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On the interchangeability of potentiostatic and galvanostatic boundary conditions for fuel cells

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ABSTRACT

This paper addresses the importance of the boundary conditions for the charge conservation equation in the modeling of fuel cells. In this context, we analyze the charge transport in an electric conductor, aiming to determine whether constant current and constant potential boundary conditions can be interchanged without disturbing the local current density distribution in the cell. Their interchangeability can be described with a dimensionless number, referred to as the "interchangeability number", which captures the relevant operating, geometrical and material parameters. The effect of the interchangeability number is further explored in a model for non-isothermal two-phase flow in a proton exchange membrane fuel cell, for which is it verified that the interchangeability number should be much less than 3, in order to ensure that the prediction for the local current density distribution at the catalyst layers remains the same regardless of galvanostatic or potentiostatic boundary conditions.

1. Introduction

Mathematical modeling of fuel cells with microscopic equations of change often involves the potential of one or two phases: electrons in the solid phase and ions in the electrolyte. The conservation of charge is usually formulated as the divergence of the current density, where the current density is postulated to follow Ohm's law; i.e. as a linear relation of the potential in a particular phase. The conservation of charge is expressed as an elliptic partial differential equation of second order in two- or three-dimensional geometries, which can be solved once the functional form of the electrical conductivity – usually a constant, function and/or tensor that accounts for differences in through- and in-plane conductivities – has been determined and the necessary boundary conditions (BCs) invoked. The latter typically takes the form of a Dirichlet condition with a specified potential or a Neumann condition with a specified current or insulation.

For fuel cells, mathematical models have been reported with both constant potential [1–12] (referred to as potentiostatic BC) and constant current BCs [13–18] (referred to as galvanostatic BCs). Typically, the two kinds of BCs do not have any distinct advantage over each other to predict the performance of a cell operated under constant inlet velocities; however, once a stoichiometric flow condition – which in turn depends on the average current density – is introduced, the use of the potentiostatic condition requires an iterative approach in order to determine the correct inlet velocity that corresponds to the prescribed stoichiometry [19,3,7]. In such a situation, the galvanostatic BC is more advantageous since the inlet velocities can be directly determined without any need for numerical iterations.

The galvanostatic BC, however, has been found to disturb the local current density distribution in the cell [20,13]. This is especially the case if the current density distribution at the bipolar plate is uneven – usually its exact functional form is unknown a *priori* to computations. This implies that the two kinds of BCs are not interchangeable by default. In this context, Meng and Wang [13] found that increasing the electronic conductivity of the bipolar plate reduces the difference in the current density distribution under the two kinds of BCs; a similar argument has been reported in [18] as well. However, a systematic mathematical analysis of charge transport is lacking in order to determine the conditions that have to be satisfied in order to ensure interchangeability of BCs.

The aim of this paper is therefore to address galvanostatic and potentiostatic BCs in multidimensional fuel cell models with a view to determining when these can be interchanged without

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influencing the current density distribution at the catalyst layer at leading order. This is accomplished by considering a conductive layer in which conservation of charge together with Ohm's law is solved analytically. A dimensionless number that characterizes the interchangeability of galvanostatic and potentiostatic BCs for an electrical conductor is then identified. The results of the analysis are then further studied in the context of an earlier non-isothermal two-phase flow model for a proton exchange membrane fuel cell (PEMFC).

2. Mathematical formulation

We consider steady-state conservation of charge for a slender two-dimensional rectangle that occupies $0 \le x \le L$, $-h \le y \le 0$ and is subject to insulating BCs at $x = 0$ and L, a galvanostatic BC at $y = 0$ and a prescribed current density distribution at $y = -h$:

$$\phi_{xx} + \phi_{yy} = 0 \tag{1}$$

$$\phi_x(0, y) = 0 \tag{2}$$

$$\phi_x(L, y) = 0 \tag{3}$$

$$-\sigma\phi_y(x, 0) = i_{\text{app}} \tag{4}$$

$$-\sigma\phi_y(x, -h) = I(x) \tag{5}$$

$$\phi(0, 0) = E_0 \tag{6}$$

Here, i is the current density, ϕ is the electronic potential, h is the thickness, L is the length, i_{app} is the applied current density, σ is the electronic conductivity, E_0 is a reference potential that is prescribed in an arbitrary point, here taken at $(x, y) = (0, 0)$, and $I(x)$ is an arbitrary current density distribution that is constrained by the integral

$$\frac{1}{L}\int_0^L I(x)dx = i_{\text{app}}, \tag{7}$$

so as to conserve current globally.

In the above formulation, a galvanostatic BC is specified at the top, $y = 0$. If a potentiostatic condition in the form of a specified potential had instead been invoked, there would have been a uniform electric potential at the top. To explore the interchangeability of the BCs, we shall employ a galvanostatic BC whilst seeking the conditions that also ensure a uniform potential distribution at the top at leading order; i.e. variations in the potential should be negligible. As a measure of the uniformity of the potential at $y = 0$, we choose the average absolute deviation, Δ:

$$\Delta := \frac{1}{L}\int_0^L \left|E_0 - \phi(x, 0)\right| dx; \tag{8}$$

note that we take $\phi(0, 0)$ as the reference. The layer we consider here represents a bipolar plate or a current collector in a fuel cell, and we seek to determine the conditions for which $\Delta \ll E_0$.

3. Analysis

Nondimensionalizing the above set of equations with

$$\tilde{x} = \frac{x}{L}, \quad \tilde{y} = \frac{y}{h}, \quad \tilde{\phi} = \frac{\phi - E_0}{\Delta\phi}, \quad \widetilde{I}(\tilde{x}) = \frac{I(x)}{i_{\text{app}}}, \quad \varepsilon = \frac{h}{L},$$
$$\tilde{\Delta} = \frac{\Delta}{E_0} \tag{9}$$

determining the scale for the potential drop, $\Delta\phi \sim i_{\text{app}}h/\sigma$, from Eq. (4), and then solving the charge conservation equation by separation of variables yields

$$\tilde{\phi}(\tilde{x}, \tilde{y}) = -\tilde{y} + \frac{2}{\pi\varepsilon}\sum_{n=1}^{\infty}\frac{1 - \cos(n\pi\tilde{x})\cosh(n\pi\varepsilon\tilde{y})}{n\sinh(n\pi\varepsilon)} \times \int_0^1 \widetilde{I}(x')\cos(n\pi x')dx' \tag{10}$$

The dimensionless average absolute deviation of the electric potential at $\tilde{y} = 0$, $\tilde{\Delta}$, can be written as

$$\tilde{\Delta} = \frac{\Delta\phi}{E_0}\int_0^1 \left|\tilde{\phi}(\tilde{x}, 0)\right| d\tilde{x} \tag{11}$$

Substituting the analytical solution and scale $\Delta\phi$, we find

$$\tilde{\Delta} = \frac{2i_{\text{app}}h}{\sigma E_0\pi\varepsilon}\int_0^1 \left|\sum_{n=1}^{\infty}\frac{1 - \cos(n\pi\tilde{x})}{n\sinh(n\pi\varepsilon)}\int_0^1 \widetilde{I}(x')\cos(n\pi x')dx'\right| d\tilde{x} \tag{12}$$

$$\le \frac{2i_{\text{app}}h}{\sigma E_0\pi\varepsilon}\sum_{n=1}^{\infty}\frac{1}{n\sinh(n\pi\varepsilon)}\left(\int_0^1 \left|\widetilde{I}(x')\cos(n\pi x')\right| dx'\right) \tag{13}$$

Defining a dimensionless number Θ, which we shall refer to as the interchangeability number, by

$$\Theta \equiv \frac{L^2 i_{\text{app}}}{h\sigma E_0}, \tag{14}$$

we have

$$\tilde{\Delta} \le \frac{2\varepsilon\Theta}{\pi}\sum_{n=1}^{\infty}\frac{1}{n\sinh(n\pi\varepsilon)}\left(\int_0^1 \left|\widetilde{I}(x')\cos(n\pi x')\right| dx'\right). \tag{15}$$

Now, we require $\tilde{\Delta} \ll 1$, which would certainly be satisfied if

$$\frac{2\varepsilon\Theta}{\pi}\sum_{n=1}^{\infty}\frac{1}{n\sinh(n\pi\varepsilon)}\left(\int_0^1 \left|\widetilde{I}(x')\cos(n\pi x')\right| dx'\right) \ll 1, \tag{16}$$

From the Cauchy–Schwarz inequality, we know that

$$\int_0^1 \left|\widetilde{I}(x')\cos(n\pi x')\right| dx' \le \int_0^1 \left|\widetilde{I}(x')\right| dx' \int_0^1 \left|\cos(n\pi x')\right| dx' \tag{17}$$

$$\int_0^1 \left|\widetilde{I}(x')\cos(n\pi x')\right| dx' \le \int_0^1 \left|\widetilde{I}(x')\right| dx' \tag{18}$$

In fuel cells, it is always the case that $\widetilde{I}(\tilde{x}) \ge 0$, which then together with Eq. (7) implies that

$$\int_0^1 \left|\widetilde{I}(x')\right| dx' = 1 \tag{19}$$

giving that

$$\frac{2\varepsilon\Theta}{\pi}\sum_{n=1}^{\infty}\frac{1}{n\sinh(n\pi\varepsilon)} \ll 1. \tag{20}$$

i.e.

$$\Theta \ll \frac{\pi}{2\varepsilon\sum_{n=1}^{\infty}(1/n\sinh(n\pi\varepsilon))}. \tag{21}$$

Ideally, there would be a closed-form expression for the sum on the right-hand side; however, there is not, and the next best alternative is to bound it with one. Note that we want to