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A natural gas-assisted steam electrolyzer for high-efficiency production of hydrogen

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Abstract

This paper presents a description and analysis of a novel, high-efficiency, solid oxide natural gas-assisted steam electrolyzer (NGASE). In conventional solid oxide electrolyzers, most of the electric power is used in forcing the oxygen to diffuse through the electrolyzer, against a high chemical potential. In the NGASE, natural gas is reacted with the oxygen produced in the electrolysis, reducing the chemical potential across the electrolyzer, thus minimizing electricity consumption. The oxygen produced in the electrolysis is consumed in either a total oxidation or a partial oxidation reaction with natural gas. Experiments performed on single cells show a voltage reduction of as much as 1 V when compared to conventional steam electrolyzers. Analysis indicates that incorporating the electrolyzer with a heat recovery system (heat exchangers and catalytic reactor) results in a high-efficiency hydrogen production system. The system efficiency is up to 70% with respect to primary energy. © 2002 Published by Elsevier Science Ltd on behalf of the International Association for Hydrogen Energy.

1. Introduction

Hydrogen is one of the leading candidates in the search for an alternative to fossil hydrocarbon fuels. Hydrogen can be made from a diverse range of sources, reducing the economical, political, and environmental costs of energy systems. In the long term, hydrogen from renewable sources offers the potential of sustainable energy infrastructure.

Hydrogen is an energy carrier like electricity and can be produced from a wide variety of energy sources, such as natural gas, coal, biomass, solar (thermal and photovoltaic), wind, hydroelectric, as well as sewage, municipal solid waste, tires, and discarded oil [1,2]. The US market for hydrogen is currently more than 0.7×10^{18} J/yr (equivalent in energy to 115 million barrels of oil), with 60% being used in the production of ammonia. In addition, a comparable amount is produced and used in petroleum refineries [3].

Hydrogen has the highest energy content by weight of any fuel and will quickly disperse if accidentally spilled or released. It also allows combustion at high compression

ratios and efficiencies in internal combustion engines [4]. When combined with oxygen in electrochemical fuels, hydrogen can produce electricity directly, bypassing the Carnot cycle efficiency limits of today's power plants and internal combustion engine generators.

Hydrogen offers a number of features that make it a serious candidate as a 21st century vehicular fuel. However, hydrogen vehicles will not be used in significant numbers until there is a reliable hydrogen supply infrastructure. An important part of this infrastructure is the development of more efficient hydrogen production systems. Presently, almost all the hydrogen demand is met by hydrogen made in steam reforming of natural gas. Another option is production of hydrogen by water electrolysis. However, this is expensive due to the high consumption of electricity.

Conventional, low-temperature electrolyzers have about 75% efficiency with respect to electrical energy input [5]. Typical efficiencies for thermal power plants, which generate most of the electricity in the US, are in the range of 35–40%. The total thermal efficiency of hydrogen production is therefore in the range of 26–30% [5]. This efficiency will grow in the future, but it is unlikely to reach very much above 40% [5].

Hydrogen production by high-temperature electrolysis of water vapor using solid-oxide electrolyte cells has been

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Nomenclature

| | |
|--------------------------|--|
| H | absolute enthalpy (includes enthalpy of formation) |
| m | mass |
| E_{elec} | electrical energy |
| ε_{p} | preheater effectiveness |
| ε_{c} | condenser effectiveness |
| ε | heat exchanger effectiveness |
| η | efficiency |
| η_{elec} | efficiency of electricity generation |
| T | temperature, K |
| LHV | lower heating value |

Subscripts

| | |
|-----------------|----------|
| CH ₄ | methane |
| H ₂ | hydrogen |

demonstrated to be a very efficient method, with an overall efficiency of 39–44% for 38% efficiency of electrical energy generation [6–9]. Overall efficiency is higher than the efficiency of power generation because fuel is used directly to generate steam at the operating temperature, therefore reducing the electricity consumption. Doenitz et al. [9] predict a maximum efficiency of hydrogen production of over 50% by using this technology.

The main drawback of electrolyzers is their high electricity consumption. Electricity is an expensive form of energy. As a result, electrolytic hydrogen is more expensive than steam-reformed hydrogen by a factor of at least two to three [9]. 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 is low. In addition, less than 30% of the overall electricity production in the United States involves renewable or nuclear energy. As a consequence, electrolysis using electricity coming from the grid is not a carbon-free process, but actually involves a large amount of greenhouse gases due to the use of electricity that is mostly produced from burning coal or natural gas.

The long-term objective of this project is to develop a high-efficiency steam electrolyzer for carbon-free production of hydrogen. However, this can only be accomplished when renewable and nuclear energies become the major sources of electricity production. In the meantime, the goal is to develop a transitional electrolyzer technology that operates efficiently and economically under current conditions, considering that most electricity is generated from fossil fuels. The goal for the transitional electrolyzer technology is a distributed, modular, hydrogen production system with lower electricity consumption, higher overall efficiency and lower greenhouse gas emissions.

2. The natural gas-assisted steam electrolyzer (ngase)

Water is best electrolyzed at high temperatures (700–1000°C) where the chemical potential necessary to separate the water into hydrogen and oxygen is lower. In addition to this, the high temperature accelerates the reaction kinetics, reducing the energy loss due to electrode polarization and increasing the overall system efficiency. In addition, the steam can be preheated by heat recovery or by fuel burning [9].

The HOT ELLY system is an example of a high-efficiency, high-temperature electrolyzer. However, despite its high-efficiency with respect to electricity, the HOT ELLY still produces hydrogen at about twice the cost of steam-reformed hydrogen [9]. According to the analysis of the HOT ELLY system, about 80% of the total hydrogen production cost comes from the electricity cost [9]. Therefore, to make electrolytic hydrogen competitive with steam-reformed hydrogen, the electricity consumption of the electrolyzer must be reduced. Currently, there is no solution because the high electricity consumption is dictated by the thermodynamics of water decomposition.

In conventional solid oxide steam electrolyzers, the gas that circulates in the cathode side (where water is decomposed) is usually a mixture of steam and hydrogen, while the gas circulating in the anode side is oxygen. At zero current, the system has an open-circuit voltage of 0.8–0.9 V, depending on the hydrogen/steam ratio and on operating temperatures. In order to electrolyze water, a voltage higher than the open-circuit voltage must be applied in order to pump oxygen from the steam side to the oxygen side. Clearly, much of the electricity used, 60–70% of the total electric power, is used in forcing the electrolyzer to operate against the high chemical potential gradient for oxygen.

In order to lower the open-circuit voltage, and thus the electricity consumption, natural gas can be circulated in the anode [11]. The reducing character of natural gas helps to bring down the chemical potential difference between the two sides of the electrolyzer. There are two different modes of operation: partial oxidation or total oxidation of natural gas. In the partial oxidation mode, an appropriate catalyst on the anode side promotes the partial oxidation of natural gas to carbon monoxide and hydrogen. The resulting gas mixture, commonly called syn-gas, can be used in important industrial processes such as the synthesis of methanol, liquid fuels, etc. Most importantly, CO can also be shifted to CO₂ to yield 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. As opposed to steam reforming reactors, the modular characteristics of the electrolyzer, along with the absence of the extensive heat exchangers, makes it possible to build small-scale hydrogen production units.

In the total oxidation mode, natural gas is used in the anode side of the electrolyzer to burn out the oxygen generated in the electrolysis, thus reducing or eliminating the

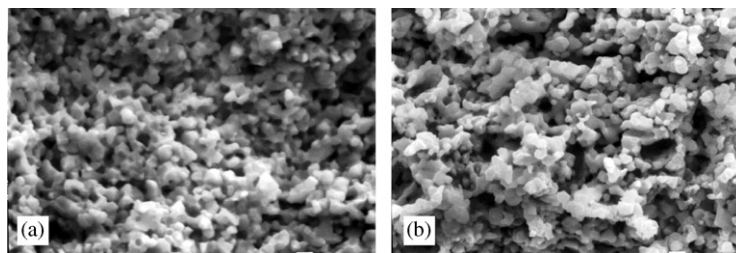


Fig. 1. Scanning electron microscope (SEM) pictures of: (a) 1999 anode with low porosity; (b) 2000 anode with optimized porosity.

potential difference across the electrolyzer membrane, reducing the electricity consumption. The products of the reaction are CO_2 and steam. This mode replaces one unit of electrical energy by one equivalent energy unit of natural gas at one-fourth the cost. For thermodynamic reasons, the total oxidation mode is restricted to temperatures up to 700°C . Above 800°C , carbon monoxide becomes more stable and total oxidation is not possible. We have chosen to focus our effort on the total oxidation mode because it is simpler and does not require any additional water shift or CO clean-up units.

In both cases, the key point of the approach is to use natural gas directly in the electrolyzer instead of using natural gas to make electricity at the central plant and then use that electricity to split water. The efficiency and the carbon emissions are lower than in conventional electrolysis. The 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.

2.1. Design of the NGASE electrodes

Early characterization has shown that the anode performance is mainly diffusion-limited. Therefore, improving the anode porosity should improve the gas phase diffusion and thus the anode performance. Various pore former materials, including carbon, polymers and starches have been tested. The optimum pore former amount has also been identified. Figs. 1a and b show the scanning electron microscopy (SEM) pictures of the cross-sectional view of the anode materials without (1999 cell design) and with pore former (2000 cell design), respectively. The black dots correspond to the pores. Clearly, the sample in Fig. 1b is significantly more porous than the sample in Fig. 1a. The pores introduced are homogeneous and uniformly distributed in the matrix of the anode. Fig. 2 shows the performance of the new cells with optimum porosity. The I - V curve of the HOT ELLY steam electrolyzer [9] as well as that of a previous design is reproduced for comparison. The performance of the 1999 NGASE cell is similar to that of the HOT ELLY as indicated by the same slope. However, the voltage is about 1 V lower due to the use of methane depolarizer. The 2000 NGASE cell

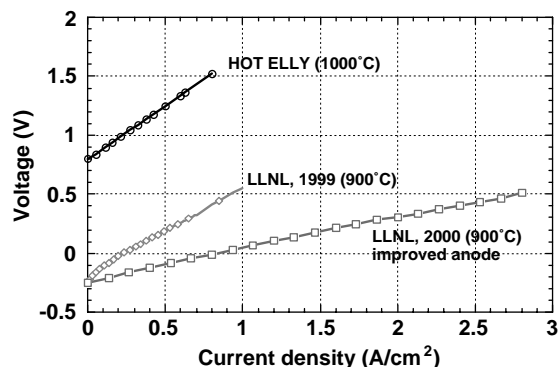


Fig. 2. Current–voltage characteristics of various steam electrolyzer cells.

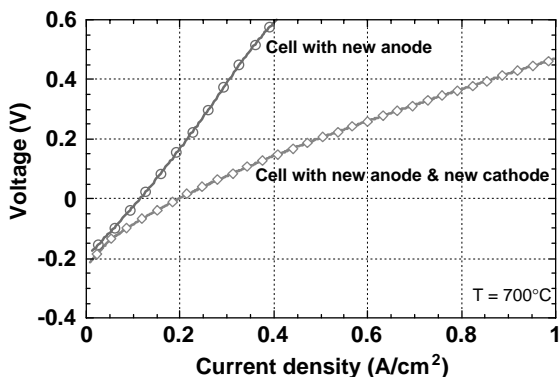


Fig. 3. Current–voltage characteristics at 700°C of two LLNL steam electrolyzer cells.

with optimum anode porosity outperforms the other cells. At only 0.5 V, the electrolytic current is as high as 2.8 A/cm^2 , compared to 1 A/cm^2 for the 1999 cell. The introduction of pore former has thus improved the electrolytic current by almost a factor of three. This is probably the highest electrolytic current per unit area ever reported to date.

The problem with operating at 900°C is that it is necessary to introduce steam in the methane side in order to avoid carbon deposition. The presence of steam can cause excessive steam reforming of methane, which is undesirable because the reaction is highly endothermic. Thus, it is

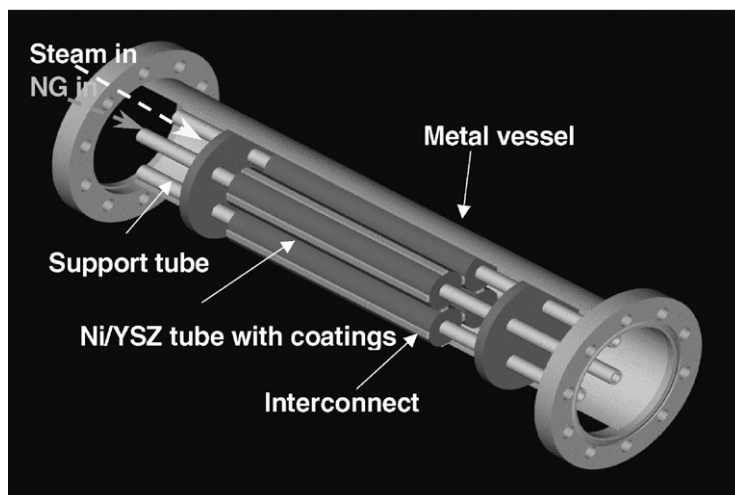


Fig. 4. Drawing of a four-tube electrolyzer stack.

highly desirable to reduce the operating temperature to minimize the amount of steam and also to favor the total oxidation of methane. Fig. 3 shows the I - V plot of the new cell with improved anode at 700°C. The performance at 700°C is significantly lower than at 900°C. The electrolytic current at 0.5 V is down from 2.8 A/cm² at 900°C to 0.35 A/cm² at 700°C. This poor performance was identified as due essentially to the cathode. The cathode material Nickel/yttrium stabilized zirconia (Ni/YSZ) was then replaced with a better electrode/catalyst. The I - V curve of the cell with both improved anode and cathode is also shown in Fig. 3. At 0.5 V, the current increases to 1 A/cm², about three times the current of the cell with the old cathode. Overall, the development of the improved cathode and anode has allowed reducing the operating temperature from 900°C to 700°C while preserving excellent cell performance. The main advantage is that carbon deposition is suppressed even with steam concentration as low as 10%.

2.2. Design of the electrolyzer stacks

Most of the current uses of hydrogen require hydrogen under some pressure. Thus the cost analysis of various hydrogen production methods must take into account the need to pressurize hydrogen. If hydrogen is produced at low pressure and a hydrogen compressor is used for pressurization, then the overall production cost could be high due to the high cost, high maintenance and low reliability of hydrogen compressors.

As mentioned above, pure electrolysis is not attractive for hydrogen production due to the high electricity consumption. However, electrochemical devices are known to be the most efficient devices for the pressurization of hydrogen. One of the most attractive features is that electrochemical compressors only require an extra ~ 100 mV to pressurize

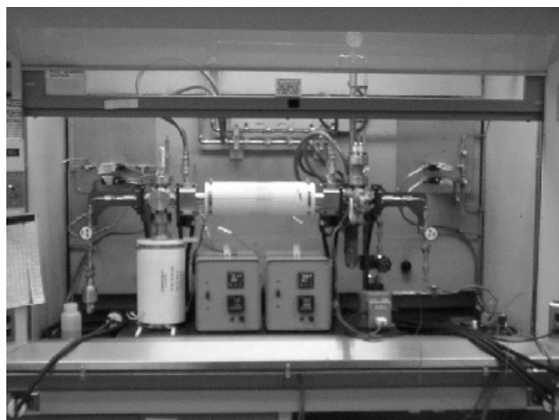


Fig. 5. Bench-scale reactor for a 100 W electrolyzer stack.

hydrogen from ambient pressure to 34.5 MPa (5000 psi). Therefore, the design of the electrolyzer stack must take advantage of the possibility to pressurize hydrogen in situ.

Since the electrolyzer is basically a fuel cell operating in reverse mode, the various stack designs developed for fuel cells can be considered for use for the electrolyzer. There are two major stack designs: tubular or planar configurations. The planar configuration can be made compact and is potentially cheaper than the tubular design. However, planar stacks are much more difficult to pressurize because they are more subject to mechanical fractures due to differences in pressure between the sides. For this reason, we chose to pursue the tubular configuration since this design allows pressurizing the exterior compartment while having ambient pressure inside the tubes. Fig. 4 shows a drawing of the

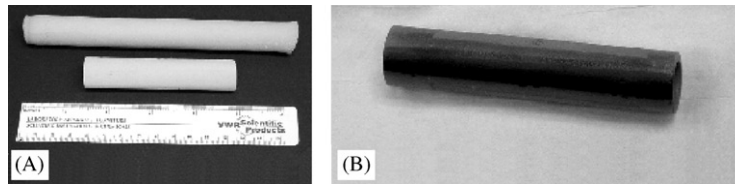


Fig. 6. Electrolyzer tubes: (a) green tube after cold isostatic pressing; (b) after completion.

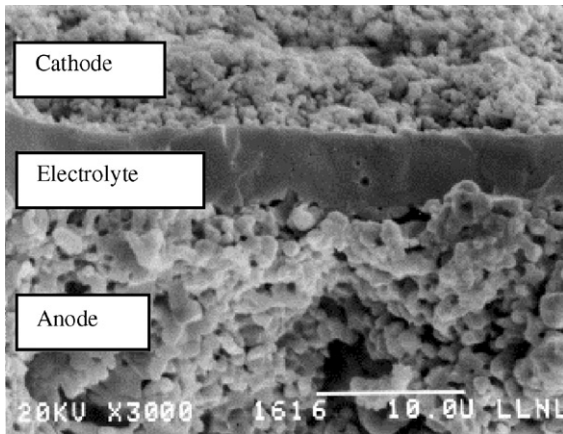


Fig. 7. Scanning electron microscope (SEM) cross-sectional view of an electrolyzer tube.

tubular electrolyzer stack with four tubes. The electrolyzer stack is located inside a metal vessel that can withstand high pressures. Natural gas flows inside the tubes at ambient pressure while the outside compartment is exposed to steam/hydrogen mixture at high pressure. Fig. 5 shows the experimental reactor where the electrolyzer stack is being tested. Although the short-term objective is for hydrogen production at ambient pressure only, the system was designed for operation up to 1 MPa (150 psi) for future research.

2.3. Tube fabrication process

A complete tube fabrication process has been developed. Nickel oxide/yttrium stabilized zirconia (NiO/YSZ) anode support tubes were made by cold isostatic pressing or by extrusion. The green tube was masked, and an interconnect thin film was deposited in the form of a thin stripe along the tube. YSZ electrolyte thin film was then coated on the tubes, followed by sintering at high temperature [10]. The thin film cathode was subsequently deposited. All thin films were processed using colloidal spray deposition, a low-cost thin film deposition technique that we have recently developed [11]. Figs. 6a and b show the tube after cold isostatic pressing and after completion, respectively. An SEM cross-sectional view of the electrolyzer tube is shown in

Fig. 7. The performance of the individual tubes is currently being evaluated.

3. Integration of the electrolyzer with a heat recovery system

Previous sections have described the materials development and electrolyzer testing that are being conducted as a part of this project. In addition to these activities, a thermodynamic analysis has been conducted to find the configuration of a heat recovery system that can be incorporated into the electrolyzer to produce a high-efficiency hydrogen generation system. This section describes the analysis of a conceptual design of an electrolyzer and heat recovery system. The analysis is focused on finding system thermodynamic efficiencies.

Fig. 8 shows the schematic of the conceptual design of the electrolyzer and heat recovery system for hydrogen production. First, methane flows through a heat exchanger where it is heated to 700°C (the electrolyzer temperature) by recovering energy from the exhaust stream. This hot methane then enters the anode section of the electrolyzer. This analysis assumes that between 70% and 90% of the methane is oxidized in the electrolyzer with the oxygen generated from the electrolysis in the cathode side. A catalytic reactor is therefore incorporated into the system to take advantage of the energy of combustion of the remaining methane. The exhaust anode gases (CO₂, steam, and methane, point 3, Fig. 8), enter the catalytic reactor to burn the remaining methane. The air necessary to burn the methane in the catalytic reactor is heated in the preheater by using the thermal energy of the exhaust gas. The catalytic reactor exhaust is a hot mixture of CO₂, steam and nitrogen (point 4, Fig. 8). This mixture heats up the electrolyzer feed water through a heat exchanger. The exhaust gases are then circulated through two more heat exchangers where they are used for heating the methane fuel and the air fed into the catalytic reactor. The mixture of hydrogen and steam produced in the electrolyzer (point 14, Fig. 8) is passed through a condenser to separate steam and hydrogen. The cooling water used in the condenser is then circulated through the electrolyzer to remove the thermal energy generated by methane combustion. The water leaves the electrolyzer as high-temperature

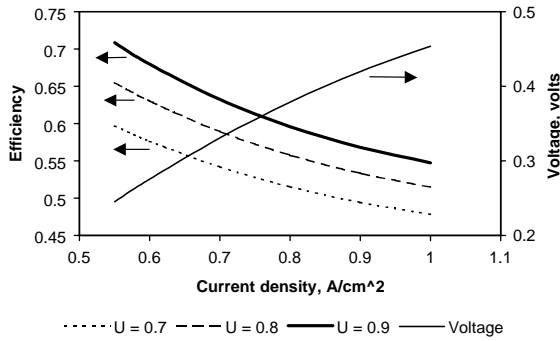


Fig. 9. Efficiency (with respect to primary energy consumption, Eq. (7)) of the hydrogen production system for three values of methane utilization (0.7, 0.8 and 0.9) as a function of current density in the electrolyzer. The figure also shows operating voltage of the electrolyzer as a function of current density.

The system of equations (1)–(8) is solved with an iterative equation solver by using computer-based tables of properties for all the substances involved (water, oxygen, nitrogen, methane and hydrogen). Table 1 shows the values of the system parameters used in the analysis.

3.1. Results

Fig. 9 shows the efficiency of the NGASE system with respect to primary energy consumption (Eq. (7)), as a function of current density in the electrolyzer, assuming 40% efficiency for electricity generation. The figure also shows the voltage across the electrolyzer as a function of current density. Fig. 9 shows that, as the current density is decreased, the voltage in the electrolyzer drops. This reduces the electricity consumption and increases the efficiency of the system. This gain in efficiency is obtained at the expense of reducing the rate of production of hydrogen in the system. A bigger, more expensive electrolyzer can generate hydrogen at a higher efficiency with less methane consumption by reducing the electrolyzer loading. An optimum current may be determined from economics, by balancing the cost of fuel and electricity consumed with the capital cost of the electrolyzer.

Fig. 9 shows system efficiency for three fractions of methane utilization: 0.7, 0.8, and 0.9. $U = 0.8$ indicates that 80% of the methane that enters the electrolyzer is oxidized inside the electrolyzer and the remaining is oxidized in the catalytic reactor. The figure shows that the system efficiency increases as methane utilization increases. Clearly, it is more efficient to use the methane directly in the electrolyzer rather than burning it in the catalytic reactor to preheat air. However, a practical limit of the methane utilization in the electrolyzer may be 90%.

Fig. 10 shows the efficiency of the system with respect to total energy consumption (Eq. (8)). The efficiency shown in Fig. 10 is much higher than in Fig. 9, because Fig. 10

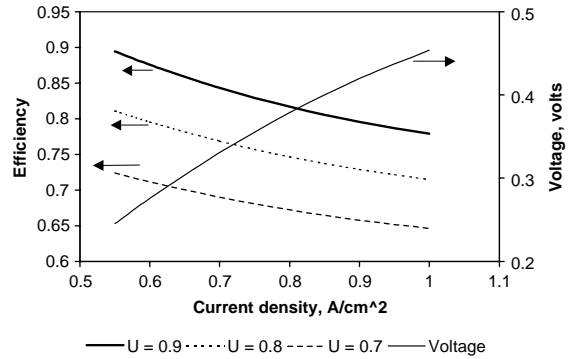


Fig. 10. Efficiency (with respect to total energy into the electrolyzer, Eq. (8)) of the hydrogen production system for three values of methane utilization (0.7, 0.8 and 0.9) as a function of the current density in the electrolyzer. The figure also shows operating voltage as a function of current density.

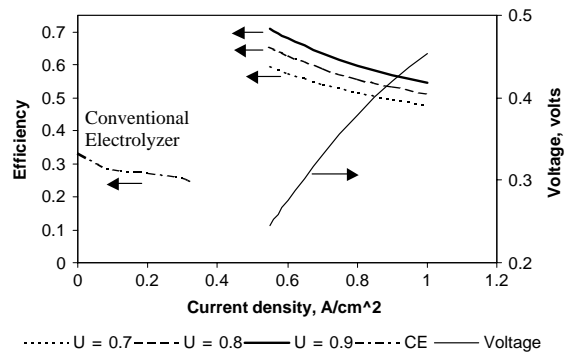


Fig. 11. Efficiency (with respect to primary energy consumption, Eq. (7)) of the hydrogen production system for three values of methane utilization (0.7, 0.8 and 0.9) as a function of current density in the electrolyzer and conventional low-temperature electrolyzer efficiency [6].

does not take into account the energy lost in the electric power plant. The efficiency in Fig. 10 increases as the current density is reduced, although the slope of the lines is smaller than in Fig. 9. This is again because energy losses in the power plant are not considered. Fig. 10 also shows system efficiency for three fractions of methane utilization: 0.7, 0.8, and 0.9. Again, the efficiency increases as methane utilization in the system increases.

Fig. 11 shows the efficiency based on primary energy consumption (Eq. (7)) of the NGASE electrolyzer (repeated from Fig. 9) and a conventional low-temperature electrolyzer [6] as a function of current density. The NGASE electrolyzer has a much higher efficiency and current density than the conventional low-temperature electrolyzer. The maximum efficiency of the conventional electrolyzer is only 32%. Maximum efficiency for the NGASE is 70%.

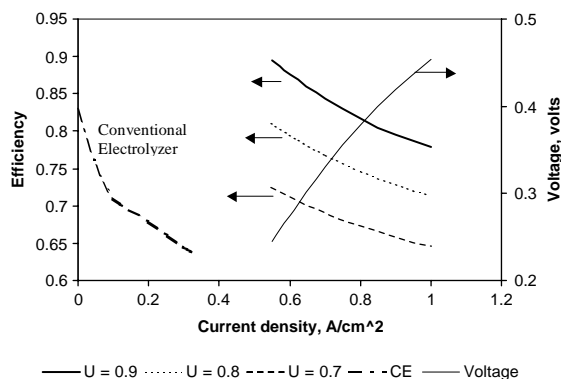


Fig. 12. Efficiency (with respect to total energy into the electrolyzer, Eq. (8)) of the hydrogen production system for three values of methane utilization (0.7, 0.8 and 0.9) as a function of the current density in the electrolyzer and conventional low-temperature electrolyzer efficiency [6].

Fig. 12 shows the efficiency based on total energy consumption (Eq. (8)) of the NGASE electrolyzer (repeated from Fig. 10) and a conventional low-temperature electrolyzer [6] as a function of current density. In this case, the efficiency of the conventional electrolyzer is comparable to the efficiency of the NGASE, because the efficiency calculation does not include losses at the electricity power plant.

4. Conclusions

This paper presents a description and analysis of a novel, high-efficiency, solid oxide natural gas-assisted steam electrolyzer (NGASE). In the NGASE, natural gas is reacted with the oxygen produced in the electrolysis, reducing the chemical potential across the electrolyzer, thus minimizing electricity consumption. Experiments performed on single cells show a voltage reduction of as much as 1 V when compared to conventional electrolyzers. In addition to this, the current density is very high, even at relatively low temperature (700 K).

A conceptual design of a heat recovery system has been analyzed. The heat recovery system includes heat exchangers and a catalytic reactor, which are incorporated into the electrolyzer. The thermodynamic analysis shows that the system can reach up to 70% efficiency based on primary energy, or up to 90% efficiency based on total energy input into the electrolyzer. Efficiency is observed to increase as the fraction of methane utilization in the electrolyzer is increased. The efficiency also increases as the current

density in the electrolyzer is decreased. Conventional low-temperature electrolyzers have a maximum efficiency of 83% with respect to electrical energy input, and 32% with respect to primary energy.

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