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Polymer electrolyte membrane electrolysis

Polymer electrolyte membrane (PEM) electrolysis is the electrolysis of water in a cell equipped with a solid polymer electrolyte (SPE)[2] that is responsible for the conduction of protons, separation of product gases, and electrical insulation of the electrodes. The PEM electrolyzer was introduced to overcome the issues of partial load, low current density, and low pressure operation currently plaguing the alkaline electrolyzer. [3][1] It involves a proton-exchange membrane.

However, a recent scientific comparison showed that state-of-the-art alkaline water electrolysis shows competitive or even better efficiencies than PEM water electrolysis.[4] This comparison moreover showed that many of the advantages such as gas purities or high current densities that were ascribed to PEM water electrolysis are also achievable by alkaline water electrolysis. Electrolysis is an important technology for the production of hydrogen to be used as an energy carrier.

With fast dynamic response times, large operational ranges, and high efficiencies, water electrolysis is a promising technology for energy storage coupled with renewable energy sources.

Polymer electrolyte membrane electrolysis

Diagram of PEM electrolysis reactions.

Typical Materials	
Type of Electrolysis:	PEM Electrolysis
Style of membrane/diaphragm	Solid polymer
Bipolar/separator plate material	Titanium or gold and platinum coated titanium
Catalyst material on the anode	Iridium
Catalyst material on the cathode	Platinum
Anode PTL material	Titanium
Cathode PTL material	Carbon paper/carbon fleece
State-of-the-art Operating Ranges	

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History

The use of a PEM for electrolysis was first introduced in the 1960s by General Electric, developed to overcome the drawbacks to the alkaline electrolysis technology.[5] The initial performances yielded 1.88 V at 1.0 A/cm² which was, compared to the alkaline electrolysis technology of that time, very efficient. In the late 1970s the alkaline electrolyzers were reporting performances around 2.06 V at 0.215 A/cm²,[6] thus prompting a sudden interest in the late 1970s and early 1980s in polymer electrolytes for water electrolysis.

A thorough review of the historical performance from the early research to that of today can be found in chronological order with many of the operating conditions in the 2013 review by Carmo et al.[1]

Advantages of PEM electrolysis

One of the largest advantages to PEM electrolysis is its ability to operate at high current densities.[1] This can result in reduced operational costs, especially for systems coupled with very dynamic energy sources such as wind and solar, where sudden spikes in energy input would otherwise result in uncaptured energy. The polymer electrolyte allows the PEM electrolyzer to operate with a very thin membrane (~100-200 µm) while still allowing high pressures, resulting in low ohmic losses, primarily caused by the conduction of protons across the membrane (0.1 S/cm) and a compressed hydrogen output.[7]

The polymer electrolyte membrane, due to its solid structure, exhibits a low gas crossover rate resulting in very high product gas purity.[1] Maintaining a high gas purity is important for storage safety and for the direct usage in a fuel cell. The safety limits for H_2 in O_2 are at standard conditions 4 mol-% H_2 in O_2.[8]

Cell temperature	50-80C[1]
Stack pressure	<30 bar[1]
Current density	0.6-2.0 A/cm²[1]
Cell voltage	1.75-2.20 V[1]
Power density	to 4.4 W/cm²[1]
Part-load range	0-10%[1]
Specific energy consumption stack	4.2-5.6 kWh/Nm³[1]
Specific energy consumption system	4.5-7.5 kWh/Nm³[1]
Cell voltage efficiency	57-69%[1]
System hydrogen production rate	30 Nm³/h[1]
Lifetime stack	<20,000 h[1]
Acceptable degradation rate	<14 μV/h[1]
System lifetime	10-20 a[1]

Science

An electrolyzer is an electrochemical device to convert electricity and water into hydrogen and oxygen, these gases can then be used as a means to store energy for later use. This use can range from electrical grid stabilization from dynamic electrical sources such as wind turbines and solar cells to localized hydrogen production as a fuel for fuel cell vehicles. The PEM electrolyzer utilizes a solid polymer electrolyte (SPE) to conduct protons from the anode to the cathode while insulating the electrodes electrically. Under standard conditions the enthalpy required for the formation of water is 285.9 kJ/mol. A portion of the required energy for a sustained electrolysis reaction is supplied by thermal energy and the remainder is supplied through electrical energy.[9]
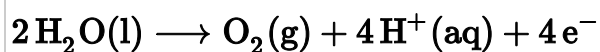
Reactions

The actual value for open circuit voltage of an operating electrolyzer will lie between the 1.23 V and 1.48 V depending on how the cell/stack design utilizes the thermal energy inputs. This is however quite difficult to determine or measure because an operating electrolyzer also experiences other voltage losses from internal electrical resistances, proton conductivity, mass transport through the cell and catalyst utilization to name a few.
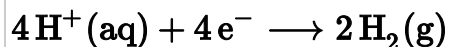
Anode reaction

The half reaction taking place on the anode side of a PEM electrolyzer is commonly referred to as the Oxygen Evolution Reaction (OER). Here the liquid water reactant is supplied to catalyst where the supplied water is oxidized to oxygen, protons and electrons.

$$2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$$

Cathode reaction

The half reaction taking place on the cathode side of a PEM electrolyzer is commonly referred to as the Hydrogen Evolution Reaction (HER). Here the supplied electrons and the protons that have conducted through the membrane are combined to create gaseous hydrogen.

$$4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2(g)$$

The illustration below depicts a simplification of how PEM electrolysis works, showing the individual half-reactions together along with the complete reaction of a PEM electrolyzer. In this case the electrolyzer is coupled with a solar panel for the production of hydrogen, however the solar panel could be replaced with any source of electricity.
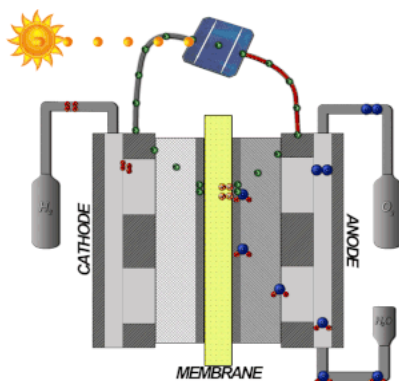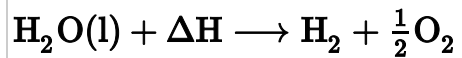

Diagram of PEM electrolyzer cell and the basic principles of operation.
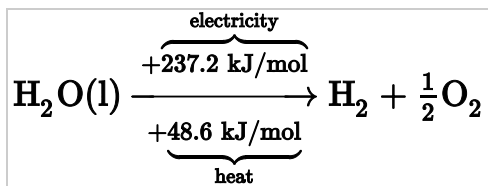
Second law of thermodynamics

As per the underlined second law of thermodynamics the underlined enthalpy of the reaction is:

$$\Delta H = \underbrace{\Delta G}_{\text{elec.}} + \underbrace{T\Delta S}_{\text{heat}}$$

Where ΔG is the Gibbs free energy of the reaction, T is the temperature of the reaction and ΔS is the change in entropy of the system.

$$\mathrm{H_2O(l)} + \Delta H \longrightarrow \mathrm{H_2} + \tfrac{1}{2}\mathrm{O_2}$$

The overall cell reaction with thermodynamic energy inputs then becomes:

$$\mathrm{H_2O(l)} \xrightarrow[\underbrace{+48.6\ \text{kJ/mol}}_{\text{heat}}]{\overbrace{+237.2\ \text{kJ/mol}}^{\text{electricity}}} \mathrm{H_2} + \tfrac{1}{2}\mathrm{O_2}$$

The thermal and electrical inputs shown above represent the minimum amount of energy that can be supplied by electricity in order to obtain an electrolysis reaction. Assuming that the maximum amount of heat energy (48.6 kJ/mol) is supplied to the reaction, the reversible cell voltage V_{rev}^0 can be calculated.

Open circuit voltage (OCV)

$$V_{\text{rev}}^0 = \frac{\Delta G^0}{n \cdot F} = \frac{237\ \text{kJ/mol}}{2 \times 96,485\ \text{C/mol}} = 1.23 V$$

where n is the number of electrons and F is Faraday's constant. The calculation of cell voltage assuming no irreversibilities exist and all of the thermal energy is utilized by the reaction is referred to as the lower heating value (LHV). The alternative formulation, using the higher heating value (HHV) is calculated assuming that all of the energy to drive the electrolysis reaction is supplied by the electrical component of the required energy which results in a higher reversible cell voltage. When using the HHV the voltage calculation is referred to as the thermoneutral voltage.

$$V_{\text{th}}^0 = \frac{\Delta H^0}{n \cdot F} = \frac{285.9\ \text{kJ/mol}}{2 \times 96,485\ \text{C/mol}} = 1.48 V$$

Voltage losses

The performance of electrolysis cells, like fuel cells, are typically compared by plotting their polarization curves, which is obtained by plotting the cell voltage against the current density. The primary sources of increased voltage in a PEM electrolyzer (the same also applies for PEM fuel cells) can be categorized into three main areas, Ohmic losses, activation losses and mass transport losses. Due to the reversal of operation between a PEM fuel cell and a PEM electrolyzer, the degree of impact for these various losses is different between the two processes.[1]

$$V_{\text{cell}} = E + V_{\text{act}} + V_{\text{trans}} + V_{\text{ohm}}$$

The performance of a PEM electrolysis system is typically compared by plotting the overpotential versus the cells current density. This essentially results in a curve that represents the power per square centimeter of cell area required to produce hydrogen and oxygen. Conversely to the PEM fuel cell, the better the PEM electrolyzer the lower the cell voltage at a given current density. The figure below is the result of a simulation from the Forschungszentrum Jülich of a 25 cm² single cell PEM electrolyzer under thermoneutral operation depicting the primary sources of voltage loss and their contributions for a range of current densities.
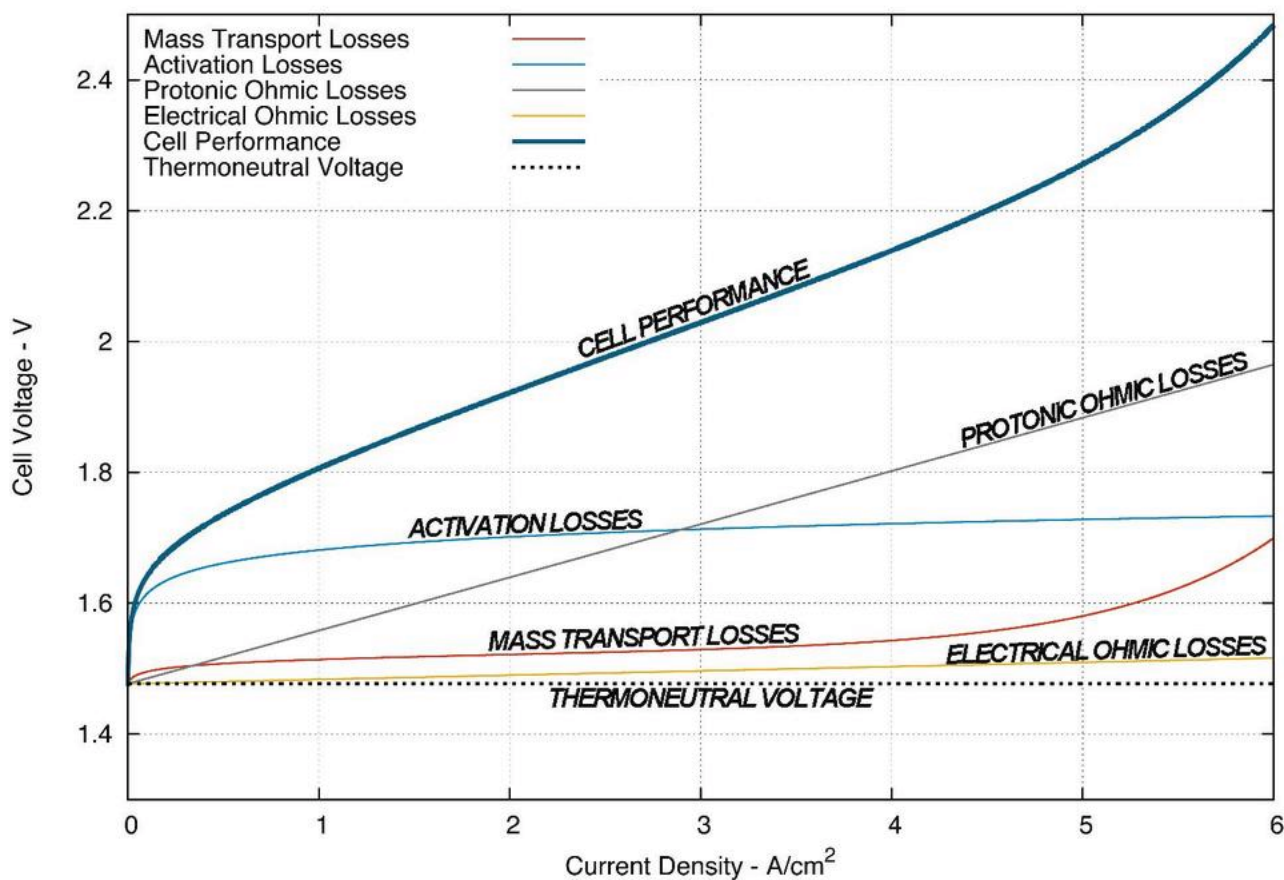
Polarization curve depicting the various losses attributed to PEM electrolysis cell operation.

Ohmic losses

Ohmic losses are an electrical overpotential introduced to the electrolysis process by the internal resistance of the cell components. This loss then requires an additional voltage to maintain the electrolysis reaction, the prediction of this loss follows Ohm's law and holds a linear relationship to the current density of the operating electrolyzer.

$$V = I \cdot R$$

The energy loss due to the electrical resistance is not entirely lost. The voltage drop due to resistivity is associated with the conversion the electrical energy to heat energy through a process known as Joule heating. Much of this heat energy is carried away with the reactant water supply and lost to the environment, however a small portion of this energy is then recaptured as heat energy in the

electrolysis process. The amount of heat energy that can be recaptured is dependent on many aspects of system operation and cell design.

$$Q \propto I^2 \cdot R$$

The Ohmic losses due to the conduction of protons contribute to the loss of efficiency which also follows Ohm's law, however without the Joule heating effect. The proton conductivity of the PEM is very dependent on the hydration, temperature, heat treatment, and ionic state of the membrane.[10]

Faradaic losses and crossover

Faradaic losses describe the efficiency losses that are correlated to the current, that is supplied without leading to hydrogen at the cathodic gas outlet. The produced hydrogen and oxygen can permeate across the membrane, referred to as crossover.[10] Mixtures of both gases at the electrodes result. At the cathode, oxygen can be catalytically reacted with hydrogen on the platinum surface of the cathodic catalyst. At the anode, hydrogen and oxygen do not react at the iridium oxide catalyst.[10] Thus, safety hazards due to explosive anodic mixtures hydrogen in oxygen can result. The supplied energy for the hydrogen production is lost, when hydrogen is lost due to the reaction with oxygen at the cathode and permeation from the cathode across the membrane to the anode corresponds. Hence, the ratio of the amount of lost and produced hydrogen determines the faradaic losses. At pressurized operation of the electrolyzer the crossover and the correlated faradaic efficiency losses increase.[10]

Hydrogen compression during water electrolysis

Hydrogen evolution due to pressurized electrolysis is comparable to an isothermal compression process, which is in terms of efficiency preferable compared to mechanical isotropical compression.[10] However, the contributions of the afore mentioned faradaic losses increase with operating pressures. Thus, in order to produce compressed hydrogen, the in-situ compression during electrolysis and subsequent compression of the gas have to be pondered under efficiency considerations.

PEM electrolysis system operation

The ability of the PEM electrolyzer to operate, not only under highly dynamic conditions, but also in part-load and overload conditions is one of the reasons for the recently renewed interest in this technology. The demands of an electrical grid are relatively stable and predictable, however when coupling these to energy sources such as wind and solar, the demand of the grid rarely matches the generation of the renewable energy. This means energy produced from renewable sources such as wind and solar must have a buffer, or a means of storing off-peak energy.

PEM Efficiency

When determining the electrical efficiency of PEM electrolysis, the higher heat value (HHV) can be used.[11] This is because the catalyst layer interacts with water as steam. As the process operates at 80 °C for PEM electrolysers the waste heat can be redirected through the system to create the steam, resulting in a higher overall electrical efficiency. The lower heat value (LHV) must be used for alkaline

electrolysers as the process within these electrolysers requires water in liquid form and uses alkalinity to facilitate the breaking of the bond holding the hydrogen and oxygen atoms together. The lower heat value must also be used for fuel cells, as steam is the output rather than input.

PEM electrolysis has an electrical efficiency of about 80% in working application, in terms of hydrogen produced per unit of electricity used to drive the reaction.[12][13] The efficiency of PEM electrolysis is expected to reach 82-86%[14] before 2030, while also maintaining durability as progress in this area continues at a pace.[15]

PEM high pressure electrolyzer system

See also

- Electrochemistry
- Electrochemical engineering
- Electrolysis
- Hydrogen production
- Gas cracker
- Photocatalytic water splitting
- Water purification
- Timeline of hydrogen technologies
- Electrolysis of water
- PEM fuel cell
- Hydrogen economy
- High-pressure electrolysis

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