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Developments in Renewable Hydrogen Electrolysis by Supercritical Geothermal Cogeneration

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ABSTRACT

Geothermal energy is growing in importance because its power is needed to balance the intermittent sources of energy, primarily wind and solar, and to produce non-polluting hydrogen to replace the fossil fuels that are burned to enable transportation and many other necessary uses of energy, such as responding to emergencies and ending climate change. The current methods of producing geothermal are not adequate in producing energy to resolve the foregoing issues. Supercritical geothermal resources can provide energy in large quantities. Unfortunately, new technologies and materials are needed to reach that stage, including the performance of electrolysis at temperatures in the range of 600 to 800°C. The current technology for geothermal energy is usually very reliable, with 94% availability. Unfortunately, such supercritical electrolysis is occasionally stopped by "breakaway" oxidation. Advances in techniques and materials are being introduced to supercritical geothermal technology that can prevent "breakaway" oxidation in supercritical geothermal and achieve a new availability of energy.

1. Introduction

The burning of coal to generate electricity was the primary cause of greenhouse gas emissions for many years. Following the Paris Accords of 2015 regarding climate change, however, a number of countries around the world and several states in the United States have reduced their reliance on the combustion of coal to generate electricity. In fact, the market for coal has fallen so much that a number of coal mining companies have filed for bankruptcy. California, for example, has changed its rules so that, within the next few years, the burning of coal to generate electricity for California is scheduled to stop. The curtailment of coal burning to generate electricity has been met in part by the adoption of wind and solar power, but those resources are both intermittent. These changes have resulted in a significant reduction in the creation of greenhouse gas in California. The reduction in combustion of coal over the years has largely caused the electric utilities to increase the combustion of natural gas to balance the grid.

Unfortunately, the goals that California has set for reduction in such emissions are still far short of being met on schedule. Now, the leading cause of greenhouse gases is the burning of fossil fuels for transportation. California is seeking to replace fossil fuels for transportation with electricity and hydrogen, but the state needs additional energy resources to meet the demand. Wind and solar companies are seeking to satiate the needs, but a baseload source of electric power is needed. Geothermal can provide a major source of such energy because it is baseload, so it can replace natural gas in balancing the electric grid when needed, and also build inventories of energy as needed for transportation. Supercritical geothermal resources are particularly valuable and adaptable because they have properties different from those of ordinary water, such as higher diffusivity and self-ionization, higher specific conductance, but lower polarity, less surface tension and viscosity and lower relative permittivity (Franck, 1970; McDonald et al., 1986)

California has for some years encouraged the adoption of hydrogen to reduce the emission of greenhouse gases as a result of transportation needs. The state is launching a plan to spread the use of hydrogen to power transportation, which is a concept that has widespread popular support, and creates hope for reducing greenhouse gas and climate change. Unfortunately, the most common method of producing hydrogen commercially is steam reformation of methane, or other similar methods involving removal of the hydrogen from fossil fuels, which releases greenhouse gases. Over ninety percent (90%) of commercial hydrogen gas is produced by such means. (Shnell et al., 2019) The reason that such means are used so commonly is that the hydrogen so produced is much less expensive than other current sources of hydrogen. California authorities have expressed a preference for hydrogen that is "renewable," such as hydrogen produced by electrolysis using renewable electricity, which is more expensive. We must reduce the cost of renewable hydrogen with more efficient technology. The objective is to develop an affordable method of producing renewable hydrogen using electrolysis. Recent successes have demonstrated the ability to build a protonic ceramic electrolysis cell ("PCEC") that operates at an "intermediate temperature" in the range of 600°C to 800°C. The ability to combine PCECs into commercially viable "stacks" will require durable interconnects.

2. Supercritical Geothermal Cogeneration

One of the leading alternatives for the supply of renewable hydrogen is the use of electrolysis powered by electricity. One of the most expensive cost factors in electrolysis is the cost of electricity. One of the suggestions for this objective is to use "wasted" electricity from the grid. Once transportation uses establish a large need for such cheap energy, however, the cost will rise. Moreover, if the electricity comes from the grid, it will require transmission and distribution, which can be expensive. If, however, supercritical geothermal cogeneration ("SGC") is used, the generator can be collocated with the supercritical resource. The Iceland Deep Drilling Project has already demonstrated that supercritical geothermal resources can be reached and produced. The supercritical generator will use a new technology, the "Brayton" cycle, which is fifty percent (50%) more efficient (Fleming et al., 2012) and is therefore expected to be less expensive, than the "Rankine" cycle, which is commonly used with lower-enthalpy resources. Since the generator will also be collocated with the electrolysis plant, no transmission or distribution network will be necessary, further reducing the cost.

The electrolyzer will be the companion part of the SGC, and it will be highly efficient because it will be powered by supercritical resources and it will benefit from some of the efficient characteristics of the generator with which it is collocated. So, the efficiency will make the hydrogen cost competitive. (Elders et al., 2018; Shnell et al., 2016) The uses for hydrogen are also very flexible, so the SGC will be very adaptable and serve many purposes.

3. The Ceramic Proton Conducting Membrane

The alkaline water electrolysis system has long been the dominant system for the commercial production of hydrogen, but it has limitations regarding the maximum operating temperature. Polymer electrolyte membrane electrolysis has recently achieved the commercialization stage and is replacing the alkaline water electrolysis system. Polymer electrolysis systems have somewhat higher maximum operating temperature limits, but they are still well below the operating temperatures of solid oxide electrolysis cells ("SOECs"), which have not yet achieved commercialization but which can operate efficiently at high temperatures. Unfortunately, the SOECs are not very durable at high temperatures. The ceramic proton conducting membrane ("CPCM") has been in development for years because it operates at intermediate temperatures, well above those of polymer electrolyte systems (and therefore is more efficient than polymer electrolyte systems). The CPCM also produces purer hydrogen, and is more durable, than the SOEC, which is at the more extreme end of the spectrum, and the SOEC has not commercialized the types of materials that will be needed to withstand the 800°C to 1000°C high-temperature range that enables the SOEC to operate efficiently enough to compete economically.

The CPCM will reach its maximum efficiency at 650°C with materials that will enable the CPCM to be highly efficient and durable (Dubois et al., 2017) decreasing the cost of the hydrogen below the cost of the current, greenhouse gas-producing steam reformation of methane. Recent developments on mixed ionic and electronic conducting membranes will enable the CPCM to achieve new levels of efficiency. Perovskites have been major factors in research and developments regarding proton conducting membranes for a number of years, but progress is still being made (see Armstrong, 2013).

4. Metallic Support for Electrolysis Cells

Research and development of high-temperature SOECs has been growing for more than a decade, focused on cells supported primarily by hydrogen electrodes. Much less attention has been focused on metal-supported SOECs, with stainless steel supports on both sides, electrolyte and electrode back bones, and structured catalysts infiltrated on the side of both hydrogen and oxygen electrodes. Metal-supported solid oxide cells ("MS-SOCs") could perform well on intermittent operations with advantages including relatively low-cost materials and mechanical ruggedness. (Wang, Dogdibegovic, et al., 2019) On the other hand, potential challenges for MS-SOCs may include oxidation of the metallic support. "Because of the unique characteristics of metal-supported cells including their low manufacturing cost, excellent redox cycling and thermal cycling tolerance, and fast start-up capability, the high-performance MS-SOECs developed in this study are considered to have high potential for certain novel applications, such as buffering intermittent excess electricity and heat from renewable energy, and hydrogen production for mobile applications." (Ibid.)

Proton-conducting oxide ceramics, as opposed to conventional oxide conductors, are widely researched because the proton conductors display higher conductivity in electrolysis cells and enables efficient operation at lower temperatures, reducing thermal stress and allowing the use of less expensive stack materials and balance of plant components. “Transport of protons across the electrolyte offers other advantages at all temperatures; for electrolysis, pure hydrogen is produced so steam does not need to be removed from the product stream.” (Wang, Byrne et al., 2019) Barium cerium zirconate doped with yttria (“BZCY”) or another dopant is a widely used proton conductor for SOCs due to its high conductivity. “The limited work on cosintering BZCY with stainless steel support indicates, however, that significant challenges exist for this approach.” (Wang, Lau et al., 2019)

While PCEC development has made good progress, it has to date focused on the single cell. One study of oxidation of austenitic stainless steel in supercritical water investigated the effect of thermo-mechanical processing. Strips of stainless steel were cold-rolled to varying thicknesses. The strips were then oxidized in supercritical water at 600°C and a pressure of 25 MPa in an autoclave for up to 1,000 hours. Following studies of the oxidation mechanism and forms, it was concluded that the oxidation resistance of the stainless steel improved by a factor of up to four, and that oxide scale exfoliation was completely prevented when the thickness of the stainless steel was reduced by fifty percent (50%) or more by the thermo-mechanical cold-rolling process. Also, the reduction of grain sizes in the stainless steel caused the formation of a protective chromium oxide layer on the stainless steel (Nezakat et al., 2014).

Another study, investigating the oxidation of ferritic steel and ferritic-martensitic steel, was focused on comparing flowing and static supercritical water at temperatures of 550 to 600°C. The study does, however, discuss the effect of the concentration of chromium in the metal, and states that “Generally speaking, the higher the Cr concentration is, the lower the oxidation rate is” (Zhang et al., 2015)

Stack development of PCECs has not been reported and the development of a stack/system scale requires interconnect materials compatible with operating atmospheres and temperatures of the PCEC. In electrolysis, one side of the interconnect is exposed to high steam content in an oxidizing environment which could cause rapid degradation of the interconnect at intermediate temperatures. (Wang, Sun, et al., 2019) Although such rapid degradation might be avoidable if the temperature was lowered to 450°C, the performance of the PCEC is much lower at such a temperature, and it will not be commercializable. Recent experimentation with four state of the art coatings, based on Y_2O_3, Ce-MC, CuMn, and Ce/Co, respectively, developed to protect the stainless steel interconnects have been demonstrated to lower the oxidation rate of the stainless steel even in harsh, humidified air. “A protective coating on the metallic interconnect is deemed necessary to mitigate corrosion at higher stack operating temperature.” (Ibid) The ongoing development of protective coatings is creating possibilities for preventing the breakaway oxidation of stainless steel interconnects and for developing the interconnects that will enable the creation of stacks that will accomplish supercritical electrolysis.

5. Conclusion

Several of the studies described above have suggested, as one potential approach to solving the issues posed, combinations of innovations such as the use of thermo-mechanical processing to improve the grain structure of an alloy, to be combined with coating particularly vulnerable parts of the interconnect to protect it from oxidation and improve the supply of renewable energy. The implementation of such improvements, especially if they are mutually supporting of their goals, have the potential to curtail more quickly the use of fossil fuels for transportation and reduce the creation of greenhouse gases, and to balance wind, solar and other intermittent forms of energy, for the benefit of the electric grid.

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