  - structurally (composites exit criteria)
  - electrochemically (2.1 v, 1,800 A exit criteria)
  - thermally (derived)
  - economically (DOE goal met @ 1,000 units/yr exit criteria)
- We feel that demonstration of the large cell nested operation is very low risk.
- We feel that demonstration of composite overwrap to achieve containment is also very low risk.

Future Directions

- Demonstrate large diameter cell operation at 1,000 psi.
- Test long-term 6,500 psi operation approaches:
  - Using existing small cell apparatus.
  - Purified gas "recirculation/dilution" approach as required to achieve the lower explosive limit (see Figure 3).
  - Neutral electrolyte chamber approach – membrane related effort.