DEVELOPMENT OF A HIGH PRESSURE PEM ELECTROLYZER:
ENABLING SEASONAL STORAGE OF RENEWABLE ENERGY

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ABSTRACT

Energy-efficient generation of hydrogen at high pressure would aid the transition to a hydrogen economy by eliminating the need for mechanical compression, a costly and inefficient parasitic load found in existing hydrogen generation systems. The Schatz Energy Research Center (SERC) has worked since 2001 on the development of a proton exchange membrane (PEM) electrolyzer capable of generating hydrogen at high pressure in useful quantities for small-scale power systems.

With financial support from the California Energy Commission’s Energy Innovations Small Grants (EISG) program, SERC developed and successfully operated one-cell and two-cell electrolyzer modules at pressures up to 2,000 pounds per square inch gauge (psig) with an average hydrogen delivery rate of 0.22 standard liters per minute (slm) per cell at a current density of 700mA/cm². By comparison, commercially available alkaline electrolyzers deliver hydrogen at a few hundred psig or less, and at lower voltage efficiency than the SERC electrolyzer. Thus, SERC’s design appears to offer a significant total energy efficiency advantage over an alkaline electrolyzer/mechanical compressor combination.

This paper will discuss the technical challenges identified and overcome in this research, the details of the results obtained thus far, and plans for continuing this work to produce a multi-cell electrolyzer module capable of delivering 3 slm. Finally we will also discuss plans to field test the electrolyzer as part of a complete SERC-built solar hydrogen system including a solar array, hydrogen storage, a fuel cell, and a real-world electric load.

1. BACKGROUND

SERC has been designing, building and operating solar hydrogen energy systems since 1989. These systems demonstrate the feasibility of using hydrogen to store renewable energy for reliable, year-round availability. Major components of a solar hydrogen system include a solar photovoltaic (PV) array, an electrolyzer, hydrogen storage, and a fuel cell. The electrolyzer uses electric power from the PV array to convert water to hydrogen and oxygen gas, while the fuel cell is able to generate electric power from the stored energy during periods when the primary energy source (solar insolation) is not available.
Our solar hydrogen projects have used an alkaline electrolyzer, specifically the Teledyne Altus 20, capable of generating 20 standard liters per minute of hydrogen using an electrical input of approximately 6 kW DC. Output pressure is approximately 100 psig. In the case of the Schatz Solar Hydrogen Center, our first solar hydrogen installation, the system was built to store hydrogen at the Altus 20’s 100 psig output pressure, requiring three 500-gallon tanks for storage of approximately 60 kWh of recoverable electrical energy. Clearly, storage volume on this scale would be unacceptably cumbersome for most applications. Higher pressures are required in order to make hydrogen sufficiently energy-dense to be practical for portable or transportation applications, or stationary applications where fuel storage space is limited. Thus a compressor is normally needed to boost gas storage pressure.

Other commercially available electrolyzers only improve modestly on the Altus 20’s hydrogen output pressure. Some currently available models include:

- Hamilton-Sundstrand ES 12280 (100 psig)
- Proton Hogen Series (200 psig)
- Stuart-Vandenborre HES (25 Bar, or 363 psig)

Hazardous materials are another concern in using alkaline electrolyzers such as the Altus 20. Not only is the electrolyte highly caustic potassium hydroxide, but the matrix in which the electrolyte is suspended is made up of asbestos fibers.

Our Altus 20 electrolyzers have performed reliably for many years; however, it would be valuable to devise an electrolyzer free of hazardous materials and capable of generating hydrogen at high pressure. Such an electrolyzer would be of even greater value if it were capable of operating at higher efficiency than existing electrolyzers.

SERC’s many years of experience designing, fabricating, and using proton exchange membrane (PEM) fuel cells have given us a thorough understanding of this solid electrolyte technology. We have been aware for a number of years that companies such as Proton Energy Systems were working to develop a commercial high-pressure electrolyzer using a PEM design related to that of PEM fuel cells. However, no high-pressure PEM electrolyzer has yet reached the market. The only PEM electrolyzers commercially available were small-scale, low-pressure benchtop units intended for use in laboratory gas chromatography, such as those produced by Packard and Balston.

In January 2001, SERC approached the California Energy Commision’s Energy Innovations Small Grants (EISG) program with a proposal to support development of a high-pressure PEM electrolyzer. EISG agreed to fund the project. SERC’s goals for this initial, EISG-funded phase of electrolyzer development were to build a prototype capable of generating 3 slm at 2,000 psig while matching or exceeding the overall efficiency of existing electrolyzers. The EISG program’s stated goal in supporting this and other projects is to establish the feasibility of energy-related products and technologies of benefit to Californians. Work began in August 2001.
2. PROJECT DESCRIPTION

After completing a literature and patent review to familiarize ourselves with the state of the art in electrolyzer design and any possible intellectual property issues, we proceeded with the design of a single-cell electrolyzer and its ancillary subsystems. For safety reasons, we chose to design the electrolyzer for low-pressure oxygen delivery. While this eliminated the hazard of handling high-pressure oxygen, it created the challenge of supporting the membrane electrode assembly (MEA) across a very high pressure differential.

Another design issue was the choice of whether to circulate water on both sides of the electrolyzer cell. Some electrolyzer designs we reviewed in the literature supply water to both the cathode and anode sides of the cell. We determined that it would be unnecessary to circulate water on the cathode side of the cell, and that supplying water only to the anode would simplify the design without sacrificing safety or performance.

Other immediate design issues included material strength and oxygen compatibility. After reviewing the range of oxygen-compatible materials and rejecting some as too expensive or lacking sufficient strength, we settled on using square stainless steel endplates joined by insulated stainless steel tie rods arrayed around a circular active area of 45.6 cm$^2$. Each of the two endplates has a circular pocket machined into it to accommodate a circular diffuser disc. In the single-cell configuration, an MEA is sandwiched between the two endplates, with the MEA’s active area positioned between and in contact with the two diffusers. In the multi-cell stack configuration, one or more bipolar plates, also made of stainless steel, are located between the endplates. Each bipolar plate has diffuser pockets on both sides. The end plates and bipolar plates are also equipped with manifolds for the introduction of water and the removal of hydrogen, oxygen, and water.

Various materials tests were conducted in the early stages of the project, including cell pressure testing using raw Nafion, disc testing for water permeability, compression strength and conductivity and single cell operational tests. The pressure testing results indicated that the sealing design of the module was adequate for hydrogen side operating pressures of 2000 psig. The other tests were used to eliminate unsuitable sample materials until satisfactory materials were identified.

In addition to the design of the electrolyzer itself, it was also necessary to create a test station for benchtop operation and monitoring of the electrolyzer. Major components of the test station include a DC power supply, a control and data acquisition computer using LabVIEW virtual instrumentation, a set of backplanes for signal processing between the computer and the electrolyzer system, a water circulation subsystem, gas plumbing, and containment for the electrolyzer module.

Given the experimental nature of our electrolyzer cell design and our plans to operate at pressures up to 2,000 psig, we decided to install the electrolyzer in a benchtop containment vessel. The vessel is built of welded quarter-inch stainless steel with two-inch bullet-resistant glass covering the viewing ports on the front.
of the vessel and an illumination port on top. The front panel of the vessel is removable. Electric power cables; stainless steel tubing for water, hydrogen and oxygen; and data acquisition wiring all pass through the rear of the vessel.

Another design challenge was the selection of a suitable diffuser material. This needed to be an electrically conductive material safe for use in a pure oxygen environment, capable of withstanding compressive forces of 2,000 psig, and permeable enough to allow free passage of water and oxygen on the anode side and hydrogen on the cathode side of the cell. The surface texture of the material needed to be smooth enough not to puncture or tear the delicate proton exchange membrane. After numerous experiments with stainless steel foam, fiber, and wire mesh materials, we settled on a multi-layer stainless steel woven mesh material. We tested several such mesh products before selecting one with adequate electrical conductivity, compressibility, and elasticity.

Once all design and materials issues were resolved, we proceeded to development of a test procedure. Our standard electrolyzer test procedure is as follows:

1. Begin circulation of water, heating it to a steady-state temperature of either 36° C or 50° C.
2. Set the power supply to deliver a constant current (21 to 33 A at 36° C or 30 to 46 A at 50° C) and a voltage not to exceed 2 V/cell.
3. Adjust the hydrogen back pressure regulator to the desired pressure for hydrogen generation.

3. RESULTS

Initial operation of the electrolyzer revealed problems with the module design. Poor performance appeared to be due to high contact resistance between adjacent components. In addition, corrosion and staining of metal surfaces suggested that undesired electrolysis reactions were taking place at sites other than on the MEA. Even the rugged stainless steel end plates and diffuser discs showed unacceptable levels of rusting after several hours of service in the oxygen-rich environment of the cell anode. Furthermore, metallic ions freed from the stainless steel by this oxidation appeared to be rapidly poisoning MEAs, causing rapid deterioration in cell performance, typically within an hour of the start of a test. These problems were eventually solved by gold plating these components, as discussed below.

Despite initial challenges in identifying suitable materials for our electrolyzer module, we were finally able to construct a single-cell module that operated at 2,000 pounds per square inch gauge (psig) at a current density of 700 mA/cm², producing on average approximately 0.22 standard liters per minute of hydrogen. Figure 1 shows hydrogen production rate, current density, and hydrogen pressure recorded over more than six hours of continuous operation during a recent test of the single cell electrolyzer. We have achieved comparable performance with a two-cell module at 2,000 psig, demonstrating the feasibility of our bipolar plate design for multi-cell configurations (see Figure 2). Given our continuing advances in cell performance, we anticipate that a 10-cell module will soon allow us to meet our performance goal of 3 slm total hydrogen generation.
Observed voltage efficiency for our PEM module is markedly better than that of a Teledyne Altus 20 alkaline electrolyzer, based on performance measurements made using both devices at the Schatz Energy Research Center. Similarly, current density (and thus hydrogen generation rate) at a given cell voltage is significantly better in our unit than in the Altus 20. Figure 3 shows a comparative cell voltage-current density graph of the two electrolyzers, each operating at a hydrogen output pressure of 100 psig. At 200 mA/cm², our electrolyzer has a voltage efficiency of 95%, compared to 87% per cell for the Teledyne electrolyzer. At a higher current density of 350 mA/cm², the relative efficiency difference is even greater: 92% for the SERC electrolyzer and 81% for the Altus 20. Clearly, our PEM electrolyzer design offers greater efficiency than a typical commercial electrolyzer. This translates to more hydrogen generated per unit cell area, which in turn could result in more compact and economical electrolyzer designs.

Figure 1. Single-cell electrolyzer module performance
Figure 2. Two-cell electrolyzer module performance

Figure 3. Comparison of SERC PEM electrolyzer and Teledyne electrolyzer
Initially, the stainless steel endplates and discs were not plated, resulting in rapid poisoning of the membrane. An initial attempt to reduce this problem by nickel-plating the components was not successful. The endplates, bi-polar plate and discs were then gold-plated and cell performance improved slightly; however, the membranes eventually became poisoned after an eight-hour test. It was suspected that the interior surfaces of the multi-layered discs were not getting plated, and this bare stainless steel was the source of unwanted ions. The discs were given a thicker gold plating and cell performance improved dramatically.

De-lamination of plating is a problem and has occurred in three regions of the module: the bottom of the disc pockets, the outer surfaces of the discs, and in the hydrogen o-ring groove. The disc and o-ring groove de-lamination evidently takes place when the membrane is pulled off the disc for a gasket replacement or when the hydrogen o-ring is removed for replacement. Possible solutions could be minimizing module disassemblies and improving surface preparation prior to plating, perhaps by roughening.

We have identified the minimization of uncontrolled hydrogen losses as key to optimizing performance of our electrolyzer. Hydrogen loss is calculated using:

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\% \text{ hydrogen loss} = \frac{Q_{H_2} \text{ (theoretical)} - Q_{H_2} \text{ (measured)}}{Q_{H_2} \text{ (theoretical)}}
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Where \( Q_{H_2} \) = hydrogen production rate in standard liters per minute (slm)

Theoretical hydrogen production rate is based on current provided to the electrolyzer.

Hydrogen loss was measured at levels between 2.0% and 12.8% in the course of our electrolyzer tests, with most of the recent tests showing less than 5% loss. Loss generally increases with hydrogen pressure. Hydrogen production below theoretical level can be attributed to one or more of three factors:

1. hydrogen leaks external to the electrolysis site, such as leaks across an o-ring or from the hydrogen plumbing upstream of the mass flow controller;
2. hydrogen crossover at the membrane to the anode side; and
3. current consumed in undesirable reactions other than electrolysis.

In order to calculate the percent loss in hydrogen the following must be known: average electrolysis current, average hydrogen flow rate, hydrogen ballast pressure at start and end of run, and run time. In order to improve accuracy of the calculation it is desirable to remove the ballast pressure variable from the equation by targeting a near zero net change in ballast pressure. The hydrogen mass flow controller is adjusted to maintain a constant ballast pressure and the data is analyzed for a period of the run where initial and final pressures are identical.

Numerous practical lessons have been learned in the process of our bench testing of the electrolyzer. Test bench program and plumbing modifications were made to address the following issues:

• **Hydrogen flow rate fluctuations.** Two modifications, a program subroutine to control the power supply at a constant current and the addition of a
hydrogen ballast system to buffer the back pressure regulator fluctuations, were implemented in order to produce a steady hydrogen flow measurement.

- **Hydrogen crossover.** When operating the electrolyzer at high hydrogen pressures, hydrogen crossover to the oxygen side produced mixtures approaching hydrogen’s lower explosive limit in oxygen. An initial attempt at a solution to this problem was the use of membranes with integral platinum catalyst, but results were minimal. A catalyst bed was added to the water/oxygen outlet line to promote the recombination of the hydrogen and oxygen prior to entering the gas/water separator. This solution was far more effective.

- **Humidity in hydrogen gas stream.** Wet gas causes the mass flow controller to indicate a flow rate higher than the actual flow rate. A molecular sieve bed was added to the plumbing system on the outlet of the hydrogen water knockout drum.

Four causes of damage to the electrolyzer MEAs have been observed:

- **Over-compression.** Compression on the MEA surface is a function of disc thickness, disc yield strength, gasket thickness, o-ring groove depth, and amount of torque applied during assembly. Over-compression between the diffuser discs can result in minute perforations over the MEA surface.

- **Ruptures.** Under microscopic examination, ruptures are sometimes found on the part of the membrane adjacent to the outer perimeter of the diffuser discs. This area of the MEA is vulnerable because of the lack of support and the sharp edges of the discs’ wire mesh.

- **Tearing.** Tearing appears to occur most commonly during disassembly of the cells between tests. The MEA and adjacent gaskets can adhere strongly to the diffuser discs.

- **Poisoning of the membrane.** As discussed above, this problem has been largely resolved by gold plating of stainless steel components, although the de-lamination of gold-plated components continues to be a problem.

Measures implemented to reduce wear and tear on the MEA, and thus reduce likelihood or degree of hydrogen crossover include:

- fine-tuning of the torquing of the module tie rods, to achieve an optimum balance between cell leakage (due to inadequate torque) and embossing of the MEA surface (resulting from excessive torque); and

- use of diffuser material having a finer-textured diffuser surface, also to reduce surface embossing of the MEA.

- addition of gaskets on both the oxygen and hydrogen sides of the cell to prevent over-compression of the MEA. The gaskets provided the additional benefit of improving electrical insulation between the anode and cathode side end plates, eliminating unwanted electrolysis reactions away from the MEA surface that had caused corrosion on the interior surfaces of the end plates. However, the gaskets can introduce increased contact resistance between conductive components if their thickness is not
adequately compensated for by adjusting diffuser pocket depths in the end plates and bipolar plates.

We have achieved our 2,000 psig hydrogen delivery pressure objective and are approaching our target hydrogen delivery rate of 0.3 slm per cell. This electrolyzer design is therefore expected to exceed our 3 slm delivery objective when expanded to a 10-cell stack format. In our most recent tests, we have operated the electrolyzer in a two-cell configuration at 1500 psig at 50°C at 1 A/cm² and a voltage of only 1.93 V/cell.

4. NEXT STEPS

We have made considerable progress in developing a high-pressure PEM electrolyzer and continue to see improved performance as we make incremental changes to our design. However, a number of problems remain to be resolved. Key problems include:

- The module has a chronic problem with water leaking out of the tie rod penetrations in the end plates.
- The gold plating on the end plates and diffusers tends to delaminate over time, with repeated assembly and disassembly of the module.
- Corrosion of metal components is still occurring, particularly in locations where gold plating has delaminated.
- Efforts continue to find an optimal combination of diffuser pocket depth and diffuser and gasket thickness that will perform well over a range of pressures with minimal impact on the MEA surface and minimal leakage.

Having achieved considerable success in benchtop testing of our prototype electrolyzer, SERC is looking ahead to field installation of a high pressure PEM electrolyzer as part of a complete solar hydrogen energy system. The proposed system would be the first field test of a high pressure PEM electrolyzer as part of a stand-alone solar hydrogen system. We have also initiated a search for a partner to commercialize our high pressure PEM electrolyzer design.

5. CONCLUSIONS

Our prototype high pressure PEM electrolyzer forms the basis of a high-performance hydrogen generator with great commercial potential. As we continue to make improvements to our component designs, performance is improving incrementally. We have exceeded our original output pressure goal of 2,000 psig in sustained single-cell and two-cell tests. Our results indicate that our short-term goal of 3 slm hydrogen output is achievable simply by increasing the total number of cells in the module. Now that we have a proven bipolar plate design, such a multi-cell electrolyzer is within our reach. With expected improvements in cell performance, we anticipate achieving 3 slm output with a 10-cell module.

Based on electrolyzer cell efficiency, our design appears to offer a significant total energy efficiency advantage over an alkaline electrolyzer/mechanical compressor combination. This performance advantage could help to make small, decentralized hydrogen generation systems for vehicular fueling and stationary and portable fuel cell power plants economically feasible.
6. ACKNOWLEDGEMENTS

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