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Humidity and Fuel Cell Testing

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The need for reactant humidification in PEM fuel cells

The performance of a polymer electrolyte membrane fuel cell (PEMFC) is influenced by its operating conditions, including temperature, pressure, and moisture content of the inlet gases. These factors all directly affect membrane water content, which in turn impacts fuel cell performance.

Hydration of the membrane is a very important determinant of the performance and durability of a PEMFC. If not properly hydrated, the membrane exhibits higher ionic resistance and in extreme cases can be physically damaged. *Figure 1* demonstrates the effect of the hydrogen (H_2) fuel water vapor content, expressed as dewpoint and relative humidity, on the resistance of a PEMFC. For this particular cell operating under the indicated conditions, a 2 °C change in the dewpoint of the anode reactant resulted in a 2% to 5% change in membrane resistance.

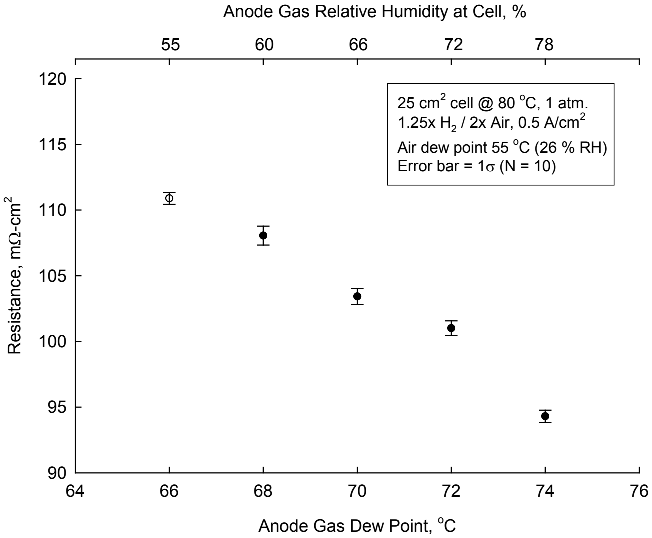

Figure 1. Resistance of a PEM fuel cell as a function of the dewpoint of the anode reactant (H_2 fuel) highlights the need for accurate, stable and repeatable control of the water content of fuel cell reactants.

Membrane hydration is affected by the water transport phenomena in the membrane itself, which in turn are affected by the condition of the inlet gases and the operating parameters of the fuel cell. Water is transported through the membrane in three ways: electro-osmotic drag by protons from the anode to the cathode, back diffusion due to concentration gradients from the cathode to the anode (or vice versa in limited cases), and convective transfer due to pressure gradients within the stack. At high current densities, where electro-osmotic drag of water from the anode to the cathode often exceeds the rate of back diffusion of water, the anode side can dry out if the inlet gases are not sufficiently humidified. Without reactant gas humidification, the fuel cell membrane will become dehydrated leading to high ohmic losses and potential damage to the membrane.

Conceptually, relative humidity is an indication of how close a gas is to being saturated; a gas with 100% RH is saturated in water vapor. Note that specific humidity is unaffected by temperature whereas relative humidity can be changed by changing the temperature of the gas and/or quantity of water vapor present in the gas. Relative humidity is empirically useful because most materials respond, absorb or adsorb in proportion to relative humidity rather than specific humidity. Specific humidity is useful when considering chemical equilibrium because it is related to the absolute amount of water vapor in a gaseous mixture.

Dewpoint is the temperature at which the gas will become saturated. Dewpoint is a direct measure of vapor pressure (p_v) expressed as a temperature. The dewpoint temperature is always less than or equal to the temperature of the gas. The closer the dewpoint is to the temperature of the gas, the closer the gas is to saturation and the higher the relative humidity. If the gas cools to the dewpoint temperature it is saturated in water vapor and the RH is 100 %. Condensation will occur on any surface cooled to or below the dewpoint of the surrounding gas.

Dry bulb temperature is the commonly measured temperature from a thermometer. It is called "dry bulb" since the sensing tip of the thermometer is dry (see "wet bulb temperature" for comparison). Since this temperature is so commonly used, it can be assumed that temperatures are dry bulb temperatures unless otherwise designated.

Wet bulb temperature is roughly determined when air is circulated past a wetted thermometer tip. It represents the equilibrium temperature at which water evaporates and brings the air to saturation. Inherent in this definition is an assumption that no heat is lost or gained (*i.e.*, adiabatic system) and the heat loss due to evaporation is balanced by thermal conduction from the air. In practice only carefully constructed systems approach this ideal condition. Wet-bulb temperature differs from dewpoint. The latter is the balance point where the temperature of liquid or solid water generates a vapor pressure (a tendency to evaporate) equal to the vapor pressure of water in the gas so that no net evaporation occurs. Therefore the dewpoint is always lower than the wet bulb temperature because at the surface temperature of the wet bulb the water must evaporate to maintain a cooling rate whereas at the dewpoint temperature the water must be so cold that it will not evaporate (but not so cold that condensation occurs).

Methods for measuring humidity

Common approaches employed to measure humidity and dewpoint temperature are described below; pros and cons of each are summarized in Table 1.

- Wet bulb: In the wet bulb method, water is allowed to evaporate and so cool itself to the point where the heat loss through evaporation equals the heat gain through thermal conduction. This method usually involves a wicking material to bring replacement water to the wet bulb, a sufficient wicking distance (with evaporation) to achieve temperature equilibrium for the replacement water, sufficient gas flow rate and precise temperature measurement.

- Polymer humidity sensor: The operating principle of solid state humidity probes is measurement of some material property of a water-sensitive material. Polymeric materials are generally used for this type of moisture sensor. Water vapor permeates the plastic and changes its electrical properties such as dielectric constant or conductivity. Sorption or desorption of water from the polymeric material occurs as the humidity of the surrounding environment changes. The change in the materials property are measured and converted to various humidity-related values using established calibration data.

- Chilled mirror: In this approach, a sensor head is heated to a temperature well above the expected dewpoint and a mirror within the sensor is cooled until dew just begins to form on its reflective surface. An optically-controlled servo loop controls the mirror temperature so that the dew neither evaporates nor continues to condense (*i.e.*, the definition of dewpoint). The temperature at which this equilibrium occurs is measured as the dewpoint. The chilled mirror technique is a first principles method meaning that the dewpoint is measured directly as opposed to via correlation of some other measured parameter to a response (calibration) curve.

- Optical: In this method, light of specific frequencies is passed through a cavity of known dimensions. Water vapor absorbs some of the light and the decrease in transmitted light is measured. The reduction in transmitted light is then correlated to the amount of water in the path of the light, and from this the various parameters related to water vapor content of the gas can be calculated.

Methods to humidify fuel cell gases

In fuel cell operation and fuel cell test equipment, one generally controls the moisture content of the *inlet gas stream*. Water is a product of the fuel cell reaction. The rate at which it is produced in the cell is a function of the reaction rate which relates to the electrical current through Faraday's Law. Water is also transported from one electrode to the other through the membrane. The direction and rate of net water transport through the membrane is a complex function of the cell conditions including anode and cathode RH, current density, and membrane water permeability, among others. For these reasons, the water content of gases within anode and cathode compartments and exit streams can differ from the water content of the respective inlet gas.

Most fuel cell test systems include some method for externally humidifying reactant gases. Three common humidification systems are illustrated in Figure 2(b)-(d): membrane humidifiers, bottle humidifiers, and flash evaporation humidifiers.

Table 1. *Comparison of common humidity and/or dew point measurement methods.*

Method	*Advantages*	*Disadvantages*
Wet Bulb	• low cost • easy to perform measurement • easy to maintain equipment • robust (not damaged by liquid water) • accurate at very high humidity where there is little or no evaporation • response time is moderate	• relies on established relationships of wet bulb T *vs.* water content (function of gas; published tables / formula are for air not H_2 or O_2) • requires addition of water to the system (problematic for small systems) • flow rate dependant • requires a water source and feed • requires cleaning • replacement of the some components (wick)
Polymer Sensor	• moderate cost ($100s-$1000s) • in-situ, real-time monitoring possible • rapid response • little or no maintenance required • reasonably reliable • easy to use • water mist entering the sensor can be evaporated and measured (if super heated chamber is used)	• probe susceptible to damage on exposure to liquid water • periodic recalibration required • periodic replacement of the sensing element required • accurate local temperature measurement is critical for conversion of %RH to other humidity units.
Chilled Mirror	• very accurate with drift and accuracy comparable to a good thermometer (better than 0.1°C). • mirror and sensor can be made from inert materials • water mist entering the sensor chamber is evaporated and measured • robust (not damaged by liquid water)	• relatively expensive ($1000s) • operation can be temperamental • mirror must be kept clean • sensor must be heated to prevent condensation • gas to be tested must be passed through heated chamber (may not be suitable for in-situ applications)
Optical	• very rapid response • sensor cavity can be made from inert materials • water mist entering the sensor can be evaporated and measured (if super heated chamber is used)	• relatively expensive • cavity must be kept clean • will respond to other gasses which absorb same frequencies of light • periodic calibration required due to drift in performance of optical components

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Most fuel cell test systems include some method for externally humidifying reactant gases. Three common humidification systems are illustrated in Figure 2(b)-(d): membrane humidifiers, bottle humidifiers, and flash evaporation humidifiers.

Membrane humidifiers are water exchange devices employing water permeable membrane tubes such as Nafion® (DuPont Company) that allow water transmission but resist transmission of reactant gas or other components. A tube-in-tube membrane humidifier is illustrated in Figure 2(b). Membrane humidifiers can operate as either water-to-gas or gas-to-gas humidifiers. In the former, hot, de-ionized water is circulated on one side of the membrane tube and the gas to be humidified on the other. Gas-to-gas humidifiers use a wet gas such as the fuel cell cathode exhaust stream as the water vapor source for the (dry) gas to be humidified, the two gases being separated by the membrane. In both types, water transport through the membrane is due to the difference in chemical potential (*i.e.*, concentration) of water on either side of the membrane.

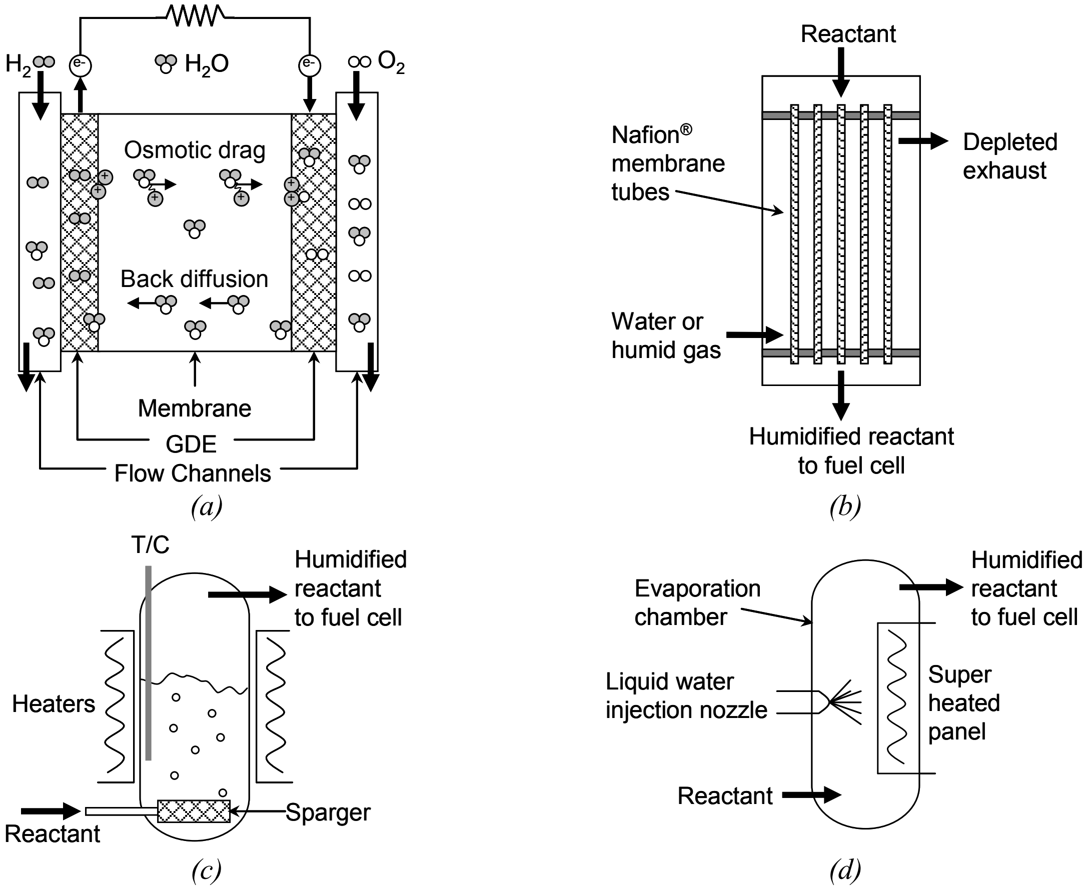
Bottle humidifiers, illustrated in Figure 2(c), are based on passing the gas to be humidified through a heated water bath. Water vapor is absorbed by the gas as the bubbles rise through the water. Water uptake by the gas is a function of the water-gas interfacial area and therefore a sparger (porous frit) is commonly used to produce fine bubbles thereby increasing the humidification efficiency. Well designed bottle humidifiers can fully saturate a gas stream, meaning that the dewpoint of the humidified gas equals the temperature of the water. Bottle-type humidifiers are simple and cost-effective. The primary disadvantages of this humidification method is it limited water transfer capacity and the inability to provide rapid changes in humidity level, although these can be addressed through proportional mixing of wet and dry gases as described below.

As shown in Figure 2(d), flash evaporation humidifiers spray water onto a super heated surface to instantly produce water vapor which mixes with the flowing gas. In some cases, the rate of liquid water injected is dynamically controlled to achieve a desired water vapor content or dewpoint of the exit gas. When operating in such a mode, the system attempts to produce humidified gas of the user-defined dewpoint by controlling the liquid water flow rate. This method of operation requires sophisticated feedback control and a built-in, real-time humidity sensor. Alternatively, one can operate under constant flow control mode wherein water is delivered to the hot plate at a rate pre-determined to produce the required humidity level. A metering pump injects water into the flash evaporation chamber at the user-specified rate. Precise cntrol of the humidity level can require that corrections to the water injection rate be made to more closely approach the desired dewpoint.

Steam injection is another common approach (not shown in Figure 2), in particular for high-capacity test stands (> 1 kW) where water transfer rates can be significant. In this method, steam is introduced directly to the reactant gas. The steam has enough thermal energy that it heats the reactant gas to a temperature sufficient to entrain all of the water vapor. Temperature-controlled coolers, such as tube-in-tube condensers, are used to decrease the gas temperature to the desired value. As the gas is cooled excess moisture condenses leaving a water vapor saturated mixture at the desired inlet temperature to the fuel cell. An advantage of the direct steam injection system is its high water transfer capacity.

Proportional mixing of wet or water vapor saturated gas and dry gas is another means to achieving a desired RH of inlet reactant. Computer-controlled mass flow controllers are used to mix in the correct proportion a fully saturated gas and a dry gas to achieve a desired relative humidity. This approach allows the water vapor content of the gases to which the fuel cell is exposed to be quickly changed, which facilitates rapid assessment of fuel cell performance over a range of conditions and measurement of the dynamic response of the fuel cell to changes in reactant humidity.

One issue common to all external humidification water will condense out of the gas, which decreases the nominal dewpoint of the gas and leads to liquid water entering the fuel cell. To counter act this, well-designed external humidification systems employ heated gas transfer lines between the humidifier and the fuel cell.



(a) *(b)*

(c) *(d)*

Figure 2. Common humidification methods. (a) Internal or self-humidification relies on diffusion of cathode-generated water through the membrane which is at least partially counterbalanced by osmotic drag of water by protons (H^+) from the anode to the cathode. (b) Membrane humidifiers are moisture-exchange devices using Nafion® tubes. (c) For bottle humidifiers, reactant gas is sparged through a temperature-controlled water bath. (d) The flash evaporation humidifier produces humidified gas by spraying a stream of water on to a super-heated panel where the water very rapidly vaporizes. T/C = thermocouple.

Things to look for in a humidification system for fuel cell testing

Reactant humidification is an important consideration when choosing a fuel cell test system. The test system needs to be able to maintain stable, accurate reactant humidity and flow levels to the fuel cell at all times. The response time, or the speed at which a desired humidity level can be reached, is also a consideration for some users. As mentioned previously, some humidification methods can more rapidly achieve or change humidification level than other schemes. The test system also needs to be able to supply anode and cathode flow rates sufficient for the cell testing to be performed.

Bottle-type humidifiers provide humidification from a fixed volume of water in a chamber. This water is consumed over time and needs to be replaced. Although a manual fill valve allows the water level to be restored, an automatic filling system reduces the number of tasks required by the test operator and also can provide less disruption to the test conditions when the filling is performed. Automatic water filling also allows long-term unattended operation of the fuel cell test system.

Regardless of the humidification system used, the water from the humid gas will condense on the walls of the tubing exiting the humidifiers unless the lines are heated to a temperature above the dewpoint of the gas. If the water condenses on the tubing, the dewpoint is reduced and droplets or "slugs" of liquid water may enter the fuel cell and potentially disturb the cell's operating condition and performance. It is therefore important that the test system heat the entire anode and cathode gas transfer lines up to the point that they enter the fuel cell. Many test systems incorporate heated cell lines for this reason.

While a basic fuel cell demonstration or experiment can allow the unconsumed gases to exit the anode and cathode outlets of the fuel cell without any restrictions (through a vent to outside the building, for example), many practical fuel cell applications pressurize the anode and cathode compartments. This is typically achieved with a manual or automated regulator on the outlets of both compartments of the fuel cell. The cell is generally not pressurized to more than a few atmospheres.

Summary

The performance of a PEMFC is strongly influenced by the moisture content of the reactants via their influence on the water content of the membrane. Hydration of the membrane is a very important determinant of the performance and durability of a PEMFC. As such, the stability, accuracy and capacity of the humidification system of fuel cell device and fuel cell test systems are an important consideration.