Data Analysis of Fuel Cells
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Proton Exchange Membrane Fuel Cells

A fuel cell is an electrochemical device which uses the reaction between hydrogen gas and oxygen gas to produce electric current. This reaction is exergonic. Under normal conditions, however, it proceeds very slowly due to a high activation energy barrier. This energy barrier may be explained by a simplified model of the reaction mechanism. The reaction product, water, is formed from the reduction of oxygen ions at a catalyst site via addition of hydrogen radicals. Cleavage of the hydrogen and oxygen diatoms contributes significantly to the high activation barrier. Oxygen ions are especially short-lived and a large amount of energy must be provided in order to produce ions in sufficient numbers to react with the hydrogen ions before recombining into oxygen gas. The chemical potential energy of the covalent bonds of the gasses is converted, in part, into electric potential. This electric potential may be used to drive electrons through an external load, i.e. electric current is produced.

A Proton Exchange Membrane Fuel Cell (PEMFC) utilizes a platinum catalyst and a membrane to lower the activation energy of the hydrogen-oxygen reaction. A hydrogen diatom is cleaved on the surface of a platinum site, which releases two electrons to the collector plate. The remaining protons are carried away from the catalyst site by protonation of water. Proton exchange membranes, such as Naflon®, contain negatively-charged side chains. The positive hydronium ions formed are attracted electrically to the side chains, enabling them to pass through the membrane to the cathode (oxygen side of the membrane). Consequently, reactant gasses are humidified to provide water and ensure operation of the membrane. Reaction with an oxygen ion then occurs. The separation of charge-the radical electrons residing on the collection plate and unreacted hydronium ions at the cathode-is the source of the electric potential. Basically, the catalyst provides an alternate energy pathway and the membrane acts as a salt bridge by promoting the transfer of protons.

A PEMFC is simple in construction. The proton exchange membrane is sandwiched between two porous electrolyte layers and two collector plates. The electrolyte layer is the means of species transfer between the gas streams and the surface of the membrane. The hydrogen gas stream and oxygen gas stream (usually air) pass over the outside surface of the porous diffusion plates.

There are three primary sources of resistance to the transfer of protons and electrons. The activation energy required to cleave gas diatoms at the catalyst sites is the activation resistance. The resistance associated with the transfer of ions is the ohmic resistance. The third resistance is due to mass transfer. Transfer of water occurs because of gas humidification and product formation. At high current, the amount of water at the cathode significantly rises until the continued transfer of oxygen from the gas stream to the membrane halts due to blockage of the pores. When this occurs, the voltage across the cell terminals drops dramatically.

Data Analysis

Evaluation of fuel cell performance is usually conducted using a polarization curve; a plot of voltage versus current density (current divided by cross-sectional area of the membrane). A typical polarization curve is shown in Figure 1.

The primary resistances are represented on separate sections of the plot. The sharp decline in voltage at low current densities is the activation resistance of the catalyst/exchange membrane. The ohmic resistance is best seen in the linear portion of the curve, approximately 0.50-1.4 A/cm^2 in Figure 1. Finally, the sudden decrease in voltage at high current densities indicates the mass transfer resistance has become significant at that point.

The expression describing the kinetic behavior of a fuel cell can be stated as $i = i_o^* \varepsilon P_{O_2}^b e^{\beta \Delta V}$, where i is the current density, P_{O2}^b is the oxygen partial pressure in the fuel cell, and ε is an effectiveness factor. The term i_o^* is a pre-exponential constant defined as $i_o^* = i_o \big/ P_{O_2,Ref}$. The reference oxygen pressure, $P_{O2,Ref}$, is usually defined as 1 atm. The specific current density, i_o, is a constant unique to the operating conditions. The voltage drop, ΔV, is given by the equation $\Delta V = V_T - V_E - V_\Omega$. The voltage predicted by thermodynamics, V_T, is offset by the external voltage V_E (this is the measured voltage) and the voltage drop due to ohmic resistance, $V_\Omega = iR_\Omega$. The thermodynamic voltage is calculated
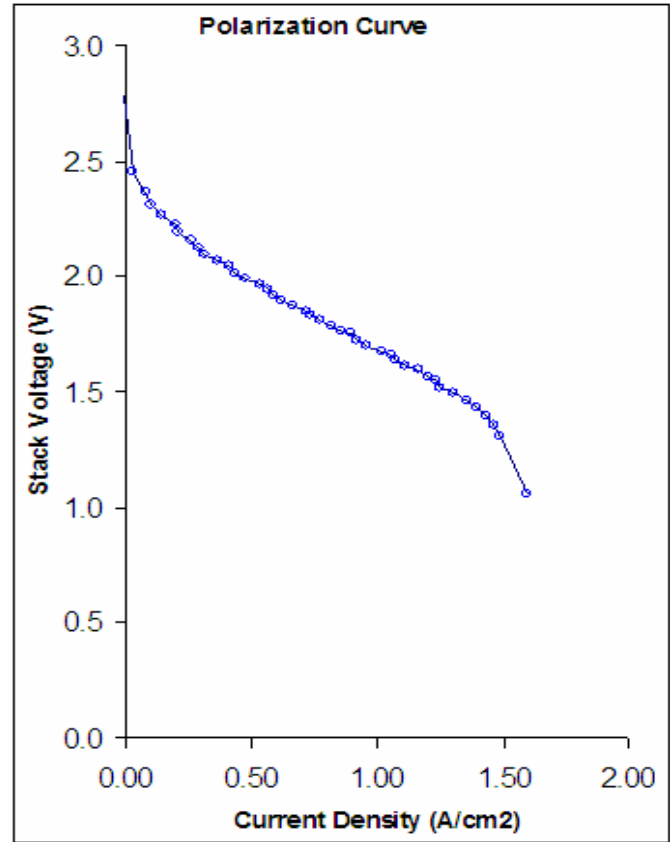

Figure 1: Typical Polarization Curve

by the expression $V_{thermo}(V) = 1.23(V) - 0.0009(T(K) - 298) + \dfrac{RT(K)}{4F} \ln\left[P_{H_2}^2 (atm)P_{O_2}(atm) \right]$. The ohmic resistance R_Ω can be estimated reliably as 0.7-0.75 times the slope of the linear region of the polarization curve.

The determination of the kinetic parameter β is accomplished by casting the kinetic expression in a linear form. A linear form is constructed by taking the natural log of both sides of the equation, $\ln(i) = \ln(i_o^* \varepsilon P_{O_2}^b e^{\beta \Delta V}) = \beta \Delta V + \ln(i_o^* \varepsilon P_{O_2}^b)$. In the linear region of the polarization curve the effectiveness factor is about 1. A plot of $ln(i)$ versus ΔV in the linear region yields a line of slope β and intercept $ln(i_o^* P_{O2}^b)$. The term β is related to the transfer coefficient α by the expression $\beta = \alpha F \big/ RT$. The term T is the absolute temperature, F is the Faraday constant, and R is the ideal gas constant.