Mass Transport Limitations in Proton Exchange Membrane Fuel Cells and Electrolyzers

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1. Introduction

The performance of Proton Exchange Membrane Fuel Cells (PEMFC) and Electrolyzers (PEME) is subject to mass transport limitations. Within this chapter we will discuss the origination of those limitations and the current research efforts for mitigation. Hydrogen powered fuel cells operate based on the reaction of hydrogen and oxygen, (Figure 1) where the anode reaction is found in Eq. 1, the cathode reaction in Eq. 2 and the overall reaction in Eq. 3. The reverse of this reaction (Eq. 4) is electrolysis. Where, in the electrolyzer the anode reaction is Eq. 5 and the cathode reaction is Eq. 6.

\[
\begin{align*}
H_2 & \rightarrow 2H^+ + 2e^- \quad E= 0V \quad (1) \\
\frac{1}{2}O_2 + 2H^+ + 2e^- & \rightarrow H_2O \quad E= 1.229V \quad (2) \\
H_2 + \frac{1}{2}O_2 & \rightarrow H_2O \quad E= 1.229V \quad (3) \\
H_2O & \rightarrow H_2 + \frac{1}{2} O_2 \quad E= -1.229V \quad (4) \\
H_2O & \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e^- \quad E= -1.229V \quad (5) \\
2H^+ + 2e^- & \rightarrow H_2 \quad E= 0V \quad (6)
\end{align*}
\]

Basic cell construction is very similar for both PEMFC and PEME. During electrolysis a voltage is applied to the cell while an ion conductor with electrocatalyst layers, such as Pt black on Nafion®, is used to split water into hydrogen and oxygen, as in Figure 2. As water is split into hydrogen and oxygen ions at the anode, the hydrogen ions travel across the PEM and oxygen is collected and exhausted at the bipolar plate. At the cathode, hydrogen ions recombine to create diatomic hydrogen, which can be then be stored for later use. The cell components are similar to those used in a PEM fuel cell, but different bipolar plates must be used due to the corrosive environment. PEMFCs typically use graphite bipolar plates that will degrade under the conditions used in a PEME. Corrosion resistant bipolar plates are substituted for graphite. Titanium plates are typically used, but are very expensive. Stainless steel bipolar plates have also been used, but there is a risk of leaching iron into the water, which would affect the performance of the catalysts and the membrane.
Typically, the electrolyte is a solid polymer electrolyte, such as Nafion®, a sulfonated polytetrafluoroethylene based ionomer. One of the most widely sited structures in found in...
Figure 3 (Yeager and Steck 1981). In this model, the structure of Nafion® is represented in three separate regions. Zone A is the fluorocarbon based backbone of the polymer. Zone C represents the ionic clusters, where ion transport occurs via either a vehicular motion or through the Grothaus mechanism. Zone B is representative of the interfacial region between A and C, consisting mostly of sulfonated ether side chains of the fluorocarbon backbone.

The solid polymer electrolyte is in contact with the catalyst layer. Typically, the catalyst layer consists of a carbon supported Pt based catalyst mixed with ionomer (typically similar materials as the polymer electrolyte). The catalyst electrode must provide channels for the transport of reactants and products, and electrically conductive path for the transport of electrodes from the electrochemical reaction and an ion conductive path for the transport of protons from the electrode to the membrane. As it is shown in Figure 4, the electrode must have a balance in order to avoid performance losses and maximize the utilization of the Pt base catalyst.

The theoretical open circuit voltage for a PEMFC with a pure hydrogen feed is 1.23V. However, actual performance of the fuel cell is considerably lower due to cell resistances, slow reaction kinetics and gas transport limitations. At potentials above 0.9V, losses are attributed slow reaction kinetics at the cathode. Between 0.9 and 0.5V, internal cell resistances govern the incurred losses, while below 0.5V losses can be attributed to gas transport, or the availability of fuel supply for the reaction.

PEME are operated at higher potentials in order to drive the electrolysis reaction of water. During operation of a PEME in the voltage range below approximately 1.4 V the cell is
Fig. 4. Schematic representation of the catalytic layer. (A) where at low Nafion content not all the catalyst particles are connected to the membrane for ionic conduction (B) the optimal Nafion content where there is good ionic and electronic conduction for all the catalyst particles. (C) When there is too much Nafion and not all of the catalyst particles are electronically connected to the diffusion layer. Reproduced from (Passalacqua, Lufrano et al. 2001)
kinetically limited and the current increases exponentially with the cell potential. Between 1.4 V and 1.7 V the cell is transitioning to a mass transfer limited mode of operation. Above 1.7 V, the cell current is completely limited by the diffusion rate of water across the membrane and further increases in the cell voltage do not result in higher cell current. The steady state current that is reached above 1.7 V is known as the mass transfer limited current density. At the mass transfer limiting current density, the rate of water diffusion across the membrane minus the rate of electroosmotic drag is equal to the reaction rate of water at the anode.

In general, the net water flux occurs from the anode to the cathode and higher water content is related to higher performance (Falcao, Rangel et al. 2009). Thus, the influence of water content at the cathode has a higher impact than the water content at the anode. At lower humidification levels, the hydrophilic fraction of the membrane, where the water travels, decreases and overall membrane permeation becomes limited by water diffusion (Majsztrik, Bocarsly et al. 2008).

Figure 4 and 5 shows the representative fuel cell performance outlining the different losses arising from the different components. At low current densities the losses are dominated by the activation polarization, which occur at the cathode under operation with clean hydrogen. The losses are followed by the ohmic resistance, which is mostly attributed to the solid electrolyte. Finally at high current densities, the performance is limited by the mass transport of reactants and products. Semi-empirical approaches have been used to predict and analyze the fuel cell performance. Such an approach is the one by (Pisani, Murgia et al. 2002), where the performance curve can be represented by:

\[
V_{cell} \approx E_0 - R_{cell}I - b \ln(I) + a \ln \left(1 - \frac{I}{I_l} S^{(1 - \frac{I}{I_l})\mu} \right)
\]

with

\[
E_0 = E(I = 0) + K, \quad b = \frac{1 + N^0_d}{\alpha_c \beta_F}, \quad a = \frac{\gamma + N^l_d}{\alpha_c \beta_F}
\]

where \(V_{cell}\) is the cell potential, \(E_0\) is the standard cell potential, \(R_{cell}\) cell resistance, \(I\) is the current density, \(b\) is the Tafel slope, \(I_l\) cell current density at the limiting current density, \(S\) flooding parameter, \(I_l\) cell current density at the limiting current density, \(S\) flooding parameter, \(\mu\) is an empirical constant, \(E\) is the potential, \(K\) is the proportionality constant, \(N^0_d\) is the diffusion mechanism parameter at the zero current density, \(\alpha_c\) is the cathode transfer coefficient, \(\beta_F\) is the Faraday constant, \(\gamma\) is the kinetic exponent of the species in the Butler-Volmer equation, \(N^l_d\) is the diffusion mechanism parameter at the limiting current density.

In real life operation, the use of pure fuel and oxidant gases results in an impractical system. A more realistic and cost efficient approach is the use of air as an oxidant gas and hydrogen from hydrogen carrier molecules (i.e., ammonia, hydrocarbons, hydrides). The short and long term effect of impurities in these gases may have an overriding effect on the fuel cell performance. Common atmospheric impurities in the cathode gas stream that have an effect on the performance of the fuel cell include \(SO_2, NO_2, H_2S, O_3\) (Veldhuis, deBruijn et al. 1998). Even though the hydrogen oxidation reaction occurs at higher rates than the oxygen reduction reaction at the cathode (Sukkee, Wang et al. 2000), the effect of hydrogen
Fig. 5. Performance curve of a PEMFC. Reproduced from the DOE Fuel Cell Handbook (2004)

Fig. 6. Cell loses due to feed. Reproduced from the DOE Fuel Cell Handbook (2004)
Fig. 7. Modified cell performance curve to include losses from impurities in cell feed:

- **No impurities**
- **With catalyst and membrane impurities**

Theoretical EMF or Ideal Voltage

![Graph showing cell voltage and current density with and without impurities.]

Fig. 8. Modified cell loss curves to include feed impurities:

- **Anode Loss (with impurities)**
- **Cathode Loss (Air)**
- **Cathode Loss (O₂)**
- **Electrolyte IR Loss (with impurities)**
- **Electrolyte IR Loss**
- **Anode Loss (H₂)**

![Graph showing polarization and current density with different types of losses.]

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impurities on fuel cell performance can be devastating. Trace impurities arising from different hydrogen production processes include carbon monoxide, carbon dioxide, ammonia, water, sulfur, hydrocarbons, oxygen, helium, nitrogen, argon, formaldehyde, formic acid and halogenates. The effect of the impurities can alter the catalytic activity of the catalyst, the ohmic resistance due to poisoning on the solid electrolyte and changes in the hydrophobicity of the pores affecting the water management in the system, which in turn affects the mass transport. Figures 7 and 8 shows a simplified schematic of the losses on the performance.

2. Cell feed contributions to mass transport losses

2.1.1 Fuel cells

It has been determined that when a PEMFC is operating under dilute hydrogen feed streams (as low as 40% H₂ and a high utilization up to 90%) stack power losses should not exceed 10% of the power achieved with neat hydrogen (Springer, Rockward et al. 2001). When carbon monoxide was present in the dilute feed stream, the power losses were amplified significantly over the neat hydrogen feed stream. The authors suggest this problem may not be solved alone by changing anode catalysts and that a method such as air bleeding may need to be employed to achieve necessary power limits.

This work has been confirmed both experimentally and theoretically (Bhatia and Wang 2004) by other groups. The feed gases tested contained hydrogen contents as low as 40% and as high as 100%. The authors noted that the poisoning of CO was a quick process, taking less than 10 minutes for effects to be seen on the polarization curves for the fuel cell, taking two hours to reach steady state conditions. Yet, the poisoning process was reversible by feeding the cell with pure hydrogen for 2 hours. It was noted that CO preferentially adsorbs on the catalyst surface and when hydrogen is present in a dilute feed stream CO slows hydrogen adsorption even further, resulting in polarization losses. The hydrogen purity standard of the gas will depend dramatically on the dilution level of hydrogen.

The influence of ammonia on PEMFCs has been analyzed by only a few groups (Uribe, Gottesfeld et al. 2002; Soto, Lee et al. 2003; Halseid, Vie et al. 2006). In general, it was found that ammonia exposure has detrimental effects on the fuel cell performance. There was a steady loss of performance associated with the increase in current density and an overall increase in cell resistance. When the exposure was studied exposure from 1-30ppm NH₃, it was found that the poisoning process was slow, up to 24 hours (Halseid, Vie et al. 2006). This poisoning was also reversible in most cases, but only after exposure to neat hydrogen for several days, while exposure to as low as 1ppm was found to have had detrimental effects on the fuel cell system performance. Ammonia was highly soluble in the membrane, but had no significant adsorption on the gas diffusion layer. This adsorption on the membrane by ammonia impurity was determined to have the largest effect on the oxygen reduction reaction, requiring an increase in power to drive the reaction to occur. The authors suggest that all ammonia must be removed from the feed stream before hydrogen can be used as a fuel and that the nitrogen content is closely monitored to prevent formation by metal-hydride alloys for hydrogen storage. The effects of ammonia at ppm and sub-ppm concentrations have been studied by (Martinez-Rodriguez, Fox et al. 2011) In their testing it was demonstrated during hydrogen pump experiments and electrochemical impedance spectroscopy that at concentrations of 10 ppm the effects of ammonia not only affect the solid electrolyte membrane, but at high current densities the resistance by the ionomer in the
electrode is significantly higher than on the membrane. On the other hand during fuel cell testing, at 0.1 ppm the performance is unaffected by the ammonia. An investigation on the effects of slightly higher concentrations of ammonia on PEMFC performance (Uribe, Gottesfeld et al. 2002), found the damage to the fuel cell to be irreversible, unlike previous results (Halseid, Vie et al. 2006). Even at 30ppm levels it was found the cell performance to drop considerably after several hours of exposure. The authors were able to successfully trap the ammonia using an ion exchange resin and continue use of the fuel cell without further damage. Fuel cell systems are even more sensitive to sulfur containing compounds, yet few systematic studies have been completed on the phenomenon. Mohtadi et al. found that exposure to 5ppm of \( \text{H}_2\text{S} \) would cause a 96% performance loss in a Pt catalyst based PEMFC (Mohtadi, Lee et al. 2005). This rate of poisoning was approximately 69% lower at 50°C than at 90°C. There was also evidence that sulfur crossed over at the cathode and affected the oxygen reduction reaction. Recent research by Ballard Power Systems on a commercial stack suggests that not only is the source of a hydrogen impurity important, but it’s point of induction also (Knights, Jia et al.). The following impurities were found to effect cell performance in decreasing order: \( \text{H}_2\text{S} \) in fuel > \( \text{SO}_2 \) in air > \( \text{NO}_2 \) in air > \( \text{NH}_3 \) in air > CO in fuel > \( \text{NH}_3 \) in fuel. This suggests that the control of environmental air pollutants is as important for PEMFC operation as a high purity hydrogen standard. The changes in air quality could result in up to 30mV performance loss, which was most noticeable on cold, clear days. In order to address problems such as performance loss due to impurity effects, new catalysts or membranes are being developed. Recent studies have been investigating the effect of trace halide contaminants on performance (Martínez-Rodríguez, Fox et al. 2011). The study of tetrachloroethylene, a common cleaning and degreasing agent, found that even at levels equal to the current ISO standards for hydrogen purity (ISO under development) detrimental impacts on fuel cell performance occur. At overpotentials above 0.2V, cell performance was fully recoverable. Poisoning that occurred at lower potentials was recoverable either by purging the cell or by changing the operating voltage.

### 2.1.2 Electrolyzers

PEM electrolyzers have a thermoneutral voltage of 1.48V, below which \( \text{H}_2 \) or \( \text{O}_2 \) cannot be generated. Testing of single cell PEM electrolyzers, operated at 75°C, have produced cell efficiencies of 82% at 1 A/cm\(^2\) and 69% at 2 A/cm\(^2\) (Badwal, Giddey et al. 2006). Results indicate that the voltage losses experienced are ohmic in nature, or the voltage drop is the resistance of electron flow across the electrodes and interconnects of the cell. The cell was found to have better performance with thinner membranes, but these membranes have a shorter lifetime and are more fragile. The optimal operating current density of a water electrolyzer is between 0.5-1 A/cm\(^2\), where resistances are minimized (Wendt and Imarisio 1988). Minimizing the ohmic resistance of the cell is important due to the high internal resistance and overvoltages experienced during operation. Cell efficiency will increase with decreasing resistance. Cell voltages will decrease with increasing cell temperature due to the decrease in overpotential and resistive losses (Onda, Murakami et al. 2002). If the individual cell is upgraded to small stacks of approximately fourteen cells, enough heat is generated due to internal resistive losses to make the cell thermally self-sustaining (Badwal, Giddey et al. 2006).
Uniform current density is an important factor to the lifetime of the membrane. A uniform current density is important to prevent the formation of hotspots, which can further decrease the performance of the electrodes and membranes. If the electrolyzer ratio (flow rate of electrolyzed water divided by the flow rate of the feed water) is less than 10%, the current density distribution in the cell is uniform in the cell (Onda, Murakami et al. 2002). At higher ratios, the current density will increase upstream where there is sufficient water and the current density will decrease downstream where there is insufficient water for the reaction. The performance of PEM electrodes has been found to be sensitive to differential pressures as low as 20 mbar between the cathode and anode sides of the cell (Millet, Andolfatto et al. 1996). If high operating pressures are used, the differential pressure must be controlled. Stainless steel pipes in contact with deionized water can cause a steady decrease in cell voltage. Low concentrations of Fe, Ni and Cr from the stainless steel became concentrated in the membrane, limiting cell performance. On-line deionizers were found to give a more stable performance, but can impose limitations when used with high operating pressures and temperatures.

Demonstration electrolyzer plants, rated at 100kW, have been successfully run for up to 15,000 hours (Stucki, Scherer et al. 1998). One plant was shut down after 15,000 hours due to hydrogen concentrations in the oxygen off-gas of higher than 3 percent. A second demonstration plant, run for only 2300 hours with 50,000 hours of standby operation, was shut down for the same reason. During the standby period, a protective polarization current of 0.34 mA/cm$^2$ was applied in order to prevent corrosion of the current collectors at the cathode. Post mortem analyses of membranes from both plants indicate that stack failure was due to thinning of the Nafion® 117 membrane. The non-uniform membrane thinning coincided with an observed decrease in cell voltage. The ion exchange capacity of the membranes remained consistent throughout operation.

![Cell polarization comparison for anode liquid feed and cathode vapor feed PEM electrolyzer cells at 30°C.](greenway2009)

Fig. 9. Cell polarization comparison for anode liquid feed and cathode vapor feed PEM electrolyzer cells at 30°C. (□) Anode liquid feed (△) Cathode vapor feed. Reproduced from (Greenway, Fox et al. 2009)
The efficiency of PEME are greatly affected by the water content of the feed. The mass transfer model presented in previous work (Fox, Greenway et al. 2008) predicted that the current for an anode liquid water feed electrolyzer would be around 8 times larger than the limiting current in a cathode water vapor feed electrolyzer. The difference in the cell polarization between these two feed configurations is shown in Figure 9. The mass transfer limiting current density for the cathode water vapor feed system is around 92 mA/cm$^2$ while the current for the cathode water vapor feed system is near 475 mA/cm$^2$ at 1.8V at 30°C. This current density could most likely be increased to 1000-1400 mA/cm$^2$ if the a higher current density is desired and if it was determined that the higher voltage did not significantly affect the lifetime of the MEAs. Therefore, the cell current density produced by the anode liquid water feed system and thus the water reaction rate could be between 5-8 times larger than a similarly sized cathode water vapor feed system. To get an equivalent water processing rate between the two systems, either the reaction area of the cathode water vapor feed system or the number of cells used for processing the water would need to be increased proportionally to the difference in current density.

3. Mitigation of mass transport losses

Membrane development is of particular interest due to the limitations of current Nafion® membranes such as temperature restrictions due to dehydration and subsequent loss of conductivity. In order to meet these demands researchers have attempted to improve the membrane by doping or by investigating new polymer membranes. These alternate routes may also be used to increase fuel cell performance in the presence of gas impurities such as carbon monoxide. For example, the effects of carbon monoxide on alternative membranes such as poly(2,5-benzimidazole) have been investigated (Krishnan, Park et al. 2006). These polymers, doped with phosphoric acid, had the ability to be operated at temperatures up to 210°C with 1% CO without performance losses, which are higher temperatures and higher carbon monoxide concentrations than conventional MEA configurations are tolerant. Other investigations involve using alternatives such as glass papers to support organic membranes (Tezuka, Tadanaga et al. 2005). The membranes cast from 3-glycidoxypropyltrimethoxysilane and tetraalkoxysilane would otherwise be too thick and have to high of a resistance for viable fuel cell use. These membranes were able to achieve a maximum power density of 80mW/cm$^2$ at 130°C and 7% relative humidity. Other methods of development include (Jalani, Dunn et al. 2005) impregnating Nafion® to create more stable composite materials. The authors found that when Nafion® was impregnated with ZrO$_2$, SiO$_2$ and TiO$_2$ the composite membranes has better water retention and thermal stability than Nafion® alone. ZrO$_2$ impregnated Nafion® had the best performance overall and this is believed to be due to the increased acidity and surface area of the membrane. ZrO$_2$ impregnated Nafion® was the only modified membrane that showed increased conductivity over Nafion®. Leading the authors to conclude that the distribution of water between the surface and bulk of a system is as important as the amount of water absorbed.

Other than membrane development, an alternative method of improving the MEA is through catalyst development. A current area of interest is the use of non-precious metals or new binary catalysts for the oxygen reduction reaction at the cathode. Presently Pt and Pt alloys are widely used as anode and cathode materials in Proton Exchange Membrane.
(PEM) Fuel Cells. Despite a cathodic over potential loss of 20%, Pt and Pt alloys are still preferred for their resistance towards corrosion in acidic media. Pt however, being an expensive metal of low abundance, it is of interest for researchers to develop a corrosion resistant non noble metal substitutes. These non-noble metal catalysts can range from metalloporphyins and bimetallic transition metals to heat treated metal catalyst (Wang 2005; Colón-Mercado and Popov 2006; Li, Qiao et al. 2009). The main advantage of the use of non-noble metal catalysts is the reduction in cost and ease of availability, although the precious metal based catalysts consistently have higher activity for the reaction, the results are promising.

4. Conclusion
Mass transport limitations in PEME and PEMFC may be due to several factors. Poor control of humidification levels within the cell can result in substantial losses in potential. In addition, good electrical and ionic conduction must be achieved between the electro catalyst layer and the membrane and diffusion layers. This will enable better utilization of the catalyst and limit cell losses through mass transport.
In addition, the feed provided to the PEMFC or PEME can greatly attribute to cell losses. If there are impurities present in the feed, it may affect the electrocatalyst performance or conductivity of the electrolyte. In both cases, substantial potential losses may be achieved, which may or may not be reversible, depending on the impurity present. In order to mitigate these effects, there is an on going effort to develop more tolerant electrocatalyst and membranes for these systems.

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6. References


Our knowledge of mass transfer processes has been extended and applied to various fields of science and engineering including industrial and manufacturing processes in recent years. Since mass transfer is a primordial phenomenon, it plays a key role in the scientific researches and fields of mechanical, energy, environmental, materials, bio, and chemical engineering. In this book, energetic authors provide present advances in scientific findings and technologies, and develop new theoretical models concerning mass transfer. This book brings valuable references for researchers and engineers working in the variety of mass transfer sciences and related fields. Since the constitutive topics cover the advances in broad research areas, the topics will be mutually stimulus and informative to the researchers and engineers in different areas.

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