

Water Management in a PEM Fuel Cell by Material Design and Engineering of the MEA

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Abstract

PEMFCs depend on proper water management to obtain high power density and energy efficiency. Traditionally, water management has been addressed by system design and engineering. That is, by adding auxiliary systems to the basic fuel cell system to provide humidification to the anode and remove water from the cathode. This approach adds significant complexities and costs and reduces the overall efficiency of the PEMFC system. To simplify the complexity of the PEM fuel cell system, an alternative approach is explored. In this new approach, components with the right properties will be used in the membrane and electrode assemblies so that the zero-net-water-transport-across-the-membrane condition can be achieved. This presentation discusses the components and the properties required to achieve the condition of zero-net-water-transport-across-the-membrane.

Introduction

Proton Exchange Membrane (PEM) fuel cell is being considered as a power source for a variety of applications because of its high efficiency, simplicity in design and operation, and environmentally friendly characteristics. Significant efforts in multiple areas in the past two decades have brought this technology to a point that commercialization in a near future is now considered a possibility. The biggest obstacle to the commercialization of this technology currently is its cost. If the cost issue could be addressed, the remaining technical issues such as durability and low temperature startups would be quickly resolved.

There are mainly two reasons for the current high cost of the PEM fuel cell system. The first one is due to the cost of the materials. The second one, arguably the more significant one, is due to the complexity and the cost of the auxiliary systems needed to operate a fuel cell system. These auxiliary systems are used mainly to provide proper gas, water and thermal management to the system. Of the gas, water and thermal management requirements, water management is believed to be the most crucial one.

PEM fuel cells depend on proper water management to obtain high power density and energy efficiency. During operation water is dragged from the anode to the cathode by electro-osmosis leading to dehydration at the anode. Concurrently, in addition to water transported from the anode by electro-osmosis water is also generated at the cathode by the oxygen reduction reaction. When the water created in the cathode is not properly removed its accumulation leads to poor fuel cell performance by blocking the gas pores used for oxygen gas transport and forming an additional transport barrier over the reactive area. In some applications and conditions, cathode humidification is desired.

Traditionally, water management has been addressed by system design and engineering. That is, by adding auxiliary systems to the basic fuel cell system to provide humidification to the anode and to remove water from the cathode. This approach has added significant complexities and costs to the system. Furthermore, these auxiliary systems reduce the net power output of the fuel cell system leading to lower conversion efficiency. Some of the traditional approaches of water management in PEM fuel cells are listed below.

Old Paradigm: Water Management by System Design and Engineering

Anode/Cathode Gas Humidification: To provide humidification to the anode/cathode, various humidification strategies and systems have been adopted. Figure 1 lists some of the strategies employed by various fuel cell developers.^[1] Each system has its own advantages and disadvantages. Regardless of which one is used, additional complexity, cost and parasitic power loss are involved.

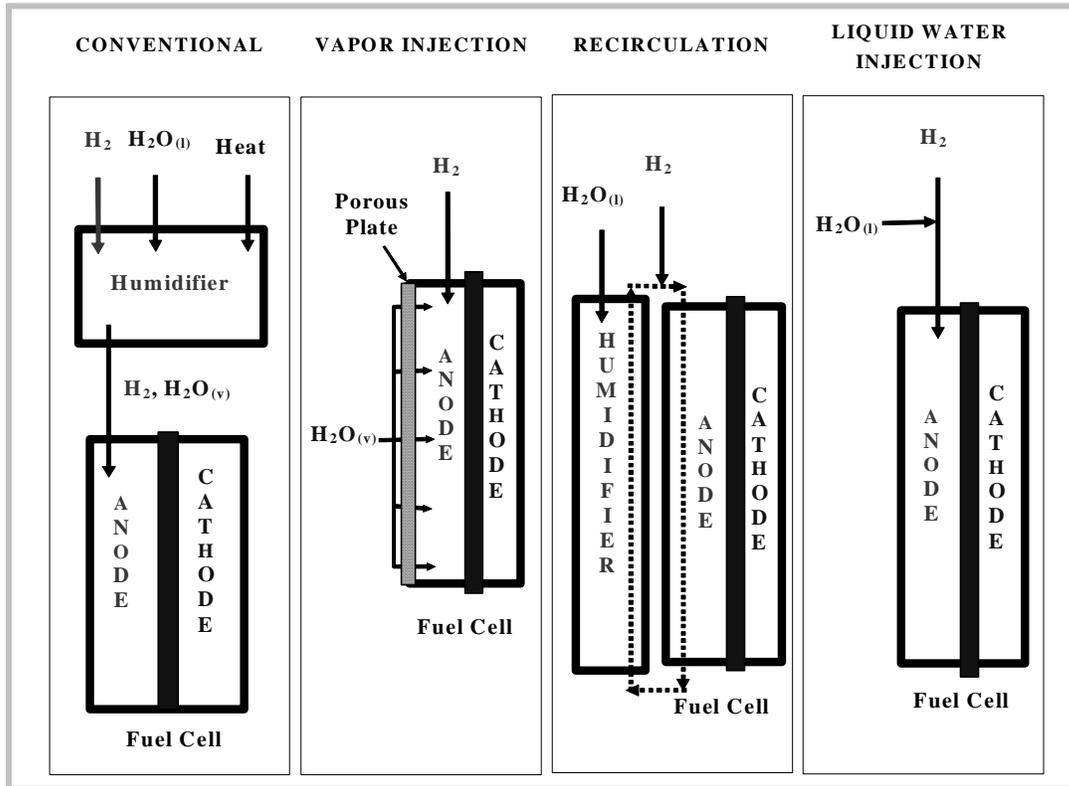


Figure 1. Humidification strategies used in PEM fuel cells.

- **Conventional:** The feed stream is humidified with water externally prior to entering the fuel cells. In this approach, the amount of water that can be added to the gas stream is limited by the saturated vapor pressure of the system.
- **Vapor Injection:** A porous gas flow plate with control pore size is used in which liquid water is fed to one side and gas is flown on the other side. Liquid water permeates through the porous plate and evaporates into the gas stream to provide humidification. This approach has been proven to provide more uniform humidification along the flow channels. However, manufacturing a material with consistent and uniform pore size and distribution is a complex and expensive process. Furthermore, freezing is a major problem for this design.
- **Recirculation:** An external humidifier similar to the first system is used. However, a recirculation loop is added to increase the humidification rate. This approach has shown to be very effective in providing humidification to the anode. The main drawback is the durability of the recirculation pump. Since the fluid being used is hydrogen, the pump has to be hermetically sealed from the environment, making these pumps quite expensive.
- **Liquid Water Injection:** Liquid water is injected directly into the anode gas stream. This approach has a higher humidification capability and can be used for simultaneous heat removal. However, handling two-phase flow effectively is a major problem.

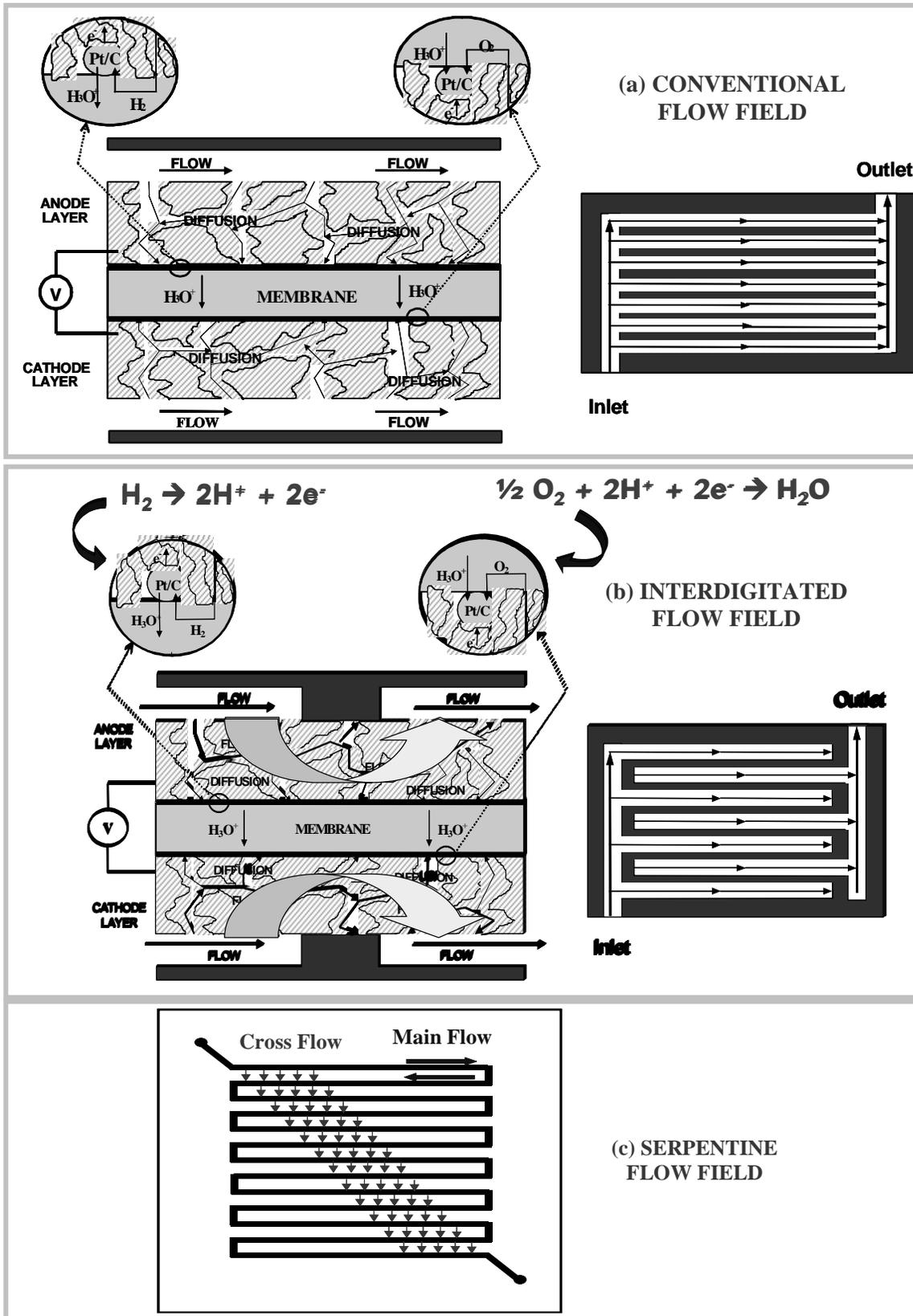


Figure 2. Most widely used flow field designs in PEM fuel cells (not to scale).

Water Removal by Flow Field Design: To remove water from the cathode so that electrode flooding of the gas pores needed for active gas transport from the flow channels to the catalyst surface can be prevented, three main flow field designs have been considered: the conventional flow field consisting of straight parallel channels, the interdigitated flow field, and the serpentine flow field (see Figure 2).^[2,3]

- In the flow field design with straight parallel channels, flow is mainly within and along the channels. Transport of the reactants and products to and from the electrode is mainly by diffusion through the porous backing layer. Consequently, the electrochemical performance could be limited by the transport rate of these species. This design is suitable for applications in which high gas flow rate and low-pressure drop are required.
- In the interdigitated flow field, gas is forced to flow through the backing layer of the electrode. The shear force of gas flow is used to flush the liquid water out of the backing layer to prevent flooding of the cathode. Due to its convective flow characteristic, this design provides the highest transport rate of the reactants and products to and from the electrode and, consequently, the best fuel cell performance. However, since gas is forced to flow through the porous backing layer instead of along the channel, high pressure is required. Furthermore, there is a concern that the porous backing layer could become a gas filter, and in this role it could become clogged with dirt. Finally, if dry feed gases are used, it could result in electrode/membrane dehydration at low current densities because of the enhanced mass transport in the backing layer.
- In a serpentine flow field, a single or multiple parallel serpentine channels are used. Flow is mainly along the channels. However, depending on the length of each turn of the channels and corresponding pressure drop along each turn, sufficient pressure difference could promote the gas to short-circuit through the porous backing layer to reach the next turn. This short-circuit flow allows the serpentine flow field design to have some of the interdigitated cross flow characteristics and their inherent benefits.

Water Removal by Differential Pressure: An alternative way to remove water from the cathode is to transport it back to the anode. This can be achieved by creating a differential gas pressure between the cathode and the anode. This differential pressure can increase the water transport rate back to the anode by creating an additional water transport mechanism: forced permeation through the membrane by a pressure gradient.^[4] This leads to lower water accumulation level in the cathode and higher reactant gas transport rate to the cathode catalyst sites. However, this also leads to a higher gas crossover rate of the cathode gas to the anode, especially at low power densities where the membrane is less hydrated because less water is generated. Another major drawback is the need to compress the cathode gas, a significant source of parasitic power.

Thinner Membranes: This is probably the first attempt of using materials to address water management in PEM fuel cells. It was recognized very quickly by the late 1980's that if more of the water generated at the cathode could be transported back to the anode, then the requirement of anode humidification could be reduced. This reduction could be achieved by shortening the distance of the back diffusion process, or essentially using thinner membranes. Membranes down to 10 μm have been used. Thinner membranes also offer an additional benefit of lower ionic resistance. However, the difficulty associated with manufacturing thin membranes that are pinhole-free and the concerns associated with durability and gas crossover rates have limited the membranes used in practical fuel cell applications to 25-40 μm . At these membrane thicknesses, the water transport rate from the cathode to the anode by diffusion is still not sufficient to significantly reduce or eliminate the need for anode gas humidification, especially for operating conditions above 60°C.^[5,6]

Figure 3 shows the water requirement calculations for various tasks in a PEMFC operating at 70°C, 2 atm, 1.2 H₂ stoich, and 2.0 air stoich. The electro-osmotic drag coefficient is assumed to be 1 H₂O/H⁺. Note that the amount of water associated with proton or electro-osmotic drag is quite large relative to the amounts generated by reaction and for anode feed and cathode feed humidification. Even though the

effect of electro-osmotic drag does not change the net system water requirement when the water added to the anode to compensate for electro-osmotic drag is recovered from the cathode exhaust and recycled back for use at the anode, the redistribution of water from the anode to the cathode is a major water management problem with significant effect on the electrochemical performance of the fuel cell. Excess water must be added to the anode stream in a way that avoids flooding of the anode electrode structure. Simultaneously, the combined amount of water generated in the cathode by electro-osmosis and reaction must be removed fast enough to prevent flooding of the cathode electrode structure and in a way to have minimal impact on the counter-current transport of the reactant (O_2) to the reactive sites. As a matter of fact, cathode flooding is the main cause of poor performance in a PEM fuel cell at high current densities.

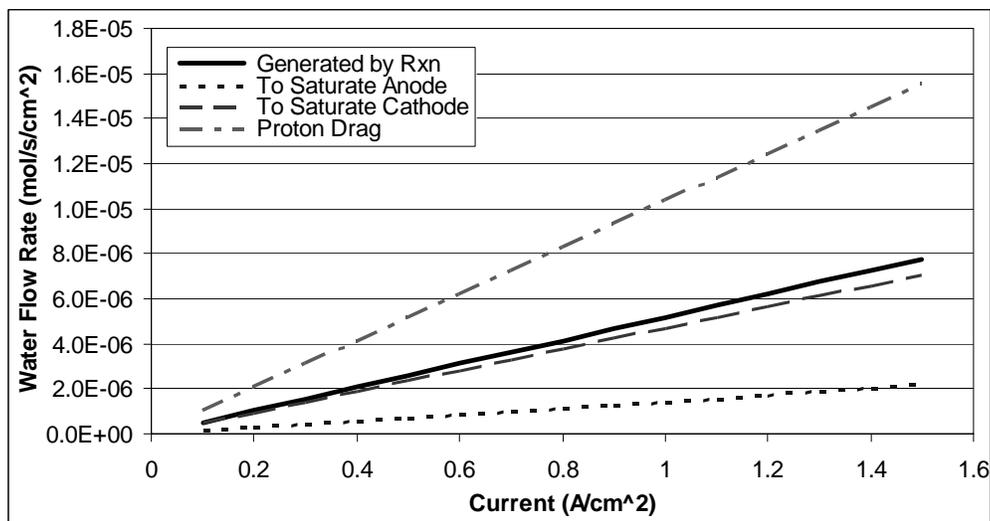


Figure 3. Water requirements for various processes in a PEM fuel cell

It is quite clear from the processes described above that unless the water transported from the anode to the cathode by electro-osmosis could be transported directly through the membrane back to the anode, the current approach of supplying water to the anode gas stream to compensate for the water loss by the electro-osmosis process is a self-defeating exercise both in terms of water management and thermal management. Energy is used to vaporize water so that it can be transported along with hydrogen through the anode electrode structure to the membrane/gas interface. When water vapor is absorbed by the membrane, energy is released and must be removed. After this water is transported across the membrane by electro-osmosis, it has to be removed from the cathode either in the form of liquid water or water vapor. In the form of liquid water, the transport rate is too slow and results in water accumulation that causes electrode flooding and poor fuel cell performance. To form water vapor that can be transported more quickly out of the cathode, energy is needed.

In summary, water is added into the anode and then removed from the cathode, and thermal energy is added into the cell in the form of water vapor in the anode stream, and then removed later from the cell. This is why this approach is considered to be self-defeating. Until a membrane that can operate with minimal or no water is found, the optimal water management approach is to find a way to force the water transported from the anode to the cathode by electro-osmosis back to the anode through the membrane so that there is no net transport of water across the membrane. Consequently, the only water that a fuel cell would need is for humidifying the cathode feed, and this water could be obtained from the water generated by the cathode reaction. This approach will eliminate the need for an on-board “de-ionized” water source and allow the water management system to be greatly simplified. Water management approaches in which the water transported from the anode to the cathode by electro-osmosis is forced back to the anode through the membrane to achieve the condition of no net-water-transport-across-the-

membrane and the achievement of this condition solely by material engineering are the merits of this new approach.

To simplify the complexity and to reduce the cost of the current PEM fuel cell system due to the water management requirements, a new water management approach based on material engineering is explored. Components used in the membrane and electrode assembly (MEA) of a PEM fuel cell will be “material engineered” to have the proper morphological, transport and surface properties to create a condition in which the water transported from the anode to the cathode by electro-osmosis is forced to flow back to the anode to maintain optimal membrane hydration without the need of anode gas humidification. Furthermore, this condition is to be achieved without any negative effect on the electrochemical performance of the fuel cell. Note that the approach of using material properties to achieve zero-net water transport across the membrane as proposed here constitutes a major paradigm shift in water management in PEM fuel cells. The components that are being investigated for this study consist of the following porous media.

New Paradigm: Water Management by Material Engineering

Macro-porous Gas Diffusion Layers: This layer, which is made of either carbon paper or carbon cloth, was first developed as a porous support for the catalyst layer. Carbon was selected because its corrosion does not lead to contamination of the membrane. As a support it provides electronic conductivity and access for the reactant and product (both gas and liquid) between the flow distribution plate and the catalyst layer. When it was recognized that liquid water could exist in the PEM fuel cell electrodes and result in flooding of the gas diffusion layers during operation, a hydrophobic phase such as Teflon[®] was added to create hydrophobic channels for gas transport. Experimental data obtained by my group using commercially available gas diffusion materials have shown that better fuel cell performance was obtained when a hydrophobic phase was added. These results also showed that the performance increased with wet-proof level up to a certain amount, beyond which additional amounts of wet-proof materials appeared to lower the performance. The optimal content appeared to vary with the thickness of the samples.

Hydrophobic Micro-porous Layers: A few years ago, multi-layer gas diffusion materials consisting of a dense, hydrophobic micro-porous layer supported by a high-porosity, macro-porous backing layer were introduced. The micro-porous layer was used to provide a better support and more intimate electrical contact with the catalyst layer. This is especially important for the case in which the catalyst layer was directly applied onto the gas backing layer to create an electrode for the membrane and electrode assembly. Without this dense micro-porous layer it was found that either a continuous catalyst layer could not be formed or the catalyst ink penetrates deeply into the macro-porous backing material, resulting in low catalyst utilization. Furthermore, the hydrophilicity of the Nafion[®] phase in the catalyst layer that penetrated into the gas diffusion material resulted in severe flooding of the gas diffusion material. The fuel cell performance was found to increase significantly when these multi-layer gas diffusion materials are used as the electrodes in the MEA of a PEM fuel cell.^[7,8,9] See Figure 4.

There had also been suggestions that the hydrophobic micro-porous layer lowers the liquid water saturation level in the macro-porous backing layer and enhances the transport rate of liquid water from the cathode porous backing layer to the gas channels. Earlier models from Kaviani’s group at The University of Michigan and Wang’s group from The Pennsylvania State University supported the concept above.^[10,11] However, recent models from Weber and Newman at The University of California at Berkeley^[12], Wang’s group from The Pennsylvania State University^[13] and my group at The University of Kansas^[14] showed that in addition to the benefits listed above, the micro-porous layer at the cathode also forces a significant amount of water through the membrane back to the anode. This significantly reduces the amount of water at the cathode that has to be removed by the gas-backing-layer-to-gas-channel route leading to lower electrode flooding condition in the cathode at high current densities. Furthermore, and most importantly, this back transport of water through the membrane to the anode helps to reduce the anode humidification requirement and maintain high membrane hydration and conductivity.

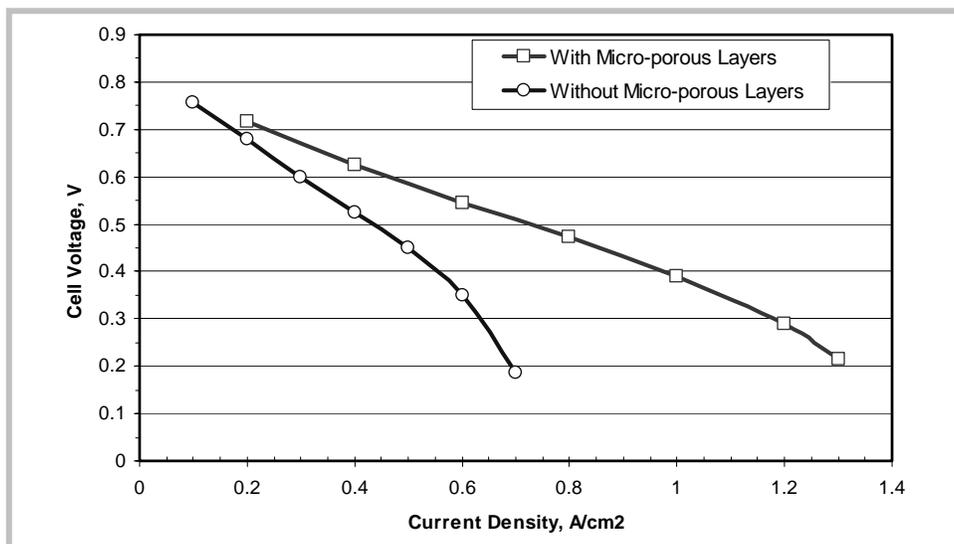


Figure 4. Fuel cell performance increases when MEA with the micro-porous layers is used.

Summary

Proton Exchange Membrane fuel cells (PEMFCs) are being considered as power sources for various applications because of their high efficiency, simplicity, and environmentally friendly characteristics. PEMFCs depend on proper water management to obtain high power density and energy efficiency. Traditionally, water management has been addressed by system design and engineering. That is, by adding auxiliary systems to the basic fuel cell system to provide humidification to the anode and to remove water from the cathode. This approach adds significant complexities and costs and reduces the overall efficiency of the PEMFC system. Recent development of new materials has led to a paradigm shift as to how water management can be implemented in a PEMFC system.

The new revelation on the forced transport of water from the cathode to the anode by the micro-porous hydrophobic layer is the foundation of the new approach of using material engineering to develop materials with the proper two-phase transport properties to force the water that is transported by electro-osmosis to the cathode back to the anode to achieve zero net water transport across the membrane. In this approach, gas diffusion materials with different two-phase transport and morphological properties are explored to determine the optimal combination of material properties and electrode configuration that will generate sufficient liquid water pressure gradient across the membrane to help force all the water transported by electro-osmosis back to the anode to meet the objective of zero-net water transport across the membrane.

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