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Membrane polarization in mixed-conducting ceramic fuel cells and electrolyzers

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ABSTRACT

This paper focuses on modeling membrane-polarization processes within mixed-conducting electrolyte membranes. Because a complete set of thermodynamic and transport properties is available, the electrolyte material used for the study is a yttrium-doped barium zirconate ($BaZr_{0.9} Y_{0.1} O_{3-\delta}$, BZY10). Unlike Polymer Electrolyte Fuel Cells (PEMFC) and Solid-Oxide Fuel Cells (SOFC), the open-circuit voltage cannot be evaluated using gas-phase compositions alone. Using a Nernst-Planck-Poisson (NPP) model, an important aspect of the present paper is to develop the theory needed to evaluate open-circuit potential. Focusing on the mixed-conducting membrane alone, the present model neglects all activation and concentration overpotentials. The model is exercised in both fuel-cell and electrolyzer modes, revealing significantly different polarization behaviors. The model-based results show how the membrane polarization depends upon operating conditions, including temperature and gas-phase compositions.

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Introduction

Protonic ceramic fuel cells (PCFCs) and electrolyzers (PCEC) are based on ceramic, solid-electrolyte, membrane materials that exhibit good protonic conductivity at intermediate temperatures (400—700 °C) [1—4]. Compared to traditional solid-oxide fuel cells (SOFC), the intermediate operating temperature of the PCFCs enables the use of inexpensive ferrite steel for interconnects, more reliable sealing, relatively rapid start-up, lower thermal stresses resulting from thermal-expansion mismatch of dissimilar materials, and negligible electrode sintering.

Doped-perovskite proton-conducting oxides have been widely investigated as PCFC electrolyte materials [1—3,5]. Particularly, the acceptor-doped $BaCeO_3$, $BaZrO_3$, or mixed solid solutions of $BaCeO_3$ and $BaZrO_3$ have been demonstrated to have good proton conductivity at intermediate temperatures. However, although $BaCeO_3$ has high conductivity, it is not useful for PCFC because it is chemically unstable in H_2O and CO_2 environments [6—8]. The acceptor-doped $BaZrO_3$ materials (i.e, $BaZr_{1-x} Y_x O_{3-\delta}$, BZY) demonstrate good chemical stability in H_2O and CO_2 environments, and are considered to be one of the most promising electrolyte materials for PCFCs [8—10].

Fig. 1 illustrates a protonic ceramic fuel cell (PCFC) and a protonic ceramic electrolysis cell (PCEC). Although the physical structure of the cells are identical, the difference between PCFC and PCEC are in the gas composition and the external electrical circuit. The fuel cell delivers electrical power by electrochemically oxidizing hydrogen. The electrolyzer uses electrical power to produce hydrogen from steam. In fuel-cell
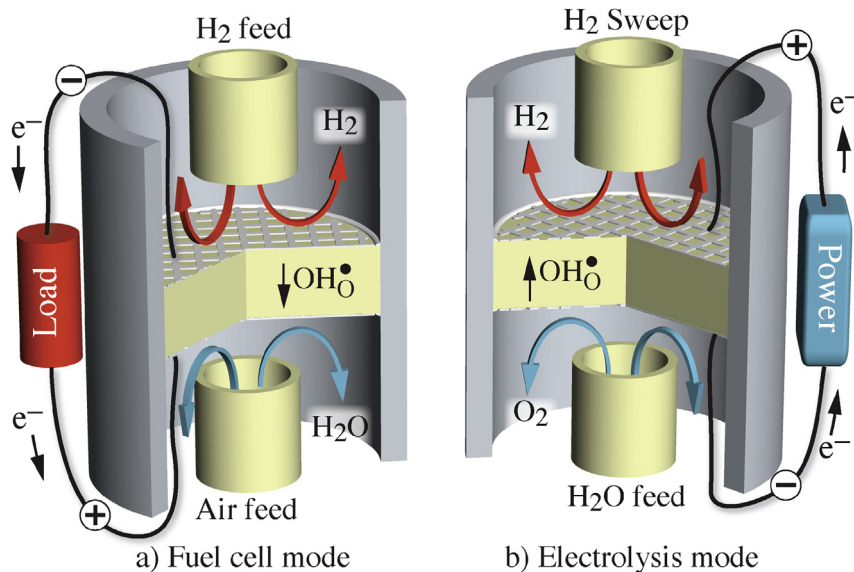
Fig. 1 – Illustrations of a Protonic Ceramic Fuel Cell (PCFC) and a Protonic Ceramic Electrolysis Cell (PCEC), both in button-cell configurations. Note that the role of the anode (negative electrode) and cathode (positive electrode) are reversed between fuel-cell and electrolyzer operation.

operation, hydrogen dissociatively adsorbs on the anode electro-catalyst surfaces. Adsorbed hydrogen on the membrane surface migrates toward the three-phase boundary (TPB) regions where electrons can be removed. Electrochemical incorporation chemistry delivers protons into the perovskite lattice. Protons are transported through the electrolyte toward the cathode where they react electrochemically with the oxygen to form water. At the same time, the electrochemical potentials drive the electrons from the anode through an external circuit to deliver power before returning back to the cathode. In electrolysis mode, the processes occur in the opposite direction, producing fuels from electricity.

The overall half-cell charge-transfer reaction for the oxidization of hydrogen to protons at the anode-electrolyte interfaces can be written globally as [11−19].

$$H_2(g) + 2O_O^\times(el) \rightleftharpoons 2OH_O^\bullet(el) + 2e'(ed). \tag{1}$$
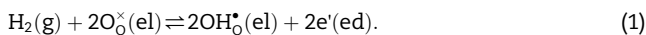
The overall half-cell charge-transfer reaction of protons with oxygen to form water at three-phase boundaries of the cathode can be represented as [20−25].

$$O_2(g) + 4OH_O^\bullet(el) + 4e'(ed) \rightleftharpoons 2H_2O(g) + 4O_O^\times(el). \tag{2}$$
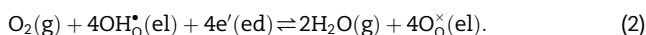
In this Kröger−Vink notation, the protons are designated as $OH_O^\bullet$. The parenthetical identifiers indicate gas-phase (g), electrode phase (ed), and electrolyte phase (el).

The protonic ceramics are usually not pure proton conductors. They are mixed ionic-electronic conductors (MIEC), which typically have two or three mobile charge-carrying defects. Taking BZY10 ($BaZr_{0.9}$ $Y_{0.1}$ $O_{3-\delta}$) as an example, there are three mobile charge-carrying defects—protons $OH_O^\bullet$, oxygen vacancies $V_O^{\bullet\bullet}$, and O-site small polarons $O_O^\bullet$ [26]. Each of these defects can participate in reactions at the BZY10 membrane−gas interface. Because of the multiple mobile charge-carrying defects within the electrolytes, there is usually a loss of potential to do electrical work (manifested as

reduced open-circuit voltage). As discussed subsequently, mixed conduction within the membrane significantly influences the open-circuit potential, operating potential, and resistive losses through electrolyte membrane.

Although BZY10 is chosen for the present study, the theory and computational approaches are the same as for other mixed-conducting electrolytes. The reason to chose BZY10 is that a complete set of thermodynamic and transport properties are available [26]. Tables 1 and 2 show the needed properties.

Early work by Riess [27,28] introduced the notion of developing solid-oxide fuel cells with mixed-conducting membranes. The underpinning theory in the Riess papers is similar to the approach in the present paper. However, the present paper develops a computational model, while Riess made approximations that enabled analytic solutions. Also, Riess was concerned with materials that were dominantly oxygen-conducting membranes, not proton-conducting membranes.

Cell voltage

The measurable cell voltage can be represented in terms of the electrochemical potential of the electrons within the electrodes as [29−31].

Table 1 − Thermodynamics for defect reactions.			
Reactions	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	K_p (750°C)
$\frac{1}{2}H_2 + O_O^\bullet \rightleftharpoons OH_O^\bullet$	−146.01	−0.89	$2.56 \times 10^{+07}$
$\frac{1}{2}O_2 + O_O^\times + V_O^{\bullet\bullet} \rightleftharpoons 2O_O^\bullet$	−36.08	−125.48	1.94×10^{-05}
$H_2O + V_O^{\bullet\bullet} + O_O^\times \rightleftharpoons 2OH_O^\bullet$	−80.00	−71.78	$2.16 \times 10^{+00}$
$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$	−248.11	−55.48	$5.87 \times 10^{+09}$