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Analysis of non-isothermal effects on polymer electrolyte fuel cell electrode assemblies

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ABSTRACT

A non-isothermal, single phase membrane electrode assembly (MEA) mathematical model accounting for most applicable heat sources, *viz.*, reversible, irreversible, ohmic heating, phase change, heat of sorption/desorption, is presented. The mathematical model fully couples a thermal transport equation with an MEA model and allows the study of non-isothermal effects, such as thermal osmosis through the membrane, local relative humidity variations in the catalyst layers and water sorption into the membrane. A detailed breakdown of various heat sources in the MEA at different current densities is provided and the impact of various thermal effects previously neglected in the literature such as thermal-osmosis, reversible heat distribution, and heat of sorption are studied. Results show that sorption heat cannot be neglected as it contributes up to 10% of the total heat under normal operating conditions. Reversible heat distribution can significantly affect the temperature distribution shifting the hottest location of the cell from anode and cathode. Analyzing the water transport across the membrane, results show that thermal-osmosis contributes up to 25% of the water flux inside the membrane at moderate and high current densities.

1. Introduction

Thermal management can significantly influence polymer electrolyte fuel cell (PEFC) operation [1,2]. At high current density, the temperature inside the fuel cell can be significantly higher than at the end plates. In automotive applications, where high power densities are achieved, the temperature variations in the cell might be of the order of several degrees. Temperature influences mass, charge and reaction rates. Reaction rates and species transport rates improve at high temperatures. However, high temperatures also result in: i) a reduction of the open cell potential; ii) a reduction in local relative humidity (RH), due to the increased saturation pressure of water, resulting in a significant decrease in membrane hydration levels and thereby proton conduction; and iii) increased fuel crossover through the membrane. Local hot spots might also cause pin holes and degeneration of the membrane significantly reducing fuel cell performance and durability.

Experimental results have recently shown that the temperatures are not constant inside the membrane electrode assembly (MEA) of a PEMFC [3,4]. A temperature difference of 5 °*C* or more between the membrane-catalyst layer interface and the gas channel was observed by Vie and Kjelstrup [3], thereby showing the limitations of the isothermal modeling assumption commonly used in the literature [2]. Nguyen and White [5] and Fuller and Newmann [6] first analyzed heat transfer in fuel cell MEAs. Assuming local thermal equilibrium between the different phases in the electrode, a single heat transfer equation was proposed. Then, an overall heat transfer coefficient for each layer was assumed in order to predict the heat transport inside the PEFC. In these preliminary studies, several heat sources, such as reversible and irreversible losses associated with the electrochemical reactions, were neglected. There are numerous heat generation mechanisms inside the PEMFC, *viz.*, reversible and irreversible heat generation due to the electrochemical reactions, ohmic heating due to electron and ion transport, and heat released/absorbed due to phase change of water. In recent years, non-isothermal models have therefore been extended to account for each one of these mechanisms as shown in Table 1. Table 1 shows that, even though non-isothermal fuel cell model in the literature account for many of the heat sources, the heat released due to water sorption has been neglected in the majority of models. Furthermore, a complete MEA model that couples

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Nomenclature

$\Delta\bar{S}$	Change in entropy per mole of fuel, $J/(mol \cdot K)$
$\hat{T}$	Temperature, $^{\circ}C$
λ	Sorbed water content
F	Universal Faraday's constant, $A \cdot s/mol$
H^{+}	Proton
k	Thermal conductivity, $W/(cm \cdot K)$
p_{tot}	Total pressure, Pa
Q_{rev}	Reversible heat released per mole of fuel, J/mol
T	Temperature, K
x_{H_2O}	Water mole fraction
ACL	Anode Catalyst Layer
CCL	Cathode Catalyst Layer
CGDL	Cathode Gas Diffusion Layer
CMPL	Cathode Microporous Layer
FEM	Finite Element Method
GDL	Gas Diffusion Layer
HOR	Hydrogen Oxidation Reaction
MEA	Membrane Electrode Assembly
ML	Membrane Layer
MPL	Microporous Layer
ORR	Oxygen Reduction Reaction
PEMFC	Polymer Electrolyte Membrane Fuel Cell
RH	Relative Humidity

all heat generation terms with an accurate membrane water transport model has not yet been developed. The development of such a model would allow researchers to better understand the relative importance of each heat generation term and the impact of thermal management on water transport in the cell.

Even though several non-isothermal models have been proposed in the literature, the analysis of the relative importance of each heat generation term in the MEA has only seldom been analyzed. Ju et al. [7] estimated the distribution of major heat source terms, *viz.*, reversible heat, irreversible heat, and ohmic heating. They found the distribution of major heat sources to be roughly 35%, 45%, and 17% respectively at cell voltage of 0.6 V under 75%/0% anode/cathode RH conditions. However, water sorption effects were neglected and the reversible heat term was formulated for liquid water product even though the model was single phase, thereby over-predicting the heat generated in the cell. For a single phase model to be consistent, a heat sink due to complete evaporation of water should be included in the model, which is ignored in their work.

Ramousse et al. [8] introduced the heat source/sink term corresponding to sorption/desorption of water into the electrolyte taking place at the catalyst layers in a one-dimensional heat transfer simulation of the MEA. Ostrovskii and Gostev [9] has shown that the enthalpy of sorption decreased from 68 kJ/mol (at $\lambda \simeq 0$) to nearly 45 kJ/mol (at $\lambda \simeq 5$), but values below the latent heat of water vaporization are not reached. On considering the enthalpy of sorption the same as the latent heat of vaporization, the heat term corresponding to sorption/desorption of water is observed to be of similar magnitude as the irreversible heat in a two-dimensional thermal model [10]. The model however does not solve for transport of other species (except temperature) and reaction kinetics.

The reversible heat release in the fuel cell is usually accounted for in most non-isothermal models. The total entropy change associated to the overall reaction producing liquid water per unit mole of fuel (H_2), $\Delta\bar{S}$, is well known in the literature [11]. At $T = 353$ K, it results in a reversible heat release of 55.99 kJ/mol-H_2 inside the fuel cell. However, this heat is not evenly distributed amongst the anode and cathode reactions. Efforts to determine the entropy changes in a single half cell reaction are marred with difficulties because of a lack of reliable knowledge of the entropy values of hydronium ions (H_3O^+) and electrons (e^-). To date, most non-isothermal models in the literature assume that almost all of the reversible heat is produced inside the cathode electrode. This might not be the case. Ramousse et al. [12] reported a wide discrepancy in the literature data for the hydrogen oxidation reaction (HOR), from -133.2 J/(mol-K) (Exothermic) to 84.7 J/(mol-K) (Endothermic). The HOR half cell reaction is reported to be slightly exothermic [13], athermic [14] and slightly endothermic [15]. On studying proton solvation in water, Ramousse et al. [12] calculated that the entropy change is -133.2 J/(mol-K) (highly exothermic). These values are opposite to the normally modelled values in the literature. Kjelstrup et al. [16] performed experiments on a hydrogen-hydrogen cell under the Soret equilibrium conditions (no current is being generated in the cell). They reported that at 340 K, the entropy change for the HOR is -66 ± 5 J/(mol-K). However, it is also concluded that as current is being generated in the cell (moving away from the Soret equilibrium), there can be a considerable enthalpy transport along with water and protons shifting the reversible heat production towards the cathode side. Hence there is ambiguity in the literature for the reversible heat production distribution inside the cell. Therefore, the impact of the reversible heat distribution should be studied.

Thermal and water management must be studied simultaneously since they severely affect one another. It has been shown that water sorption/desorption will release/absorb energy. Temperature gradients across the membrane also affect water management across the membrane. Water in sorbed phase is transported under temperature gradients inside the polymer electrolyte membrane [17,18]. This so-called thermal osmosis effect can be explained by the second law of thermodynamics, since water moves from the cold side (ordered state inside the hydrophillic membranes) to the hot side in order to increase the entropy.

Table 1

Summary of non-isothermal models in the literature with respect to various heat source terms and other limitations.

Ref.	Irrev.	Rev.	Ohm.	Sorp.	Other remarks
[7]	√	√	√	×	Reversible heat formulated for liquid water product in single phase
[8]	√	√	√	√	1D model with independent heat transfer analysis
[10]	√	√	√	√	1D heat transfer only
[53,54]	√	√	×	×	-
[55]	√	√	×	×	Global heat source terms instead of location-specific
[56]	√	√	√	×	1D model, fully hydrated membrane (undermined ohmic heating)
[57]	×	×	√	×	Interface CL
[58]	√	×	√	×	-
[59–63]	√	√	√	×	-
[13,64]	√	√	√	×	Interface CL
[65]	×	√	√	×	-
[66]	√	√	√	×	Cathode electrode only
[67]	√	√	√	×	Two equation thermal model