Modelling of PEM Electrolyzer Dynamics for Green Hydrogen Production

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Abstract

In the current paradigm of sustainable chemical production, Green Hydrogen production using electrolysis of water is gaining popularity. This necessitates the development of rigorous first principles-based electrolyzer simulation models that can be leveraged during design and for training of operators in optimal and safe operation of the equipment. PEM electrolysis is one of the efficient routes for Green Hydrogen generation. Given the complexity of the operation, unique challenges are faced in modelling the dynamic behavior. The study here involves developing a high-fidelity dynamic model of PEM Electrolyzer leveraging AVEVA Dynamic SimulationTM. Modelling of electrolyzers is challenging, as standard reactor models cannot be used for electrolysis since electrolysis has a strong dependency on electrical current flowing in the cell. The model should be capable of predicting correct pressure and temperature responses for any changes in feed water flow and/or electrical load. The model should be also capable of accurately modelling the heat generation in the system due to low material inventory at cathode and should have provision for the heat extraction. In addition, the model should also have provision to handle gas leakage through membrane as well as water permeation due to electro-osmatic drag and diffusion through the membrane. The model developed here was used to study the cell voltage, ohmic, activation and mass transfer losses along with the typical relationship between voltage and current density in the electrolyzer cell. The use case of Hydrogen leakage based on electrical load was also simulated using user specified diffusion coefficient. Membrane rupture which leads to direct flow from cathode to anode is another use case that was studied. These together provided the ability to test the boundary case of explosion limit. Multiple electrolyzer arrangements, connected in series and in parallel, were also simulated and studied. The results generated from the studies using the model were in close match with the expected dynamic response and results. In summary, the PEM Electrolyzer model developed using AVEVA Dynamic SimulationTM has the rigor to train engineers in operating this complex piece of equipment.

**Keywords**: Sustainability, green hydrogen production, proton exchange membrane (PEM) electrolyzer, water permeation, electro-osmatic drag, membrane hydrogen leakage.

* 1. Introduction

Hydrogen is an important chemical that is widely used in the Oil & Gas, Refining and Chemical industries to produce other chemicals. Hydrogen demand is also increasing globally as a clean source of energy, as it emits only water on combustion. Hydrogen has been traditionally manufactured using hydrocarbon feedstock via steam reforming, coal gasification or methane pyrolysis process. However, of late, the focus is on green hydrogen, where hydrogen is produced via water electrolysis, using electricity generated from a renewable source like solar or wind energy. The process gives high purity hydrogen, with oxygen as a by-product, and has minimal impact on the environment. The commercial electrolyzers used for hydrogen production are Proton Exchange Membrane (PEM) and Alkaline Electrolyzers. The study presented here simulates PEM electrolyzer using AVEVA Dynamic SimulationTM (ADS), which is a commercial high fidelity dynamic process simulator used for building Operator Training Simulators (OTS).

* 1. Description

In PEM electrolyzer, water is electrochemically split into hydrogen and oxygen at the cathode and anode respectively. Pure water, used as the electrolyte solution, is pumped to the anode section, where it splits into oxygen (O2), protons (H+) and electrons (e−). These protons migrate via the polymer-based proton conducting membrane towards cathode. At the cathode, migrated protons re-combine with electrons to produce hydrogen gas.

2.1 Design

Anode and Cathode are considered as holdups in ADS where the fluids can be accumulated for some time before moving forward. These holdups have their own pressure dynamics and mass/energy balance. The Hydrogen and Oxygen formation is based on the electrochemical reaction. The flow at cathode and anode sides are based on the differential pressure and mass balance equation. The temperature is determined based on the energy balance equation.

2.2 Voltage calculations

In the electrochemical model, the cell voltage is calculated by adding the open circuit voltage, the maximum voltage, and various losses (activation and ohmic losses) based on Abdol et al., 2015 [1] as shown below:

$V\_{cell}= V\_{ocv }+V\_{act }+V\_{Ω}$

The open-circuit voltage is calculated based on Saebea et al., 2017 [2].

$$V\_{ocv}= V\_{rev}+ \frac{R\*T\_{m}}{2F}ln⁡(\frac{pp\_{H\_{2}}}{P\_{std}}\* \sqrt{\frac{pp\_{O\_{2}}}{P\_{std}}})$$

where *Vrev* is the reversible voltage i.e., the minimum voltage required for each reaction at the electrodes, *F* is Faraday constant i.e., 96485 C/mol, R is gas constant, ppH2 and ppO2 are partial pressures of Hydrogen and Oxygen respectively.

Activation over-potential at each electrode is defined based on Abdol et al., 2015 [1]:

$V\_{act,x }= \frac{R\*T\_{x}}{2α\_{x}F}ln⁡(\frac{J}{2i\_{ax }}+ \sqrt[2]{\left(\frac{J}{2i\_{ax }}\right)^{2}+1} )$

where *x* is either anode or cathode, *αx* is charge transfer coefficient for the electrode which is user-defined and dimensionless, *J* is current density on the PEM stack electrodes and iax is current density at each electrode.

Ohmic overpotential is caused by the membrane resistance to the flow of ions. This can be expressed as (Abdol et al., 2015 [1]):

$$V\_{ohm}= R\_{mem }\*I$$

*Rmem* is an ionic resistance as a function of membrane thickness conductivity (σmem, S/m), membrane height (ϕ, m), $I$ is electrolyzer current to each electrolyzer.

2.3 Material Balance

Simplified form of equations based on Paolo et al., 2017 [3], are used in the simulation model. The hydrogen production rate is calculated using the equation:

$FH\_{2,prod}\*1000=\frac{etaF\*Ncell\*I}{2\*F} $

where *Ncell* is Number of electrolyzer cells, *I* is Electrolyzer total current (Amp), and *etaF* is Faraday efficiency (1.0).

The permeation rate can be represented as being proportional to the diffusivity in the membrane and the concentration gradient between two flow channels, which is described as:

$FH\_{2}\_{permeated}=D\_{H2}\frac{(C\_{H2,c}-C\_{H2,a})N\_{Cell}A\_{e}}{t\_{m}}$

where *tm* is the thickness of the membrane and *CH2 c*and *CH2,a*are hydrogen concentration for the cathode and anode surface of the membrane, respectively.

Diffusivity of hydrogen in membrane (m2/s),

 $D\_{H\_{2}}= DiffCoeff\_{H\_{2}}\* e^{(- \frac{16510}{RT\_{m}})}$

where *DiffCoeff*H2 is diffusion coefficient for hydrogen which is user-defined, and the default is 4.9E-5, *R* is Gas Constant and is equal to 8.314 kJ/kg-mol/K and *Tm* is electrolyzer temperature.

The large fraction of permeated hydrogen from the membrane decomposes at the anode. The current understanding is that 80% of the permeated hydrogen decomposes, while the remaining 20% mixes with oxygen at the anode.

$$FH\_{2}\_{anode}= 0.2\*FH\_{2}\_{permeated}$$

Oxygen production rate is half of FH2. Oxygen undergoes the same membrane migration phenomenon in the opposite direction as hydrogen permeation.

$FO\_{2}\_{cathode}= DiffCoeff\_{O2}\frac{(C\_{O2,a}-C\_{O2,c})N\_{Cell}A\_{e}}{t\_{m}}$

where *CO2,c*and *CO2,a* are oxygen concentration for the cathode and anode surface of the membrane, respectively. *DiffCoeff*O2 is diffusion coefficient for oxygen which is user-defined, and default is 6.5E-7.

Water permeates through membrane due to electro-osmatic drag and diffusion which are functions of the water content of the membrane and are based on Paolo et al., 2017 [3].

Water permeation due to electro-osmatic drag,

$$FH\_{2}O\_{eod}=EODragCoeff\*\frac{M\_{H2O}n\_{d}JN\_{cell}A\_{e}}{1000\*F}$$

where *Ae* is the area of the electrolyzer cell, *J* is current density, *ƛ* is degree of humidity in membrane and *nd* is the electro-osmotic drag coefficient calculated based on degree of humidity as follows:

$$n\_{d}=0.0029ƛ^{2}+0.05ƛ-3.4\*10^{-19}$$

*EODragCoeff* is user-defined factor to tune electro-osmatic drag flow rate.

Water diffusion through the membrane is given from Fick’s first law of diffusion as follows:

$$FH\_{2}O\_{Diff}=D\_{w}\frac{(C\_{wa}-C\_{wc})NCellA\_{e}}{t\_{m}}$$

where Cw*,c*and *Cw,a* are water concentration for the cathode and anode surface of the membrane, respectively. The water diffusion coefficient is computed as:

$$D\_{w}=1.25\*10^{-10}DiffCoeff\_{ }e^{2416(\frac{1}{303}-\frac{1}{T\_{cat}})}$$

*DiffCoeff* is user-defined factor to tune water flow rate due to diffusion, *Tcat* is cathode side temperature.

2.4 Energy Balance

Overall energy balance includes the heat of reaction as well as the electrical power including heat loss from fluid to metal (Paolo et al., 2017 [3]).​

$M\_{m}Cp\_{m}\frac{dT\_{m}}{dt}= (Q\_{loss}- Qf\_{Ano}-Qf\_{Cat}-HRxn+ Power)$

where *QfAno* and *QfCat* are heat losses from fluid to metal at the corresponding electrodes,

*Hrxn* is the heat of reaction and *Qloss*is the heat loss from metal to ambient.

* 1. Simulation model details and results of case study

3.1 Simulation model

In ADS, the PEM electrolyzer model consists of an anode chamber with one inlet and one outlet stream and a cathode chamber with two process outlet streams. An electrical source is connected to the cell using electrical stream. A fan-based cooler is used to remove excess heat generated in the electrolyzer. Water enters the anode chamber, where it is split into hydrogen and oxygen using electrical potential. Hydrogen then flows to cathode, along with permeated water. The mixture is separated in a gas-liquid separator and hydrogen is sent to storage. Oxygen flows out of anode along with the unused water and is separated in a gas-liquid separator. Oxygen is taken to storage, while water is recycled back to electrolyzer. Diffusion coefficients are used to simulate cross-over of hydrogen and oxygen through the membrane. The schematic representation of the simulation model is depicted in Figure.1.



Figure.1. Schematic representation of electrolyzer process and corresponding ADS simulation model.

3.2 Impact of membrane thickness

Current density is a key parameter that determines the operating efficiency of PEM Electrolyzer.  The effect of membrane thickness on performance was modeled using the ADS simulation model (Figure.2) and the results match with literature (Saebea et al., 2017 [2]). It is found that at high pressure operation thinner membranes provide higher performance because when membrane gets thicker, ohmic resistance increases, thereby necessitating higher voltages.

Figure.2. Effect of Current Density and membrane thickness on Cell Voltage

3.3 Impact of cathode pressure

When hydrogen leak accumulates over time or if the leakage increases to such an extent that it is near the explosion limit i.e., 4% of H2 in O2, it poses safety risk. So, the detection of hydrogen leakage is very important. The effect of pressure on hydrogen permeation towards anode is modelled using the PEM model (Figure.3) and the results match with literature (Saebea et al., 2017 [2]). The rise in pressure increases hydrogen permeation towards anode, i.e., hydrogen leakage.

Figure.3. Effect of Current Density and Pressure on Hydrogen leakage

3.4 Impact of membrane degradation

Membrane degradation takes a long time to observe in actual operation. Its effect on electrolyzer can be simulated at an accelerated rate using the ADS model. For this purpose, a malfunction scenario is created where in membrane degradation is simulated. Membrane degradation causes a decrease in the performance of electrolyzer; thereby, a decrease in hydrogen production and increase in hydrogen leakage. The results are plotted in Figure.4.

Figure.4. Effect of Membrane Degradation on Hydrogen Production and Current Density

3.5 Impact of external cooling source

Excess heat produced is removed by fan to maintain the temperatures at around 350 C. Upon fan failure, it is observed that the temperature of electrolyzer increases along with the increase in hydrogen leakage. This led to the formation of explosive mixture within 2 minutes of fan cut off. The results are plotted in Figure.5.

Figure.5. Cooling source cut off vs Hydrogen Leakage and Electrolyzer Temperature

Conclusions

PEM electrolyzer was successfully simulated using AVEVA Dynamic SimulationTM. The impact of various parameters like membrane thickness, current density, and cooling source on the electrolyzer performance were studied. The model results are in close match with the expected dynamic response. In conclusion, the electrolyzer model has the necessary rigor to simulate various operating scenarios and could be used to train engineers in the effective and safe operation of PEM electrolyzer based plants.

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