Proceedings of the 1999 U.S DOE Hydrogen Program Review
NREL/CP-570-26938

HIGH EFFICIENCY STEAM ELECTROLYZER

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Abstract

A novel steam electrolyzer has been developed. In conventional electrolyzers, oxygen produced from electrolysis is usually released in the air stream. In our novel design, natural gas is used to replace air in order to reduce the chemical potential difference across the electrolyzer, thus minimizing the electrical consumption. The oxygen from the electrolysis is used to partially oxidized natural gas to CO and hydrogen. CO can be subsequently shifted to yield extra hydrogen. Preliminary testing on thin film electrolyzer shown a voltage reduction as much as 1V for an equivalent electrolytic current as in conventional systems. The system efficiency with respect to primary energy can be higher than 60% while that of conventional electrolyzers is lower than 40%.

Introduction

Currently, most of the total hydrogen demand is met by hydrogen production from fossil fuels, i.e., by steam reforming of natural gas and by coal gasification. However, most of these central plants are located in remote areas. The produced hydrogen must then be delivered to the users either by trucks or by using hydrogen pipelines. Because of the inherently low energy density of hydrogen, hydrogen transportation is not a viable option. Due to the high cost of the hydrogen pipelines (about $1 million/mile), hydrogen delivery using pipelines is not cost effective either. Thus, the ideal hydrogen production for the future hydrogen economy is likely to be a distributed system where hydrogen is produced close to where it is used. Such a distributed hydrogen production using distributed small steam reforming reactors is not possible due to the very high cost of the reactors at small scales.

Hydrogen can be produced from water or steam electrolysis using much simpler technology. Due to the modularity of the electrolyzer, electrolysis can be done at a central plant as well as at a refueling station or at home. In addition, electrolysis using renewable electricity offers the possibility to produce hydrogen without any green house gas emissions. However, water electrolysis has not had significant commercial impact because it has not been possible to make it cost effective.

The main drawback of the electrolyzers is the high electricity consumption. Electricity is known to be by far the most expensive form of energy. As a result, electrolytic hydrogen is more expensive than the steam-reformed hydrogen by a factor of at least two to three (Donitz 1990). Moreover, electricity is not a primary energy but must be produced using fossil fuels, nuclear fuels or renewable energy. Considering the fact that the production of electricity has an average efficiency of less than 40% with respect to primary energy, the overall efficiency of the electrolyzer in general is low. In addition, currently, less than 20% of the overall electricity production in the United States involves renewable energy. As a consequence, electrolysis using electricity coming from the grid is not a carbon free process, but actually involves a large amount of green house gases due to the use of electricity that is mostly produced from burning coal and natural gas.

The long-term objective of this project is to develop a high efficiency steam electrolyzer for carbon free production of hydrogen. This approach will be viable only when renewable energy becomes the major source for electricity production. The short-term goal is to develop a transitional electrolyzer technology that takes into account the current situation of electricity production and the current economic infrastructure. The goal for the transitional electrolyzer technology is a distributed hydrogen production system with lower electricity consumption, higher overall efficiency and lower green house gas emissions.

Background

From the thermodynamic viewpoint of the water decomposition, it is more advantageous to electrolyze water at high temperature (800-1000°C) because the energy is supplied in mixed form of electricity and heat (Donitz 1980). In addition, the high temperature accelerates the reaction kinetics, reducing the energy loss due to electrode polarization and increasing the overall system efficiency. Typical high temperature electrolyzer such as the German HOT ELLY system achieves 92% in electrical efficiency while low temperature electrolyzers can reach at most 85% efficiency only (Donitz 1990). Despite this high efficiency with respect to electricity, the German system still produces hydrogen at about twice the cost of the steam-reformed hydrogen (Donitz 1990). According to the German analysis of the HOT ELLY system, about 80% of the total hydrogen production cost comes from the electricity cost (Donitz 1990). Therefore, to make the electrolytic hydrogen competitive versus the steam-reformed hydrogen, the electricity consumption of the electrolyzer must be reduced to at least 50% of its current value. Currently, there is no solution because the high electricity consumption is dictated by the thermodynamic of the decomposition of water.

In conventional electrolyzers, the gas supplied to the cathode side (where water is decomposed) is usually a mixture of steam and hydrogen, while the gas supplied to the anode side is usually air. At zero current, the system has an open circuit voltage of 0.8 to 0.9 V, depending on the hydrogen/steam ratio and on operating temperatures. In order to electrolyze water, a voltage that opposes and is higher than the open circuit voltage must be applied in order to pump oxygen from the steam side to the air side. Clearly, much of the electricity used, 60 to 70% of the total electrical power, is wasted forcing the electrolyzer to operate against the high chemical potential gradient for oxygen. In addition, the liberation of oxygen coming from the decomposition of water into the air stream at the anode side is clearly a waste.

Approach

In order to lower the open circuit voltage, and thus the electricity consumption, our approach is to replace air in the anode side by natural gas. The reducing character of natural gas will help to bring down the chemical potential difference between the two sides of the electrolyzer. One can distinguish two different modes of operation: total oxidation or partial oxidation of natural gas. In the first case, natural gas is used in the anode side of the electrolyzer to burn out the oxygen coming from the electrolysis, thus reducing or eliminating the potential difference across the electrolyzer membrane. The products of the reaction will be CO_2 and water. The role of natural gas is just to lower the chemical potential gradient, thus the electricity consumption. This mode replaces one unit of electrical energy by one equivalent energy unit of natural gas at one fourth the cost. Due to the thermodynamic, the total oxidation mode is restricted to temperatures lower than 700 to 800°C. Above 800°C, carbon monoxide becomes more stable and total oxidation is not possible.

In the second operation mode, an appropriate catalyst on the anode side will promote the partial oxidation of natural gas to carbon monoxide and hydrogen. The resulting gas mixture, also called syn-gas can be used in important industrial processes such as the synthesis of methanol, liquid fuels... Most important of all, CO can also be shifted to CO_2 to give additional hydrogen. In this process, hydrogen is produced at both sides of the steam electrolyzer. The overall reaction is equivalent to the steam reforming of natural gas. However, as opposed to the steam reforming reactors, the modular characteristics of the electrolyzer, together with the absence of the extensive heat exchangers, make possible the small-scale hydrogen production units.

In both cases, the key point of the approach is to use natural gas directly on the electrolyzer instead of using natural gas to make electricity at the central plant, then to use that electricity to split water. The efficiency and the carbon emissions will be lower than in conventional electrolysis. The Natural-Gas-Assisted Steam Electrolyzer or NGASE is not a carbon free hydrogen production system because it still involves natural gas. However, by combining both natural gas and electricity, which have existing infrastructures, the NGASE is an ideal transitional technology for distributed hydrogen production.

Experimental

Since the electrolyzer is essentially a fuel cell operating in reverse mode, most of the materials and the fabrication technologies that have been developed for fuel cell can be used for the electrolyzer. One of the key technologies for fuel cell manufacturing is the thin film processing technique. Thin film is critical to the electrolyzer performance because it lowers the resistive loss in the electrolyte material. Although a number of techniques are available, most of them are not appropriate for fuel cell and electrolyzer applications. For instance, physical vapor deposition techniques can yield good dense films but are too expensive. Although much cheaper, tape casting and tape calendering techniques cannot be used to deposit thin films on tubular substrates. Recently, we have developed a proprietary low cost thin film deposition technique that can be used for both planar and tubular substrates (Pham 1999). The technique is an improved version of the well known colloidal deposition. This technique is used to deposit thin film electrolytes for the present electrolyzer.

A mixture of NiO/yttria-stabilized-zirconia (YSZ) powder was prepared. The powder was pressed into pellets and partially sintered at 1000°C. The thin film YSZ electrolyte was subsequently deposited on the NiO/YSZ disks using our novel thin film deposition technique. The substrate and the film were co-sintered at 1400°C for 2 hours. Two different types of cells were prepared: for conventional electrolyzer cell, platinum paste was painted on top of the thin film electrolyte and annealed at 900°C. For NGASE cell, another thin film of NiO/YSZ layer was subsequently deposited on the sintered YSZ film. The complete cell was annealed at 1200°C for 2 hours. The cell was then sealed to an alumina tube using a gold O ring. The tube with the sample was put in a quartz tube and the whole system was put in a tube furnace. The cell was brought to 900°C. Then hydrogen was flown on both sides of the cell in order to reduce nickel oxide to nickel metal. The thin film Ni/YSZ side was then exposed to a hydrogen, nitrogen and steam mixture while the substrate side was exposed to methane with 3% steam. Steam was introduced to the system by passing hydrogen in a heated gas bubler filled with water. The steam concentration was varied by controlling the bubler temperature. The current-voltage characteristics of the cell was determined using a Solartron potentiostat model 1287. The outlet gas from both sides was analyzed using a Shimadzu gas chromatograph.

Results and Discussion

Thin Film Electrolyzer Cell

Fig. 1 shows a scanning electron microscopy picture of the thin film electrolyzer cell. The Ni/YSZ substrate, which also served as the anode, is clearly porous, with pore size typically less than a few microns. The porosity is necessary for the gas to access the reaction zone located at the interface between the electrolyte and the electrode. The thin film electrolyte is fully dense and has no crack. The electrolyte film thickness was 20 μm. The cathode, also made of Ni/YSZ, was 18 μm thick. As opposed to conventional electrolyzers and fuel cells, the NGASE has a symmetrical electrode configuration. This alleviates significantly the problems associated with materials incompatibility and thermal expansion mismatch.

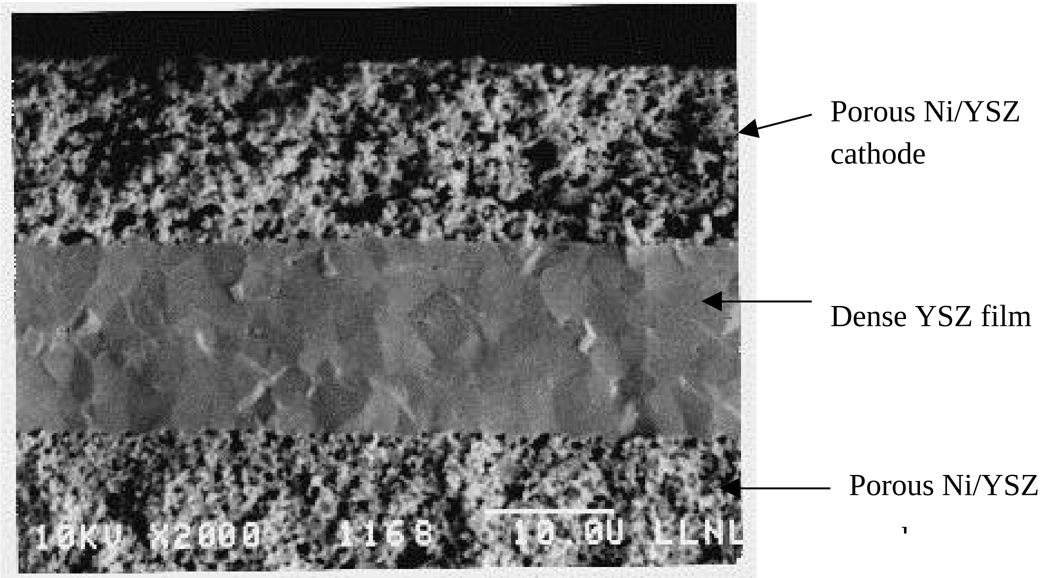

Figure 1: Scanning electron microscopy picture of a cross-section of the NGASE thin film cell.

Performance Characteristics of NGASE

Fig. 2 shows the current-voltage curves of the conventional electrolyzer and NGASE cells. For comparison purpose, the curve corresponding to the German HOT ELLY electrolyzer was reproduced (Donitz 1990). The open-circuit voltage of the HOT ELLY electrolyzer is 0.8V at 1000°C. A similar open-circuit voltage was observed for our conventional cell. However, for a same current, and despite a lower operating temperature, 900°C, our conventional cell exhibits a slightly smaller voltage than that of the HOT ELLY, indicating a lower electrical consumption. This is due to the reduction of the resistive lost in the electrolyte, due to the use of thin films.

When air is replaced with methane as in the NGASE cell, the open-circuit voltage (emf) drops from + 0.8 V to – 0.24 V. The presence of methane clearly induces a large voltage reduction. The open-circuit voltage becomes even negative, indicating that the methane side becomes more reducing than the steam/hydrogen side. If dry methane is used, no stable emf was observed. The presence of a small amount of steam (3% in this case) was thus critical to maintain the reducing atmosphere in the methane side. Indeed, in wet gas, and in the presence of the Ni/YSZ catalyst, a small fraction of methane undergoes the steam reforming reaction to yield H_2 and CO. In dry gas, the steam reforming reaction is impossible; methane behaves like an inert gas.

When a current flows through the NGASE cell, in the negative voltage region, the cell is actually a fuel cell that generates both electricity and hydrogen. When the voltage becomes positive, the cell operates in the electrolysis mode, meaning that electricity must be supplied to the system to generate chemicals. In all regions, the NGASE voltage is lower by 1 V or more compared to the conventional cell that is operated in similar conditions. The use of natural gas to reduce the electrical consumption in the electrolyzer is clearly demonstrated.

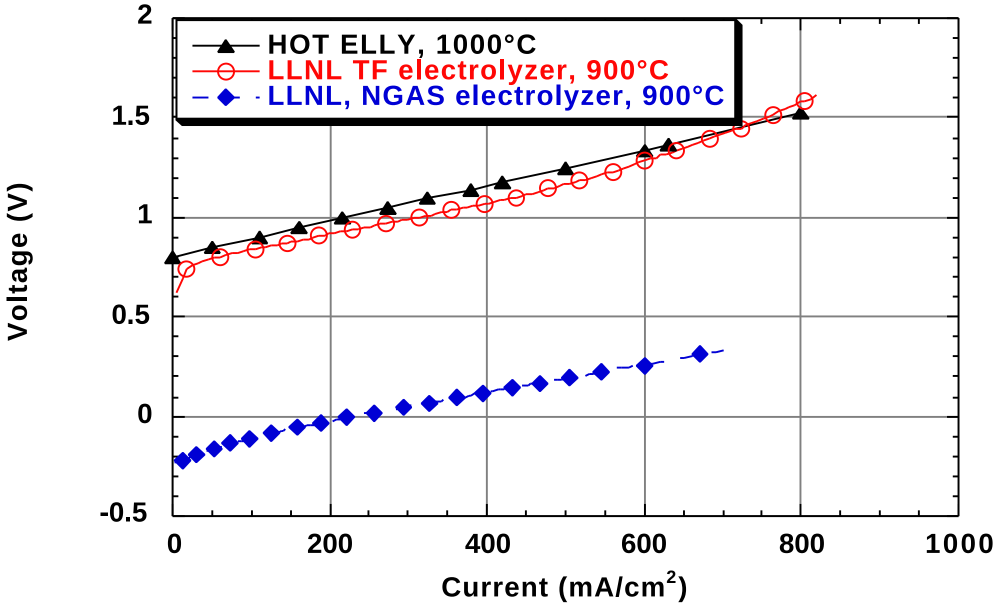

Figure 2: Current-voltage plots of conventional electrolyzer and NGASE. The cathode inlet gas was H_2 (3%) + H_2O (70%) + N_2 (balance). The anode inlet gas was CH_4 (97%) + H_2O (3%).

Gas chromatography analysis showed an electrical current efficiency for hydrogen generation in the steam side approaching 99%. This is a well-known characteristics of solid oxide electrolyzers. Attempts to analyze the gas composition on the methane side has not been successful because the test cell was too small and thus the amount of methane converted in the reaction was too small compared to the methane gas inlet. Experiments using larger cells are in progress.

In actual electrolyzer stack, the fuel composition as well as the steam composition are not constant due to fuel and steam consumptions respectively. The fuel and/or steam depletion can significantly reduced the electrolyzer performance, i.e. gas depletion will increase the electrical energy demand while less hydrogen will be produced. Fig. 3 shows two plots corresponding to two different fuel compositions in the methane side of the electrolyzer. The gas composition in the cathode side was kept constant. Clearly, decreasing the methane concentration reduces the open-circuit voltage (in absolute value). Most important of all, for lower methane concentration, a higher voltage is necessary to yield a same electrolytic current. The plot even shows a saturation at about 300 mA, meaning that beyond 300 mA, forcing a higher current through the electrolyzer requires a large increase in the applied voltage. The actual electrolyzer stack must avoid operating in this region.

Fig. 4 shows the I-V plots corresponding to different steam compositions. The fuel composition in the anode side was kept constant. Just as for the fuel composition effect, decreasing the steam concentration in the cathode side decreases the open-circuit voltage (in absolute value) and increases the voltage required for a constant electrolytic current.

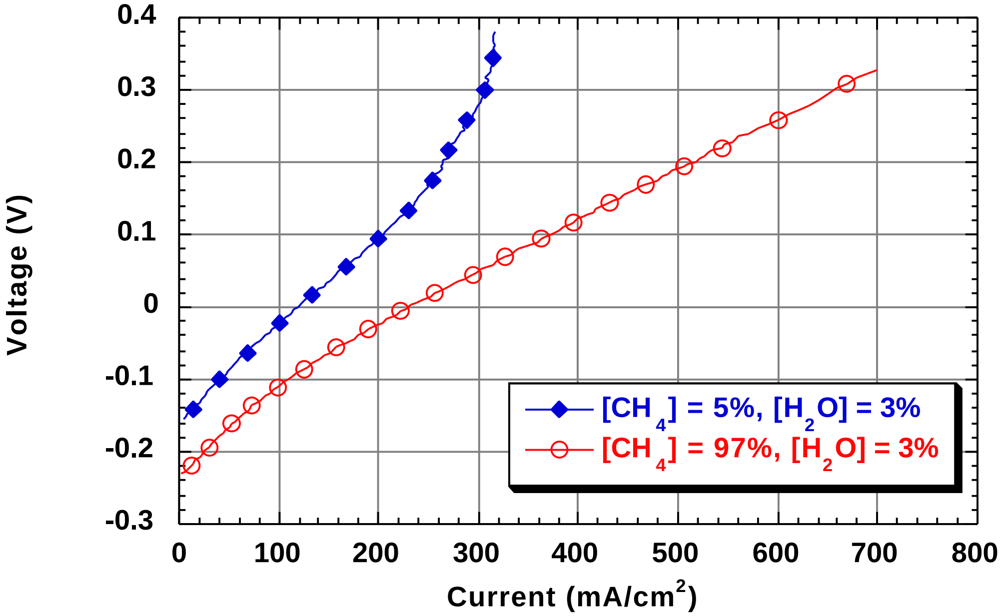

Figure 3: Current-voltage plots of NGASE cell for different fuel compositions. The cathode inlet gas was H_2 (3%) + H_2O (70%) + N_2 (balance).

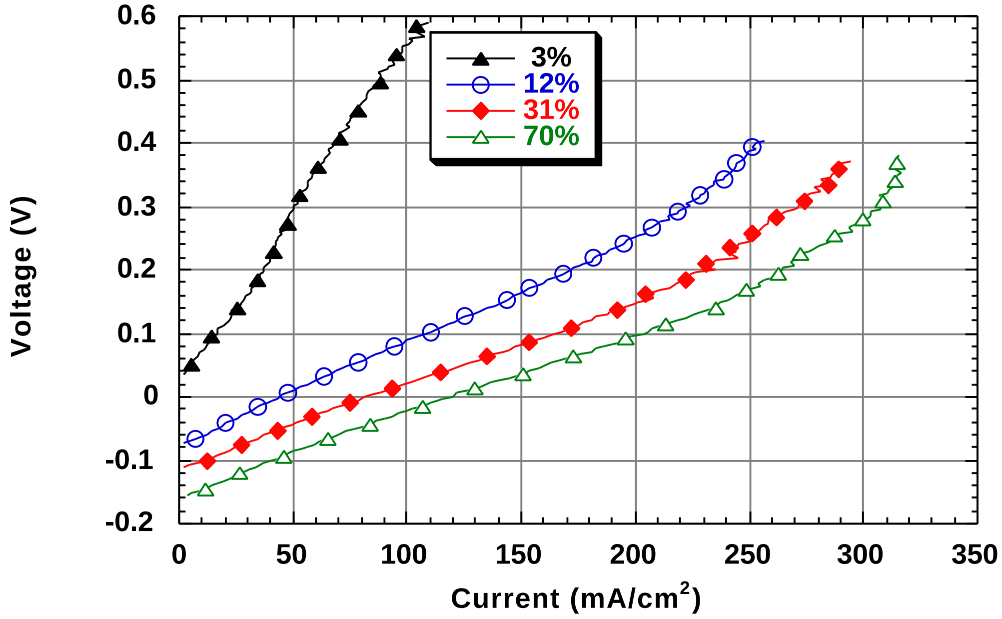

Figure 4: Current-voltage plots of NGASE cell for different steam compositions. The anode inlet gas was CH_4 (5%) + H_2O (3%) + N_2 (balance).

Development of a New Water Splitting Catalyst

Ni/YSZ is currently used as water splitting catalyst as well as partial oxidation catalyst of natural gas. In order to increase the electrolyzer performance, we are developing new catalyst materials for both cathode and anode sides. One of the materials evaluated has shown promising performance (patent application in progress). Fig. 5 shows the current-overpotential curves of Pt electrode alone and Pt electrode with a catalytic interfacial layer on a conventional electrolyzer cell (anode is exposed to air). In the presence of the interfacial layer, a clear voltage reduction is observed for a same electrolytic current. The voltage reduction can be as large as 0.4 V for high enough electrolytic current. More characterization is in progress.

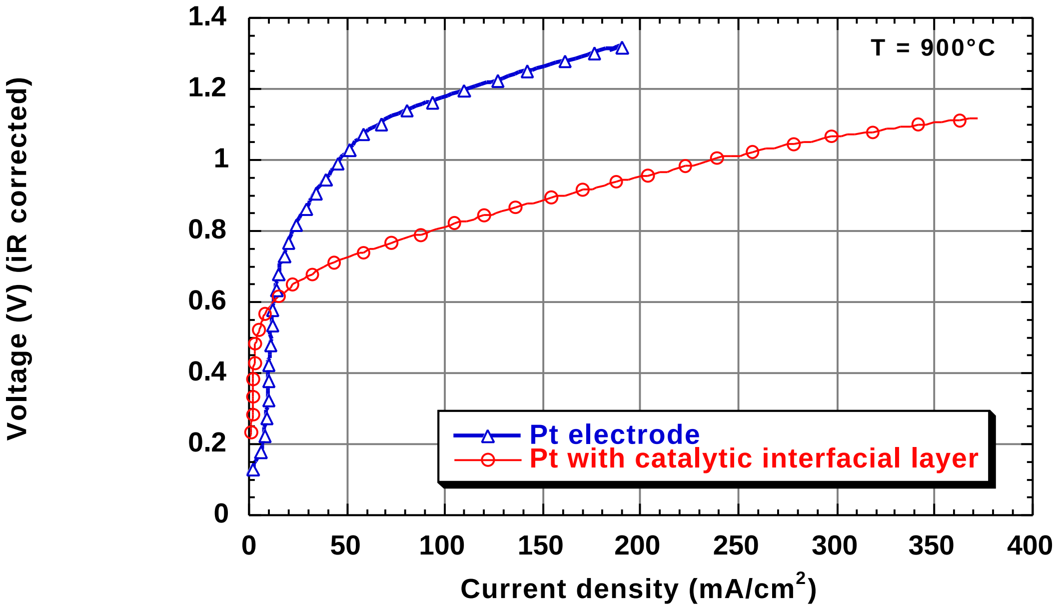

Figure 5: Current-voltage plots showing the effect of the interfacial catalytic layer. The cathode inlet gas was H_2O (31%) + N_2 (balance). The anode inlet gas was air.

Preliminary System Analysis

The above data were obtained for small size cells and the information on the gas composition in the methane side has not been well determined. Therefore, a precise system analysis is not possible at this point. However, assuming some hypotheses, it is possible to have a rough idea of the system efficiency.

From the HOT ELLY data, the production of 1 kWh of hydrogen requires 0.2 kWh energy for converting water to steam and 1.07 kWh electricity for electrolysis (at a current density of 0.5 A/cm^2). From the I-V curve of the NGASE, it can be calculated that a same amount of hydrogen would require only 0.12 kWh electricity and 1.3 kWh of methane (assuming total oxidation at

80% fuel conversion). The electricity consumption of the NGASE is thus reduced by one order of magnitude compared to conventional electrolyzers. The majority of the energy required is supplied by natural gas, which is much cheaper than electricity.

The HOT ELLY electrolyzer had an electrical efficiency of 92%. However, assuming an efficiency of 38% for the electricity generation, the overall efficiency drops to 39.3% (Donitz 1990). In contrast, the NGASE efficiency is as high as 62%, assuming a total oxidation mode. More detailed analysis will be reported in the future.

Future Work

Our plan is to further characterize the NGASE using large size cells. In addition, we will continue the development of the different catalysts for improved electrolyzer performance. We will do engineering calculations in order to determine the best stack design and to identify the most efficient and the most interesting mode of operation. Then, we will build a 100 W followed by a 1 kW prototype units. Ultimately, we will consider pressurized systems for better efficiency. The Institute of Gas Technology will be our partner in the stack development effort.

Conclusion

We have demonstrated the feasibility of the Natural-Assisted Steam Electrolyzer concept. The use of natural gas to partially replace the more expensive electricity has been shown to lower the electricity consumption by as much as one order of magnitude. In the partial oxidation mode, hydrogen is generated on both side of the electrolyzer making the system highly efficient. In this mode, the NGASE yields similar products as the steam reforming reactor with the advantage of the modular characteristic of the fuel cell.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

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Figure Captions

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