Multi-Physical and Electrochemical Coupling Model for the Protonic Ceramic Fuel Cells with H⁺/e⁻/O²⁻ Mixed Conducting Cathodes

Dongping Yan 1, Wansheng Wang 1, Runhua Li 1, Shanshan Jiang 1, Liu Lu 2,*; Aleksey Levtsev 3 and Daifen Chen 1,*©

Abstract: A protonic ceramic fuel cell (PCFC) has great potential for medium temperature power generation. Its working process, however, is complicated and quite different from the traditional oxygen solid oxide fuel cell (O²⁻-SOFC) and proton exchange membrane fuel cell (PEMFC). In this paper, a multi-physical model for the PCFC with H⁺/e⁻/O²⁻ mixed conducting cathode is established, in which the fuel- and oxidant-diffusing processes; electron-, oxygen ion-, and proton-conducting processes; three electrochemical reactions; and their coupling working details are carefully considered. Taking Ni-BZCY/BZCY/BZCY-LSCF PCFC as an example, the validation of the model is well verified by good agreements with the experiment i_op-V_op curves at different temperatures. The result shows that the cathodic electrochemical reactions will be concentrated to a small thickness near the electrolyte because of the greatly decreased ionic conductivity compared with the high electronic conductivity at an intermediate temperature. O²⁻ within the PCFC cathode is only an intermediate transform substance between the electrons and protons. Thus, there is a peak oxygen ion current distribution within the composite cathode of PCFC. The cathodic oxygen reduction half reaction is found to be a key factor to dominate the total PCFC voltage loss at the intermediate temperature zone. The concentration polarization of anode-supported PCFC is small, due to the vapors that are generated in the cathode side instead of anode side.

Keywords: protonic ceramic fuel cell; mixed electronic and ionic conductor; protonic conductor; multi-physics process; electrochemical process

1. Introduction

Solid oxide fuel cells (SOFCs) have become the focus of the research community due to the relatively high energy efficiency and power density, all-solid state, cleanliness, and capability of working with various fuels [1–3]. In the past decade, extensive efforts have been devoted to lowering the working temperature of SOFC to 350–650 °C [4], because the low operating temperature would make it possible to apply these cells to portable devices [5], reduce material costs [6–8], and extend the lifetime of fuel cells [6].

The ionic conductivity of traditional electrolyte materials (i.e., yttria-stabilized zirconia: YSZ) decreases exponentially as the operation temperature drops [9,10]. Proton-conductive electrolyte materials have been used to replace oxygen ionic electrolyte materials to overcome SOFC difficulties, while the operation temperature is reduced [11]. Compared with oxygen ionic electrolyte materials, proton-conductive electrolyte materials (i.e., BaZr0.1Ce0.7Y0.2O3−δ (BZCY) [12], BaZr0.1Ce0.7Y0.1Yb0.1O3 (BZCYYb) [13,14]) have higher proton conductivity around the intermediate temperature zone [15,16]. Furthermore,
unlike the O\textsuperscript{2−}-SOFCs, protonic ceramic fuel cells (PCFCs) have the following advantages: (a) low energy loss during H\textsuperscript{+} transport \cite{17–19}, (b) the cathode produces water to avoid dilution of the fuel in anode side \cite{20}, (c) faster fuel shipments lead to low concentration at anode \cite{21,22}, and (d) transference of H\textsuperscript{+} increases with the decreasing temperature \cite{23}.

The choice of cathode material is crucially important to the performance of PCFC \cite{24,25}. The cathode material, La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3} (LSM), which is widely used at high temperature is restricted, while the temperature drops below 800 °C due to the lack of oxygen vacancies \cite{26–28}. Therefore, ion/e\textsuperscript{−} mixed conducting cathode materials (i.e., Ba\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3−δ} (BSCF) \cite{29}, La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3−δ} (LSCF) \cite{30,31}) are widely used in intermediate temperature fuel cells. C. Duan et al. \cite{32} pointed out that the poor performance of most PCFCs is attributed to having no suitable cathode material. H\textsuperscript{+}/e\textsuperscript{−}/O\textsuperscript{2−} mixed conducting material (i.e., BaCo\textsubscript{0.4}Fe\textsubscript{0.4}Zr\textsubscript{0.1}Y\textsubscript{0.1}O\textsubscript{δ−δ}; BCFZY\textsubscript{0.1} \cite{33}) helps to improve the oxygen reduction reaction kinetics at intermediate temperature PCFC. M. Liu et al. \cite{34} proposed a H\textsuperscript{+}/e\textsuperscript{−}/O\textsuperscript{2−} mixed conducting composite cathode BZCY-LSCF in PCFC. Many H\textsuperscript{+}/e\textsuperscript{−}/O\textsuperscript{2−} mixed conducting materials \cite{35–37} (i.e., Pr\textsubscript{0.5}Ba\textsubscript{0.5}Co\textsubscript{0.7}Fe\textsubscript{0.3}O\textsubscript{3−δ}) have also been invented as the PCFC cathode materials and good performances have been achieved.

Compared with the conventional composite electrodes, the reaction sites and reaction process in the mixed conducting cathode of PCFCs are very different. The reaction in H\textsuperscript{+}/e\textsuperscript{−}/O\textsuperscript{2−} mixed conducting cathodes is divided into two parts. The electrochemically active sites (EAS) for oxygen reaction (O\textsubscript{2}→O\textsuperscript{2−}) are the percolated double-phase boundary sites (DPBs) (i.e., LSCF-pore), while the EAS for vapor formation reaction is the percolated LSCF-BZCY-pore three-phase boundary sites (TPBs).

With the development of PCFC electrode manufacturing technology, in order to improve the performance of PCFC, a variety of electrode materials have been invented, and the structures/components are also more complex \cite{38,39}. The microstructure of electrodes has a great influence on the PCFC performance \cite{40,41}. There is an increasing need to predict the effect of the microstructure parameters on the PCFC working details. Numerical simulation of PCFC system has been studied in some papers \cite{42,43}. However, as far as we know, different from the O\textsuperscript{2−}-SOFC, little scholarly attention has been devoted to the multi-physical simulation related to PCFC. The performance of PCFC varies greatly at different temperatures \cite{44}, but the key parameters that cause a rapid voltage drop with decreasing temperature are not clear. In order to evaluate PCFC composite cathodes more effectively, we need a multi-physical model to explore the influence of microscopic parameters on PCFCs working details.

In current paper, the percolation theory is adopted to obtain the effective physical and electrochemical properties from the microstructure parameters of PCFC. Then, after careful analysis of the electrochemical reactions and multi-physical transporting processes within the PCFC, the governing equations and boundary conditions of the PCFC cell are obtained. A multi-model is established to observe the working details in the PCFC. Finally, the calculation results are compared with the experimental \textit{i}_\text{op}–V\textit{op} curves to verify the accuracy of the multi-physical model for PCFC with H\textsuperscript{+}/e\textsuperscript{−}/O\textsuperscript{2−} mixed conducting cathodes, and some conclusions are drawn.

2. Materials and Methods

Taking Ni-BZCY/BZCY-BZCY-LSCF PCFC as an example, the electrochemical and multi-physical coupling model for the PCFC with H\textsuperscript{+}/e\textsuperscript{−}/O\textsuperscript{2−} mixed conducting cathodes is developed. It should be noted that the model is not limited to Ni-BZCY/BZCY-BZCY-LSCF, but can also be used for other PCFCs with the similar working processes.

The PCFC cell consists of three parts: (a) the anode is a porous structure consisting of Ni- and BZCY- particles, (b) the electrolyte is made of dense BZCY, and (c) the cathode is a porous structure consisting of LSCF- and BZCY- particles. Figure 1a displays the schematic diagram of the microstructure and the working processes of a typical PCFC. The corresponding equivalent circuit of e\textsuperscript{−}, O\textsuperscript{2−}, and H\textsuperscript{+} electric processes and two activation overpotentials within the LSCF-BZCY composite cathode are also illustrated in Figure 1b.
Because LSCF in the cathode can conduct both electrons and oxygen ions, the oxygen reduction half reaction \( \text{O}_2 \rightarrow \text{O}_2^- \) occurs on the surface of the percolated LSCF-pore DPBs. Percolated means that there is a connection path between the DPBs and the oxygen inlet and electronic current collector. Steam formation half reaction \( \text{O}_2^- + 2\text{H}^+ = \text{H}_2\text{O} \) occurs at the percolated LSCF-BZCY-pore TPBs. Percolated TPBs means that there are three paths connected with TPBs, including vapor transport (pore) from the TPBs to the cathode inlet, proton transport (BZCY) from TPBs to the electrolyte layer, and electron transport (LSCF) from TPBs to the electronic current collector. \( \text{O}_2^- \) is the intermediate transform substance between electrons and protons.

**Figure 1.** (a) Illustration of the electrochemical and physical coupling processes within a typical Ni-BZCY/BZCY/BZCY-LSCF PCFC button cell; (b) the corresponding equivalent circuit of \( e^- \), \( \text{O}_2^- \), and \( \text{H}^+ \) electric processes within the LSCF-BZCY composite cathode.

With hydrogen as the fuel and air as the oxidant, the basic electrochemical reactions based on the mutual electric charge conversions among the electrons, oxygen ions, and protons can be described as follows:

\[
\text{Anode: } 2\text{H}_2(\text{pore}) = 2\text{H}^+(\text{BZCY}) + 2e^- (\text{Ni}) \tag{1}
\]

\[
\text{Cathode: } 0.5\text{O}_2(\text{pore}) + 2e^- (\text{LSCF}) = \text{O}_2^- (\text{LSCF}) \tag{2}
\]

\[
\text{O}_2^- (\text{LSCF}) + 2\text{H}^+ (\text{BZCY}) = \text{H}_2\text{O}(\text{pore}) \tag{3}
\]

The contents in parentheses indicate the carriers of the reactants and products. As PCFC has quite different working processes from the conventional \( \text{O}_2^- \text{-SOFC} \), the multi-physical model would be more complicated. There are two different electromotive forces (\( e^- /\text{O}_2^- \) and \( \text{O}_2^- /\text{H}^+ \) interfaces) within the cathode side; thus, there are two different
activation overpotentials for the charge transfer rates between e\(^-\) and O\(^2-\) and O\(^2-\) and H\(^+\), respectively. More details can be found from the Supplementary Materials, in which the relevant local electrochemical equilibriums are carefully illustrated.

In order to verify the effectiveness of the model, the Ni-BZY/BZY/BZY-LSCF PCFC reported by Ref. [34] is selected in this paper to develop and verify the numerical model. The percolation micro model in Ref. [16] is used to calculate the effective properties of the anode, electrolyte, and cathode in PCFC from the experiment-specified microstructure parameters [34].

Accurate and proper electrochemical and physical properties are essential to solve the coupled governing equations of physical–chemical processes. Table 1 lists the basic microstructure parameters of each PCFC component layer with the experimental sources specified. Most of the other effective electrode properties in Table 1 are evaluated by our previously developed percolation micro model [16] as a function of the reported microstructure parameters.

### Table 1. Microstructure parameters and the effective properties of each PCFC component.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (µm)</td>
<td>LSCF-BZY</td>
<td>BZY</td>
<td>Ni-BZY</td>
</tr>
<tr>
<td>Mass ratio</td>
<td>25 [34]</td>
<td>55 [34]</td>
<td>500 [34]</td>
</tr>
<tr>
<td>Particle diameter (µm)</td>
<td>1/1 [34]</td>
<td>1 [34]</td>
<td>1/1 [34]</td>
</tr>
<tr>
<td>(\phi_S)</td>
<td>30% [34]</td>
<td>40% [34]</td>
<td></td>
</tr>
<tr>
<td>(\sigma_{\text{eff}} (\text{S m}^{-1}))</td>
<td>(2.54 \times 10^4) 750 °C</td>
<td>(3.32 \times 10^5) 750 °C</td>
<td></td>
</tr>
<tr>
<td>(\sigma_{\text{eff}} (\text{S m}^{-1}))</td>
<td>(2.81 \times 10^4) 650 °C</td>
<td>(3.48 \times 10^5) 650 °C</td>
<td></td>
</tr>
<tr>
<td>(\sigma_{\text{eff}} (\text{S m}^{-1}))</td>
<td>(2.92 \times 10^4) 550 °C</td>
<td>(3.64 \times 10^5) 550 °C</td>
<td></td>
</tr>
<tr>
<td>(\sigma_{\text{eff}} (\text{S m}^{-1}))</td>
<td>(0.012) 750 °C</td>
<td>(2.457) 750 °C</td>
<td>(0.064) 750 °C</td>
</tr>
<tr>
<td>(\sigma_{\text{eff}} (\text{S m}^{-1}))</td>
<td>(0.007) 650 °C</td>
<td>(1.538) 650 °C</td>
<td>(0.040) 650 °C</td>
</tr>
<tr>
<td>(\sigma_{\text{eff}} (\text{S m}^{-1}))</td>
<td>(0.004) 550 °C</td>
<td>(0.708) 550 °C</td>
<td>(0.022) 550 °C</td>
</tr>
<tr>
<td>(\sigma_{\text{eff}} (\text{S m}^{-1}))</td>
<td>(0.452) 750 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\sigma_{\text{eff}} (\text{S m}^{-1}))</td>
<td>(0.121) 650 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\sigma_{\text{eff}} (\text{S m}^{-1}))</td>
<td>(0.023) 550 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\tau)</td>
<td>0.476</td>
<td>0.556</td>
<td></td>
</tr>
<tr>
<td>(\lambda_{\text{TPB,eff}} (\text{m}^{-2}))</td>
<td>(8.0 \times 10^{12})</td>
<td>(1.69 \times 10^{12})</td>
<td></td>
</tr>
<tr>
<td>(\rho_{\text{LSCF}} (\text{m}^{-1}))</td>
<td>(1.74 \times 10^6)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The governing equations to describe the transports of electrons, protons, and oxygen ions, and their mutual transfers processes can be resolved by the following equations.

\[
\nabla \cdot i_e = \nabla \cdot \left( -\sigma_{\text{eff}} e^{-} \nabla \Phi_e \right) = \begin{cases} \nabla \cdot i_{e^{-},LSCF}^{V,e} & \text{Cathode} \\ -\nabla \cdot i_{e^{-},H^{+},TPB}^{V,a} & \text{Anode} \end{cases}
\]

\[
\nabla \cdot i_{H^{+}} = \nabla \cdot \left( -\sigma_{\text{eff}} H^{+} \nabla \Phi_{H^{+}} \right) = \begin{cases} \nabla \cdot i_{H^{+},LSCF}^{V,e} & \text{Cathode} \\ 0 & \text{Electrolyte} \\ -\nabla \cdot i_{e^{-},H^{+},TPB}^{V,a} & \text{Anode} \end{cases}
\]

\[
\nabla \cdot i_{O^{2-}} = \nabla \cdot \left( -\sigma_{\text{eff}} O^{2-} \nabla \Phi_{O^{2-}} \right) = -\nabla \cdot i_{e^{-},O^{2-},LSCF}^{V,e} + \nabla \cdot i_{e^{-},H^{+},TPB}^{V,a}
\]

where \(\sigma_{\text{eff}}\) are the effective conductivities. \(\Phi_e, \Phi_{H^{+}}, \Phi_{O^{2-}}\) are the local electronic, protonic, and oxygen ionic electric potentials, respectively. \(i_{e^{-}}, i_{H^{+}}, \text{ and } i_{O^{2-}}\) are their corresponding electrochemical current densities, respectively.

\[
i_{V,a}^{N,a} = \frac{i_{V,a}^{N,a}}{\sigma_{\text{TPB,eff}}} \left[ \text{A m}^{-3} \right]
\]
where $\lambda_{\text{TPB,ref}}^V$ is the Ni-BZCY-pore TPB lengths per unit volume. $j_{\text{TPB}}^a$ is the $e^−-H^+$ charge transfer rate per unit TPB length, which can be evaluated by Butler–Volmer equation,

$$j_{\text{TPB}}^a = j_{\text{TPB,0,ref}}^a \exp \left( - \frac{E_{\text{H}^+}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \left( \frac{p_{\text{H}_2}}{p_0} \right)^{0.25} \left[ \exp \left( \frac{2a F}{RT} \eta_{\text{act}}^a \right) - \exp \left( - \frac{2a F}{RT} \eta_{\text{act}}^a \right) \right]$$

(8)

where $\eta_{\text{act}}^a$ is the anodic activation; more details can be found in the Supplementary Materials.

$$\eta_{\text{act}}^a = \Phi_e - \Phi_{\text{H}^+} + E^{\text{st}} + \frac{RT}{2F} \ln \frac{p_{\text{H}_2}}{1\text{ atm}}$$

(9)

$i_{\text{e}^--O^{2-},\text{LSCF}}^V$ is the conversion rate between $e^-$ and $O^{2-}$ electric charges over the percolated LSCF surface per cathode volume.

$$i_{\text{e}^--O^{2-},\text{LSCF}}^V = i_{\text{LSCF}} S_{\text{LSCF}}^V \text{ [A m}^{-3}]$$

(10)

where $S_{\text{LSCF}}^V$ is the LSCF-pore DPB area per unit cathode volume (m$^{-1}$). It is determined by detailed electrode microstructure parameters [16].

The $e^−-O^{2-}$ charge transfer rate per LSCF-particle area can be analogously evaluated as follows:

$$i_{\text{LSCF}} = i_{\text{LSCF,0,ref}} \exp \left( - \frac{E_{\text{O}_2}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \left( \frac{p_{\text{O}_2}}{p_0} \right)^{0.25} \left[ \exp \left( \frac{2a_{\text{LSCF}} F}{RT} \eta_{\text{act}}^c \right) - \exp \left( - \frac{2a_{\text{LSCF}} F}{RT} \eta_{\text{act}}^c \right) \right]$$

(11)

where the local cathode activation overpotential-c1 referring to the oxygen-reducing half reaction $O_2 = 2O^{2-} + 2e^−$ can be estimated as follows (more details can be found in the Supplementary Materials):

$$\eta_{\text{act}}^c = \Phi_{\text{O}_2} - \Phi_e + \frac{RT}{4F} \ln \frac{p_{\text{O}_2}}{1\text{ atm}}$$

(12)

where $i_{\text{H}^+-O^{2-},\text{L-B}}^V$ is the conversion rate of about $H^+-O^{2-}$ electric charges over the BZCY-LSCF-pores TPB lengths per cathode volume.

$$i_{\text{H}^+-O^{2-},\text{L-B}}^V = j_{\text{L-B}} \lambda_{\text{L-B}}^V \text{ [A m}^{-3}]$$

(13)

where $\lambda_{\text{L-B}}^V$ is the LSCF-BZCY-pore TPB lengths per unit volume.

The $H^+-O^{2-}$ charge transfer rate per LSCF-particle area can be evaluated by Butler–Volmer equation as follows:

$$j_{\text{L-B}} = j_{\text{L-B,0,ref}} \exp \left( - \frac{E_{\text{O}_2-H^+}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \left( \frac{p_{\text{H}_2 \text{O}}}{p_0} \right) \left[ \exp \left( \frac{2a_{\text{L-B}} F}{RT} \eta_{\text{act}}^c \right) - \exp \left( - \frac{2a_{\text{L-B}} F}{RT} \eta_{\text{act}}^c \right) \right]$$

(14)

where the local cathode activation overpotential-c2 referring to the vapor-producing half reaction $O^{2-} + 2H^+ = H_2O$ can be estimated as follows (more details can be found in the Supplementary Materials),

$$\eta_{\text{act}}^c = \Phi_{\text{O}_2} - \Phi_{\text{O}^{2-}} + \frac{RT}{2F} \ln \frac{p_{\text{H}_2 \text{O}}}{1\text{ atm}}$$

(15)

The extended Fick’s model is adopted to describe the species transfers within the porous mediums.

$$\nabla \cdot N_a = R_a$$

(16)

$$\nabla (-D_{\text{eff}}^{\text{a}} \nabla c_a) = R_a$$

(17)
where \( c_\alpha \) is the molarity of species \( \alpha \). \( D_{\alpha}^{\text{eff}} \) is the effective diffusion coefficient. The species sources/leaks \( R_\alpha \) (mol m\(^{-1}\) s\(^{-1}\)) for \( \text{O}_2, \text{N}_2, \text{H}_2, \text{H}_2\text{O} \) in different component layers are as follows:

\[
\begin{align*}
\text{RO}_2 & = -i_{\text{V,c}} e^{-\text{O}_2^-,\text{LSCF}/(4F)} \quad \text{Cathode} \\
\text{RH}_2\text{O} & = i_{\text{V,c}} \text{O}_2^-,\text{L}-\text{B}/(2F) \quad \text{Cathode} \\
\text{RN}_2 & = 0 \quad \text{Cathode} \\
\text{RH}_2 & = -i_{\text{V,a}} e^{-\text{H}^+,\text{TPB}/(2F)} \quad \text{Anode} \\
\text{RH}_2\text{O} & = 0 \quad \text{Anode}
\end{align*}
\] (18)

The corresponding boundary conditions for all the component interfaces are illustrated in the Supplementary Materials. Most of the microstructure parameters used by the electrochemical–multi-physical model were obtained from Ref. [34] directly. The other unillustrated effective properties of each component were calculated by the percolation micro model [16]. The corresponding results are summarized in Table 1. Then, all the above equations were coupling resolved by COMSOL software.

3. Results and Discussion

In Figure 2, the calculated \( i_{\text{op}}-V_{\text{op}} \) curves at operating temperatures of 550, 650, and 750 °C are compared with the that obtained by experimental in Ref. [34]. \( i_{\text{op}} \) and \( V_{\text{op}} \) are the operating electric current density and the corresponding output voltage, respectively. Good agreements between the simulated and experimental results in various temperatures verifies the validation of the established electrochemical and multi-physical coupling model.

As can be seen from Figure 3, the cathode activation overpotential \( c_1 \) of \( \text{O}_2 = 2\text{O}_2^- + 2\text{e}^- \) increases with the decreasing temperature, and the electrochemical active region of the PCFC cathode increases gradually. At 550 °C, the oxygen reduction reaction occurring at the LSCF-pore DPB areas mainly occurs within 8 µm from the electrolyte surface. At the same time, similar results can be obtained for other output voltages. Therefore, for PCFCs using LSCF-BZCY 7/3 mixed cathode, the cathode thickness of 8 µm is sufficient to support most cathodic electrochemical reactions at intermediate operating temperatures. This result is reasonable. For most of the SOFCs working around 800 °C, the main cathode
electrochemical active zones were found to be concentrated within 10 µm for both LSM-YSZ and LSCF-SDC composite cathodes [45,46]. For PCFC, when the working temperature decreases from 800 °C to 550 °C, the ionic conductivity greatly decreases and the electronic conductivity only slightly changes. Thus, the electrochemical active zone will be further compressed forward to the dense electrolyte direction for the minimal total energy loss.

Figure 3. The local activation overpotential distribution $\eta_{\text{act}}^{\text{c1}}$ refers to $\text{O}_2 = 2\text{O}^{2-} + 2e^{-}$ at $V_{\text{op}} = 0.5$ V.

Under the working condition $T = 550$ °C and $V_{\text{op}} = 0.5$ V, Figure 4a further shows the distributions of the local $e^-$, $O^{2-}$, and $H^+$ electric charge transfer source. The corresponding electric current densities in the PCFC cathode are also displayed in Figure 4b. Different from the cathode reaction of $O^{2-}$-SOFC, oxygen ions in the composite cathode of PCFC are not generated at LSCF-pore DPBs and consumed at the LSCF-BZCY-pore TPBs. $O^{2-}$ is an intermediate transform substance between electrons and protons. Thus, there is a peak distribution within the composite cathode of PCFC. Since the electron conductivity in the LSCF-BZCY composite cathode is much higher than that of oxygen ions and protons, in order to achieve the minimal total energy loss of all physical transporting processes, the electrochemical active zones for the $e^-$-$O^{2-}$ and $O^{2-}$-$H^+$ charge transfers are concentrated to a small distance away from the dense electrolyte. With the shortening of the distance from the electrolyte surface, the reaction between the protons and oxygen ions to produce steam becomes more intense, resulting in the rapid consumption of oxygen ion current, which makes the oxygen ion current in the cathode show a trend to first increase and then decrease.

In Figure 5, the proportion of each polarization loss in the total voltage loss at 550 and 750 °C are shown. $\eta_{\text{act}}^{a}$ refers to the active overpotential of the anodic half reaction. $\eta_{\text{act}}^{1}$ and $\eta_{\text{act}}^{2}$ refer to the active overpotentials of the oxygen reduction half reaction $0.5\text{O}_2 + 2e^- \rightarrow \text{O}^{2-}$ and vapor generation reaction $\text{O}^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{O}$, respectively. $\eta_{\text{ohm}}$ includes the ohmic loss referring to the $e^-$, $H^+$, and $O^{2-}$ transports. $\eta_{\text{con}}$ is the concentration polarization of both cathode and anode. For the current anode support PCFC with an anode thickness of 500 µm and a cathode thickness of 25 µm, the concentration polarization loss of fuel-diffusing process within anode play the dominant role.
Figure 4. The distributions of (a) the local e\(^-\), O\(^2-\), and H\(^+\) electric charge transfer source in the PCFC cathode. (b) The local e\(^-\), O\(^2-\), and H\(^+\) electric current densities in the cathode.

From Figure 5, we can observe that the concentration polarization is small, compared with the other ohmic and activation overpotentials. This result is quite different from that of traditional O\(^2-\)-SOFC [45], in which the fuel concentration voltage loss is large. This result is attribute to the reason that the vapors are generated in the cathode side of PCFC instead of the anode side. This means that high mole fraction of hydrogen can be maintained over the anode–electrolyte interface of PCFC, even if many hydrogens are consumed.

From Figure 5a,b, we can see that the proportion of the activation overpotentials is greatly increased, especially the activation overpotential of oxygen reduction half reaction in the cathode side of PCFC.
Figure 5. Proportion of each polarization loss in the total overpotential: (a) 550 °C and (b) 750 °C.

In order to more clearly compare the contributions of different overpotentials on the total voltage loss of PCFC at different $T$, Figure 6 shows the corresponding proportions at the constant output current and voltage cases, respectively. As can be seen from Figure 6a, for $i_{op} = 0.5 \text{ A cm}^{-2}$, the activation polarization loss (including $\eta_{act}^1, \eta_{act}^{c1}, \eta_{act}^{c2}$) goes from 25.0 to 244.2 mV and the ohmic polarization loss goes from 134.4 to 445.5 mV, while the temperature decreases from 1025 K to 825 K. Among them, the activation polarization loss of cathodic oxygen reduction reaction $\eta_{act}^{c1}$ is significantly increased from 8.5 to 162.1 mV.

In Figure 6b, for the same operating voltage of 0.5 V, ohmic polarization accounts for the 63.1%, 74.8%, and 82.5% of the PCFC total voltage losses, while $T$ is adjusted to 823, 923, and 1023 K, respectively. With the decrease of temperature, the proportion of cathode activation polarization loss increases from 5.4% to 24.3%. The sharp increase of cathode activation polarization loss at a relevant low temperature is considered to be one of the main factors that contributes to the performance degradation of PCFC.
Figure 6. The contributions of different overpotentials on the total voltage loss of PCFC at different operation temperatures at (a) \( i_{\text{op}} = 0.5 \, \text{A cm}^{-2} \) and (b) \( V_{\text{op}} = 0.5 \, \text{V} \).

From the above result we can find that the oxygen reduction half reaction on the cathode side is a key factor to dominate the voltage loss at the intermediate temperature zone. In Figure 7, the dependence of the PCFC performance on the reference exchange current density \( i_{\text{LSCF,0,ref}} \) is shown. It is found that the PCFC performance at 55 °C is greatly increased from 0.164 to 0.263 W cm\(^{-2}\), while the \( i_{\text{LSCF,0,ref}} \) is increased by one order of magnitude. Thus, finding materials with high electrochemical activity of oxygen reduction would be helpful to improve the performance of PCFC around the intermediate temperature zone.
Figure 7. Dependence of the PCFC performance on the reference exchange current density $i_{\text{LSCF},0,\text{ref}}$ at $T = 550 \degree C$.

Figure 8a shows the $H_2$ concentration distribution within the PCFC at $T = 550 \degree C$ and $V_{\text{op}} = 0.5 \text{ V}$. Figure 8b further shows the distribution of $H_2$ consumption rates within the composite anode of PCFC. The calculated result shows that the anode area beyond the cathode area is not electrochemically active. This result is consistent with that obtained by the $O^{2-}$-SOFC button cell [4].

Figure 8. (a) Hydrogen concentration (mol/m$^3$) distribution within the composite anode. (b) The consumption rate of hydrogen $R_{\text{H2}}$ within the composite anode (mol m$^{-3}$ s$^{-1}$).

Generally, increasing the effective conductivity of the electrode can improve the performance of PCFC. Taking the PCFC with $T = 550 \degree C$ and $V_{\text{op}} = 0.5 \text{ V}$ as an example, Figure 9 shows the dependences of the local oxygen ions and protons generation rates distributions on different ionic conductivities. As shown in Figure 9a, while $\sigma_{\text{O}^{2-}}$ is increased from 0.023 to 0.233 S m$^{-1}$, the electrochemically active region for the $O^{2-}$ generation/consumption is expanded from 8 to 14 $\mu m$. While the $H^+$ conductivity is raised from 0.004 to 0.039 S m$^{-1}$, the active region for the $H^+$ consumption is expanded from 3 to 6 $\mu m$. Obviously, the main cathodic electrochemical active zones are still concentrated within the 10 $\mu m$ thickness area away from the dense electrolyte, and the electrochemical contribution of the extending zone is still negligible. This result is attributed to the larger electronic conductivity of composite cathode, compared with both the oxygen ionic and protonic conductivities at intermediate temperature zones.
Figure 9. The dependences of the distributions of the local oxygen ions and protons generation rates on different ionic conductivities. (a) Different oxygen ionic conductivity; (b) different protonic conductivity.

4. Conclusions

In this paper, a multi-physical and electrochemical coupling model was well established for the typical PCFC with \( \text{H}^+/e^-/\text{O}^{2-} \) mixed conducting cathode. Taking a typical Ni-BZCY/BZCY/BZCY-LSCF PCFC as an example, the validation of the model was verified by good agreements with the experimental results, and the following conclusions were achieved.

(i) Compared with the \( \text{O}^{2-}-\text{SOFC} \), the ionic conductivity of PCFC greatly decreased, and the electronic conductivity only slightly changed, while the working temperature decreased from 800 °C to 550 °C. Thus, the cathodic electrochemical active zones for both the oxygen reducing and vapor producing half reactions would be further compressed to a smaller distance (i.e., 8 μm in the current situation) away from the electrolyte than that of \( \text{O}^{2-}-\text{SOFC} \) to achieve the minimal total energy loss (Figures 3, 4, and 9). The electrochemical contribution of the extending thickness would be negligible.

(ii) Different from the \( \text{O}^{2-}-\text{SOFC} \), \( \text{O}^{2-} \) within the PCFC cathode is only an intermediate transform substance between the electrons and protons. Thus, there is a peak oxygen ion current distribution within the composite cathode of PCFC (Figure 4). The oxygen reduction half reaction on the cathode side of PCFC is found to be a key factor to dominate the total PCFC voltage loss at intermediate temperature zone (Figure 6).

(iii) Compared with the \( \text{O}^{2-}-\text{SOFC} \), the concentration polarization of anode-supported PCFC is small. This result is attributed to the reason that the vapors are generated in the cathode side of PCFC instead of the anode side (Figure 5). This means that high mole fraction of hydrogen can be maintained over the anode-electrolyte interface of PCFC, even if many hydrogens are consumed.
It should be noted that the model is not limited to Ni-BZCY/BZCY/BZCY-LSCF, but also can be further used for other PCFCs with similar H⁺/e⁻/O²⁻ mixed conducting characteristics.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app12083889/s1, Supplementary: Multi-physical and Electrochemical Coupling Model for the Protonic Ceramic Fuel Cells with H⁺/e⁻/O²⁻ mixed conducting cathodes.

**Author Contributions:** Data curation, D.Y., W.W., S.J. and R.L.; Investigation, L.L. and D.C.; Writing—Original Draft Preparation, D.Y. and R.L.; Writing—Review and Editing, A.L. and D.C. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by National Natural Science Foundation of China (22179054), Ministry of Science and Technology of China (CU03-10), and Postgraduate Research and Practice Innovation Program of Jiangsu Province (KYCX21_3463).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

12. Yu, T.; Mao, X.; Ma, G. Performance of cobalt-free perovskite La0.6Sr0.4Fe1−xNbxO3−δ cathode materials for proton-conducting IT-SOFC. *J. Alloy. Compd.* 2014, 608, 30–34. [CrossRef]
13. VahidMohammadi, A.; Cheng, Z. Fundamentals of Synthesis, Sintering Issues, and Chemical Stability of BaZr0.1Ce0.7Y0.1yb0.13δProton Conducting Electrolyte for SOFCs. *J. Electrochem. Soc.* 2015, 162, F803–F811. [CrossRef]
17. Fabbri, E.; D’Epifanio, A.; Di Bartolomeo, E.; Licoccia, S.; Traversa, E. Tailoring the chemical stability of Ba(Ce0.8-xZrx)Y0.2O3-delta protonic conductors for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs). *Solid State Ion.* 2008, 179, 558–564. [CrossRef]


24. Loureiro, F.J.A.; Ramasamy, D.; Graca, V.C.D.; Holz, L.I.V.; Mikhailov, S.V.; Fagg, D.P. Analysis of La4Ni3O10 +/-delta-BaCe0.9Y0.1O3-delta Composite Cathodes for Protonic Ceramic Fuel Cells. *Appl. Sci.* 2021, 11, 3407. [CrossRef]


33. Rauf, S.; Zhu, B.; Shah, M.A.K.Y.; Tayyab, Z.; Attique, S.; Ali, N.; Mushtaq, N.; Wang, B.; Yang, C.; Asghar, M.I.; et al. Application of a Triple-conducting Heterostructure Electrolyte of Ba1.5Sr0.5Co1.0Fe0.7Zr0.1Y0.3-delta and Ca0.04Ce0.80Sm0.16O2-delta in a High-Performance Low-Temperature Solid Oxide Fuel Cell. *ACS Appl. Mater. Interfaces* 2020, 12, 35071–35080. [CrossRef] [PubMed]


35. Tao, Z.T.; Fu, M.; Liu, Y.; Gao, Y.J.; Tong, H.; Hu, W.J.; Lei, L.B.; Bi, L. High-performing proton-conducting solid oxide fuel cells with triple-conducting cathode of Pr0.5Ba0.5(Co0.7Fe0.3)O3-delta tailored with W. *Int. J. Hydrog. Energy* 2022, 47, 1947–1953. [CrossRef]


40. Li, J.; Huang, Q.; Lei, Q.; Maxim, T.; Chen, D. The effects of microstructural parameters on the electrochemical properties of LSM-LSCF composite cathode by the particle-based discrete element method. *Ionics* 2021, 27, 2901–2907. [CrossRef]


