Supporting Information

Open-cell voltage and electrical conductivity of a protionic ceramic electrolyte under two chemical potential gradients

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**Calculation of proton and oxygen vacancy mobilities**

The number of oxygen sites in BZY20 is restricted to 3 in total as follows:

\[
[\text{OH}_0^*] + [\text{V}_{o}^{**}] + [\text{O}^*_{o}] = 3
\]  

(S1)

By combining Eq. (S1) with Eqs. (1) and (3) in the main text, \( K_w \) can be expressed as a function of proton concentration.

\[
K_w = \frac{[\text{OH}_0^*]^2}{a\text{H}_2\text{O}(3 - \frac{1}{2}[\text{Y}_{Z_r}^*] - \frac{1}{2}[\text{OH}_0^*])(\frac{1}{2}[\text{Y}_{Z_r}^*] - \frac{1}{2}[\text{OH}_0^*])}
\]  

(S2)

The \( K_w \) for BZY20 at 500°C is reported by Yamazaki et al.\(^1\), and thus the proton and oxygen vacancy concentrations can be calculated at a given \( a\text{H}_2\text{O} \).

The total electrical conductivity for BZY20 at 500°C can be obtained from the pre-factors and activation energies of the partial ionic conductivities reported by Nomura and Kageyama.\(^2\)

From the best fit of the general expression for the total conductivity expressed in Eq. (S3) to the actual values, the mobility of oxygen vacancies, \( \mu_{\text{VO}} \), and that of protons, \( \mu_{\text{OH}_0^*} \), can be obtained.

\[
\sigma_{\text{tot}} = \sigma_{\text{OH}_0^*} + \sigma_{\text{VO}} = e[\text{OH}_0^*]\mu_{\text{OH}_0^*} + (2e)[\text{V}_{o}^{**}]\mu_{\text{VO}}
\]  

(S3)

Figure S1 shows the fit result, giving \( \mu_{\text{VO}} = 1.81 \times 10^{-7} \) and \( \mu_{\text{OH}_0^*} = 2.14 \times 10^{-5} \) (cm\(^2\)/V\(\text{s}\)).
Figure S1. Total electrical conductivity reported by Nomura and Kageyama\textsuperscript{2} and the best fit for BZY20 at 500°C.
Calculation of $aO_2$ at 500°C

To calculate $aO_2$ at fixed $aH_2O$, the reaction for thermolysis of $H_2O(g)$ is considered with the assumption that thermolysis is negligible at low temperature. Hereafter, subscripts $LT$ and $HT$ indicate low and high temperatures, respectively, and $p\Psi$ does partial pressure of species $\Psi$.

\[
\begin{align*}
\text{initial (LT)} & \quad \frac{H_2O(g)}{\rightarrow} \frac{H_2(g)}{+} \frac{1}{2}O_2(g) \\
\text{change} & \quad (pH_{2O_{LT}}/p_{tot}) - \chi \quad (pH_{2,LT}/p_{tot}) \quad (pO_{2,LT}/p_{tot}) \\
\text{final (500 °C)} & \quad (pH_{2O_{LT}}/p_{tot}) - \chi \quad (pH_{2,LT}/p_{tot}) + \chi \quad (pO_{2,LT}/p_{tot}) + \frac{1}{2}\chi
\end{align*}
\]

(S4)

In the above, $p_{tot}$ is total pressure considered as 1 atm at low temperature and even at 500°C after thermolysis, and $\chi$ is the fractional concentration of $H_2O$ consumed by thermolysis. All activity values at 500°C are expressed in Eqs. (S5-S7), and the value of $aH_2O_{HT}$ is fixed as $A$.

\[
aH_2O_{HT} = \frac{pH_{2O_{HT}}}{p_{tot}} = \frac{(pH_{2O_{LT}}/p_{tot}) - \chi}{(pH_{2O_{LT}}/p_{tot}) + (pH_{2,LT}/p_{tot}) + (pO_{2,LT}/p_{tot}) + \frac{1}{2}\chi} = A
\]

(S5)

\[
aH_2_{HT} = \frac{pH_{2,HT}}{p_{tot}} = \frac{(pH_{2,LT}/p_{tot}) + \chi}{(pH_{2O_{LT}}/p_{tot}) + (pH_{2,LT}/p_{tot}) + (pO_{2,LT}/p_{tot}) + \frac{1}{2}\chi}
\]

(S6)

\[
aO_{2,HT} = \frac{pO_{2,HT}}{p_{tot}} = \frac{(pO_{2,LT}/p_{tot}) + \frac{1}{2}\chi}{(pH_{2O_{LT}}/p_{tot}) + (pH_{2,LT}/p_{tot}) + (pO_{2,LT}/p_{tot}) + \frac{1}{2}\chi}
\]

(S7)

The expression for the thermodynamic equilibrium constant at 500 °C, $K_{H_2O}$, is given by

\[
K_{H_2O}(500 \degree C) = \frac{pH_{2,HT} \cdot (pO_{2,HT})^{\frac{1}{2}}}{pH_{2O_{HT}} \cdot (p_{tot})^{\frac{1}{2}}}
\]

(S8)

For the anode side, since water-saturated hydrogen is normally used, $pO_{2,LT}$ can be considered to be 0, and thus, $pH_{2O_{LT}} + pH_{2,LT} = 1$. Overall, we have three unknown, $x$, $pH_{2O_{LT}}$, and $pH_{2,LT}$,
and three equations, Eqs. (S5), (S8), and $p_{\text{H}_2\text{O}_{LT}} + p_{\text{H}_2\text{O}_{LT}} = 1$. Thus, $a_{\text{O}_2,\text{HT}} (= p_{\text{O}_2,\text{HT}} / p_{\text{tot}})$ can be obtained by solving these simultaneous equations.

For the cathode side, $p_{\text{H}_2\text{O}_{LT}}$ can be considered to be 0, and thus, $p_{\text{O}_2,\text{LT}} = 0.21 \times (1 - p_{\text{H}_2\text{O}_{LT}})$. Overall, we have three unknowns, $x$, $p_{\text{H}_2\text{O}_{LT}}$, and $p_{\text{O}_2,\text{LT}}$, and three equations. Thus, $p_{\text{O}_2,\text{HT}}$ can be obtained by solving the simultaneous equations in the same way. The results of $a_{\text{O}_2,\text{HT}} (= p_{\text{O}_2,\text{HT}} / p_{\text{tot}})$ for given $a_{\text{H}_2\text{O}_{HT}} (= p_{\text{H}_2\text{O}_{HT}} / p_{\text{tot}})$ are summarized in Table S1.

Table S1. Thermodynamic calculation of $a_{\text{O}_2}$ at 500 °C

<table>
<thead>
<tr>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{\text{H}_2\text{O}}$ at 500 °C</td>
<td>$a_{\text{O}_2}$ at 500 °C</td>
</tr>
<tr>
<td>(calculation)</td>
<td>(calculation)</td>
</tr>
<tr>
<td>1.00 $\times$ 10$^{-5}$</td>
<td>1.98 $\times$ 10$^{-38}$</td>
</tr>
<tr>
<td>1.00 $\times$ 10$^{-4}$</td>
<td>1.98 $\times$ 10$^{-36}$</td>
</tr>
<tr>
<td>1.00 $\times$ 10$^{-3}$</td>
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<td>1.00 $\times$ 10$^{-2}$</td>
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<td>3.00 $\times$ 10$^{-2}$</td>
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<td>5.00 $\times$ 10$^{-2}$</td>
<td>5.48 $\times$ 10$^{-31}$</td>
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<td>7.00 $\times$ 10$^{-2}$</td>
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<td>1.00 $\times$ 10$^{-1}$</td>
<td>2.44 $\times$ 10$^{-30}$</td>
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References