Modeling Transport in *n*-Type Oxide MIECs with Potential Dependent Boundary Conditions and Non-Linear Potentials

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The transport properties of Mixed Ionic-Electronic Conductors (MIECs)—such as the spatial distribution and flux of defects—have been modeled by solving the transport laws applicable to the MIEC system; namely the Nernst-Planck equation

$$j_i = -D_i \nabla c_i - u_i c_i \nabla \phi \qquad [1]$$

and steady state material balance

$$\nabla j_i = 0 \qquad [2]$$

where j is flux density, D is diffusivity, c is concentration, u is electrical mobility (from the Nernst-Einstein equation), and ϕ is electrical potential.

In order to find a solution to the resulting system of differential equations a number of simplifying assumptions are typically made (1 - 3). This paper is concerned with two of these simplifications which have the potential to give particularly misleading results. The first is the use of fixed—i.e., independent of an external potential—boundary conditions. The usual justification for this assumption is the notion of electrode reversibility at high temperatures (> ~800 °C). However, the verity of this assumption has not been fully explored and may be incorrect. The second concern is the assumption of a linear potential, which turns out to be equivalent to assuming that the concentration of ionic defects is uniformly distributed through the MIEC. If the applied potential is not too large, this assumption is reasonable for some MIECs (e.g., cubic-stabilized zirconia). However, it is dubious for other MIECs (e.g., acceptor-doped ceria).

In this paper, defect distribution and transport in MIECs is modeled with and without these assumptions and the results are compared. As an example, The spatial distribution of electrons, modeled using both *fixed* and *potential dependent* boundary conditions, is shown in Figure 1 (where $\Phi_{\square\square\square}$ is the load voltage, Φ_{oc} the open-circuit potential and Φ_{th} the theoretical (Nernst) potential). Additionally, because of the possible impact of these assumptions on the design of devices such as fuel cells, their impact on power efficiency (ζ_P) and current efficiency (ζ_I) is also evaluated, Figure 2. Also shown in Figure 2 are the modeled I-V characteristics and power density of an SOFC with a ceria electrolyte.

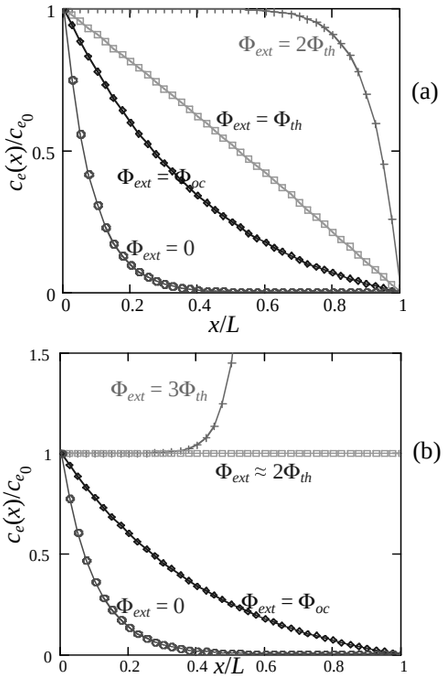

Figure 1. Electron concentration profile with (a) *fixed* and (b) *potential dependent* boundary conditions.

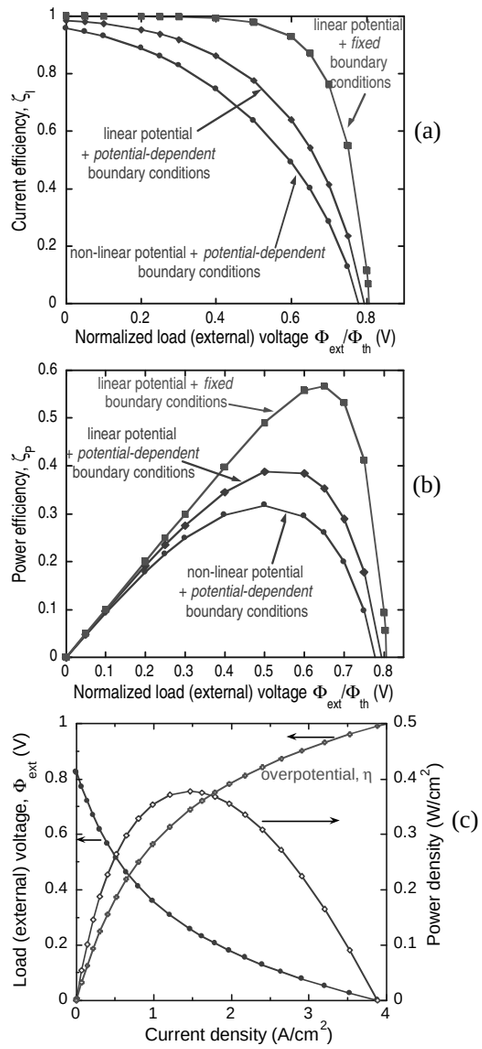

Figure 2. Predicted (a) current efficiency, (b) power efficiency and (c) I-V characteristics.

References

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