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Supporting Information

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

Ho-Il Ji,[1,*] Hyoungchul Kim,[1] Hae-Weon Lee,[1] Byung-Kook Kim,[1] Ji-Won Son,[1,2] Kyung Joong Yoon,[1] and Jong-Ho Lee,[1,2]

[1]High-temperature Energy Materials Research Center, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea

[2]Nanomaterials Science and Engineering, Korea University of Science and Technology (UST), KIST Campus, Seoul 02792, Republic of Korea

Calculation of proton and oxygen vacancy mobilities

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

$$[\mathrm{OH_O^{\bullet}}]+[\mathrm{V_O^{\bullet\bullet}}]+[\mathrm{O_O^{\times}}]=3 \tag{S1}$$

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

$$K_w=\frac{[\mathrm{OH_O^{\bullet}}]^2}{a\mathrm{H_2O}\left(3-\frac{1}{2}[\mathrm{Y'_{Zr}}]-\frac{1}{2}[\mathrm{OH_O^{\bullet}}]\right)\left(\frac{1}{2}[\mathrm{Y'_{Zr}}]-\frac{1}{2}[\mathrm{OH_O^{\bullet}}]\right)} \tag{S2}$$

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 $a\mathrm{H_2O}$.

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, $u_{\mathrm{V_O^{\bullet\bullet}}}$, and that of protons, $u_{\mathrm{OH_O^{\bullet}}}$, can be obtained.

$$\sigma_{tot}=\sigma_{\mathrm{OH_O^{\bullet}}}+\sigma_{\mathrm{V_O^{\bullet\bullet}}}=e[\mathrm{OH_O^{\bullet}}]u_{\mathrm{OH_O^{\bullet}}}+(2e)[\mathrm{V_O^{\bullet\bullet}}]u_{\mathrm{V_O^{\bullet\bullet}}} \tag{S3}$$

Figure S1 shows the fit result, giving $u_{\mathrm{V_O^{\bullet\bullet}}} = 1.81\times10^{-7}$ and $u_{\mathrm{OH_O^{\bullet}}} = 2.14\times10^{-5}$ ($\mathrm{cm^2V^{-1}s^{-1}}$).

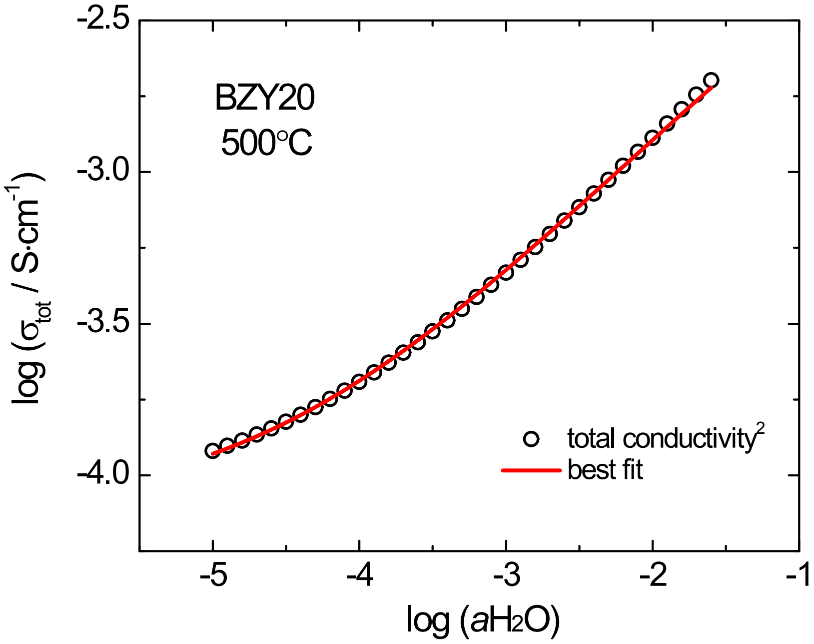

Figure S1. Total electrical conductivity reported by Nomura and Kageyama[2] and the best fit for BZY20 at 500°C.

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 Ψ.

	$H_2O(g)$ $\rightarrow$	$H_2(g)$ +	$\frac{1}{2}O_2(g)$	
initial (LT)	(pH_2O_{LT}/p_{tot})	$(pH_{2,LT}/p_{tot})$	$(pO_{2,LT}/p_{tot})$	(S4)
change	$-\chi$	χ	$\frac{1}{2}\chi$	
final (500 °C)	$(pH_2O_{LT}/p_{tot}) - \chi$	$(pH_{2,LT}/p_{tot}) + \chi$	$(pO_{2,LT}/p_{tot}) + \frac{1}{2}\chi$	

In the above, p_{tot} is total pressure considered as 1 atm at low temperature and even at 500°C after thermolysis, and χ 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.

$$aH_2O_{HT} = \frac{pH_2O_{HT}}{p_{tot}} = \frac{(pH_2O_{LT}/p_{tot}) - \chi}{(pH_2O_{LT}/p_{tot}) + (pH_{2,LT}/p_{tot}) + (pO_{2,LT}/p_{tot}) + \frac{1}{2}\chi} = A \qquad \text{(S5)}$$

$$aH_{2,HT} = \frac{pH_{2,HT}}{p_{tot}} = \frac{(pH_{2,LT}/p_{tot}) + \chi}{(pH_2O_{LT}/p_{tot}) + (pH_{2,LT}/p_{tot}) + (pO_{2,LT}/p_{tot}) + \frac{1}{2}\chi} \qquad \text{(S6)}$$

$$aO_{2,HT} = \frac{pO_{2,HT}}{p_{tot}} = \frac{(pO_{2,LT}/p_{tot}) + \frac{1}{2}\chi}{(pH_2O_{LT}/p_{tot}) + (pH_{2,LT}/p_{tot}) + (pO_{2,LT}/p_{tot}) + \frac{1}{2}\chi} \qquad \text{(S7)}$$

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

$$K_{H_2O}(500\ ^{\circ}\text{C}) = \frac{pH_{2,HT} \cdot (pO_{2,HT})^{1/2}}{pH_2O_{HT} \cdot (p_{tot})^{1/2}} \qquad \text{(S8)}$$

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 $pH_2O_{LT} + pH_{2,LT} = 1$. Thus, $aO_{2,HT}$ (= $pO_{2,HT} / p_{tot}$) can be obtained by solving these simultaneous equations.

For the cathode side, $pH_{2,LT}$ can be considered to be 0, and thus, $pO_{2,LT} = 0.21 \times (1 - pH_2O_{LT})$. Overall, we have three unknowns, x, pH_2O_{LT}, and $pO_{2,LT}$, and three equations. Thus, $pO_{2,HT}$ can be obtained by solving the simultaneous equations in the same way. The results of $aO_{2,HT}$ (= $pO_{2,HT} / p_{tot}$) for given aH_2O_{HT} (= pH_2O_{HT} / p_{tot}) are summarized in Table S1.

Table S1. Thermodynamic calculation of aO_2 at 500 °C

Anode		Cathode	
aH_2O at 500 °C	aO_2 at 500 °C (calculation)	aH_2O at 500 °C	aO_2 at 500 °C (calculation)
1.00×10^{-5}	1.98×10^{-38}	1.00×10^{-5}	2.10×10^{-1}
1.00×10^{-4}	1.98×10^{-36}	1.00×10^{-4}	2.10×10^{-1}
1.00×10^{-3}	1.98×10^{-34}	1.00×10^{-3}	2.10×10^{-1}
1.00×10^{-2}	2.02×10^{-32}	1.00×10^{-2}	2.08×10^{-1}
3.00×10^{-2}	1.89×10^{-31}	3.00×10^{-2}	2.04×10^{-1}
5.00×10^{-2}	5.48×10^{-31}	5.00×10^{-2}	2.00×10^{-1}
7.00×10^{-2}	1.12×10^{-30}	7.00×10^{-2}	1.96×10^{-1}
1.00×10^{-1}	2.44×10^{-30}	1.00×10^{-1}	1.91×10^{-1}

References

1. Y. Yamazaki, P. Babilo and S. M. Haile, *Chem. Mat.*, 2008, **20**, 6352-6357.
2. K. Nomura and H. Kageyama, *Solid State Ionics*, 2007, **178**, 661-665.