Fuel crossover and internal current in proton exchange membrane fuel cell modeling

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HIGHLIGHTS

- Identifies an error in the fuel cell modeling literature.
- Provides an explanation of the error.
- Provides the correct model.

ABSTRACT

This note discusses an inexact use of fuel crossover and internal current in the derivation of the output voltage of proton exchange membrane fuel cells in the literature.

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1. Introduction

Proton exchange membrane (or polymer electrolyte membrane, or PEM) fuel cells offer a clean, high-efficiency, high-power-density and low-temperature source of energy for both stationary and portable applications, with particular promise for future transportation applications [1,2]. Modeling of PEM fuel cells (e.g., [3–6]) is an integral part of the research on improving their durability and reducing costs. In many papers in the fuel cell modeling literature (e.g., [7–19]), the expression used for the terminal voltage of PEM fuel cells is erroneous. The present paper points out the inclusion of the fuel crossover and internal current in the calculation of the ohmic voltage drop as the source of the error. An explanation of the error and a correct expression of terminal voltage are given in the next section.

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2. The correct model

The output terminal voltage in a typical model of a proton exchange membrane fuel cell is obtained by subtracting from the thermodynamically predicted electromotive force (EMF) the irreversibilities (or losses) that take place when current is drawn from the cell [2]. The ideal open-circuit EMF, or the reversible thermodynamic potential, of a cell is given by the Nernst voltage:

$$E_{Nernst} = E_0 + \frac{RT}{2F} \ln \left(p_{H_2} \sqrt{p_{O_2}} \right) \tag{1}$$

where E_0 is the standard reference potential (dependent on temperature) of the cell, p_{H_2} and p_{O_2} are partial pressures of hydrogen and oxygen, T is the temperature, R is the universal gas constant, and F is Faraday's constant. The above equation is a simplified form of

$$E_{Nernst} = E_0 + \frac{RT}{2F} \ln \left(\frac{a_{H_2} \sqrt{a_{O_2}}}{a_{H_2O}} \right) \tag{2}$$

where a_{H_2O}, the *activity* of water, is taken to be unity (which is not unjustified for a PEM fuel cell that is operated below 100 °C so that

liquid water is produced), and the activity of an ideal gas is expressed in terms of its pressure (or partial pressure) p:

$$a_{H_2} = \frac{p_{H_2}}{p^0}, \tag{3}$$

$$a_{O_2} = \frac{p_{O_2}}{p^0}, \tag{4}$$

where p^0 is the standard pressure (1 atm).

Four types of irreversibilities [2] are usually considered:

1. Activation losses explained by the reaction kinetics taking place on the surface of the electrode:

$$\eta_{act} = \frac{RT}{\alpha nF} \ln\left(\frac{i_{den}}{i_{0,den}}\right) \tag{5}$$

where α is the electron transfer coefficient, n is the number of moles of electrons transferred for every mole of hydrogen participating in the reaction, i_{den} is the current density, and $i_{0,den}$ the exchange current density (with $i_{den} > i_{0,den}$).

2. Concentration loss (or mass transport loss) arising out of the change in concentration of the reactants at the surface of the electrodes as the fuel is used:

$$\eta_{conc} = -B \ln\left(1 - \frac{i_{den}}{i_{limit,den}}\right) \tag{6}$$

where B is a constant and $i_{limit,den}$ is the limiting current density (with $i_{den} < i_{limit,den}$).

3. Ohmic loss due to the electronic and ionic resistance (resistance of the electrodes, the interconnects, the electrolyte, and the conducting resistance between the membrane and the electrodes):

$$\eta_{ohm} = i_{den} r_{area} \tag{7}$$

where r_{area} represents the area-specific resistance (dependent upon temperature).

4. Loss due to fuel crossover (waste of hydrogen fuel passing through the electrolyte) and internal current (waste of electrons passing through the electrolyte). Let $i_{n,den}$ represent the current density for the combined effect of fuel crossover and internal current.

Under the standard assumptions, approximations and limitations in the fuel cell modeling literature (e.g., [2]), the output voltage, V_{cell}, of a cell is given by the following equation:

$$V_{cell} = E_{Nernst} - \frac{RT}{\alpha nF} \ln\left(\frac{i_{den} + i_{n,den}}{i_{0,den}}\right) + B \ln\left(1 - \frac{i_{den} + i_{n,den}}{i_{limit,den}}\right) - i_{den} \times r_{area}. \tag{8}$$

Refs. [7–19] all gave an output voltage expression almost identical to Eq. (8) of the present paper (ignoring notational differences and the obvious difference between a single cell and a stack), but in those papers an error crept into the ohmic loss term: the ohmic loss was accounted for in those papers by

$$(i_{den} + i_{n,den}) \times r_{area}.$$

The internal current is used to model the undesired passage (leakage) of electrons from the anode through the electrolyte (not through the external circuit) onto the cathode. The fuel crossover event is used to describe the undesired passage of fuel (hydrogen molecules, not hydrogen ions) through the electrolyte, from the anode to the cathode. Thus fuel crossover and internal current can be thought of as components that are "stolen" or "lost" from the external (load) current. It is common practice in the literature (e.g., [2]) to consider the effect of fuel crossover as equivalent to that of the internal current, thereby lumping the two effects into a single phrase. The crossing over, or permeation, of the fuel (hydrogen) from the anode to the cathode via the electrolyte (membrane) takes place not as a result of any electrical potential difference (voltage gradient), but because of a concentration gradient of hydrogen. In other words, hydrogen crossover is the diffusion of uncharged H_2 through the membrane, as opposed to the conduction (through the membrane) of charged H^+ (protons) under the influence of an electric field. If we call the fuel crossover and internal current "bad" current, then the internal ohmic resistance is used to model the resistance offered to the flow of the "good" current by the material of the electrodes and the interconnections and by the electrolyte (specifically, electrical resistance by the electrodes to the flow of electrons and electrical resistance by the electrolyte to the flow of hydrogen ions). The "good" or useful current and the "bad" or useless current are disjoint or orthogonal in nature, so far as the ohmic resistance is concerned (the "bad" current does affect the reactant and product concentrations and the reaction kinetics, though). Thus it does not make sense to add the "bad" current to external (load) current in computing the irreversible ohmic drop. (At open circuit, when the "bad" current is non-zero even though the "good" current is zero, the ohmic drop is zero.)

3. Conclusion

This paper analyzed an inaccuracy in a proton exchange membrane fuel cell model that has long been circulating in the literature. An incorrect application of the fuel crossover and internal current in the derivation of the ohmic loss was shown to be the cause of the error. While this discussion is valid in general for hydrogen–oxygen fuel cells such as solid oxide fuel cells and proton exchange membrane fuel cells, the internal current and fuel crossover effects at open circuit are more pronounced for PEM fuel cells which operate at a much lower temperature than solid oxide fuel cells.

In the papers where the same model is used in different computational algorithms [7–12,14,17], the error in the model has the same effect on all the algorithms, and therefore the presence of the error does not invalidate the findings in those papers about the relative performance of the competing algorithms.

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