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 ($\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$, 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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1. 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 BaCeO₃, BaZrO₃, or mixed solid solutions of BaCeO₃ and BaZrO₃ have been demonstrated to have good proton conductivity at intermediate temperatures. However, although BaCeO₃ has high conductivity, it is not useful for PCFC because it is chemically unstable in H₂O and CO₂ environments [6–8]. The acceptor-doped BaZrO₃ materials (i.e., BaZr_{1-x}Y_xO_{3-δ}, BZY) demonstrate good chemical stability in H₂O and CO₂ 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 com-

Figure 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.

23 position and the external electrical circuit. The fuel cell delivers electrical
 24 power by electrochemically oxidizing hydrogen. The electrolyzer uses electri-
 25 cal power to produce hydrogen from steam. In fuel-cell operation, hydrogen
 26 dissociatively adsorbs on the anode electro-catalyst surfaces. Adsorbed hy-
 27 drogen on the membrane surface migrates toward the three-phase boundary
 28 (TPB) regions where electrons can be removed. Electrochemical incorpo-
 29 ration chemistry delivers protons into the perovskite lattice. Protons are
 30 transported through the electrolyte toward the cathode where they react
 31 electrochemically with the oxygen to form water. At the same time, the elec-
 32 trochemical potentials drive the electrons from the anode through an external

33 circuit to deliver power before returning back to the cathode. In electrolysis
 34 mode, the processes occur in the opposite direction, producing fuels from
 35 electricity.

36 The overall half-cell charge-transfer reaction for the oxidization of hydro-
 37 gen to protons at the anode-electrolyte interfaces can be written globally
 38 as [11–19]

39 The overall half-cell charge-transfer reaction of protons with oxygen to form
 40 water at three-phase boundaries of the cathode can be represented as [20–25]

41 In this Kröger–Vink notation, the protons are designated as $\text{OH}_{\text{O}}^{\bullet}$. The
 42 parenthetical identifiers indicate gas-phase (g), electrode phase (ed), and
 43 electrolyte phase (el).

44 The protonic ceramics are usually not pure proton conductors. They
 45 are mixed ionic-electronic conductors (MIEC), which typically have two or
 46 three mobile charge-carrying defects. Taking BZY10 ($\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$) as an
 47 example, there are three mobile charge-carrying defects—protons $\text{OH}_{\text{O}}^{\bullet}$, oxy-
 48 gen vacancies $\text{V}_{\text{O}}^{\bullet\bullet}$, and O-site small polarons $\text{O}_{\text{O}}^{\bullet}$ [26]. Each of these defects
 49 can participate in reactions at the BZY10 membrane-gas interface. Because
 50 of the multiple mobile charge-carrying defects within the electrolytes, there
 51 is usually a loss of potential to do electrical work (manifested as reduced
 52 open-circuit voltage). As discussed subsequently, mixed conduction within
 53 the membrane significantly influences the open-circuit potential, operating
 54 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 the Riess made approximations that enabled analytic solutions. Also, Riess was concerned with materials that were dominantly oxygen-conducting membranes, not proton-conducting membranes.

2. Cell Voltage

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

$$E_{\text{cell}} = \Phi_{\text{c}} - \Phi_{\text{a}} = \frac{\tilde{\mu}_{\text{e}'}(\text{c}) - \tilde{\mu}_{\text{e}'}(\text{a})}{F}, \quad (3)$$

where “c” and “a” represent cathode and anode. Assuming that all surface reactions are equilibrated, the charge-transfer reaction between the electrode and the mixed-conducting electrolyte can be expressed as

which is the combination of the electron-transfer reaction across the electrode-BZY10 interface (i.e., $\text{Nil} = \text{e}'(\text{ed}) + \text{h}^{\bullet}(\text{el})$) [32, 33] and the definition of the O-site polaron (i.e., $\text{O}_{\text{O}}^{\times}(\text{el}) + \text{h}^{\bullet}(\text{el}) = \text{O}_{\text{O}}^{\bullet}(\text{el})$) [26].

At the anode-electrolyte interface, an activation overpotential η_a can be formally defined as

$$\eta_a = (\Phi_a - \Phi_{e,a}) - E_a^{\text{eq}} \quad (5)$$

where Φ_a is the electric potential within the (metallic) anode, $\Phi_{e,a}$ is the electrostatic potential of electrolyte at the anode-electrolyte interface, and $E_a^{\text{eq}} = \Phi_a^{\text{eq}} - \Phi_{e,a}^{\text{eq}}$ is the equilibrium electric potential difference between the anode and the electrolyte. Similarly, the activation overpotential at the cathode-electrolyte interface η_c can be formally defined as

$$\eta_c = (\Phi_c - \Phi_{e,c}) - E_c^{\text{eq}} \quad (6)$$

where Φ_c is the electric potential within the cathode, $\Phi_{e,c}$ is the electrostatic potential of electrolyte at the cathode-electrolyte interface, and $E_c^{\text{eq}} = \Phi_c^{\text{eq}} - \Phi_{e,c}^{\text{eq}}$ is the equilibrium electric potential difference between the cathode and the electrolyte. The equilibrium electric-potential differences (e.g., E_c^{eq} and E_a^{eq}) describe the electric-potential difference at which Eq. 4 proceeds equally in the forward and reverse directions, but with no net charge transfer.

At equilibrium, and considering Eq. 4, the charge-transfer processes between the electrodes and electrolyte membrane can be written in terms of electrochemical potentials $\tilde{\mu}_k$ as

$$\tilde{\mu}_{\text{O}_\text{O}^\times(\text{el})} = \tilde{\mu}_{\text{O}_\text{O}^\bullet(\text{el})} + \tilde{\mu}_{\text{e}'(\text{ed})}, \quad (7)$$

where

$$\tilde{\mu}_{\text{O}_\text{O}^\bullet(\text{el})} = \mu_{\text{O}_\text{O}^\bullet(\text{el})}^\circ + RT \ln[\text{O}_\text{O}^\bullet(\text{el})] + F\Phi_{\text{el}}, \quad (8)$$

and

$$\tilde{\mu}_{\text{O}_\text{O}^\times(\text{el})} = \mu_{\text{O}_\text{O}^\times(\text{el})}^\circ + RT \ln[\text{O}_\text{O}^\times(\text{el})]. \quad (9)$$

94 In these expressions, the standard-state chemical potentials are written as μ_k°
 95 and the defect concentrations are written as $[X_k]$. The equilibrium electric-
 96 potential difference between the electrode and the electrolyte can be repre-
 97 sented as

$$E^{\text{eq}} = \Phi_{\text{ed}}^{\text{eq}} - \Phi_{\text{el}}^{\text{eq}} = \frac{\mu_{\text{O}\bullet}^{\circ}(\text{el}) - \mu_{\text{O}\times}^{\circ}(\text{el})}{F} + \frac{RT}{F} \ln \frac{[\text{O}\bullet(\text{el})]}{[\text{O}\times(\text{el})]}. \quad (10)$$

98 The cell operating potential E_{cell} can be expressed as

$$E_{\text{cell}} = \Phi_{\text{c}} - \Phi_{\text{a}} = E_{\text{c}}^{\text{eq}} - E_{\text{a}}^{\text{eq}} + \eta_{\text{c}} - \eta_{\text{a}} + \Phi_{\text{e,c}} - \Phi_{\text{e,a}} \quad (11)$$

99 The present analysis is based on assuming perfect charge transfer in the
 100 sense that the activation overpotentials vanish, $\eta_{\text{c}} = \eta_{\text{a}} = 0$. Thus, the cell
 101 potential E_{cell} can be evaluated using the predicted defect concentrations and
 102 electrostatic potentials at the electrode interfaces as

$$E_{\text{cell}} = (\Phi_{\text{e,c}} - \Phi_{\text{e,a}}) + \frac{RT}{F} \left(\ln \frac{[\text{O}\bullet]_{\text{e,c}}}{[\text{O}\bullet]_{\text{e,a}}} - \ln \frac{[\text{O}\times]_{\text{e,c}}}{[\text{O}\times]_{\text{e,a}}} \right). \quad (12)$$

103 The open-circuit potential may also be evaluated from Eq. 12. As discussed
 104 subsequently, with mixed conductors, $\Delta\Phi_{\text{e}} = (\Phi_{\text{e,c}} - \Phi_{\text{e,a}})$ does not vanish
 105 at open circuit.

106 Unfortunately, the electrostatic-potential difference within the mixed-
 107 conducting electrolyte membrane $\Delta\Phi_{\text{e}} = \Phi_{\text{e,c}} - \Phi_{\text{e,a}}$ cannot be measured.
 108 That is to say, as soon as electrodes are attached to measure the potentials,
 109 then the measurement represents the electrode potentials, not the desired
 110 internal electrostatic potentials within the electrolyte. However, the inter-
 111 nal electrostatic potential can be predicted by solving the defect transport
 112 equations (i.e., the Nernst–Planck–Poisson, NPP, problem) [26, 31, 34]. The
 113 equilibrium defect concentrations at the electrode-electrolyte interfaces can

Table 1: Thermodynamics for defect reactions

Reactions	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	K_p (750°C)
$\frac{1}{2}\text{H}_2 + \text{O}_{\text{O}}^\bullet \rightleftharpoons \text{OH}_{\text{O}}^\bullet$	-146.01	-0.89	$2.56 \times 10^{+07}$
$\frac{1}{2}\text{O}_2 + \text{O}_{\text{O}}^\times + \text{V}_{\text{O}}^{\bullet\bullet} \rightleftharpoons 2\text{O}_{\text{O}}^\bullet$	-36.08	-125.48	1.94×10^{-05}
$\text{H}_2\text{O} + \text{V}_{\text{O}}^{\bullet\bullet} + \text{O}_{\text{O}}^\times \rightleftharpoons 2\text{OH}_{\text{O}}^\bullet$	-80.00	-71.78	$2.16 \times 10^{+00}$
$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$	-248.11	-55.48	$5.87 \times 10^{+09}$

Table 2: Charged-defect diffusion coefficients, $D_k = D_k^\circ \exp(-E_k/RT)$

	D_k° (m ² s ⁻¹)	E_k (kJ mol ⁻¹)	D_k (600 °C) (m ² s ⁻¹)	D_k (800 °C) (m ² s ⁻¹)
$\text{OH}_{\text{O}}^\bullet$	9.39×10^{-9}	35.09	7.46×10^{-11}	1.84×10^{-10}
$\text{V}_{\text{O}}^{\bullet\bullet}$	1.30×10^{-8}	67.00	1.28×10^{-12}	7.12×10^{-12}
$\text{O}_{\text{O}}^\bullet$	1.70×10^{-3}	86.00	1.22×10^{-08}	1.11×10^{-07}

114 be evaluated assuming that the defect reactions at the surfaces are equi-
 115 brated.

116 3. Defect chemistry

117 3.1. Equilibrium defect reactions

118 Three mobile charge-carrying defects (protons $\text{OH}_{\text{O}}^\bullet$, oxygen vacancies
 119 $\text{V}_{\text{O}}^{\bullet\bullet}$, and O-site polarons $\text{O}_{\text{O}}^\bullet$) are involved in the defect reactions at the
 120 BZY10 ceramic-gas interface [26]. The incorporation reactions may be writ-
 121 ten as

123 The equilibrium constants K_p based on the gas-phase species partial pres-
 124 sures and defect lattice concentrations are defined as

$$K_{p,\text{H}_2} = \frac{[\text{OH}_{\text{O}}^{\bullet}]_{\text{L}}}{p_{\text{H}_2}^{1/2} [\text{O}_{\text{O}}^{\bullet}]_{\text{L}}}, \quad (16)$$

$$K_{p,\text{O}_2} = \frac{[\text{O}_{\text{O}}^{\bullet}]_{\text{L}}^2}{p_{\text{O}_2}^{1/2} [\text{O}_{\text{O}}^{\times}]_{\text{L}} [\text{V}_{\text{O}}^{\bullet\bullet}]_{\text{L}}}, \quad (17)$$

$$K_{p,\text{H}_2\text{O}} = \frac{[\text{OH}_{\text{O}}^{\bullet}]_{\text{L}}^2}{p_{\text{H}_2\text{O}} [\text{O}_{\text{O}}^{\times}]_{\text{L}} [\text{V}_{\text{O}}^{\bullet\bullet}]_{\text{L}}}. \quad (18)$$

127 The formula-unit concentrations $[X_k]_{\text{L}}$ are related to the molar concentra-
 128 tions $[X_k]$ via the molar volume V_{m} as $[X_k]_{\text{L}} = [X_k]V_{\text{m}}$. For BZY10, the
 129 lattice molar volume is $V_{\text{m}} = 44.792 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. The three equilib-
 130 rium constants K_{p,H_2} , K_{p,O_2} and $K_{p,\text{H}_2\text{O}}$ are not independent, but are coupled
 131 through the assumed gas-phase equilibrium constant $K_{p,\text{G}}$ as

$$K_{p,\text{H}_2}^2 K_{p,\text{O}_2} = K_{p,\text{H}_2\text{O}} K_{p,\text{G}}. \quad (19)$$

132 Here the gas phase is presumed to be in equilibrium according to

133 with $K_{p,\text{G}}$ being the equilibrium constant. The equilibrium constants can
 134 be evaluated from the Gibbs free energy change for the reactions $\Delta G^\circ =$
 135 $\Delta H^\circ - T\Delta S^\circ$ as

$$K_p = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{\Delta S^\circ}{R}\right) \exp\left(-\frac{\Delta H^\circ}{RT}\right). \quad (21)$$

136 Table 1 provides the needed thermodynamic properties for BZY10.

137 *3.2. Site and electroneutrality constraints*

138 On the surface and within the ceramic membrane, site constraints and
 139 electroneutrality must be preserved. The number of oxygen sites in a per-
 140 voskite lattice (per formula unit) must be maintained as 3. Thus,

$$[V_{\text{O}}^{\bullet\bullet}]_{\text{L}} + [\text{OH}_{\text{O}}^{\bullet}]_{\text{L}} + [\text{O}_{\text{O}}^{\bullet}]_{\text{L}} + [\text{O}_{\text{O}}^{\times}]_{\text{L}} = 3. \quad (22)$$

141 In this formulation, Eq. 22 is written to include the O-site polaron $[\text{O}_{\text{O}}^{\bullet}]_{\text{L}}$ in
 142 the site constraint [26]. Charge neutrality requires that

$$2[V_{\text{O}}^{\bullet\bullet}]_{\text{L}} + [\text{OH}_{\text{O}}^{\bullet}]_{\text{L}} + [\text{O}_{\text{O}}^{\bullet}]_{\text{L}} - [Y'_{\text{Zr}}]_{\text{L}} = 0. \quad (23)$$

143 Considering BZY10 ($\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$), the doping concentration is 10%, in
 144 which case $[Y'_{\text{Zr}}]_{\text{L}} = 0.1$.

145 *3.3. Defect equilibrium concentrations*

146 The defect equilibrium concentrations (i.e., $[V_{\text{O}}^{\bullet\bullet}]_{\text{L}}$, $[\text{OH}_{\text{O}}^{\bullet}]_{\text{L}}$, $[\text{O}_{\text{O}}^{\bullet}]_{\text{L}}$, and
 147 $[\text{O}_{\text{O}}^{\times}]_{\text{L}}$) on the surface as functions of the gas-phase partial pressures (i.e.,
 148 p_{O_2} , p_{H_2} , and $p_{\text{H}_2\text{O}}$) can be established by solving iteratively Eqs. 17, 18,
 149 22, and 23. Note that Eq 16 is not used because Eqs. 16, 17, and 18 are not
 150 independent of each other (i.e., Eq. 19).

151 The iteration process is initiated by first estimating a value of $[V_{\text{O}}^{\bullet\bullet}]_{\text{L}}$.
 152 Based on Eqs. 17, 18, and 23, the defect concentrations $[\text{O}_{\text{O}}^{\bullet}]_{\text{L}}$ and $[\text{OH}_{\text{O}}^{\bullet}]_{\text{L}}$
 153 can be evaluated in terms of $[V_{\text{O}}^{\bullet\bullet}]_{\text{L}}$ as

$$[\text{O}_{\text{O}}^{\bullet}]_{\text{L}} = \frac{[Y'_{\text{Ce,Zr}}]_{\text{L}} - 2[V_{\text{O}}^{\bullet\bullet}]_{\text{L}}}{1 + \Theta}, \quad (24)$$

154 where

$$\Theta = \frac{[\text{OH}_{\text{O}}^{\bullet}]_{\text{L}}}{[\text{O}_{\text{O}}^{\bullet}]_{\text{L}}} = \left[\frac{K_{p,\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{K_{p,\text{O}_2} p_{\text{O}_2}^{1/2}} \right]^{1/2}. \quad (25)$$

Figure 2: Summary of the NPP model in cartoon form. The electron and current directions are shown in fuel-cell mode.

Using Eq. 17, $[O_O^x]_L$ can be represented as

$$[O_O^x]_L = \frac{[O_O^•]_L^2}{K_{p,O_2} p_{O_2}^{1/2} [V_O^{\bullet\bullet}]_L}. \quad (26)$$

Finally, the oxygen site constraint (Eq. 22) is imposed. If all the equations above were to be explicitly substituted, the result would be one nonlinear equation with one unknown, $[V_O^{\bullet\bullet}]_L$. Once $[V_O^{\bullet\bullet}]_L$ is determined, all the other defect concentrations follow easily from Eqs. 24, 25, and 26.

4. Nernst–Planck–Poisson (NPP) membrane model

The spatial and temporal variations of defect concentrations and the electrostatic potential through the perovskite membrane can be represented using the Nernst–Planck–Poisson model. The defect transport through the

164 membrane is governed by conservation equations as

$$\frac{\partial[X_k]}{\partial t} + \nabla \cdot \mathbf{J}_k = 0. \quad (27)$$

165 Assuming dilute defect interactions, the defect transport fluxes $\mathbf{J}_k$ due to
 166 concentration gradients (diffusion) and electrostatic-potential gradients (mi-
 167 gration) can be represented using a Nernst–Planck formulation as

$$\mathbf{J}_k = -D_k \left(\nabla[X_k] + \frac{z_k F}{RT} [X_k] \nabla \Phi_e \right), \quad (28)$$

168 where D_k are defect diffusion coefficients. Table 2 provides the needed diffu-
 169 sion coefficients for BZY10.

170 The local electrostatic potential Φ_e can be related to the local charge
 171 density ρ_e through the Gauss law as

$$\nabla \cdot (\varepsilon_o \varepsilon_r \nabla \Phi_e) = -\rho_e = -\sum_{k=1} z_k F [X_k]. \quad (29)$$

172 where ε_r and ε_o are the relative and vacuum permittivities, respectively.
 173 Alternatively, the Gauss law for the one-dimensional perovskite membrane
 174 can be equivalently replaced by the displacement-current equation as [35]

$$\frac{\partial E}{\partial t} = \frac{1}{\varepsilon_0 \varepsilon_r} \left[I - \sum_k z_k F J_k \right], \quad (30)$$

175 where $E = -\nabla \Phi_e$ is the electric field, and I is the external current density.
 176 Solving the Gauss equation is nearly equivalent to, but more general than,
 177 imposing strict electroneutrality (i.e., $\sum_{k=1}^K z_k F [X_k] = 0$). Requiring strict
 178 electroneutrality leads to an implicit relationship (i.e., $\sum_k z_k F J_k = I$) from
 179 which the local electrostatic potential profiles can be determined [26, 34].

180 4.1. Equilibrium gas-phase fluxes

181 The transport fluxes of the ionic defect species manifest themselves as gas-
 182 phase fluxes at the membrane-gas interfaces. Assuming equilibrium defect
 183 chemistry at the ceramic-gas interfaces, the gas-phase fluxes of H_2O , H_2 , and
 184 O_2 can be evaluated as [34]

$$\mathbf{J}_{\text{H}_2\text{O}} = \frac{\mathbf{J}_{\text{OH}\bullet}}{\left[2 + \frac{2p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} + \frac{p_{\text{H}_2}}{2p_{\text{O}_2}}\right]} - \frac{\mathbf{J}_{\text{V}\bullet\bullet}}{\left[1 + \frac{4p_{\text{O}_2}}{p_{\text{H}_2\text{O}}} + \frac{4p_{\text{O}_2}}{p_{\text{H}_2}}\right]}. \quad (31)$$

$$\mathbf{J}_{\text{O}_2} = -\frac{1}{2}\mathbf{J}_{\text{V}\bullet\bullet} - \frac{1}{2}\mathbf{J}_{\text{H}_2\text{O}}, \quad (32)$$

$$\mathbf{J}_{\text{H}_2} = \frac{1}{2}\mathbf{J}_{\text{OH}\bullet} - \mathbf{J}_{\text{H}_2\text{O}}. \quad (33)$$

187 where $\mathbf{J}_{\text{OH}\bullet}$ and $\mathbf{J}_{\text{V}\bullet\bullet}$ are the molar fluxes of protons and oxygen vacancies
 188 at the membrane surfaces.

189 4.2. Model summary

190 Figure 2 summarizes the model in cartoon form. At the membrane sur-
 191 faces, the defect incorporation chemistry is maintained at equilibrium with
 192 the local gas composition, which is also assumed to be equilibrated. This
 193 equilibrium, together with site constraints (Eq. 22) and charge neutrality
 194 (Eq. 23) serves to establish defect-concentration boundary conditions for the
 195 NPP problem, which at steady state is an elliptic boundary-value problem.
 196 Boundary conditions are also needed for the internal electrostatic potentials.
 197 At one surface (here the cathode), a reference potential is set arbitrarily to be
 198 $\Phi_{\text{e,c}} = 0$. The other boundary is imposed implicitly in terms of the imposed
 199 current, $i = \sum z_k F J_k$. Implicit means that this boundary condition for the

electrostatic potential $\Phi_{e,a}$ does not explicitly involve $\Phi_{e,a}$ itself. At open circuit, $i = 0$. In fuel-cell mode $i > 0$ and in electrolysis mode $i < 0$. The NPP problem is solved computationally on a finite-volume mesh network. The present model is implemented in MATLAB using a method-of-lines approach.

5. Results and discussions

The present results are based on a BZY10 membrane electrolyte with a thickness of 20 μm . Equilibrium constants for the defect reactions can be evaluated using the thermodynamic properties listed in Table 1. Table 2 lists needed defect transport parameters. Assuming ideal anodes and cathodes, all associated polarization losses (i.e., activation and concentration polarizations) are neglected. Although this is not a physically realistic assumption in practice, it does facilitate the specific focus on membrane polarization processes. The fuel-cell and electrolysis performance of the PCFC and PCEC cells are represented using polarization curves and the open-circuit potentials. The primary objective of the present study is to investigate the contributions of the mixed-conducting electrolyte membrane on the cell performance.

5.1. Open-circuit potentials

The open-circuit potential (Eq. 12) contains two parts: the electrostatic-potential difference across the electrolyte membrane $\Delta\Phi_e = \Phi_{e,c} - \Phi_{e,a}$ and the electrostatic-potential difference E_{def} associated with the defect concentration differences between the anode and cathode sides of the membrane,

$$E_{\text{def}} = \frac{RT}{F} \left(\ln \frac{[\text{O}_{\text{O}}^{\bullet}]_{e,c}}{[\text{O}_{\text{O}}^{\bullet}]_{e,a}} - \ln \frac{[\text{O}_{\text{O}}^{\times}]_{e,c}}{[\text{O}_{\text{O}}^{\times}]_{e,a}} \right). \quad (34)$$

Figure 3: Open-circuit potentials as functions of the operating temperature. The gas composition is 97% H₂ and 3% H₂O on the anode side, and 20% O₂, 3% H₂O and 77% N₂ on the cathode side.

Figure 4: Equilibrium defect concentrations at the membrane-gas interfaces. Moist H₂ is on one side of the membrane and moist air is on the other side.

221 The present model assumes that the temperature and the gas-phase com-
 222 positions on both sides of the membrane are fixed. Thus, the equilibrium
 223 defect concentrations at the electrode-electrolyte interfaces are fixed based

224 on the equilibrium defect chemistry. Therefore, E_{def} depends only on the
 225 gas-phase compositions at the membrane surfaces. Furthermore, $\Delta\Phi_e$ under
 226 open-circuit conditions also depends only on the gas-phase compositions. The
 227 fixed defect concentrations on the membrane surfaces are sufficient to deter-
 228 mine the total electrostatic-potential difference across the electrolyte mem-
 229 brane. Although the electrostatic-potential gradient $\nabla\Phi_e$ across the elec-
 230 trolyte membrane varies with the membrane thickness, the net electrostatic-
 231 potential difference $\Delta\Phi_e$ does not depend on membrane thickness. Therefore,
 232 the open-circuit potential $E_{\text{cell}} = E_{\text{def}} + \Delta\Phi_e$ does not change with the mem-
 233 brane thickness.

234 Figure 3 shows the variation of E_{def} , $\Delta\Phi_e$, and E_{cell} as functions of tem-
 235 perature. The gas compositions are taken to be 97% H_2 and 3% H_2O on the
 236 anode side, and 20% O_2 , 3% H_2O and 77% N_2 on the cathode side, with net
 237 atmospheric pressure. As illustrated in Fig. 3, E_{def} decreases as the tem-
 238 perature increases from 400 to 900 °C. The electrostatic-potential loss term
 239 is approximately $\Delta\Phi_e \approx 0.003$ V at 400 °C, and increases to approximately
 240 $\Delta\Phi_e \approx 0.285$ V at 900 °C. Because of the decrease in E_{def} and the signifi-
 241 cantly greater decrease in $\Delta\Phi_e$ as the temperature increases, the open-circuit
 242 potential E_{cell} drops greatly as the temperature increases.

243 The temperature-dependent variations in E_{cell} can be explained by the
 244 effects of temperature on defect concentrations and the derivative effects on
 245 maintaing charge neutrality. Figure 4 shows illustrative equilibrium defect
 246 concentrations on both sides of the membrane as functions of temperature.
 247 In this case, one side of the membrane is maintained in a moist-hydrogen
 248 atmosphere and the other side is maintained in moist air. The proton con-

249 centration decreases and the vacancy concentration increases as temperature
 250 increases, with the temperature dependencies being very similar on both sides
 251 of the membrane. Because the temperature dependencies are very similar,
 252 the proton gradient across the membrane depends only weakly on temper-
 253 ature. Compared to the protons, the polaron concentrations behave quite
 254 differently. First, the polaron concentrations are very much lower than the
 255 other defects (right-hand axis). Although the concentrations are low, the
 256 important observation is that the air-side polaron concentrations are very
 257 much greater (approximately four orders of magnitude) than the hydrogen-
 258 side concentrations. That is, the air-side concentrations generally increase
 259 with increasing temperature, but the hydrogen-side polaron concentrations
 260 remain at essentially zero relative to the air side concentrations. Although
 261 there is a weak maximum at around 750 °C, the effective polaron gradients
 262 generally increase as temperature increases.

263 With the equilibrium behaviors in mind, consider the Nernst-Planck de-
 264 fect fluxes in Eq. 28 that contain a diffusion term due to the concentration
 265 gradient and migration due to the electrostatic-potential gradient. Because
 266 the proton and vacancy concentrations on the fuel side are higher than those
 267 at the air side, the proton and vacancy diffuse from the fuel side toward the
 268 air side. The polarons diffuse from the air side toward the fuel side due to the
 269 higher polaron concentration on the air side. Under open-circuit conditions,
 270 the electric potential on the fuel side is higher than it is on the air side. Thus,
 271 the electrostatic-potential gradient (migration) enhances the Nernst-Planck
 272 fluxes of proton and vacancy from the fuel side toward the air side, but di-
 273 minishes the polaron flux from the air side to the fuel side. Because the

Figure 5: Open-circuit potentials as functions of the fraction of O₂ consumption of the air stream. The operating temperature is 700 °C. The gas composition is 97% H₂ and 3% H₂O at the anode (fuel) side. The cathode (oxidizer) flow stream contains 21% O₂ and 79% N₂ at zero O₂ utilization, and 34.7% H₂O and 65.3% N₂ at full O₂ utilization.

274 polaron concentration gradients increase at higher temperature, the diffu-
 275 sion contribution for polaron transport flux increases. Additionally, because
 276 of higher mobility, the polaron flux is much higher than the proton and va-
 277 cancy diffusion fluxes. To maintain charge neutrality (i.e., $\sum_k z_k F \mathbf{J}_k = 0$),
 278 the magnitude of the internal electrostatic potential gradient must increase
 279 as the temperature increases. With higher electrostatic-potential gradients,
 280 the polaron diffusion flux can largely be reduced by the polaron migration
 281 flux. However, the proton and vacancy diffusion fluxes are enhanced by the
 282 migration fluxes. Therefore, the charge neutrality condition can be achieved.

283 Figure 5 shows the open-circuit potential variation as a function of O₂
 284 utilization in the cathode (oxidizer) flow stream. The operating temperature
 285 is 700 °C. The gas composition at the anode (fuel) side is fixed 97% H₂ and
 286 3% H₂O. When the O₂ utilization factor is zero, the cathode flow stream is
 287 air with 21% O₂ and 79% N₂. Because one mole of O₂ is consumed, 2 moles
 288 of H₂O are produced, the cathode flow composition at 100% O₂ utilization

Figure 6: Polarization behavior at the nominal operating temperature of 700 °C. The gas composition is 97% H₂ and 3% H₂O on the anode side, and 20% O₂, 3% H₂O and 77% N₂ on the cathode side.

289 becomes 34.7% H₂O and 65.3% N₂. As illustrated in Fig. 5, E_{def} decreases
 290 as O₂ utilization factor increases due to less available O₂ in the cathode
 291 flow stream. Meanwhile, the electrostatic-potential loss term $\Delta\Phi_e$ becomes
 292 smaller when the oxidizer flow stream contains less O₂ and more H₂O. The
 293 open-circuit potential E_{cell} decreases as the O₂ utilization factor increases.

294 5.2. Fuel-cell operation

295 For the sake of quantitative illustration, the nominal gas-phase compo-
 296 sition for fuel-cell operation at the anode is fixed as 97% H₂ and 3% H₂O,
 297 and the gas-phase species composition at the cathode is 20% O₂, 3% H₂O
 298 and 77% N₂. The nominal operating temperatures is 700 °C and the total
 299 gas-phase pressure is assumed to be atmospheric.

300 Figure 6 shows the cell potential and electric power as functions of the
 301 current density, spanning from the electrolysis mode to the fuel-cell mode.
 302 Under these conditions, the open-circuit potential is about 0.92 V. When
 303 the cell is operating in the fuel-cell mode, the limiting current density is

Figure 7: Fluxes of defects and gas-phase species at the electrode-electrolyte surfaces as functions of the current density. The operating temperature is 700 °C. The gas composition is 97% H_2 and 3% H_2O at the anode side, and 20% O_2 , 3% H_2O and 77% N_2 at the cathode side.

about 1.22 A cm $^{-2}$ and the maximum power is about 0.35 W cm $^{-2}$ when the current density is 0.63 A cm $^{-2}$ and the cell potential is about 0.55 V. In the electrolysis mode (negative current densities), higher cell potential is needed as the current density increases, and more electrical power is required to drive the system.

From Fig. 6 it is interesting to note that the membrane's area-specific resistance (i.e., slope of voltage versus current density) is significantly higher in fuel-cell mode than it is in electrolysis mode. As discussed subsequently, the

312 reasons for these differences are related to the profiles of internal electrostatic
 313 potentials and defect concentrations under different operating conditions.

314 Fig. 7a shows the defect and gas-phase species fluxes at the hydrogen side
 315 of the membrane and Fig. 7b shows the fluxes at the air side of the mem-
 316 brane. A positive flux means that the flux is in the direction from hydrogen
 317 side toward the air side. When the cell is operating in the fuel-cell mode,
 318 H_2 is consumed and $\text{OH}^\bullet_{\text{O}}$ is produced at the anode-electrolyte interface, and
 319 a small amount of H_2O is formed at the anode-electrolyte interface and re-
 320 leased to the fuel compartment. The $\text{OH}^\bullet_{\text{O}}$ produced at the anode-electrolyte
 321 interface transports through the electrolyte membrane toward the cathode
 322 side. At the cathode-electrolyte interface, $\text{OH}^\bullet_{\text{O}}$ is electrochemically oxidized
 323 to produce H_2O by consuming O_2 . When the cell is operating in the elec-
 324 trolysis mode, Fig. 7b shows H_2O is consumed and O_2 is produced at the air
 325 side.¹ The $\text{OH}^\bullet_{\text{O}}$ produced at the air side of the membrane transports toward
 326 the hydrogen side. At the hydrogen side, $\text{OH}^\bullet_{\text{O}}$ is reduced and gas-phase H_2
 327 is formed and released.

328 Under open-circuit conditions (i.e., $i = 0 \text{ A cm}^{-2}$), it is interesting to note
 329 the directions and magnitudes of the defect transport. Protons are being
 330 transported toward the air side and O-site polarons are being transported
 331 toward the hydrogen side. There is also some vacancy transport, but under
 332 these conditions it is essentially negligible. At open circuit, the net charge

¹Keep in mind that in electrolysis mode the roles of anode (negative electrode) and cathode (positive electrode) are reversed compared to fuel-cell operation (cf., Fig. 1).

333 flux through the membrane must vanish. That is, at open circuit

$$\sum z_k F \mathbf{J}_k = 0, \quad (35)$$

334 where z_k are the defect charges and $\mathbf{J}_k$ are the fluxes. However, the individual
 335 defect fluxes *do not vanish* at open circuit. This behavior is very different
 336 from a typical single-mobile-defect SOFC membrane (e.g., yttria-doped zir-
 337 conia, YSZ) that is essentially a pure oxygen-ion conductor. The fact that
 338 mixed conductors permit defect transport at open-circuit is the reason that
 339 the reversible open-circuit potential is always less than that predicted by the
 340 Nernst equation [e.g., $E_{\text{rev}} = (RT/4F) \ln(p_{\text{O}_{2,c}}/p_{\text{O}_{2,a}})$] that applies for single-
 341 ion conductors. In other words, the energy needed to support the internal
 342 defect transport diminishes the potential to do work that is associated with
 343 oxidation of the fuel.

344 Because mixed conducting membranes usually have electrical conductiv-
 345 ity, it is often said that the loss of open-circuit potential is associated with
 346 a “leakage” current. In fact, this is a bit of a misnomer. There is no net
 347 electronic “leakage” through the membrane at open circuit in the sense that
 348 any current enters an external circuit. Rather, the loss of potential is associ-
 349 ated with the energy needed to support the internal defect transport, while
 350 maintaining zero net charge flux.

351 Fig. 8 shows spatial profiles of the electrostatic potential and the defect
 352 concentrations through the electrolyte membrane at four different current
 353 densities: -1.5 , 0.0 , 0.5 and 1.2 A cm^{-2} (negative current density means
 354 electrolysis mode). The electrostatic potential at the air side is set to be zero
 355 as a reference. As illustrated in Fig. 8a, the electrostatic potential at the
 356 hydrogen side is higher than it is at the air side when operating in the fuel-

Figure 8: Profiles of electric potential and defect concentrations (formula unit) through the electrolyte membrane at four current densities: -1.5 , 0.0 , 0.5 and 1.2 A cm^{-2} . The operating temperature is $700 \text{ }^{\circ}\text{C}$. The gas composition is $97\% \text{ H}_2$ and $3\% \text{ H}_2\text{O}$ at the anode side (left), and $20\% \text{ O}_2$, $3\% \text{ H}_2\text{O}$ and $77\% \text{ N}_2$ at the cathode side (right).

cell mode (i.e., $i_e = 0.5$ and 1.2 A cm^{-2}). The electrostatic potential gradient tends to drive all the positively charged mobile defects within the electrolyte membrane from the hydrogen side toward the air side. As the current density

360 increases, the internal electrostatic potential gradient becomes larger, which
 361 drives the variation of defect concentrations closer to the air side. Hence
 362 the high concentration gradients near the air side of the membrane. Since
 363 both the fuel stream and air stream contain 3% H_2O , the overall variations
 364 of the defect concentrations, except the polarons $\text{O}_\text{O}^\bullet$, change only slightly.
 365 As the current density increases, the slope of the electric potential becomes
 366 steeper, causing higher overpotential loss for the defect transport through
 367 the electrolyte membrane.

368 At open-circuit ($i = 0$), Fig. 8a shows an electrostatic-potential difference
 369 of approximately 0.125 V from the fuel side to the cathode. It is interest-
 370 ing to note that the electrostatic potential is greater at the fuel side than
 371 it is at the cathode side. This is possibly an unexpected result because the
 372 sign of the electrostatic-potential difference within the membrane is oppo-
 373 site from the sign of the electric-potential difference between the electrodes.
 374 That is to say, in fuel cell operation the electric potential of the cathode (air
 375 side, positive terminal) is greater than the electric potential of the anode
 376 (fuel side, negative terminal). Thus, it cannot be the case that the electric
 377 potentials are the same across the electrode-electrolyte interfaces. In mod-
 378 els such as the present one, the vanishingly thin space-charge region at the
 379 electrode-electrolyte interfaces is modeled using a “jump” described in terms
 380 of activation overpotentials. Here, the activation overpotentials are assumed
 381 to vanish.

382 With increasingly high current densities in fuel-cell mode, the magnitude
 383 of the internal electrostatic-potential gradient become larger. Near limiting
 384 current in fuel-cell mode ($i = 1.2 \text{ A cm}^{-2}$), the internal electrostatic-potential

385 difference is nearly equivalent to the open-circuit potential (albiet, with oppo-
386 site sign). In electrolysis mode ($i < 0$), the sign of the electrostatic-potential
387 difference is opposite from that in fuel-cell mode. This behavior is discussed
388 subsequently, when the gas-compositions are set to represent typical electrol-
389 ysis operation.

390 Figures 8b-d show defect concentration profiles (lattice formula units)
391 within the membrane at different current densities. It is evident that the
392 defect concentration profiles depend greatly on the current density. At high
393 current density in fuel-cell mode ($i > 0$), the profiles tend to shift toward
394 the air side. In electrolysis mode, the profiles shift toward the fuel side.
395 These behaviors are caused by the relatively complex interactions between
396 the defect diffusion and migration as represented by the NPP model. The
397 qualitatively different polarization mechanisms cause the differences in inter-
398 nal membrane polarization as evidenced in Fig. 6 when shifting from fuel-cell
399 to electrolysis operation.

400 Figure 9a compares the cell potentials as functions of current density at
401 four operating temperatures (500, 600, 700 and 800 °C). The current density
402 spans from the electrolysis mode to fuel-cell mode, but the gas compositions
403 are set for nominal fuel cell operation. Figure 9b shows the corresponding
404 variation of the power density as functions current density and temperature.
405 As illustrated in Fig. 9, the cell potentials operating in fuel cell mode drop
406 faster and less power is produced as the temperature decreases from 800
407 °C to 500 °C. Under the electrolysis mode, higher cell potential and more
408 electric power are needed to maintain the same operating current density
409 as the temperature decreases. Figure 9a also shows that the open-circuit

Figure 9: Comparison of the cell voltage and power density as functions of the current density at the four different operating temperatures: 500, 600, 700, and 800 °C. The gas composition is set to represent fuel-cell operation, with 97% H₂ and 3% H₂O on the fuel (anode) side and 20% O₂, 3% H₂O, and 77% N₂ on the cathode (air) side. The total pressure is atmospheric.

410 potentials increase significantly as the temperature decreases.

Figure 10: Comparison of the cell voltage and power density as functions of the current density at the four different operating temperatures: 500, 600, 700, and 800 °C. The gas composition is set to represent electrolysis operation, with 97% H₂ and 3% H₂O on the cathode (positive electrode) side and 1% O₂ and 99% H₂O on the anode (negative electrode) side. The total pressure is atmospheric.

5.3. Electrolysis operation

The nominal gas-phase composition chosen for electrolysis operation is 97% H₂ and 3% H₂O at the cathode side (upper chamber, Fig. 1b), and 1%

Figure 11: Faradaic efficiencies as function of current density. In electrolysis mode ($i < 0$) the Faradaic efficiency measures the H_2 production efficiency relative to input current. In fuel-cell mode ($i > 0$) the Faradaic efficiency measures the electric-current production relative to H_2 consumption rate. The gas composition is set to represent electrolysis operation, with 97% H_2 and 3% H_2O on the cathode (positive electrode) side and 1% O_2 and 99% H_2O on the anode (negative electrode) side. The total pressure is atmospheric.

414 O_2 and 99% H_2O at the anode side (lower chamber, Fig. 1b). The operating
 415 conditions consider four temperatures (500, 600, 700, and 800 °C) and net
 416 atmospheric pressure.

417 Fig. 10 shows cell potential and electric power as functions of current
 418 density. Fig. 10a shows that the open-circuit potential decreases as the op-
 419 erating temperature increases (i.e., $E_{\text{cell}} \approx 0.98$ V at 500 °C, $E_{\text{cell}} \approx 0.94$ V
 420 at 600 °C, $E_{\text{cell}} \approx 0.89$ V at 700 °C, and $E_{\text{cell}} \approx 0.83$ V at 800 °C). As also
 421 seen from Fig. 9, higher operating cell potentials and more electric power are
 422 required for the cell to be operated in the electrolysis mode as the operating
 423 temperature is reduced from 800 to 500 °C.

424 5.3.1. Faradaic efficiency

425 In part because of mixed-conduction behavior, ideal operation of PCFC
 426 and PCEC usually cannot be realized. In fuel-cell mode, the hydrogen flux

427 leaving the hydrogen compartment may not be fully converted into the de-
 428 sired electric current. In electrolysis mode, the imposed electric current may
 429 not be fully converted to the desired H_2 flux. The Faradaic efficiency can
 430 be defined to represent the conversion efficiency between the fuel consump-
 431 tion/production and the electric current. Faradaic efficiency in the electroly-
 432 sis mode is defined to be the ratio of the H_2 production flux and the imposed
 433 electric current density I as

$$\varepsilon_{\text{H}_2, \text{EC}} = \frac{2F J_{\text{H}_2}}{I}. \quad (36)$$

434 In fuel-cell mode, Faradaic efficiency is defined to be the ratio of the delivered
 435 external current density and the H_2 consumption flux as

$$\varepsilon_{\text{H}_2, \text{FC}} = \frac{I}{2F J_{\text{H}_2}}. \quad (37)$$

436 Fig. 11 compares Faradaic efficiencies as functions of current density at
 437 four operating temperatures. For each temperature, the electrolysis-mode
 438 Faradaic efficiencies $\varepsilon_{\text{H}_2, \text{EC}}$ achieve maximum asymptotic values at high cur-
 439 rent densities. These maximum Faradaic efficiencies increase significantly
 440 at lower temperatures, but never achieve unity. The Faradaic efficiencies
 441 decrease dramatically (even become negative) at low current densities near
 442 open-circuit operation.

443 The Faradaic efficiency in fuel-cell mode $\varepsilon_{\text{H}_2, \text{FC}}$ is zero at the open cir-
 444 cuit, and then increases as the output current density increases, reaching
 445 maximum efficiencies very near unity at high current density. The maximum
 446 fuel-cell Faradaic efficiencies are higher than are the maximum electrolysis
 447 Faradaic efficiencies. The maximum $\varepsilon_{\text{H}_2, \text{EC}}$ is approximately 0.97 at 500 °C,
 448 but drops to approximately 0.91 at 600 °C, 0.78 at 700 °C, and 0.61 at

800 °C. Although the maximum $\varepsilon_{\text{H}_2, \text{EC}}$ at 500 °C is much higher than it is at 800 °C, much higher operating cell potential, and thus higher power, are required to achieve the high Faradaic efficiencies (cf., Fig. 10). Thus, achieving high Faradaic efficiency alone does not necessarily lead to the best operating conditions for the cell.

5.3.2. Profiles and fluxes

Reduction in Faradaic efficiency is caused by electronic transport associated with the O-site polaron. Although the $\text{O}_{\bullet}^{\bullet}$ transport is often unavoidable, the electronic transport demands energy that could otherwise be available to assist the production of desired products (electricity in PCFCs and H_2 in PCEC). In other words, energy is required to drive the $\text{O}_{\bullet}^{\bullet}$ through the resistive membrane material, but the $\text{O}_{\bullet}^{\bullet}$ flux does not contribute directly to the desired product. The reasons for Faradaic losses can be explained and interpreted by studying defect profiles within the membrane and the associated defect fluxes.

With the gas compositions nominally set for electrolysis operation, Fig. 12 illustrates profiles of electric potentials and defect concentrations within the electrolyte membrane at four current densities: -1.5 , -0.5 , 0.0 , and 0.5 A cm^{-2} . The operating temperature is fixed as 600 °C. Fig. 13 shows the defect fluxes and gas-phase species fluxes at the membrane surfaces as functions of current density. For current densities of $i = 0.0$ and $i = 0.5 \text{ A cm}^{-2}$ (i.e., open circuit and fuel-cell mode), Fig. 12 shows that the electrostatic potentials are higher on the hydrogen side than they are on the steam-oxygen side ($\Delta\Phi_e \approx -0.019 \text{ V}$ at $i = 0 \text{ A cm}^{-2}$, and $\Delta\Phi_e \approx -0.55 \text{ V}$ at $i = 0.5 \text{ A cm}^{-2}$). The positively charged defects are driven toward the steam-oxygen

Figure 12: Profiles of electric potential and defect concentrations (formula unit) through the electrolyte membrane at four current densities: -1.5 , -0.5 , 0.0 and 0.5 A cm^{-2} . The operating temperature is 600°C . The gas composition is $97\% \text{ H}_2$ and $3\% \text{ H}_2\text{O}$ on the hydrogen side and $99\% \text{ H}_2\text{O}$ and $1\% \text{ O}_2$ on the steam-oxygen side.

side as the fuel-cell current density increases. Fig. 12d shows that the polaron concentration and its gradient near the hydrogen side is essentially

Figure 13: Fluxes of charged defects and gas-phase species at the electrode-electrolyte interfaces as functions of current density. The operating temperature is 600 °C. The gas composition is 97% H₂ and 3% H₂O on the hydrogen side, and 1% O₂ and 99% H₂O on the steam-oxygen side.

476 zero at $i = 0.5 \text{ A cm}^{-2}$. Therefore, as shown on the right-hand side (fuel-cell
 477 mode) of Fig. 13, the $\text{O}_\text{O}^\bullet$ transport flux is negligible and resulting charge flux
 478 from $\text{O}_\text{O}^\bullet$ transport also becomes negligible at high operating current density.
 479 The Nernst–Planck flux (Eq. 28) has two terms—diffusion and migration.
 480 When the concentration gradient vanishes, the diffusion contribution van-
 481 ishes. When the concentration itself vanishes, the migration contribution
 482 vanishes. Thus, from Fig. 12d at $i = 0.5 \text{ A cm}^{-2}$ it is evident that the $\text{O}_\text{O}^\bullet$
 483 transport flux must vanish. Because of the negligible losses associated with

484 $\text{O}_{\text{O}}^{\bullet}$, the fuel-cell Faraday efficiency achieves nearly unity at high operating
485 current in fuel-cell mode.

486 Consider now the electrolysis-mode operation. Fig. 12a shows that $\Delta\Phi_{\text{e}} \approx$
487 0.42 V at $i = -0.5 \text{ A cm}^{-2}$ and $\Delta\Phi_{\text{e}} \approx 1.27 \text{ V}$ at $i = -1.5 \text{ A cm}^{-2}$.
488 Because of the electrostatic potential at the steam-oxygen side is higher than
489 it is at the hydrogen side, the defects are driven toward the hydrogen side
490 (Fig. 12). Under these electrolysis conditions, the $\text{O}_{\text{O}}^{\bullet}$ concentration through
491 the electrolyte membrane is not close to zero, and a large $\text{O}_{\text{O}}^{\bullet}$ concentration
492 gradient is formed near to the hydrogen side as the imposed current density
493 increases. Therefore, the $\text{O}_{\text{O}}^{\bullet}$ flux increases as the electrolysis current density
494 increases (Fig. 13). The $\text{O}_{\text{O}}^{\bullet}$ transport causes a loss of the Faradaic efficiency
495 (Fig. 11).

496 In electrolysis mode ($i < 0$), Fig. 11 shows that the Faradaic efficiency
497 decreases below zero in the regions around open-circuit. Independent of any
498 imposed current density, the BZY10 acts as a hydrogen-separation mem-
499 brane. At open-circuit, there is a net flux of protons from the hydrogen side
500 toward the steam-oxygen side. This behavior is more evident at higher tem-
501 peratures (cf., Fig. 7) than that at lower temperature (cf., Fig. 13). In elec-
502 trolysis mode, the objective is the transport protons from the steam-oxygen
503 side toward the hydrogen side. This is just the opposite from the direction of
504 the pressure-driven membrane flux. Thus, the imposed electrolysis current
505 density must be sufficiently high as to overcome the counter flux associated
506 with the gas-phase chemical-potential gradient across the membrane.

507 In a practical protonic-ceramic electrolysis cell, depending on the steam
508 flow rate, oxygen can accumulate on the steam side. Thus, it is interesting to

Figure 14: Faradaic efficiencies as function of current density. The gas composition is set to represent electrolysis operation, but with significant oxygen accumulation on the steam side. The gas compositions are 97% H₂ and 3% H₂O on the cathode (positive electrode) side and 50% O₂ and 50% H₂O on the anode (negative electrode) side. The total pressure is atmospheric.

509 consider the effect of oxygen concentration on the cell performance. Figure 14
 510 shows the predicted Faradaic efficiency for a cell with 50% O₂ and 50% H₂O
 511 on the steam side. Comparing with Fig. 10, it is evident that increased
 512 oxygen concentration on the steam side significantly decreases the Faradaic
 513 efficiency, especially at higher temperatures. In fuel-cell model, however, the
 514 Faradiac efficiency is only weakly affected by the oxygen concentration.

515 These results suggest that a material such as BZY10 is likely to per-
 516 form well in fuel-cell mode. However, performance in electrolysis model is
 517 likely to be less effective. The performance differences are attributed to the
 518 fact that BZY10 has *p*-type conductivity in the form of the O-site polarons.
 519 Although required to maintain charge neutrality, the polaron transport rep-
 520 represents a deleterious loss mechanism. However, as discussed in the previous
 521 paragraphs, the O_•O transport is largely suppressed in fuel-cell mode. On the

contrary, $\text{O}_\text{O}^\bullet$ transport is active in electrolysis mode, representing a significant efficiency loss.

6. Summary and conclusions

A Nernst–Planck–Poisson (NPP) model has been developed to evaluate polarization behavior within mixed-conducting ceramic electrolyte membranes. By neglecting all activation and concentration overpotentials, the analysis focuses specifically on the defect transport within the membranes. Although the theory and modeling approaches are generally applicable, the present study considers BZY10, for which a complete self-consistent set of thermodynamic and transport properties is available. The model is exercised in fuel-cell mode and electrolysis mode. Results reveal quantitative polarization behaviors as functions of temperature and imposed current density. Operating cell potential, including open-circuit potential, depend strongly on operating conditions. With mixed-conducting membranes, the open-circuit potential is always lower than the Nernst potential that is typically evaluated for single-ion-conducting membranes such as YSZ. Unlike the single-conducting membranes, where the open-circuit potential can be evaluated in a straightforward way from gas composition, predicting open-circuit potential in mixed conductors requires a more sophisticated model, such as the one presented here. The results suggest that protonic-ceramic mixed conductors with p -type electronic conductivity are likely to perform well as fuel-cell membranes, but not as well as electrolyzer membranes.

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