

Intro to PEM Electrolyzer Modeling

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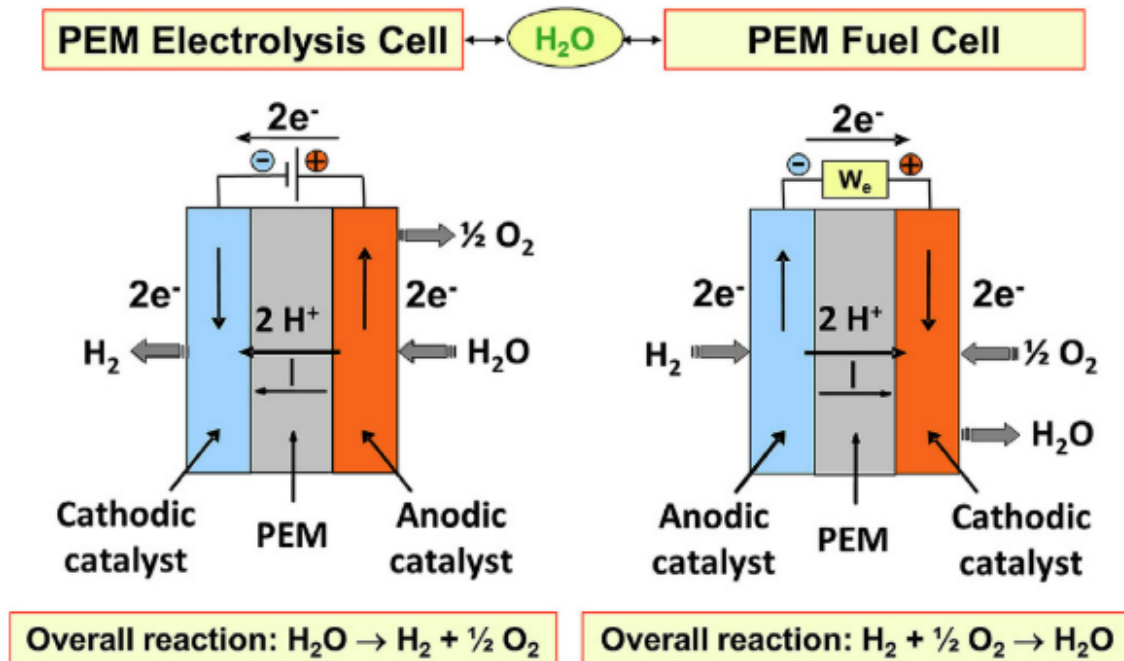


Figure 1: Schematic representation of PEM EL and PEM FC (Lamy, 2016, Falcao, 2020)

1 Background

1.1 Definition

Electrolysis is the electrochemical reaction which splits water into hydrogen and oxygen using electricity. This is the reverse setup of a fuel cell which seeks to combine hydrogen and oxygen to generate electricity. With a clean electricity source, the produced hydrogen can be considered "green" and be used to produce cleaner (significantly less relative to no carbon dioxide) electricity when coupled with a fuel cell or other source of clean energy. The most common kind of electrolyzer is a Proton Exchange Membrane (PEM) hydrogen electrolyzer, which uses water to shuttle ions across a semi-permeable, ionically conductive electrolyte membrane, often sandwiched between two catalyst layers.

1.2 Motivation

Increasing energy demand amidst rising carbon emissions drive motivation for "green" energy alternatives. Proton Exchange Membrane (PEM) hydrogen electrolyzers can create "green" hydrogen fuel when water transports hydrogen ions across a solid electrolyte membrane layer coated in a catalyst. This electrochemical reaction creates gaseous bubbles that must be transported away from the membrane in order to make way for more reactants, avoid damage and other sources of energy loss. The PEM hydrogen electrolyzer can be used in collaboration with the PEM hydrogen fuel cell to produce electricity from the generated hydrogen. The end-goal is to model the generation of hydrogen ions and their respective operating ranges. The ability to model hydrogen generation can lead to additional design insights and optimizations that can improve the efficiency of the system. Modeling the behavior is useful to determine the expected hydrogen ion generation and the amount of

energy the process requires.

2 Losses

2.1 Open Circuit Voltage and Overpotential

Energy loss can come from three different sources: kinetic, mass transport, and ohmic. Open circuit voltage can be considered the "baseline" potential energy that reactants have and overpotential is the deviation of energy required for the reaction to occur. The open circuit voltage can be calculated with the Nernst equation using temperature, partial pressures, Faraday's constant and reversible cell voltage (E_{rev}). The overpotentials are associated with a variety of losses that must be overcome in order for a reaction to take place [1].

$$E_{cell} = E_{rev}^0 + \frac{RT}{2F} \left[\ln \left(\frac{P_{H_2O} \rho_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \right) \right] \quad (1)$$

2.2 Kinetics

Kinetic losses result from kinetic overpotential at both the anode and cathode sides of the exchange membrane. The kinetic overpotential is defined as the additional energy necessary for a reaction to occur and is related to many chemical interactions that produce the reaction, but is often consolidated to one model that includes the diffusive, ohmic, anode and cathode models. There are many steps that must be completed in order for a reaction to occur, for instance, correct orientation of the water molecules for electrons to be collected, appropriate current density to split the hydrogen and oxygen, and diffusive potential to shuttle the water across the semi-permeable membrane. All of these phenomena are typically accounted for when calculating the exchange current density and charge transfer coefficient along with the

Butler-Volmer equation [1].

The exchange current density refers to the reaction rate at which the chemical equilibrium state operates. A higher exchange current density relates to more reactions and vice versa for lower densities. The charge transfer coefficient refers to the rate at which electrons can cross the double-layer membrane before being shuttled to the other half-cell. Charge transfer coefficient can be assumed to be constant for both oxidation and reduction for use in the Butler-Volmer equation [2].

$$E_{Nernst} = E_{rev}^0 + \frac{RT}{\eta F} \ln\left(\frac{P_{H_2} P_{O_2}^5}{P_{H_2O}}\right) \quad (2)$$

Each respective over-potential is modeled separately and includes different phenomena. Most often in literature, the Nernst equation will be used to calculate the concentration of products and reactants due to pressure differentials. This also represents the open-circuit voltage, which can be considered as the baseline kinetic potential held by the product and reactants.

$$V_{Act} = \frac{RT_a}{\alpha_a F} \operatorname{arcsinh}\left(\frac{i}{2i_{0,a}}\right) + \frac{RT_a}{\alpha_c F} \operatorname{arcsinh}\left(\frac{i}{2i_{0,c}}\right) \quad (3)$$

2.3 Kinetics Survey

Butler-Volmer is often utilized as the state-of-the-art kinetics model and is used to solve for the activation overpotential at both the anode and cathode[1, 3, 4, 5] sites. The Butler-Volmer equation is based on the Ion-transfer (IT) theory and has largely remained unchanged since it's conception [6]. The Butler-Volmer equation can be expanded upon to account for additional properties, however, it should be noted that the Butler-Volmer equation is most

often seen in it's hyperbolic sine form in order to have the ability to use nonlinear curve fitting [3]. It is assumed that the reactions are symmetrical in order to apply the Butler-Volmer equation to both anode and cathode sides.

Additionally, the Electron Transfer theory (ET) is the lesser-known counterpart and originally sought to model the proton transfer and therefore the reaction rate. The ET theory is closely related to quantum mechanics due to the process of quantum tunneling. Butler expanded upon this theory to approximate the ion transfer (IT) and thus derived the Butler-Volmer equation. However, there were attempts between R. W. Gurney and J. A. V. Butler to propose a coupling of the IT and ET theories resulting in the Gurney-Butler theory which would later be expanded upon with further ET extensions [6]. Due to an inability to validate Tafel's Law, the ET theory fails to provide the same consistency for electrochemical kinetics as the BV equation. With that said, it can still be used in addition to the BV equation as is the focus of [6].

As explained in [7], the Butler-Volmer equation must assume negligible mass-transport affects. It is noted that including such phenomena requires accounting for local reactant concentrations in what is referred to as microkinetic modelling. This model includes separate anode and cathode models that rely on the effective charge transfer coefficient and effective exchange current density.

A successful model was produced that calculated the Oxygen Reduction Reaction (ORR) through a dense series of equations [8]. Although this method uses Boltzmann relationships, it varies in it's methodology by directly modeling many different phenomena instead of encompassing many parameters in the BV equation. This method assumes steady state and performs dimensionless models as a function of concentrations of the reactants.

2.4 Diffusion and Mass Transfer

It has also been observed to model the diffusion with molar concentration [9] in which ancillaries are calculated for the cathode, anode, membrane and voltage. This method can be expanded upon by using the Butler-Volmer to relate anode and cathode sides using a symmetry factor on each side to account for the respective additional oxidation and reduction energy requirements. This method seeks to model the pressure in the storage container as a result of the produced hydrogen.

$$\eta_{\omega,e} = R_{ele}i \quad (4)$$

$$R_{ele} = \frac{\rho l}{A} \quad (5)$$

It could be beneficial to provide a review that analyzes the different modeling methods and map out the specific similarities and differences for each parameter's respective model. There is some papers that fulfill this to some degree [1], however, the analysis of each paper largely discusses the benefits and issues with a given model, but does not do any comparative analysis between the models.

2.5 Mass Transport Loss

Mass transport loss is often neglected by many authors due to it's minimal affects at low current density. However, with larger densities or scaling, the losses would become more prominent and the affects could become significant. Mass transport loss occurs when the current density and transport of reactants is not balanced. As the reaction takes place, the reactants either fail to clear the active sites or gaseous byproducts impede fresh reactant material from coming into contact with the membrane.

$$i_0 = i_{0,ref} \exp\left[-\frac{E_{act}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \quad (6)$$

It should be noted that as temperature and hydration increase, ionic conductivity also increases and resistivity decreases. The related conduction is dependent upon the limiting current density (i_0) at which the overpotential begins to exponentially increase, effectively creating a barrier that limits your diffusive potential. This will often require design concessions that will determine future parameters and behavior as limiting current density is modeled dependent on design characteristics.

$$V_{Diff} = \frac{RT}{nF} \ln\left(1 - \frac{i}{i_{lim}}\right) \quad (7)$$

Diffusion transports water via water concentration and pressure differentials between the anode and cathode side. These phenomena drive water transport through the membrane. Hydrogen ions are shuttled with water across the membrane and rejoin electrons on the anode side, producing electro-osmotic drag across the membrane [9]. This drag must be opposed by diffusion and both phenomena contribute largely to the mass transport losses. [10]

2.6 Ohmic Loss

$$E_{ohmic} = \frac{\phi}{\sigma} j \quad (8)$$

Ohmic potential can be calculated simply, relating the electrical resistances from two primary sources, membrane and interfacial resistances [1], [2], [3], [9], [4], [5], [10]. Ohmic overpotential is most commonly calculated with the previous equation representing the ionic resistance. In literature, some authors will elect to model the effects of the electronic resis-

tance with the following equation as equivalent to the previous, while others will separately model the resistance due to the bipolar plates with ohm's law. [9], [4], [5]

Electric losses' behavior primarily follows Ohm's Law and therefore resistivity is proportionally related to voltage and inversely related to current. Losses stem from material resistance to the charged particles and largely depends on material properties. Resistance can also be related to design parameters, largely the cross-sectional area of the ionically conductive membrane. Due to the relationship to Ohm's Law, the ohmic losses follow a linear relationship, which contrasts the nonlinear, logarithmic and exponential behavior of both the kinetic and mass transport losses respectively, motivating the need to model all phenomena separately.

$$V_{ohm} = RI \quad (9)$$

3 Modeling

Modeling PEM Electrolyzers is a complicated and difficult task due to the large number of input parameters. Each parameter is related to other properties and they are often dependent upon another phenomena requiring it's own model. Each model has it's advantages and disadvantages, while no model covers all necessary components of the system. Models are often performed on the two half-cells in order to isolate the anode and cathode reactions. Models come in a wide variety and the challenge becomes selecting the appropriate model to simulate the desired phenomena for the given system.

3.1 Dynamic Behaviour and Thermal Effects

In literature, "dynamics" are modeled in many numerous ways. The definition of what is being modeled is often vague and difficult to narrow down the desired phenomena. The term "dynamic" typically refers to the rate of change of any given parameter, often with respect to time. The intent is to model the way certain properties evolve opposed to more constant, or "static" parameters that can be treated as steady. These processes can be modeled with Ordinary (ODE) or Partial Differential Equations (PDE) and are often zero-dimensional empirical models, however, few are validated with experimental results.

Often, the dynamic behavior that is of importance is heat transfer and it's affect on electrolyzer efficiency and durability. Due to the reactive nature of the electrochemical system, heat is intermittently produced and taken away by chemical reaction, electrical conduction and mass flow. Therefore, heat is generated from more than one source and dissipated similarly. This produces challenges in appropriately modeling the temperature at any given time. If left unwetted, the surface of the membrane can become cracked and worn from undue thermal stress and dehydration. This creates a temporal aspect in which the relevant property observes a rate of change with respect to fundamental quantities such as time or space.

Thermal effects have an added complexity due to the relationship to material, electrical and chemical properties that interact at the interfaces of distinct materials. Each surface must be modeled accordingly including operating ranges for current and temperature.

Due to the difficult nature of modeling some phenomena, some authors will elect to disregard or design their system so that said phenomena is negligible. This is due to a number of reasons, but is only possible because of the volume of parameters and manipulating their

relationships to other properties. For instance, the ability to neglect mass transfer loss at lower current densities due to the lower reaction rate and therefore lower bubble generation. The necessity for accurate modeling of the mass transfer decreases, eventually allowing it to be thrown out completely. The same goes for thermal effects in many cases throughout literature.

3.2 Empirical and Semi-Empirical Models

It is often desirable to utilize empirical or semi-empirical models to analyze different effects on efficiency such as temperature and pressure on the electrolysis reaction. Empirical models work utilizing experimental data to generate parameters. On the other hand, semi-empirical models derive physically meaningful parameters from physical laws. These models are ideal for generating polarization curves, although must be individually tailored to the desired conditions and relevant design.

4 Two-phase Flow

4.1 Bubble Generation

In a PEM Hydrogen Electrolyzer, water transports ions across a semi-permeable, ionically conductive electrolyte membrane. The membrane has a current and when water comes in contact with the external catalyst layer, an electrochemical reaction takes place which splits water and generates heat, hydrogen and oxygen. Those oxygen bubbles generate on the surface of the membrane and are carried away by the water flow. This flow is now two-phase and is necessary to model effectively in order to gain insight to the ideal operating conditions to maximize the chemical reaction taking place. If the current density is high enough, the

reaction is limited by mass transport and consequently, the bubbles can form and stay on the interface of the membrane which can reduce wetness, generate unnecessary heat and as a result cause damage to the membrane. On the other hand, if mass transport is too high, there is a large volume of material that does not get a chance to react and therefore limits the reaction.

These two-phase flow models are used to evaluate the electrochemical performance of the model. The expected behavior of the models can be verified through predicted values derived from polarization curves coupled with experimental results. Molecular interactions between the two phases are dependent upon the molar fraction of each phase. It is desirable to maintain high fluid content in order to continuously remove gaseous bubbles, however, the gaseous bubbles are a product of the electrochemical reaction, a function of the fluid mass transport itself and current density.

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