Knowledge Based Materials

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High Temperature Polymer Electrolyte Membrane Water Electrolysis Cells

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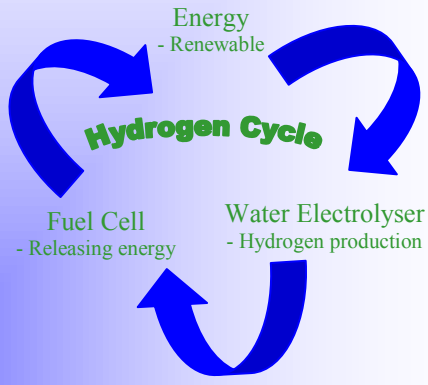
General abstract

In resent years production of electricity from sustainable energy sources has increased considerably. This is partly due to increasing political willingness to invest in sustainable energy projects and that the technology for utilizing wind, solar, and other sustainable energy sources has become both cheaper and more effective. The political interest in sustainable energy has mainly been caused by a worldwide increased demand for energy, higher prices on fossil fuels, instability in the most oil rich regions, as well as by increased awareness in the public of many countries of environmental consequences of burning of fossil fuels. Especially evolution of CO_2 has been subject to much discussion. Replacement of fossil fuels with sustainable energy sources does, however, have the shortage that the energy production from sustainable energy sources varies with changing conditions. During high production or low consumption periods it would be desirable to convert the excess energy into transportable and lasting fuels as a mean of energy storage. The first step of this could be to produce hydrogen by water electrolysis. To produce hydrogen by water electrolysis in an as inexpensive and effective way as possible is the main aim of the present project. The first steps toward succeeding in this is presented.

Technical abstract

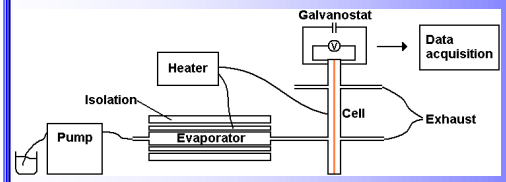
Most PEM water electrolysers are based on Nafion membrane electrolytes. This causes a similar temperature limitation as for Nafion based fuel cells (working temperatures only below 100 °C). This can be overcome in the same manners as for fuel cells, e.g. using H_3PO_4 doped PBI as electrolyte material. However, conditions in the electrolysis mode are more corrosive, thus some modifications are necessary concerning materials selections, e.g. carbon can not be used on the anode side of the membrane. MEAs and cell houses have been fabricated and preliminary experiments on high-temperature PEM electrolysis conducted at temperatures above 120 °C. The main source of resistance in the electrolyser cells were the anode including contact resistances. Therefore different materials for the catalyst layer as well as the gas diffusion layer at the anode side were prepared and tested in the electrolyser cells. The materials comprise conducting oxides such as IrO_2 and RuO_2 alone or in combination with non-noble metal oxides. It was also found that the membrane needs to be thicker in the electrolysis mode than the 40-50 µm that are sufficient for use in high-temperature PEM fuel cells.

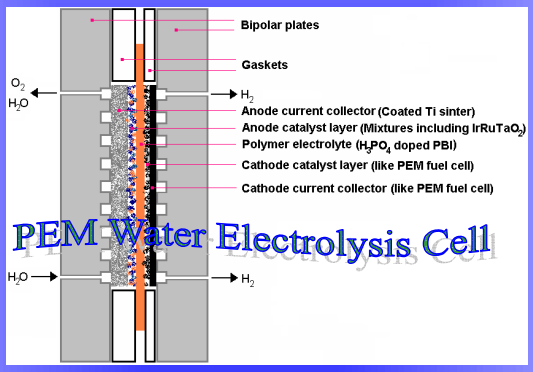


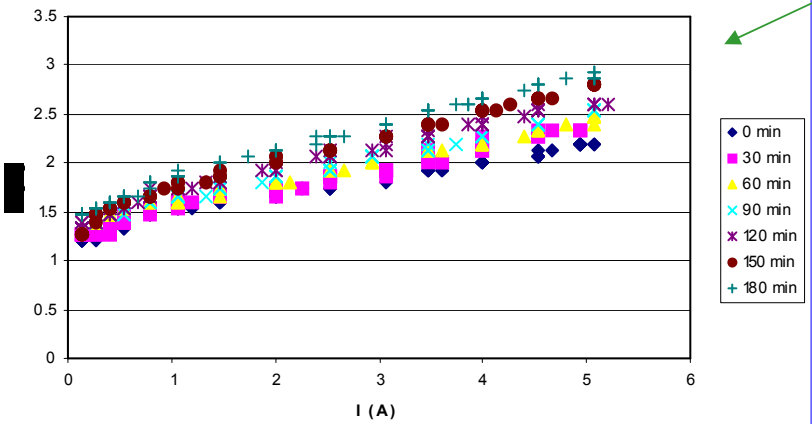
Method of water electrolysis

Water is pumped into a heated reactor and evaporated to steam of temperature120 –170 °C, which is let in to the anode part of the cell through gas channels and the gas diffusion layer. The cell is heated to the same temperature as the steam.

A potential higher than the standard water splitting potential (1.18 V for steam and 1.23 for liquid water) is applied to the cell. Thereby at the anode three phase boundaries the water is split into gaseous oxygen, electrons, and H^+ ions. These ions migrate through the H_3PO_4 doped poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole (PBI) electrolyte. At the cathode three phase boundaries ions combine with electrons to form H_2.

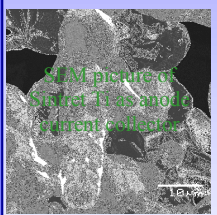






Results

Polarization curve of steam electrolysis at 130 °C and a steam flow equivalent of 0.2 ml liquid water per min. is shown in the graph. Each current point in the measurement is measured for 10 sec.. There is no current nor potential applied in the time intervals between the measurements, however, water is kept running through the cell. Severe degradation is observed over time. This may be due to dilution of the phosphoric acid by the steam as well as oxidation , thus passivation of the anode current collector.



The overall ohmic resistance of the cell (of 10 cm^2) is 0.18 V during the first measurement and increases with 0.03 V per hour of water flow. Other experiments has shown that if bubbling steam through H_3PO_4 water is absorbed in the acid.

Conclusion and future work

The first high temperature (steam) PEM electrolysis cell has been made and polarization curves obtained. Compared with low temperature PEM electrolysers (Nafion based working at temperatures below 100 °C, unless the cell is pressurized) the resistance as well as overpotential of the cells are quite high and thus the amount of energy required to operate the cells are larger. If, however, the better electrically conducting materials, which are stable in the harsh environment can be found the system may have potential, because the theoretical overpotential for electrolyzing steam is comparatively lower than that of liquid water electrolysis. The energy that is needed to evaporate the water can to some extent be reused in the system.

There are two major of the system which needs improvements. The current collector at the anode side of the electrolyte, which at present is not sufficiently corrosion resistant. This problem also apply to low temperature electrolysis cells, though the amount of corrosion increases with increased temperature. Different oxide materials will be tested regarding their conductivity and stability. The other part is the electrolyte strength and conductivity. The conductivity of H_3PO_4 doped polybenzimidazole is only about 0.1 times that of a water doped Nafion electrolyte. Additionally the presence of steam softens the membrane. This causes the a need for the membranes to be thicker (above 100 µm) than needed in fuel cells (40-50 µm) which again increases the ohmic resistance of the cells. Measurements using different modifications of PBI will be conducted.

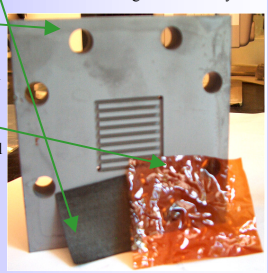
Glossary

Membrane Electrode Assembly (MEA) - A flat sheet of solid polymer electrolyte with anode and cathode on each side of it.

Dimensionally Stable Anodes (DSA) - Oxide catalyst used as anode. The idea is that it does not change composition or degrade (ideally) in the oxidising environment. They normally consists of IrO_2, RuO_2, PtO_2 or the like, sometimes combined with non-noble metal oxides, such as Ta_2O_5, TiO_2, SnO_2, and NbO_2.

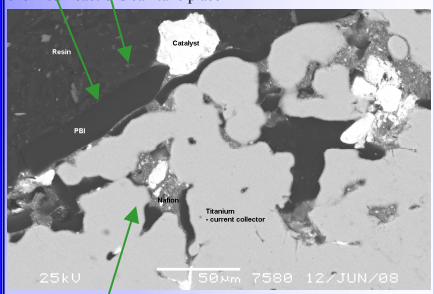
Current collector/gas diffusion layer - Layer of sinter, mesh or the like which is both electrically conducting and porous such that both electrons and gaseous reactants can get to and away for the reactive area.

Bipolar plates - In a stack of cells these are used as anode in one cell and cathode in the next.



Polybenzimidazole (PBI) - Polymer material with high thermal stability and the ability of containing considerable amounts of phosphoric acid, which makes it proton conducting.

Three phase boundary - A boundary where electrons, ions, and gaseous or liquid reactants all have access to so that electrochemical reactions can take place



Nafion - Transparent polymer with is proton conducting when doped with water. Nafion is widely used in PEM fuel cells (up to 80 °C) and electrolysis cells (up to 90 °C).

Reversible potential (E^{rev}) - The theoretically lowest potential that must be applied between two electrodes for a thermodynamically unfavorable reaction to proceed. I case of water electrolysis the reversible energy is given by:

$$E^{rev} = E^0 - \frac{RT}{nF}\ln\left[\frac{p_{H_2}\, p_{O_2}^{1/2}}{p_{H_2O}}\right]$$

(E^0 is the standard potential and R, T, n, F, and p are the ideal gas constant, temperature, number of electrons in reaction, Faradays constant, and pressure respectively). Due to overpotentials and ohmic resistances the actually needed potential is higher than E^{rev}.

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