The influence of gas-diffusion layer properties on elevated temperature operation of polymer-electrolyte fuel cells

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HIGHLIGHTS

- We study how the diffusion layer affects water behavior in fuel cells.
- High thermal resistance drives water to cathode and lowers humidity.
- High mass-transport resistance drives water to anode and raises humidity.
- Simple model supports experimental findings.

ARTICLE INFO

ABSTRACT

The performance and water management characteristics of polymer-electrolyte fuel cells depend upon the heat and mass transport properties of the components. The influences of the thermal conductivity and thickness of the cathode gas-diffusion layer on the ability to operate stably over a range of temperatures and relative humidities are investigated in this paper. Low thermal resistance is detrimental at low temperature and beneficial at high temperature. The opposite trends hold for mass transport, although the voltage losses associated with oxygen concentration polarization diminish the benefits of increasing the resistance to mass transport.

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1. Introduction

Conventional polymer-electrolyte fuel cells (PEFCs) are sensitive to operating temperature. This sensitivity primarily derives from the state of water in the cell. The water generated by reaction is liquid at low temperatures and vapor at high temperatures. This relationship is depicted in Fig. 1 where the fraction of water leaving the cell as a vapor and the relative humidity of the air and fuel leaving the cell (RH_E) are plotted as a function of coolant temperature. The definition of RH_E is given in the appendix and the conditions are reported in the figure caption. All water exits as vapor above 78 °C; 99% of the water exits as liquid at 1 °C. Liquid water tends to saturate porous media and impede reactant transport to catalyst sites at low temperature. Conversely, Ohmic losses associated with the ionomer in the membrane and catalyst layers tend to be highest at high temperature and low humidity. This conflict

makes maximizing performance over a broad range of operating conditions difficult. The relative humidity at a given temperature can be raised by increasing pressure, increasing inlet dew points, or decreasing air flow. However, compressors and water recovery devices add cost and complexity to fuel-cell systems [1]. Restricting air flow can lead to large overpotentials caused by oxygen concentration polarization.

This paper focuses on how the thermal and mass-transport resistances of the gas-diffusion layer (GDL) on the cathode side affect water movement at elevated temperatures and how this affects performance. A conventional GDL consists of carbon fiber paper (CP) coated with poly(tetrafluoroethylene) (PTFE). A typical CP is approximately 190 μm thick and >70% porous with 7 μm diameter fibers and 10–30 μm diameter pores. Graphitized binder material is also present in many CPs. A microporous layer (MPL) containing carbon particles and PTFE usually separates the CP from the catalyst layer. A typical MPL is less than 50 μm thick with 100–500 nm diameter pores [2]. This range of pore sizes corresponds to the transition between ordinary and Knudsen diffusion at atmospheric pressure.
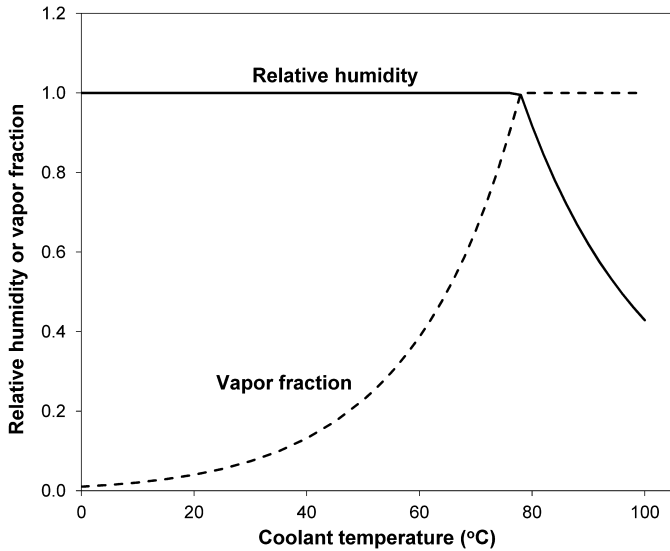
Fig. 1. Relative humidity and vapor fraction as a function of coolant temperature. Fuel: 170 kPa, 1.2× stoichiometric flow, 53 °C dew point. Air: 170 kPa, 1.5× stoichiometric flow, 0 °C dew point.

Fig. 2. Schematic diagram of region of interest showing temperature at the flow field, T_{FF}, and exiting relative humidity, RH_E, as boundary conditions at the flow field on the left. The water flux, n_w, and heat flux, q, are specified at the catalyst layer on the right. The relative humidity at the catalyst layer, RH_{CL}, is the main result.

The combined influence of thermal and mass-transport properties on water vapor movement through the GDL has been described by a number of researchers including Weber and Newman [3], Burlatsky et al. [4], Owejan et al. [5] and Caulk and Baker [6]. These authors convincingly argued that water vapor moves down the temperature gradient in the GDL caused by the heat flux and that vapor transport can dominate even when gases are fully humidified. While the results presented in the cited works are compelling, none includes water distribution measurements or examines the influence of GDL thickness.

The objective of this work is to understand how the transport properties of the CP affect behavior at high temperatures. The link between drying of the membrane-electrode assembly and the thermal resistance of the diffusion media has not been explicitly addressed in the publications cited above. This issue is explored in this work by augmenting the model presented by Caulk and Baker [6] with a relative humidity calculation that describes the hydration state of the membrane-electrode assembly. Predictions for fully humidified and sub-saturated conditions quantify how the properties of the CP influence the range of temperatures yielding stable operation. The predicted operating regimes are qualitatively compared to experimental data from cells with CPs having different thermal conductivities and thickness. In particular, the veracity of the model is interrogated by qualitative comparison to voltage–temperature responses at fixed current and measured water distributions between air and fuel.

2. Mathematical model

Fig. 2 shows a schematic diagram of the region of interest, which consists of the flow field, diffusion media, and catalyst layer on the cathode side of a PEFC. Temperature and relative humidity are specified at the flow-field (FF) boundary on the left. The relative humidity at the FF is set to RH_E in this work. Water flux, n_w, and heat flux, q, are specified at the cathode catalyst layer (CL) boundary on the right. The primary result is RH_{CL}. Heat and vapor transport are solved in the direction perpendicular to the membrane through the composite diffusion medium consisting of CP and MPL. The carbon paper contacts ribs that are separated by gas channels in conventional PEFCs; this detail is not shown in the diagram. Ribs
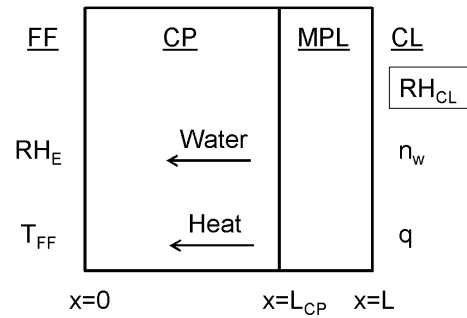
and channels are typically wider (∼1 mm) than the thickness of the diffusion media (∼200 μm), suggesting that two dimensional effects in the plane of the membrane may be important. Caulk and Baker, however, showed good agreement between predicted and measured dry to wet transitions using a one-dimensional model for heat and mass transport essentially identical to the one discussed in this work [6]. Therefore, a one-dimensional approach that uses composite rib/channel boundary conditions yields a good first approximation. Weber discussed a method for calculating an effective one-dimensional length for a GDL confined by ribs and channels [7]. Variations over the active area and transients are ignored as well. Qualitative comparison of the model to experimental data is appropriate given these approximations.

Temperature and vapor pressure profiles through the diffusion media were determined using the formulation presented by Caulk and Baker [6] with minor modifications. Complete derivations are not repeated here, instead we simply present the equations used to calculate the relative humidity in the catalyst layer, and the fraction of water exiting via the cathode. The influence of thermal conductivity on operation at low temperature has been presented before as mentioned in the introduction; however the results of these calculations are included here in order to clarify the nature of the trade between hot and cold performance arising from the selection of a particular set of materials.

Heat conduction through the CP and MPL is assumed to follow Fourier's law, and heat flux is assumed to be continuous across all boundaries. All heat is assumed to flow through the solid phase, in view of the relatively low thermal conductivity of gases. Heat generation in the diffusion media by IR is neglected. Furthermore, no attempt is made to account for enthalpy changes due to evaporation or condensation of water in the diffusion media. A thermal contact resistance between the FF and CP is included in the formula for total thermal resistance. The temperature at the catalyst layer is:

$$T_{CL} = T_{FF} + z_H i(E - V)R_t; \quad R_t = R_{t,c} + \sum_i \frac{L_i}{k_i} \tag{1}$$

where T_{FF} is the temperature at the flow field, z_H is the fraction of the heat generated that exits via the cathode, i is the current density, E is the thermo-neutral or enthalpy voltage, V is the cell voltage, R_t is the total thermal resistance, L_i is the thickness of component i, k_i is the thermal conductivity of region i, and $R_{t,c}$ is the thermal contact resistance between the ribs and CP. Index i in Equation (1) includes the MPL and CP. $R_{t,c} = 5 \times 10^{-5}$ W^{-1} m^2 K, taken from Ref. [6]. Caulk and Baker use $z_H = 0.5$ [6], Burlatsky et al. suggest $0.25 < z_H < 0.5$ [4]. In this work, z_H was estimated for the different configurations by assuming that all heat is generated in the cathode catalyst layer (Table 2 in Ref. [3] gives 77.3% with a