Supplementary Information

# Determination of partial conductivities and computational analysis of theoretical power density of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb1711) electrolyte under idiomatic PCFC conditions

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**Partial Conductivity**

The defect structure of the BCY-BZY system was well described in a previous study. In this BZCYYb1711 system, the Schottky–Wagner defect equilibrium was ignored because the errors resulting from this omission are negligible for heavily-doped systems.[1] Thus, the charge neutrality condition can be given as follows (details in previous studies[2,3])

$$n + \left[Y, Yb_{Ce,Zr}^{/}\right] = p + 2\left[V_O^{\cdot\cdot}\right] + \left[OH_O^{\cdot}\right] \tag{S1}$$

$$\frac{1}{2}O_{2(g)} + V_O^{\bullet\bullet} \Leftrightarrow O_O^x + 2h^{\bullet}; K_{OX} = \frac{p^2}{[V_O^{\bullet\bullet}]P_{O_2}^{1/2}} \tag{S2}$$

$$H_2O_{(g)} + V_O^{\bullet\bullet} + O_O^x \Leftrightarrow 2OH_O^{\bullet}; K_H = \frac{[OH_O^{\bullet}]^2}{[V_O^{\bullet\bullet}]P_{H_2O}} \tag{S3}$$

The partial conductivities of each of the charge carriers can be written in terms of the product of the concentration and diffusivity of the mobile defect species as follows

$$\sigma_{OH_O^{\cdot}} = \sigma_{OH_O^{\cdot}}^{*}\left[\left(1 + \frac{\alpha}{p_{H_2O}}\right)^{1/2} - 1\right]\left(\frac{p_{H_2O}}{\alpha}\right)\left(\frac{\alpha}{(1+\alpha)^{1/2} - 1}\right) \tag{S4}$$

$$\sigma_{V_O^{\cdot\cdot}} = \sigma_{V_O^{\cdot\cdot}}^{*}\left[\left(1 + \frac{\alpha}{p_{H_2O}}\right)^{1/2} - 1\right]^2\left(\frac{p_{H_2O}}{\alpha}\right) \tag{S5}$$

$$\sigma_p = \sigma_p^{*}\left[\left(1 + \frac{\alpha}{p_{H_2O}}\right)^{1/2} - 1\right]\left(\frac{p_{H_2O}}{\alpha}\right)^{1/2} p_{O_2}^{1/4} \tag{S6}$$

where the conductivity at standard partial pressures was selected, $\sigma_{OH_O^{\cdot}}^{*}$ represents the protonic

conductivity at $p_{H_2O}$ = 1 atm, $\sigma_p^*$ is the hole conductivity at $p_{O_2}$ = 1 atm and $p_{H_2O}$ = 0 atm, and $\sigma_{V_O^{\cdot\cdot}}^*$ is the oxygen-ion conductivity when $[V_O^{\cdot\cdot}]$ is independent of $p_{O_2}$ and $p_{H_2O}$ = 0 atm. Here, $\sigma_p \propto p_{H_2O}^{1/2}, p_{O_2}^{-1/4}$. Parameter $\alpha$ is a constant determined as follows

$$\alpha = \frac{8\left[Y,Yb_{Ce,Zr}^{/}\right]}{K_w} \tag{S7}$$

where $\left[Y,Yb_{Ce,Zr}^{/}\right] = \frac{x \cdot N_A}{V_m}$, in which $x$ is the molar dopant concentration, $N_A$ is Avogadro's number, and $V_m$ is the molar volume of the system. By considering the charge neutrality conditions (S8) and the relation between conductivities and concentrations (S9), the partial conductivities of each species could be determined as given below[4].

$$2[V_O^{\bullet\bullet}] + [OH_O^{\bullet}] + p = [Y_B^{'}] \tag{S8}$$

$$\sigma_i = z_i c_i \mu_i = \frac{z_i F}{V}[C_i]\mu_i \tag{S9}$$

$$\sigma_{OH_O^{\bullet}} = \frac{F}{4V}\mu_{OH_O^{\bullet}} K_H p_{H_2O}\left[\sqrt{\left(1+\frac{K_H^{1/2}p_{O_2}^{1/4}}{K_O^{1/2}p_{H_2O}^{1/2}}\right)^2 + \frac{8\left[Y_B^{'}\right]}{K_H p_{H_2O}}} - \left(1+\frac{K_H^{1/2}p_{O_2}^{1/4}}{K_O^{1/2}p_{H_2O}^{1/2}}\right)\right] \tag{S10}$$

$$\sigma_p = \frac{F}{4V}\mu_p \frac{K_H^{3/2}}{K_O^{1/2}} p_{H_2O}^{1/2} p_{O_2}^{1/2}\left[\sqrt{\left(1+\frac{K_H^{1/2}p_{O_2}^{1/4}}{K_O^{1/2}p_{H_2O}^{1/2}}\right)^2 + \frac{8\left[Y_B^{'}\right]}{K_H p_{H_2O}}} - \left(1+\frac{K_H^{1/2}p_{O_2}^{1/4}}{K_O^{1/2}p_{H_2O}^{1/2}}\right)\right] \tag{S11}$$

$$\sigma_{V_O^{\bullet\bullet}} = \frac{F}{8V}\mu_{V_O^{\bullet\bullet}} K_H p_{H_2O}\left[\sqrt{\left(1+\frac{K_H^{1/2}p_{O_2}^{1/4}}{K_O^{1/2}p_{H_2O}^{1/2}}\right)^2+\frac{8[Y_B']}{K_H p_{H_2O}}}-\left(1+\frac{K_H^{1/2}p_{O_2}^{1/4}}{K_O^{1/2}p_{H_2O}^{1/2}}\right)\right]^2 \quad \text{(S12)}$$

$$\sigma_T = \sigma_{OH_O^{\bullet}} + \sigma_{V_O^{\bullet\bullet}} + \sigma_p \quad \text{(S13)}$$

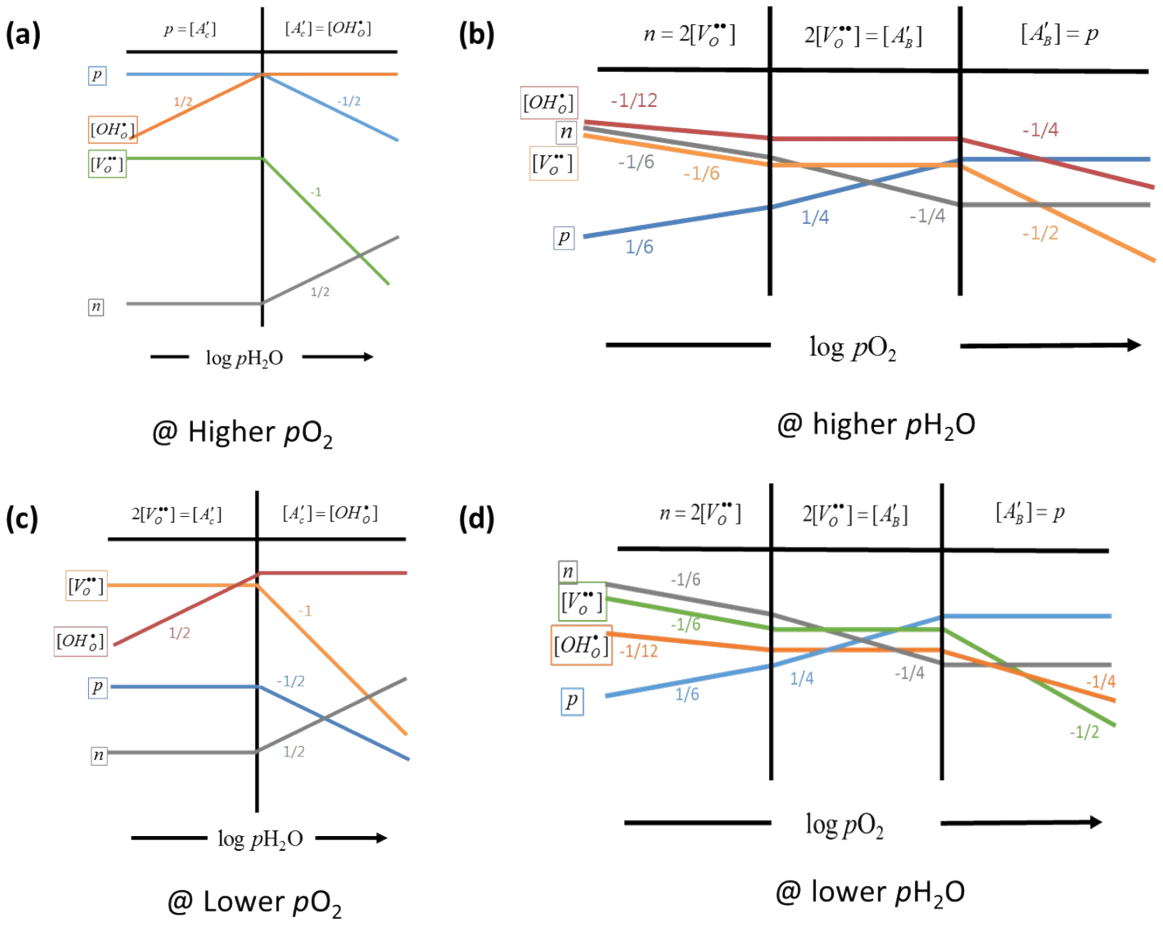


**Fig. S1.** Defect equilibrium diagrams of BZCYYb1711 as a function of $pH_2O$ at (a) higher $pO_2$ and (b) lower $pO_2$ and as a function of $pO_2$ at (c) higher $pH_2O$ and (d) lower $pH_2O$.

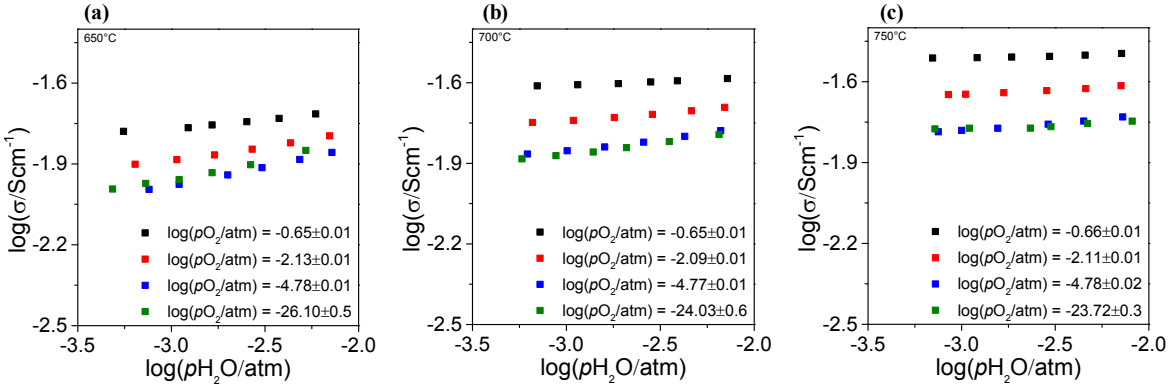


**Fig. S2.** Total conductivity of BZCYYb1711 electrolyte as a function of water vapor pressure at (a) 650 °C, (b) 700 °C, and (c) 750 °C.

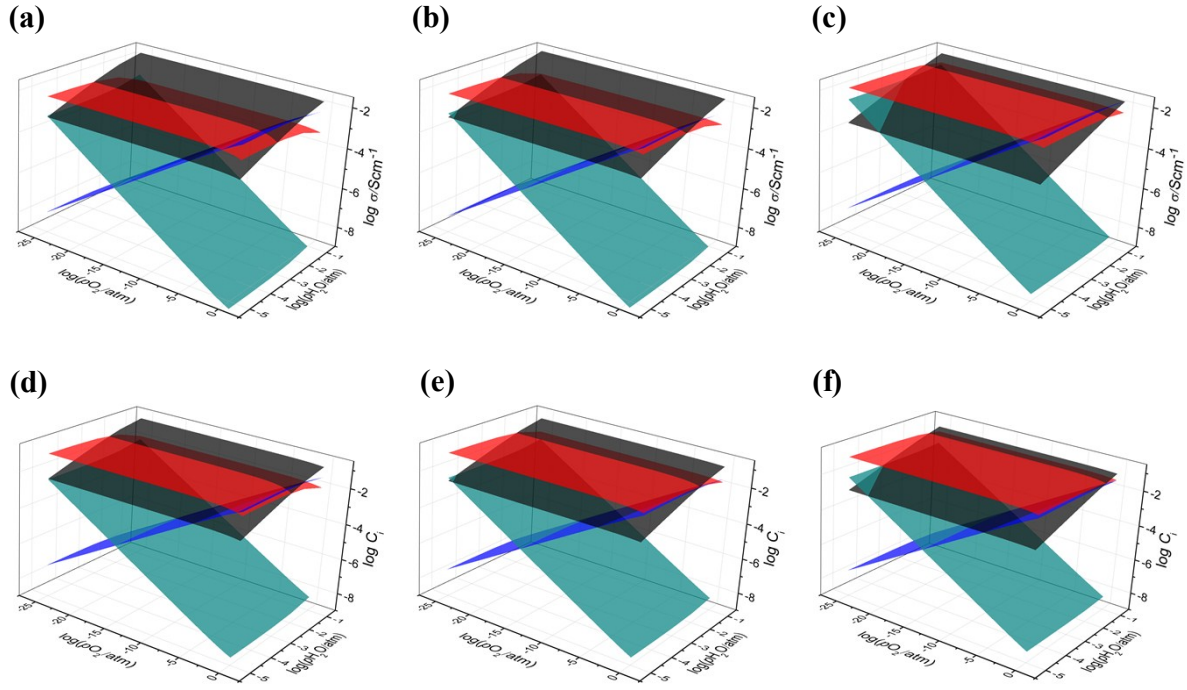


**Fig. S3.** 3D diagrams of Partial conductivities of BZCYYb1711 at (a) 650 °C, (b) 700 °C, and (c) 750 °C. Concentrations of mobile charge carriers at (a) 650 °C, (b) 700 °C, and (c) 750 °C. Here, each mobile charge carrier is denoted as- black is proton, red is oxygen, blue is hole, and dark cyan is electron.

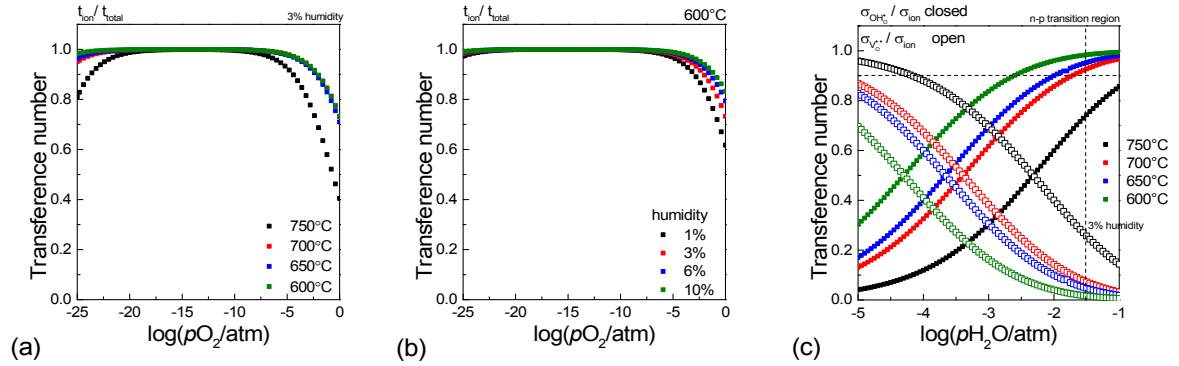


**Fig. S4.** Ratio of $t_{ion}/t_{total}$ as a function of (a) temperature and (b) humidity; (c) Proton dominant regime ($t_{proton} \geq 0.9$) at $pH_2O$/atm $\geq 0.03$.

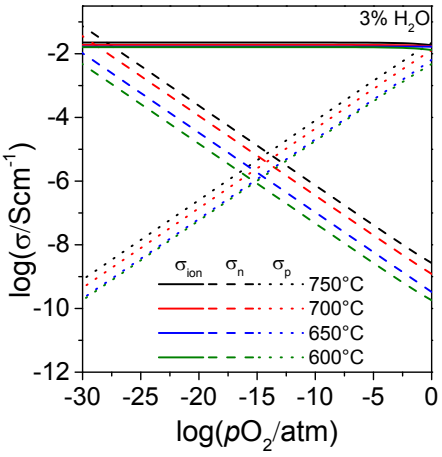


**Fig. S5.** Partial conductivity and N-P transition point of BZCYYb1711 as a function of $pO_2$ in the temperature range of 600 – 750 °C.

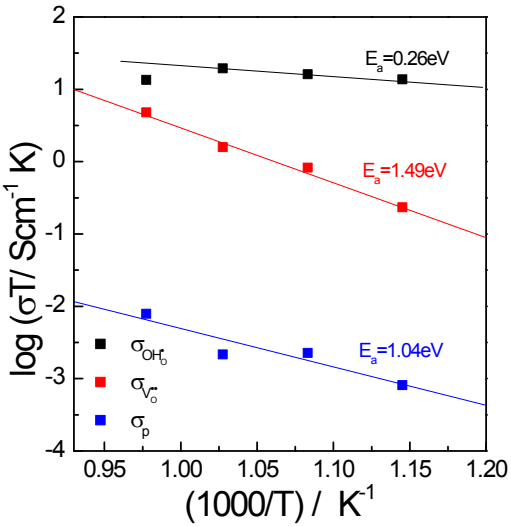


**Fig. S6.** Arrhenius curves of the partial conductivities of BZCYYb1711 and their activation energies

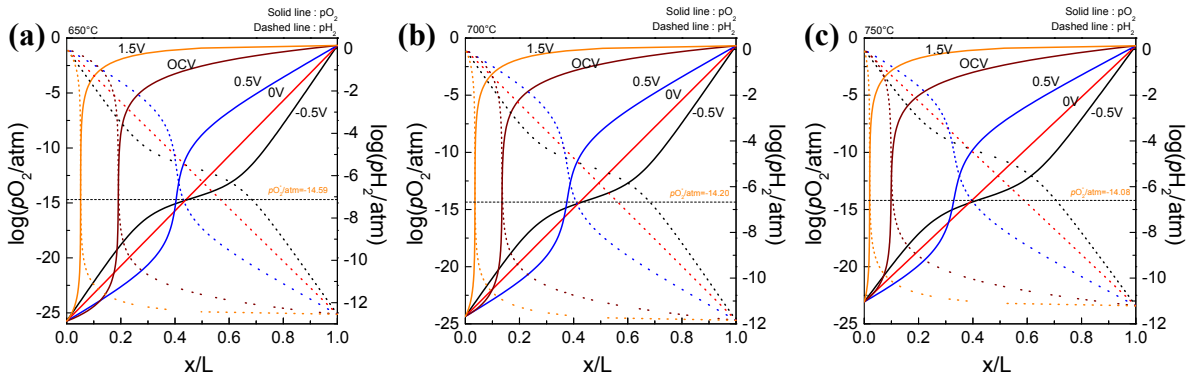


**Fig. S7.** Spatial distributions of chemical potential gradient of BZCYYb1711 under 3% humidified air at air electrode and 3% humidified hydrogen at fuel electrode at (a) 650 °C, (b) 700 °C, and (c) 750 °C.

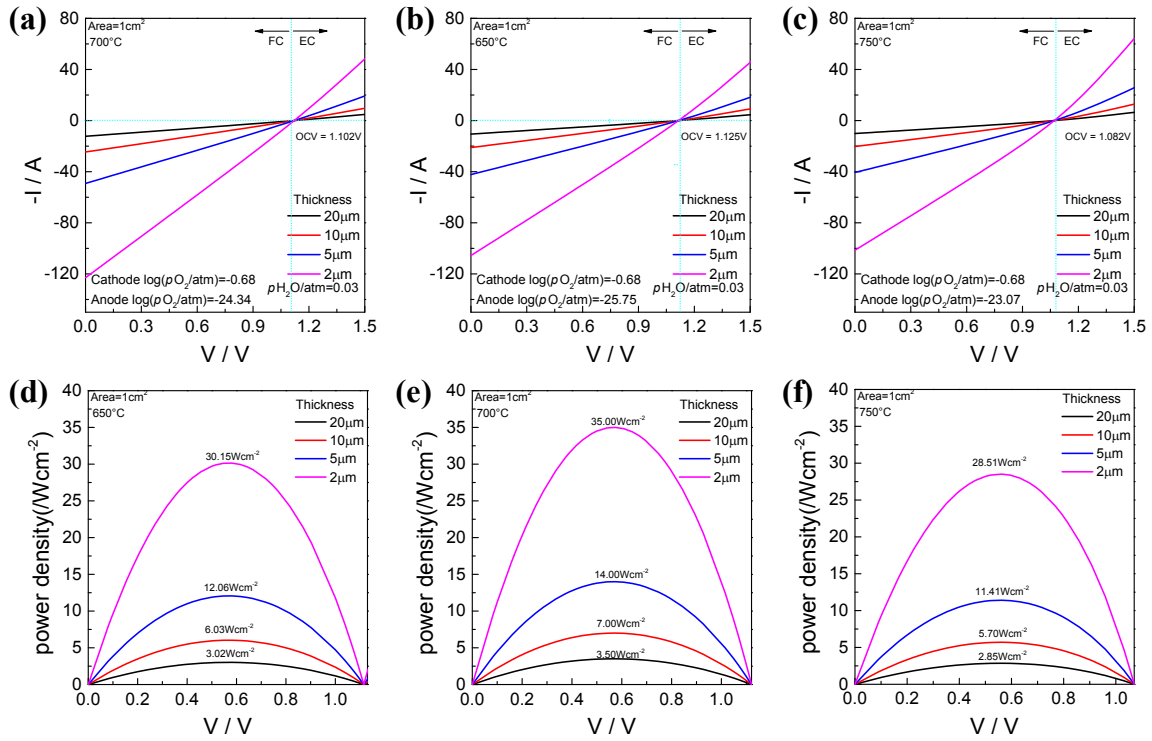


**Fig. S8.** I-V profiles (a,b,c) and powder densities (d,e,f) of BZCYYb1711 with various electrolyte thicknesses at (a,d) 650 °C, at (b,e) 700 °C, and (c,f) 750 °C under the supply of 3% humidified air/hydrogen gas to each electrode.

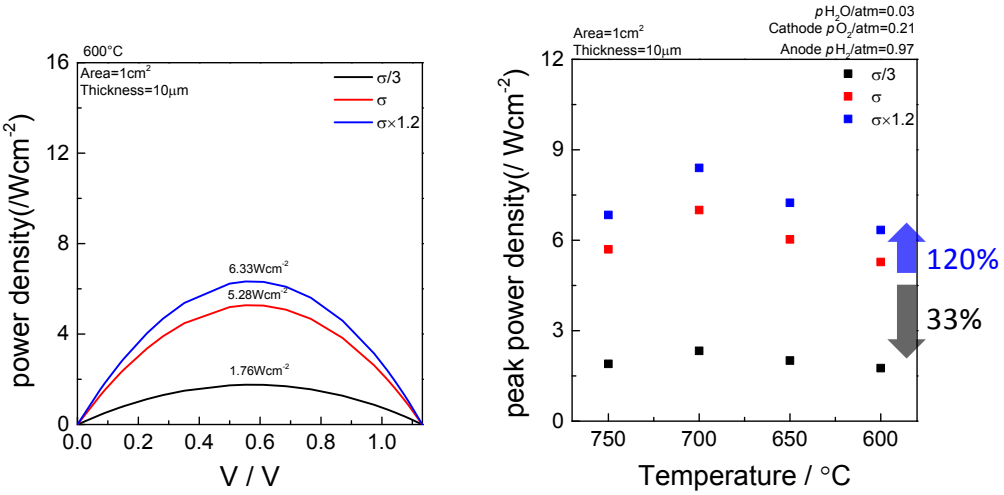


**Fig. S9.** (a) Theoretical power density at 600 ℃ and (b) peak power densities at different operating temperatures for BZCYYb1711 considering 1/3 times lower and 1.2 times higher values of calculated total conductivities.

Table S1. Theoretical peak power density of BZCYYb1711 as a function of hydrogen with various water vapor pressures in fuel electrode and gas type with 3% humidity in air electrode at 600 °C.

| Gas condition @ anode side | Thickness (μm) | Air condition @ cathode side ($W/cm^2$) | Oxygen condition @ cathode side ($W/cm^2$) |
|---|---|---|---|
| 3% humidified hydrogen | 10 | 5.27 | 5.55 |
| | 20 | 2.64 | 2.78 |
| | 30 | 1.76 | 1.85 |
| 4% humidified hydrogen | 10 | 5.34 | 5.63 |
| 5% humidified hydrogen | 10 | 5.38 | 5.66 |
| | 20 | 2.69 | 2.83 |
| | 30 | 1.79 | 1.89 |
| 6% humidified hydrogen | 10 | 5.39 | 5.68 |
| 7% humidified hydrogen | 10 | 5.40 | 5.68 |
| 8% humidified hydrogen | 10 | 5.39 | 5.68 |
| 9% humidified hydrogen | 10 | 5.38 | 5.67 |
| 10% humidified hydrogen | 10 | 5.37 | 5.66 |
| | 20 | 2.69 | 2.83 |
| | 30 | 1.79 | 1.89 |

**Reference**


1. N. Bonanos, F. W. Poulsen. Considerations of Defect Equilibria in High Temperature Proton-Conducting Cerates, J. Mater. Chem. 9 (1999) 431-434.

2. D.-K. Lim, M.-B. Choi, K.-T. Lee, H.-S. Yoon, E. D. Wachsman, S.-J. Song, Non-Monotonic Conductivity Relaxation of Proton-conducting $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ upon Hydration and Dehydration, Int. J. Hydrog. Energy 36 (2011) 9367-9373.

3. S.-J. Song, E. D. Wachsman, S. E. Dorris, U. Balachadran, Electrical Properties of p-type Electronic Defects in the Protonic Conductor $SrCe_{0.95}Eu_{0.05}O_{3-\delta}$, J. Electrochem. Soc. 150 (2003) A790-A795.

4. E. Kim, Y. Yamazaki, S. M. Hail, H.-Y. Yoo, Effect of NiO sintering-aid on hydration kinetics and defect-chemical parameters of $BaZr_{0.8}Y_{0.2}O_{3-d}$, Solid State Ionics 275 (2015) 23-28.