Encyclopedia of Electrochemical Power Sources

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PEMFC Cells

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Abstract

A PEMFC unit cell consists of a proton exchange membrane, anode and cathode catalyst layers, gas diffusion layers, sealing elements and flow-fields. In this chapter, the operational principles of a PEMFC unit cell are discussed with respect to the basic functions and desirable qualities of these individual cell components. The current-voltage (polarization or performance) curve of a unit cell is analyzed with respect to losses from kinetic, thermodynamic, ohmic, concentration, short-circuit and crossover polarizations. A brief overview of basic diagnostic tools and visualization techniques currently in practice for evaluation and characterization of a PEMFC unit cell is presented. The aspect of cell design is presented with respect to their end applications. The evolution of PEMFC performance is presented along with the developmental challenges that fuel cell component designers currently face towards commercializing this technology, including materials selection, cost and performance optimization. Finally, current approaches towards large scale manufacturing of cell components and their assembly to functional unit cells are discussed.

Keywords: Current, Design, Efficiency, PEM Fuel Cell, Voltage

Introduction

Proton exchange membrane or polymer electrolyte membrane fuel cells (PEMFCs) operating on gaseous hydrogen (H_2) and oxygen (O_2) are electrochemical energy conversion devices that directly convert hydrogen's chemical energy into electrical energy. In a PEMFC, H_2 and O_2 combine electrochemically to produce water (H_2O), power and waste heat. This direct energy conversion circumvents most of the intermediate steps of producing heat and mechanical work common to majority of power generation methods. As a result, PEMFCs are not limited by the thermodynamic limitations of conventional heat engines, such as Carnot efficiency, and are able to generate high power densities making them potentially attractive for light-duty transportation applications. Additionally, due to the absence of chemical combustion involving carbonaceous fuels, H_2 powered PEMFCs have minimal environmental impact than most power generators.

The state of the art PEMFC power plant typically consists of (1) a fuel processing unit, which supplies purified H_2 (2) a PEMFC stack module, the heart of the power plant and (3) balance of plant, which include components that provide water management, thermal management, power conditioning and other ancillary functions. The PEMFC stack module is in turn made of unit cells that are modularly combined or stacked and are electrically connected to each other. The number of unit cells and the nature of electrical connections between each unit cell are based on the desired output capacity of the PEMFC stack. A unit cell is made of (1) a proton exchange membrane, (2) anode and cathode electro-catalyst layers placed on either side of the membrane (3) an electrically conductive gas diffusion layer (GDL) or porous transport layer (PTL) placed next to the

catalyst layers (4) a sealing element and (5) cell interconnects and/or flow fields that deliver H_2 and O_2 via gas channels and electrically connect the cells. The anode, cathode and the membrane constitute the membrane electrode assembly (MEA) and together with the seal is commonly referred to as an unitized electrode assembly (UEA). The proton exchange membrane that is in wide use today consists of a polytetrafluoroethylene (PTFE) backbone with perfluorinated-vinyl-polyether side chains containing sulphonic acid end groups (e.g., Nafion®). The anode and cathode catalysts are composite structures consisting of a proton conducting polymer and a carbon supported metal catalyst. The GDLs are either carbon paper (e.g., Toray®) or cloth. Fig. 1 shows the cross-sectional schematic of a unit cell with a flow field that also serves as a current collector along with the anodic and the cathodic reactions. A three dimensional view of this unit cell as a repeat unit in a PEMFC stack is shown in Fig. 2. A non-porous bipolar plate shown in cross-flow configuration in this figure serves both as a flow-field for gas distribution as well as a conductor of current from one cell to the next.

Operational Principles of Cell Components

On the anode, H_2 is oxidized to protons and electrons. The protons move across the membrane (hence the term 'proton exchange membrane') while the electrons flow through the external circuit, both towards the cathode, where they combine with O_2 to form water (Fig. 1). This flow of electrons creates work and is proportional to the load (or resistance) on the external circuit. Due to the direction of the flow of electrons, the polarity of the anode is negative and that of the cathode is positive. These reactions can occur spontaneously at any temperature above absolute zero. However, PEMFCs are typically operated around 80 °C, where they are most efficient. Though the overall

operational principle is simple, the unit cell in itself is a highly integrated system. The unit cell is more than a simple collection of its constituent components because a change in one of them impacts the performance of the others. Each component of the unit cell performs a unique role contributing to the overall operating principle, which is described below.

Proton exchange membrane

The proton exchange membrane in a PEM unit cell serves two important purposes: (1) it keeps the fuel and the oxidant (i.e., H_2 and O_2) from mixing and reacting chemically and (2) it serves as the solid polymer electrolyte and selectively transports the protons generated at the anode to the cathode thereby completing the circuit. The functional requirements of PEM include high protonic conductivity, good thermal, mechanical and chemical stabilities, reasonable operating range (temperature and humidity), low porosity (i.e., low gas transport) and easy manufacturability. The widely used membrane in today's PEM fuel cell is Nafion® originally developed by Walther Grot in DuPont in the late 1960s by modifying Teflon®. Nafion® ionomer, a subset of poly electrolytes (i.e., ion containing polymers) consists of hydrophobic polytetrafluoroethylene (PTFE) backbone with perfluorinated-vinyl-polyether side chains containing hydrophilic sulphonic acid end groups. The hydrophobic and the hydrophilic regions come together to form clusters or aggregates and act as physical cross-links. The cluster size depends on water content and increases with water uptake, resulting in swelling. Therefore, Nafion® can be said to have the physical and chemical properties of Teflon® base material with additional ionic characteristics. These ionomeric polymers are characterized by their equivalent weight defined as the ratio of grams of dry polymer to

moles of ion exchange sites. The lower the equivalent weight, the larger the number of ion exchange sites. Though large number of ion exchange sites is desirable, polymer stability is reduced due to dissolution at low equivalent weights. Typical commercially available Nafion® membranes have an equivalent weight of 1100. The proton conductivity in these ionomers is a strong function of hydration. The proton conductivity mechanism in Nafion® is thought to be of two types: (1) Vehicular mechanism, in which the proton is attached to a solvent molecule called vehicle (i.e., H_3O^+) and moves at the rate of vehicular diffusion. The net proton transport is governed by vehicle diffusion rates. (2) Grotthuss or hopping mechanism, in which the proton hops from one stationary vehicle to the next. The solvent reorientation paves the way for H^+ conduction and ensures their continuous motion. Because of this, fully hydrated (saturation) conditions result in higher proton conductivities.

These perfluorosulfonic-acid membranes were originally developed for the chlor-alkali industry and so the fuel cell environment is relatively mild. The need for high power densities has led to much thinner membranes than those developed for the chlor-alkali industry. For example, Nafion® 117 has a thickness of 175 μm (the "7" in "117" refers to a membrane seven thousandths of an inch thick while "11" refers to an equivalent weight of 1100). Now the standard for a laboratory unit test cell is Nafion® 112, which is 50 μm thick, and that for those unit cells in commercial stacks have membranes thinner than 25 μm. These thinner membranes have less mechanical strength, which has lead several manufacturers to develop composite membranes akin to reinforced Nafion®. Another consequence of using thinner membranes is an increase in reactant crossover, which decreases fuel utilization and the cell performance. This is

especially problematic in a direct methanol fuel cell (DMFC) since methanol has similar properties to water. Thicker membranes reduce reactant crossover but at the expense of higher resistance and hence lower power density. Researchers are currently developing composite membranes with the dual properties of high proton conductivity and low reactant crossover.

Although Nafion® has been the standard for PEM fuel cells, the market is demanding alternative operating conditions, which is driving the search for new membranes. For example, the automobile companies would prefer membranes that are functional at elevated temperatures (> 100 °C) and low relative humidities (< 25% RH). The former would dramatically reduce the size of the radiator while the latter would offer quicker start-up and easier freeze-thaw cycle management. However, it is not possible to maintain adequate membrane water content, and hence acceptable proton conductivity, at higher temperatures without operating at elevated pressures. Elevated pressures introduce additional problems such as a need for an energy consuming compressor. In addition, the glass transition temperature of Nafion® is 111°C and therefore its mechanical stability is compromised at elevated temperatures.

Anode and cathode catalyst layers

The anode and the cathode catalyst layers serve the purpose of (1) catalyzing hydrogen oxidation ($H_2 \rightarrow 2H^+ + 2e^-$) and the oxygen reduction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) reactions and (2) efficiently transporting the reactants and the products. Typically, the catalyst layers on the anode and cathode are composite structures consisting of the proton conducting ionomer (e.g., Nafion®) and metal catalyst nanoparticles (e.g., Pt) supported

on a high surface area carbon (e.g., Vulcan XC-72 or Ketjen Black). Catalyst layer thicknesses vary between 10 and 20 μm depending on catalyst loading levels and ionomer content. Platinum is by far the best catalyst for both the anode and the cathode. However, the choice of the anode catalyst and loading levels also depend on the fuel source. The hydrogen oxidation reaction is thought to occur via dissociative adsorption of hydrogen (the limiting step) followed by its oxidation. When operating on pure hydrogen relatively little Pt (e.g., 0.005 mg cm^{-2}) is needed since the hydrogen oxidation reaction is facile (high exchange current density of 1 mA cm^{-2}) and the resulting overpotential is small. If the fuel is a reformate (i.e., a mixture of H_2, CO_2, N_2 and impurities such as CO, H_2S etc.) or methanol, then catalysts such as a PtRu, PtRh or PtNi alloys are used to minimize the adverse affect of CO poisoning, where CO adsorbs on Pt thereby reducing the active sites for H_2 adsorption. Typically, at least 10 ppm CO (and up to 2%) is present in the feed stream. While Pt can tolerate up to 50 ppm CO, bi-functional catalysts such as PtRu, PtAu are required for higher CO concentrations. These catalysts require lower overpotential for the formation of OH- species which scavenge CO species by oxidizing them to CO_2. In addition to using bi-functional catalysts, a small amount (up to 2%) of air or oxygen is fed with the anode fuel stream to promote the chemical oxidation of CO on these catalysts.

The oxygen reduction reaction (ORR) is the more limiting reaction in a well performing fuel cell with exchange current densities as low as 10^{-4} to 10^{-6} mA cm^{-2}. Therefore, reducing the activation overpotential for ORR is a crucial factor in improving the fuel cell performance. Increasing the cell temperature and pressure, increasing the reactant concentration (i.e. operating on pure oxygen), increasing the electrode roughness

and the catalyst loading are some of the ways to deal with the performance loss due to the sluggish ORR kinetics. For example, for a PEM fuel cell fueled by hydrogen and oxygen operating at 80ºC and 1 atmosphere, the loss due to the ORR at 0.5 A cm^{-2} can be as high as 160 mV. Currently the catalyst loading levels on the cathode side are between 0.1 and 0.2 mg cm^{-2}. This is a dramatic improvement over loadings in the 1960s which were about 28 mg cm^{-2}. At current prices, this translates into a Pt cost about $2,000 for a 1 kW stack. The two-fold decrease in loading levels since then brings Pt costs down to $10 for a similar unit. This is relatively insignificant for an estimated cost of a mass-produced fuel cell subsystem of $325/kW. However, the DOE goal of $45/kW will require further reduction or elimination in the amount of precious metals.

Though the details vary, the basic structure of the electrode in different PEMFCs is similar. The catalyst particles approximately 5-20 nm are dispersed onto a carbon support (e.g. Vulcan XC-72® Cabot). Smaller particle sizes lead to a larger active area and a better performance per mg of catalyst loading. However, smaller particles are less stable and so agglomeration of particles occurs over time. Two popular methods are currently practiced in the fabrication of the catalyst layer. In the first method, the carbon supported catalyst is mixed with an ionomer and is sprayed or electro-deposited onto a porous and conductive material such as carbon cloth or carbon paper. These catalyst loaded electrodes are then put onto each side of a proton exchange membrane and hot pressed or steam-bonded at a high temperature (between 130-150 ºC) and at considerable pressures (up to 500 psig) for 2-3 minutes. The second method involves building the electrodes directly on the proton exchange membrane. The supported metal catalyst and ionomer mixture is applied to the electrolyte membrane using rolling methods, by

spraying or through a process similar to screen-printing. Each processing step imparts known and unknown characteristics to the membrane, catalyst layer, and interfaces. Therefore, variations in the processing steps can play as big of a role in performance as variations in materials themselves.

Regardless of the composition of the catalyst, these porous layers not only contain the sites for charge transfer, but they also must have a dual conduction mechanism. That is, they must conduct protons through the ionomer to complete the ionic path and electrons through the carbon to complete the electronic path. In addition, gases and water must move easily through these layers. Therefore, an intimate three phase contact is required for the efficient operation of the unit cell. Finally, one must guard against the case of cell reversal when one of the cells in the fuel cell stack gets starved of fuel. When fuel starvation occurs at the anode, the local anode potential increases causing water electrolysis or carbon oxidation. One way to protect the carbon-based components is to incorporate an additional electro-catalyst in the anode catalyst layer to sustain the water electrolysis.

Gas diffusion layer (GDL)

The gas diffusion layers or the porous transport layer (PTL) might play the most critical and least appreciated role of all. As the name implies, the main purpose of the GDL is to distribute the reactants from the gas flow channels uniformly along the active surface of the catalyst layer. In addition, the GDL has to ensure proper transport of product water, electrons, and heat of reaction. It also forms a protective layer over the very thin layer of the catalyst. The GDLs are either carbon paper (e.g., Toray® paper) or

carbon cloth. The papers are thinner, thus producing a more compact design, while the thicker cloth absorb more water and are of superior durable, which simplifies mechanical assembly. Even the GDL is not a simple, uniform structure. Often a micro porous layer is added between the main macro porous layer and the catalyst layer. The purpose of this micro layer is to aid in the distribution of the reacting gases, improve mechanical compatibility between the layers, reduce contact resistance, and improve water management. This micro layer is usually comprised of carbon for electrical conductivity and PTFE for hydrophobicity. The in-plane and the through plane resistivities of the commercial GDLs are in the range of 25-100 mΩ cm and 6-20 mΩ cm^2 respectively. The in-plane and the through-plane resistances depend on the micro-structure of the GDL. The through-plane resistance dictates the cell resistance and the in-plane resistance affects the reaction uniformity. Further, the role of the GDL on the anode is not usually identical to its role on the cathode. For example, water formed on the cathode must be easily repelled from the catalyst surface to prevent flooding (i.e., liquid water formation). This liquid water blocks catalyst site and prevents oxygen from getting through the catalyst layer. In contrast, the anode must retain some water to keep the membrane from drying out. This is especially true if the anode gas stream is dry. Finally, the placement (such as near the gas inlet/outlet) and the hydrophobicity/hydrophilicity of the microporous layer play a crucial role in water management. For example, the presence of the microporous layer in the anode is more beneficial than in the cathode.

Seals and gaskets

The integrated seals and gaskets provide for a compact design while performing its primary function of eliminating leaks and over-compression. The thickness and the compressibility of these gaskets dictate compression levels on the GDLs. Also, contaminants from the seals can poison the catalysts or degrade over time. Also, sealing materials are required to separate the gas compartments from each other, to avoid mixing of the fuel (H_2) and the oxidant (O_2), and to prevent leakage and loss of fuel. They also serve additional functions such as electrical insulation and control of stack height. The auto industry with their long history in design of seals is expected to contribute to PEMFC stack sealing. Silicone and silicon based elastomers are commonly used as sealing materials in PEMFC stack systems due to their wide operating temperature (-40 to 300 °C), excellent hardness (20 to 60), stress relaxation (up to 25% force retained), good electrical resistivity (> 1014 Ω cm), and dielectric strength (15-17 kV/mm). Silicones also have excellent functional properties such as good pressure sealing ability (20-200 kPa), low swelling in PEMFC fluids (< 5%), and low permeability to fuel gases and coolants. However, currently used silicone based seals, gaskets and tubing materials fall short of the performance targets. Degraded or substandard seals might cause fuel leaks and may lead to reduced cell voltage due to mixed potential at the electrodes. Despite their importance, the area of seals and their durability remain the least explored area in PEM fuel cell research.

Flow-field

The flow-field or the bipolar plate serves the following important functions: (1) distribution of reactant gases to the anode and the cathode via gas channels and stack

manifolds with minimal parasitic pressure drop, (2) efficient transport of electrons from the anode of one unit cell to the cathode of the neighboring unit cell ensuring constant current in each unit cell, (3) efficient removal of heat generated by the electrochemical reactions and (4) efficient liquid water storage and transport. Flow fields commonly used in PEM fuel cells can be porous or non-porous and almost always have channel/land design features. While most flow-fields are non-porous in nature to prevent physical crossover of fuel and oxidant gas feeds, some flow fields known as water transfer plates are porous in nature. They are designed with an extra compartment adjacent to the gas distribution channels that removes excess water through vacuum while also serving as coolant. The channels transport gases to the catalyst layers through the GDL and the land region in contact with the GDL serve to collect current and transport heat. An ideal flow-field should serve all of the above mentioned functions in addition to having manufacturability and compact design features. Most flow-field designs incorporate one or a combination of the following simple channel configurations: serpentine, parallel, parallel-serpentine, mesh, spiral, interdigitated, or foam type. Fig. 3 shows some of the basic flow-field design patterns. Each design has its own pros and cons with trade-offs among pressure drops, water removal/uptake capabilities, reactant distribution and contact resistances.

Cell Performance and Diagnostics

Most laboratory diagnostics for evaluating the functional characteristics of cell components are performed in a unit cell. The most commonly used unit cell consists of an UEA with 5-25 cm^2 active electrode area, modular nonporous flow-fields and end

plates. The cell is typically assembled by bolting the end plates together with the cell components (arranged as shown in Fig. 2) with an applied torque of 35 inch-lb at 5 inch-lb increments ensuring uniform pressure. The assembly is tested for throughput (gas flow), overboard and crossover leaks. The overboard leak test checks for gas leaks through the seals while the crossover leak test checks for physical gas crossover from anode to cathode or vice versa. Both overboard and crossover leak tests are typically done at 5 psig pressure under water. A series of current-voltage (performance or polarization) curves are typically obtained with fully humidified fuel (H_2) and oxidant (O_2) at 70-80 °C as anode and cathode gases respectively, and at 1 atm as part of the cell incubation procedure. The current-voltage curve is a standard tool for evaluation of a unit cell performance. A simple schematic to show the experimental setup used to measure this polarization curve is shown in Fig. 4. The cell is usually connected to a variable load bank (or a rheostat) and is operated either at a constant current or a constant potential. The resistance level on the load bank is usually the controlling parameter in both cases. The thermodynamic open-circuit voltage (OCV) of a PEM unit cell operating on H_2 and O_2 is 1.299 V. However, due to mixed potentials caused by gas crossover, internal leakage currents, and impurities result in a measurable OCV (i.e., when $R = \infty$) of ~1 V. A polarization curve is obtained by measuring the current (and hence the current density) corresponding to a series of cell potentials or vice versa. Fig. 5 shows a typical polarization curve of a PEMFC unit cell. If the cell behaves ideally, the measured OCV should equal the ideal Nernstian thermodynamic potential at all current densities. The observed deviation from ideality is a result of several losses and can be broadly grouped into three categories: (1) losses due to kinetics (active polarization region), (2)

losses due to membrane and other contact resistances (ohmic polarization region) and (3) losses due to the transport of reactants (concentration polarization region). Though the losses due to the individual contributions are represented as distinct regions in this VI plot, all three losses contribute throughout the entire current range. In short, the operating voltage of the unit cell is a departure from the ideal Nernstian voltage caused by these various losses.

The activation polarization is the voltage lost in the process of initiating the anodic and cathodic electrochemical reactions and therefore dominates at low current densities. Since the rate of an electrochemical reaction is proportional to the exponential of the overpotential, the increase in this activation polarization is significant at lower current densities than at higher currents. The activation polarization is dependent on reaction mechanism, operating parameters such as temperature and pressure, type of catalyst and its morphology, the concentration of H_2 and O_2, impurities etc. As mentioned before, the HOR is a more facile reaction than the ORR and therefore contributes to lower activation polarization loss. All of these dependencies can be engineered to reduce the losses and increase efficiency.

At intermediate current densities, the VI curve is linear and the reduction in the cell voltage is dominated by the ohmic polarization. This can be thought of as the sum of ionic and electronic resistances due to the membrane and other components (e.g., catalyst layers, bipolar plates, GDL) between the anode and the cathode current collectors. Due to very high conductivities exhibited by the catalyst layers, GDL and the bipolar plates, the membrane contributes predominantly to this ohmic loss. Since the membrane

conductivity is highly dependent on the degree of hydration, water management plays a significant role in ohmic losses.

At higher current densities, the system is limited by transport of reactant gases to the catalyst sites and the removal of liquid water out of their point of generation. This can be seen as a knee or a bend in the VI curve at high current densities. Because of this, the power of a fuel cell when plotted against the current density goes through a peak. In addition to the reactant gases and product water transport, the build-up of inert gases and surface blockage by impurities or poisons also contribute to concentration polarization loss. In addition to the above three polarization losses, gas crossover from either side of the membrane to the other side and electrical short circuits are also detrimental to the performance of the unit cell.

Diagnostics

Though the polarization curve is the most commonly employed technique in evaluating the overall performance of a unit cell, there are several other diagnostic tools currently in practice to evaluate the performance of the individual cell components.

Cyclic voltammetry

A potential scan (typically between 5-20 mV s^{-1}) is employed on the electrode of interest (working electrode) versus the counter (and reference) electrode, usually the catalyst layer or the electrode on the other side of the membrane. The working electrode is usually in contact with an inert gas, while the counter and reference electrode is in contact with dilute H_2. Cyclic voltammetry is typically used to measure the electrochemical area (ECA) of the catalyst based on the charge obtained under the hydrogen adsorption and desorption peaks. ECA is the “real” catalyst surface area per

mass of catalyst (e.g. $m^2 g^{-1}$). This is essentially the surface area of catalyst that is in contact with both the electrolyte phase and the electronic phase. ECA is inversely proportional to the size of the particle {e.g. Area = $\pi.D^2$, Mass = $V.\rho = \pi.D^3.\rho/6$, and so ECA = Area/Mass =$6/(\rho. D)$}. Measuring the active ECA is an important and a fairly common diagnostic to measure the catalytic activity of Pt or alloy catalysts in the MEA. Other diagnostic techniques include (1) Hydrogen pump experiment to measure the resistance of the ionomer in the catalyst layer, (2) Current interrupt technique to measure the ionic resistance of the membrane, (3) the Four-probe method to estimate the in-plane and through-plane resistances of the GDL, and bipolar plates, (4) Electrochemical impedance spectroscopy to estimate carbon corrosion and kinetics of a given electrode reaction, (5) Helox experiments to characterize the transport losses and (6) Gas crossover measurements to measure gas permeability across the proton exchange membrane. Polarization losses due to various components and diagnostic tools typically used in their estimation are summarized in Table 1. Accelerated durability experiments such as load and humidity, temperature (freeze-thaw) cycling as well as open circuit voltage hold experiments are commonly employed to evaluate and predict the lifetime capabilities of unit cell components.

Cell Design and Manufacturing

Design of a PEMFC unit cell greatly depends on its intended application. All UEA producers strive to provide high power density, long and dependable lifetime, low cost, consistent and reliable performance, simplicity of use, and operational flexibility. Unfortunately these are not mutually exclusive and so there is a continuous tradeoff among these goals while continuing to drive down cost. Where that optimum lies

depends on the end use of the product as defined by the customer. For example, for stationary applications durability is the key attribute. These units must run continuously for tens of thousands of hours without fail. Because they are stationary, power density is not as important as lifetime and reliability. Also, these units are large so the incremental size and cost of additional auxiliary units (e.g., humidifiers, heat exchangers, pumps, and controllers) can be justified if they extend life and minimize maintenance.

For transportation, high power density (i.e., size of the unit) is critical since these units are moving with the load. Therefore, the efficiency of the load plus the fuel cell must be optimized. In addition, durability and flexible operation are also critical design constraints. For example, the load and temperature on these units fluctuate, especially during cold starts or prolonged operation. They must also perform well whether they are being used in the hot, sub-Sahara desert or in the middle of an Arctic winter. For portable applications, size and simplicity must be achieved with dry rather than humidified gas streams. Auxiliary units that can help optimize performance by controlling operating conditions are often not practical. Like unit cells used for transportation, portable applications have varying loads or even no loads for extended periods of time. Therefore, fuel and water management must be maintained even when the cell is not operating. A membrane cannot be allowed to dry out when the fuel cell is not in use or it will not deliver power when power is demanded. And although cost is always an issue, there are some applications where the consumer will pay premium price for the unique attributes of a fuel cell. For example, the military is willing to pay more than a typical consumer for a device that is quiet, dependable, and has a small thermal signature. As with all industries, the UEA manufacturer must work closely with their

customers (i.e., fuel cell manufacturer) and their suppliers (i.e., manufacturers of membranes, catalysts, GDLs, seals) to engineer a UEA that meets the performance requirements and operating conditions of the fuel cell. This requires numerous iterations as UEAs are designed, fabricated and tested. This process is shown in Figure 5.

The process begins with the customer providing performance requirements, design specifications and operating conditions to the MEA manufacturer. This will include such things as operating temperature, power requirements, size, application (i.e., stationary, transportation, portable), target costs, and fuel and oxygen source. The MEA manufacturer must then choose a set of membranes, catalysts, GDLs, and seals that they feel will meet these specifications. In addition, they must determine how all these layers will be assembled and if there is a need for any interfacial coatings (e.g., micro layer of a GDL). This requires close consultation with their supplies so they can get the components with the desired properties. While assessing material properties based on desired fuel cell performance, the MEA manufacturer must also try to drive down their costs by simplifying the manufacturing process without affecting quality. This in itself may affect the selection of materials. For example, a choice of carbon paper or carbon cloth may be dictated by which is more compatible for their assembly process.

Once the materials have been selected and the sequence in which layers are applied has been determined, the MEAs are fabricated, installed in a fuel cell, and tested under the specified operating conditions. These results are compared to the customer's specifications and new sets of materials, in consultation with suppliers, are selected for testing. This interactive process is continued until the customer's requirements are met.

Large scale manufacturing of the MEA follows, and if problems arise here the iterative process could start over.

What makes this interactive process so involved is that a change in one layer, or operating condition, can affect the optimization of another. For example, super-saturation of the incoming gas streams result in a very high current density at the inlet but also the formation of liquid water (i.e., flooding), which lowers the performance due to the increased film resistance for diffusion. In contrast, dry gas streams on either anode or cathode cause low membrane conductivity and low performance so components must be chosen to retain water. Since there are so many interacting parameters that need to be optimized, it is not possible to test all possible combinations within a reasonable amount of time. Therefore, the MEA manufacturer relies heavily on statistical analysis to test those combinations that have the highest probability for success.

Cell Development Challenges

Current challenges towards commercializing the PEMFC technology are (1) reducing the cost and (2) increasing the durability.

Cost

Cost of the fuel cell module consisting of the fuel cell stack, air supply system, and coolant circulation system, could amount to 50-60% of the overall cost of the fuel cell power plant. Among these, the cost of the fuel cell stack dominates (~80-85%) the fuel cell module cost. The cost distribution of the individual components of the unit cell is shown in Fig. 7. The membrane electrode assembly with the precious metal catalyst and the polymer electrolyte membrane contribute to most of the cost of a unit cell. The

current challenge in bringing down the cost of the MEA lies in the development of alternative membranes that are as functional and durable yet cheaper than Nafion and finding alternative non-precious catalysts that have similar or more activity towards HOR and ORR reactions.

Durability

While cost remains a main barricade on the road to PEMFC commercialization, durability targets also present significant challenges to design engineers. The exact degradation mechanism by which the PEM fuel cells fail has been delineated thanks to an explosion of durability centered research in the first half of the first decade of 21st century. PEMFC degradation occurs due to chemical and mechanical causes. Accelerated durability tests such as OCV decay (i.e., leaving a cell at open circuit potential), load (or potential), humidity and temperature (e.g., freeze/thaw) cycling routinely conducted as part of MEA/UEA performance evaluation indicate that the membrane loses its physical structure and disintegrates over a period of time. Drop in the cell potential, an increase in the hydrogen crossover current and optical images of failed MEAs from these durability experiments indicate that membrane thinning and/or pinholes occur over a period of time. Figure 6 shows a schematic of reactant flows across a catalyst coated membrane in a PEM unit cell. The presence of a very high potential (typical requirement for low cost stack design) on the cathode causes Pt oxidation to PtO and dissolution as Pt^{2+} . Both PtO and Pt^{2+} migrate into the membrane because of concentration gradient. Pt^{2+} species in the membrane is reduced by molecular H_2 crossing over from the anode side resulting in the chemical platinization of membrane (i.e., $2Pt^{2+} + H_2 \rightarrow 2Pt + 2H^+$). Similar

platinization of membranes has been shown to take place via chemical procedures for the metallization of membranes in which anionic metal ions in a solution in contact with one face of PEM is reduced by a reductant which diffuses through the membrane from a solution in contact with the opposite face of the membrane. Also, a two-step impregnation-reduction method exists in which the membrane (e.g., Nafion®) was ion-exchanged with a pre-cursor metal salt followed by an exposure to a reductant. Similar chemical platinization occurs in a PEM fuel cell membrane, where the Pt^{2+} ions act as the source for Pt and H_2 crossing over from the anode act as a reductant. The chemical platinization occurs in the membrane at a distance X_0 from the cathode-membrane interface. This distance is dictated by the relative fluxes of molecular O_2 and H_2 due to diffusion from the cathode and anode sides respectively. The lower potential on the anode side of the membrane together with oxygen crossing over from the cathode side drives the peroxide formation reaction. The peroxide thus formed disintegrates to $OH^{\bullet}$ radicals on the Pt in the membrane. The $OH^{\bullet}$ radicals thus formed attack the membrane and produce HF. Direct radical formation can also occur in that $OH^{\bullet}$ radicals are formed directly from the crossover O_2 if favorable potentials exist. These phenomena are very sensitive to temperature and local water content. Increased temperatures and low humidity (both crucial requirements for automotive stacks) accelerate these degradation reactions causing membrane failure and MEA degradation.

In addition to the above described chemical degradation mechanism, routine mechanical stresses induced in a membrane due to periodic swelling upon water uptake and thinning upon drying also causes failure. Therefore the current cell development

challenges include both minimizing the cost without compromising the chemical and mechanical durability of the cell components.

Main Applications

The first application of a PEM fuel cell was in the 1960s as an auxiliary power source in the Gemini space flights. Subsequent advances in the PEMFC technology was stagnant until the 1980s when the fundamental design of the cell components underwent considerable reconfiguration. Since then, PEMFCs have been used for a number of applications and can be broadly classified into the following four areas: (1) Automotive, (2) Stationary power (3) Mobile units (such as electronic devices) and (4) Military and space applications. The unit cells are typically assembled into stacks, which are then used as power modules in fuel cell power plants for these applications. (Please see applications for fuel cell stacks for an overview of the above listed applications)

Concluding Remarks

This article on PEMFC unit cell is an overview of its operational principle based on the functions of individual components. The current-voltage curve of a unit cell is discussed with respect to losses due to kinetic, ohmic and concentration polarizations. The current developmental challenges faced by the fuel cell community are in reducing the cost of the fuel cell components without sacrificing the performance and durability characteristics.

Further Reading

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List of All Non-SI Units Used

inch (in)

pound (lb)

List of All Acronyms/Abbreviations/Special Symbols

ACL	Anode Catalyst Layer
CCL	Cathode Catalyst Layer
EIS	Electrochemical Impedance Spectroscopy
GDL	Gas Diffusion Layer
HOR	Hydrogen Oxidation Reaction
MEA	Membrane Electrode Assembly
OCP/OCV	Open Circuit Potential/Open Circuit Voltage
ORR	Oxygen Reduction Reaction
PEM	Polymer Electrolyte Membrane, Proton Exchange Membrane
PTL	Porous Transport Layer
RDE	Rotating Disc Electrode
SPE	Solid Polymer Electrolyte
UEA	Unitized Electrode Assembly
VI	Current-Voltage

Glossary

Helox	Mixture of Helium (He) and Oxygen (O_2)
Nafion	Trademark name for sulfonated tetrafluorethylene copolymer used as a PEM
Teflon	Trademark name for poly(tetrafluoroethene) or poly(tetrafluoroethylene) (PTFE) is a synthetic fluoropolymer

Suggested Cross-references

History of Fuel Cells, Peter Kurzweil (MS-5)

Modeling Fuel Cells, Paola Costamagna (MS-39)

Introduction to Fuel Cells, John Appleby (MS-221)

PEMFC Anodes – Reformate, Sarah Ball (MS-222)

PEMFC Cathodes, Steve H. Bergens (MS-224)

PEMFC Gas Diffusion Layers, Don Gervasio (MS-225)

PEMFC Gas-flow Fields, Angelika Heinzel (MS-226)

PEMFC Membrane Electrode Assemblies, Ramaraja Ramasamy (MS-227))

PEMFC Stack, Jean St-Pierre (MS-229)

PEMFC Electrolytic Membranes, Giulio Alberti (MS-230)

PEMFC Ambient Temperature Membranes, Thomas J. Schmidt (MS-232)

PEMFC General Performance and Operational Conditions, Jean St-Pierre (MS-233)

PEMFC Life-limiting Considerations – Catalyst, Hubert Gasteiger (MS-234)

PEMFC Life-limiting Considerations – Membrane, Hui Xu (MS-235)

PEMFC Cold Start, Ahmad Pesaran (MS-237)

PEMFC Systems, Zhigang Qi (MS-238)

PEMFC Dynamics, Andreas Friedrich (MS-239)

Figures, Schemes, Equations and Structures

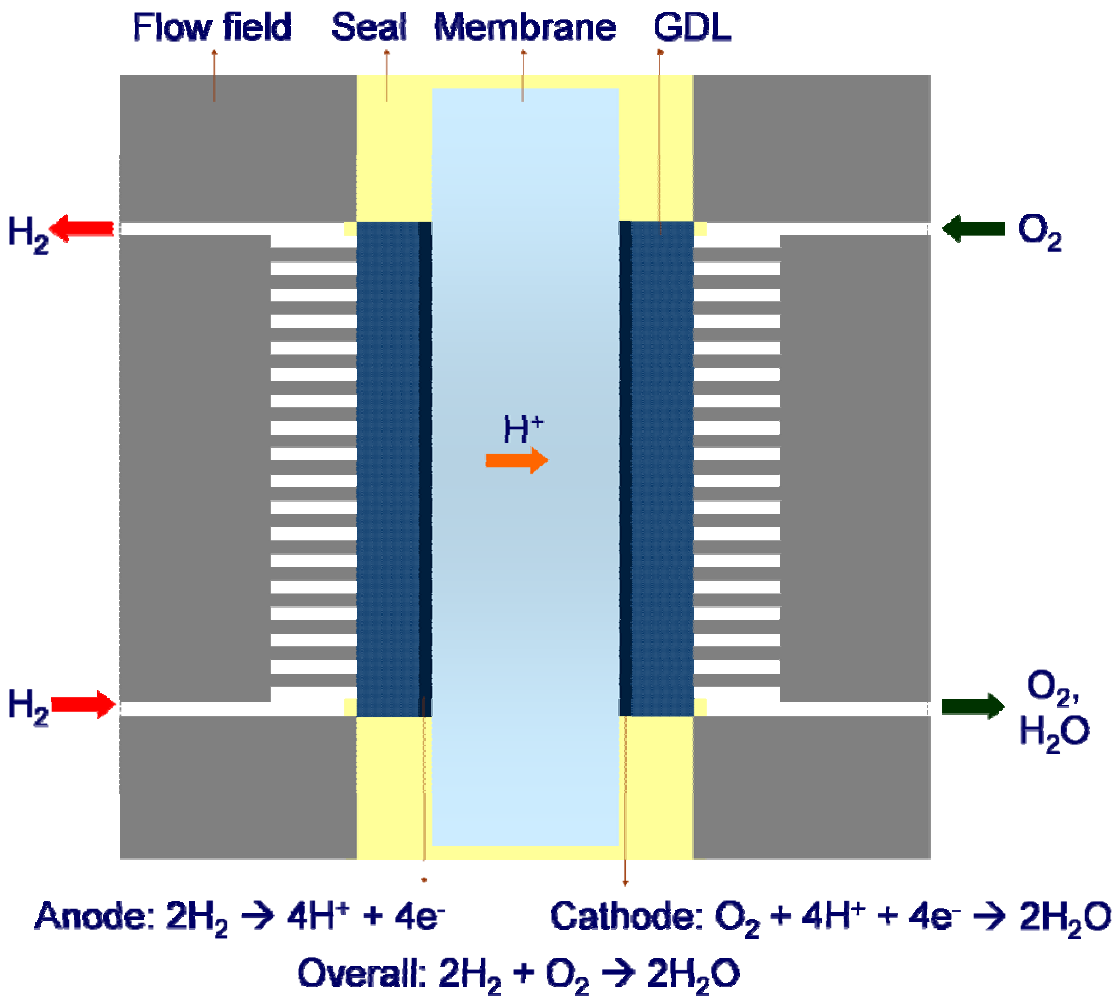

Figure 1: Cross-sectional view of a PEM unit cell. The fuel (H_2) is oxidized at the anode catalyst layer and the oxidant (O_2) is reduced at the cathode catalyst layer.

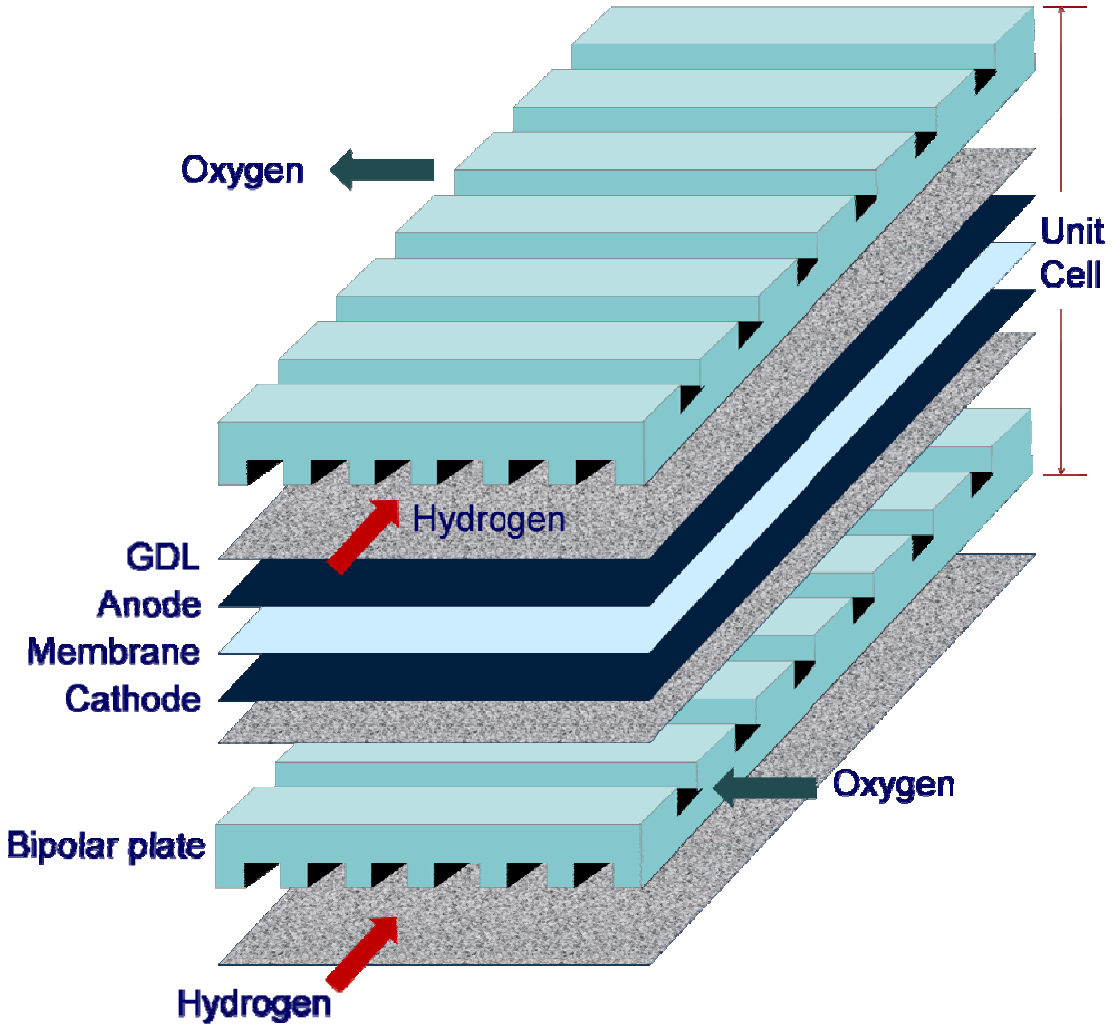

Figure 2: Three dimensional schematic of a representative section of a PEM fuel cell stack shown with cross-flow configuration. The two gas diffusion layers (GDL), the anode catalyst layer (ACL), proton exchange membrane (PEM) and cathode catalyst layer (CCL) shown here as separate layers constitute a membrane electrode assembly (MEA). An MEA together with the seal (not shown) constitutes a unitized electrode assembly (UEA). The ACL and CCL are thin layers consisting of catalyst supported on carbon and ionomer. The unit cell repeats itself in a PEM fuel cell stack.

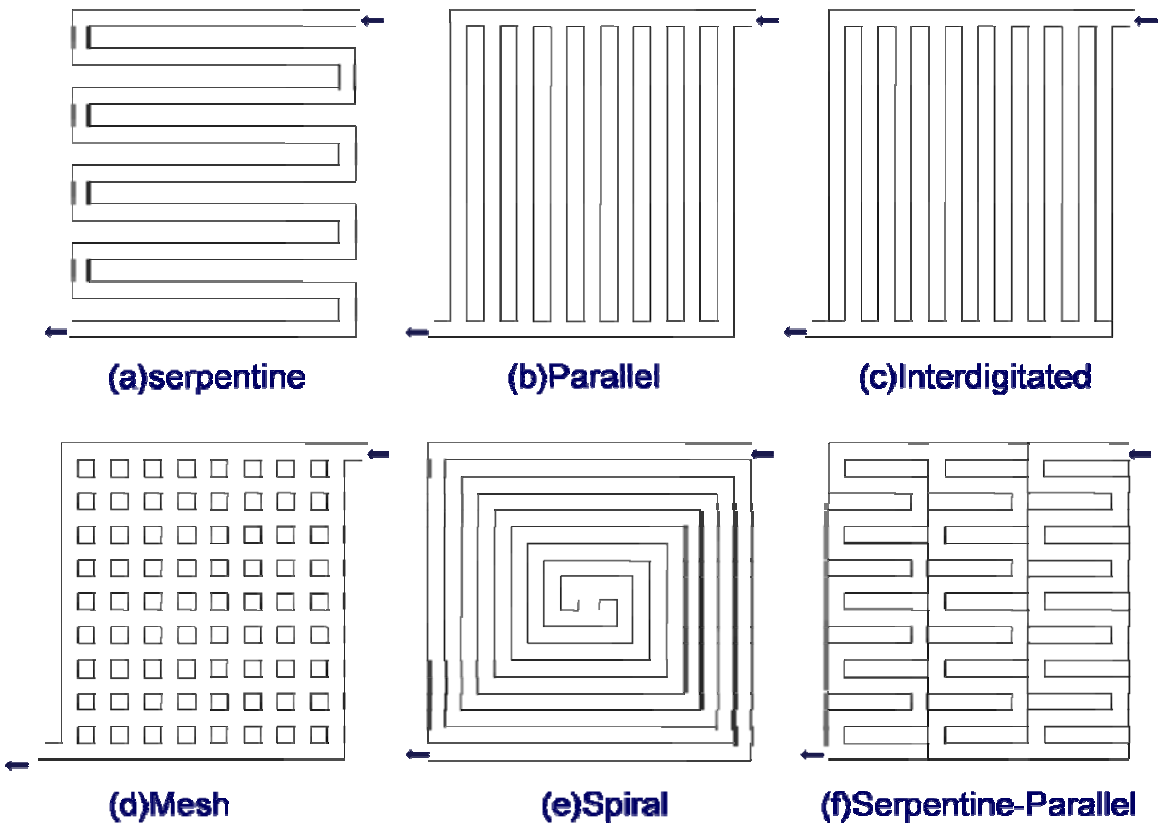

Figure 3: Schematics of flow-field design patterns. Though basic design patterns are shown, a number of combinations of these design patterns are also used.

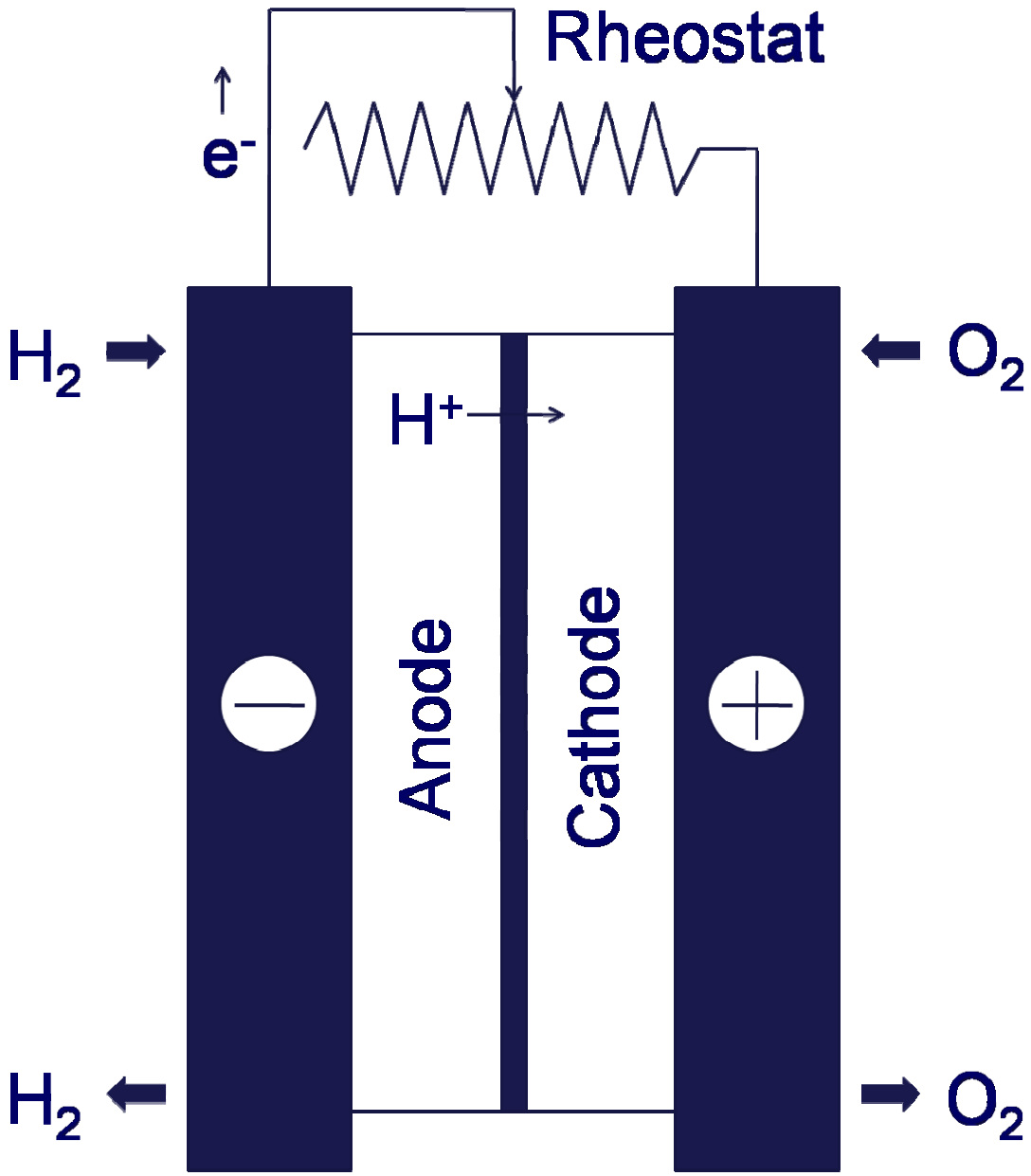

Figure 4: A simple schematic to show the experimental setup typically used to measure the current-voltage (polarization) curve, and hence the performance, of a PEM unit cell. The anode and cathode polarities are also shown.

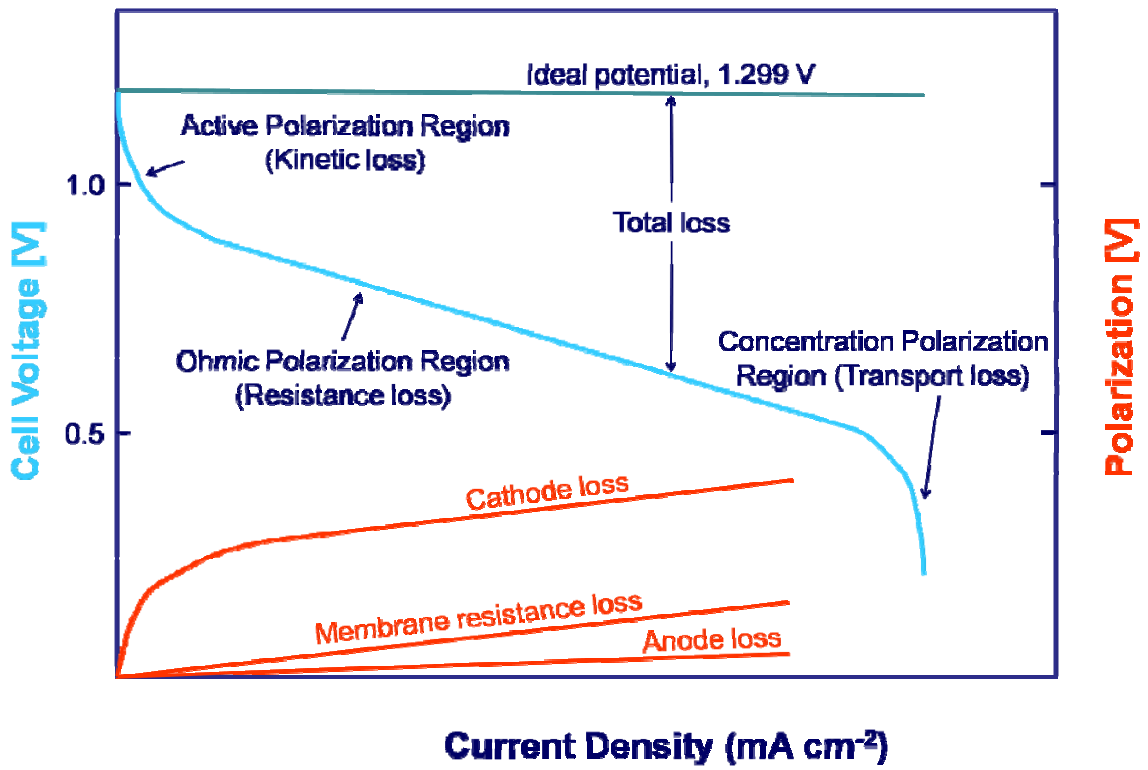

Figure 5: The current-voltage (VI) curve of a PEMFC unit cell (blue line) shown along with the ideal VI curve (green line) and polarization losses (red lines) due to oxygen reduction and hydrogen oxidation reactions and membrane resistance. Three main losses due to kinetics, ohmic and transport are also shown.

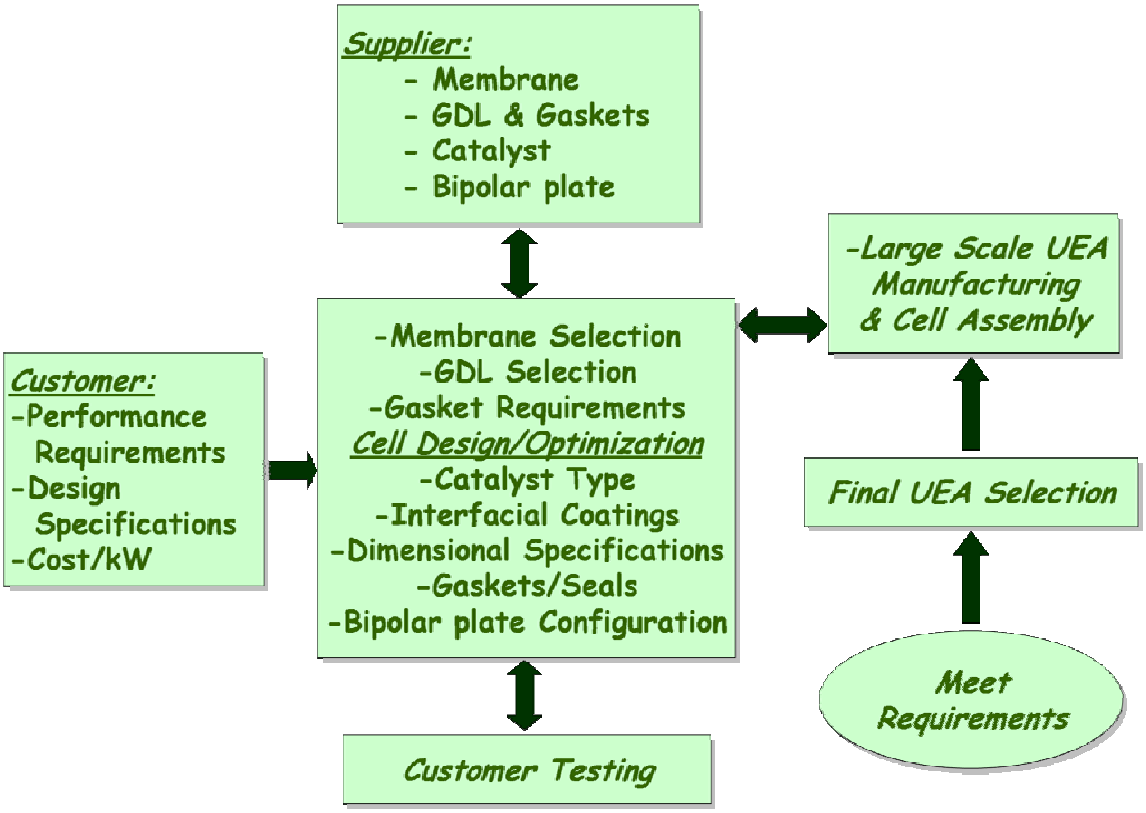

Figure 6: A quality control flow sheet for selecting components towards proper cell design and manufacturing.

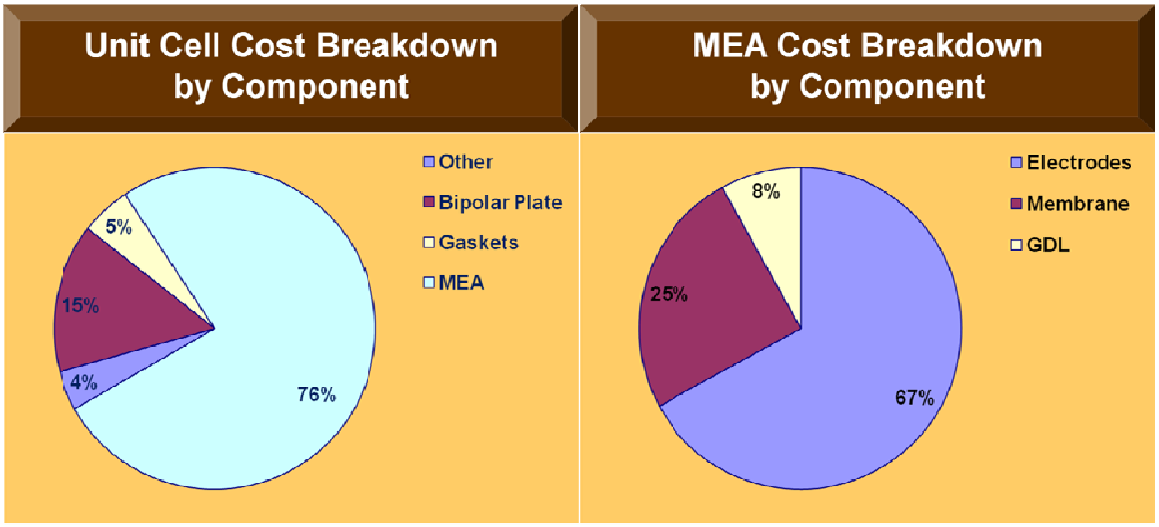

Figure 7: Unit cell cost breakdown by individual components (left) and further breakdown of the MEA cost due to membrane, electrode and GDL (right). Note that this cost analysis takes into account certain design assumptions and material selections.

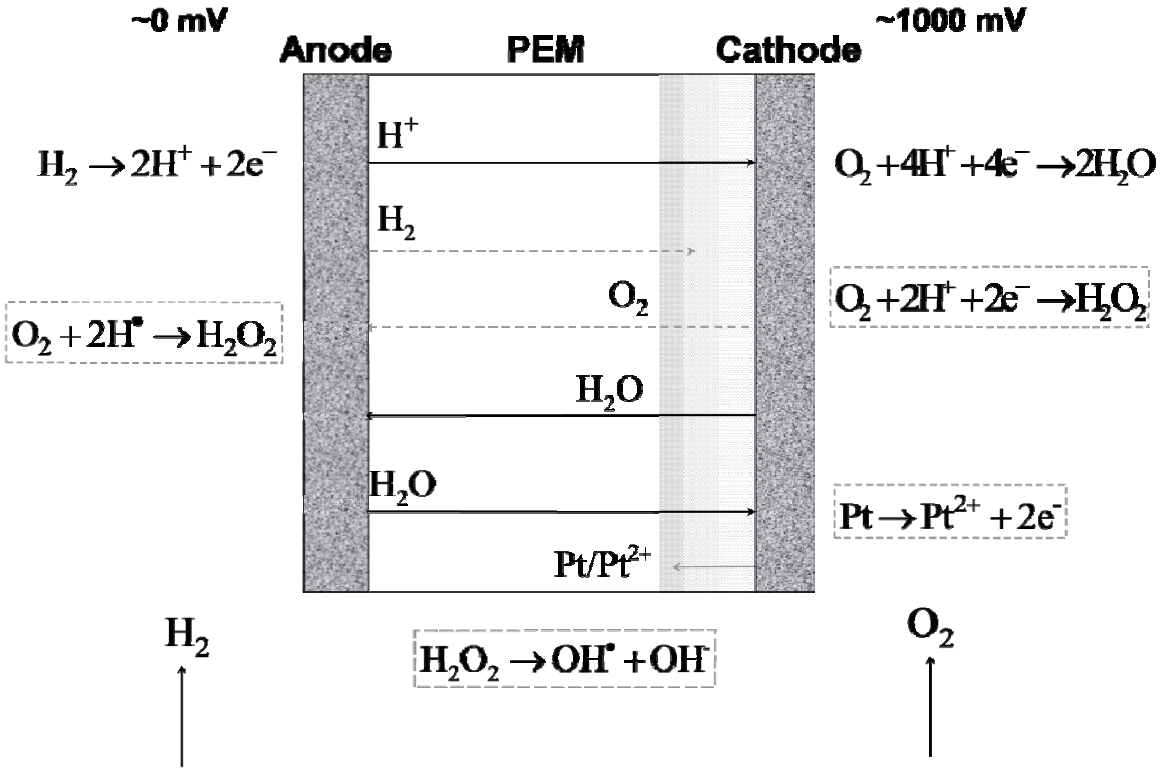

Figure 8: Schematic of the MEA showing the important reactions and fluxes of key species in a PEM unit cell. The reactions in dashed boxes cause or contribute to membrane degradation and have important consequences towards PEMFC durability.

Tables

Table 1: Polarization losses due to various components and diagnostic tools typically used in their estimation:

Polarization	**Component**	**Typical value**	**Diagnostic tool**
Kinetic	Anode	10-20 mV/decade	Half-cell (H_2/H_2)
	Cathode	120 mV/decade	RDE
Ohmic	Membrane	$I\rho l$, $\rho = 0.1\ \Omega$ m, $l = 50\text{-}175\ \mu$m	Current Interrupt
	Bipolar plate	$I\rho l$, $\rho = 0.05\ m\Omega$ m, $l = 2\text{-}5$ mm	Four probe method
	Catalyst Layer	$I\rho l$, $\rho = 0.2\text{-}1\ \Omega$ m, $l = 5\text{-}20\ \mu$m	EIS, H_2 pump
	Contact resistances	IR, R = ~15-30 $m\Omega\ cm^2$	-
	GDL	$I\rho l$, $\rho = 0.1\text{-}0.2\ m\Omega$ m, $l = 100\text{-}300\ \mu$m	Four probe method
Concentration	H_2, O_2	Nernstian	Helox

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