Electronic Supplementary Information

Space Charge Layer Effect at the Platinum anode/$BaZr_{0.9}Y_{0.1}O_{3-\delta}$ electrolyte Interface in Proton Ceramic Fuel Cells

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1. Derivation of Equation 7 in the manuscript

As the ECT reaction (Equation 6) is in equilibrium, the relationship of

$$\mu_{H_{int}} + \tilde{\mu}_{O^{2-}_{O}} = \tilde{\mu}_{OH^{-}_{O}} + \tilde{\mu}_{e^{-}}$$

(S1)

can be obtained, where μ and $\tilde{\mu}$ represent chemical potential and electrochemical potential, respectively. Considering the relationship between $\varphi(0)$ (electrical potential at x = 0) and $\varphi(Pt)$ (electrical potential at the Pt electrode), Equation S1 can be further written as:

$$\mu_{H_{int}} + \mu_{O^{2-}_{O}} - 2F\varphi(0) = \mu_{OH^{-}_{O}} - F\varphi(0) + \mu_{e^{-}} - F\varphi(Pt)$$

(S2)

giving the expression of Equation 7 in the manuscript.

2. Derivation of space charge layer resistance ($R_{SCL}(PT)$)

As presented in Figure 2, the resistance of protons transport through the space charge layer ($R_{SCL}(PT)$) can be expressed as:

$$R_{SCL}(H^+) = \rho_{SCL}^{eff}\frac{\lambda}{S} = \frac{\int_0^\lambda \rho_{SCL}(x)dx}{S} = \frac{\int_0^\lambda \frac{1}{\sigma_{SCL(x)}}dx}{S} = \frac{\int_0^\lambda \frac{1}{euC_{H^+}^{SCL}(x)}dx}{S}$$

(S3)

where $\rho_{SCL}(x)$ and $\sigma_{SCL}(x)$ represents the resistivity and conductivity at the position of x in the SCL, respectively. And also, u is the mobility of protons and S is the effective area of $R_{SCL}(H^+)$.

The concentration of protons ($C_{H^+}^{SCL}$) in the SCL is given by:

$$C_{H^+}^{SCL} = C_{H^+}^{bulk}\exp\left(\frac{-zF\Delta\varphi(x)}{RT}\right) \quad (z = 1) \qquad \text{(S4)}$$

where $C_{H^+}^{bulk}$ represents the concentration of protons in the bulk of the electrolyte,

Introducing (S4) in (S3) results in:

$$R_{SCL}(H^+) = \frac{1}{euSC_{H^+}^{bulk}}\int_{x_1}^{x_1+\lambda} \exp\left(\frac{F\Delta\varphi(x)}{RT}\right)dx$$

(S5)

2. Configuration of three electrode electrochemical cells

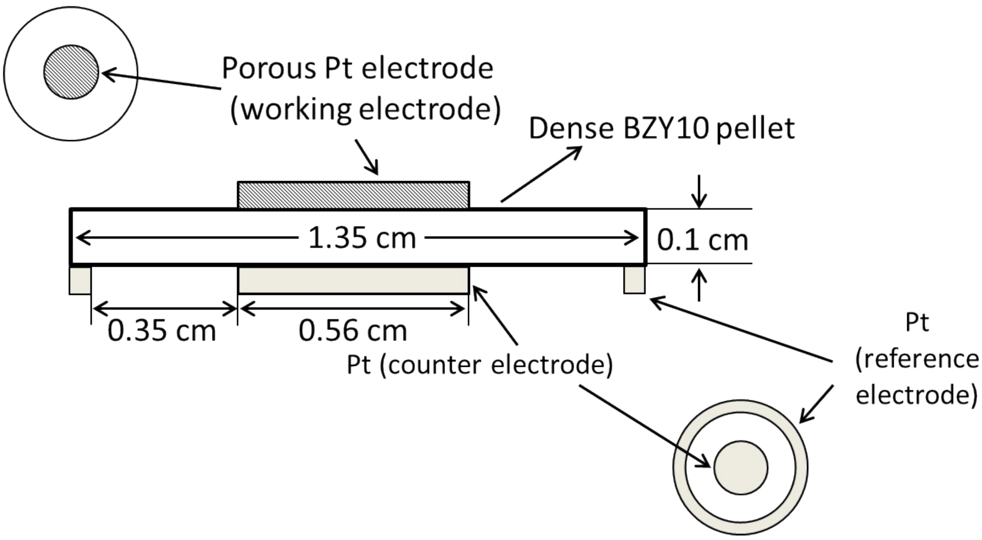

Figure S1. Schematic diagram and geometrical parameters of the three electrode electrochemical cells.

3. Derivation of coverage of atomic hydrogen (θ^H) as a function of pH₂

The H_2 dissociative absorption on the porous Ni electrode can be expressed by:

$$H_{2,\ ads} 2H_{ads} \underset{k_2^b}{\overset{k_2^f}{\rightleftarrows}} \quad \text{(S6)}$$

where the superscripts of f and b represent the forward and backward reaction, respectively, and k_2 is the rate constant. The net reaction rate υ_2 of this reaction can be written as:

$$\upsilon_2 = \upsilon_f - \upsilon_b = k_2^f(1 - \theta^H)pH_2 - k_2^b(\theta^H)^2 \tag{S7}$$

Equation (S7) solved for the equilibrium state ($\upsilon_f = \upsilon_b$) gives:

$$\frac{{pH_2}^{0.5}}{\theta^H} = \frac{1}{K^{0.5}} + {pH_2}^{0.5} \ (K = \frac{k_2^f}{k_2^b})$$

(S8)

representing the typical linearized Langmuir isotherm for dissociative adsorption. In addition, the experimental data in the inset of Figure 4(a) gives:

$$\frac{1}{R_{ECT}^{OCP}} \propto {pH_2}^{0.18} \tag{S9}$$

Introducing Equation S9 into Equation 22 gives (Assuming $\alpha_f = 0.5$)

$$\theta^H \propto {pH_2}^{0.36} \quad (\theta^H = A \cdot {pH_2}^{0.36}) \tag{S10}$$

Further introducing Equation S10 into S8 gives:

$${pH_2}^{0.14} = \frac{A}{K^{0.5}} + A \cdot {pH_2}^{0.5} \tag{S11}$$

Subsequently applying the linear fitting on Equation S11 gives the values of A and $K^{0.5}$, as displayed in Figure S2. Finally, introducing the $K^{0.5}$ value into Equation S8 gives the variation of θ^H value as a function of pH_2, as presented in Figure 5.

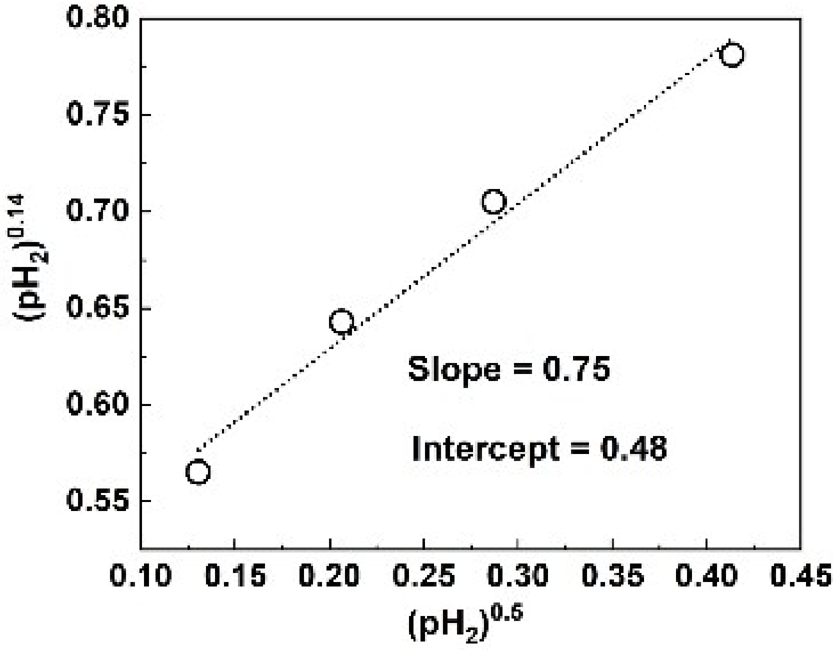

Figure S2 Linear fitting of ${pH_2}^{0.14}$ as a function of ${pH_2}^{0.5}$ in terms of Equation S11

4. Dependency of $C_{H^+}^{bulk}$ of BZY10 ceramics on pH_2O

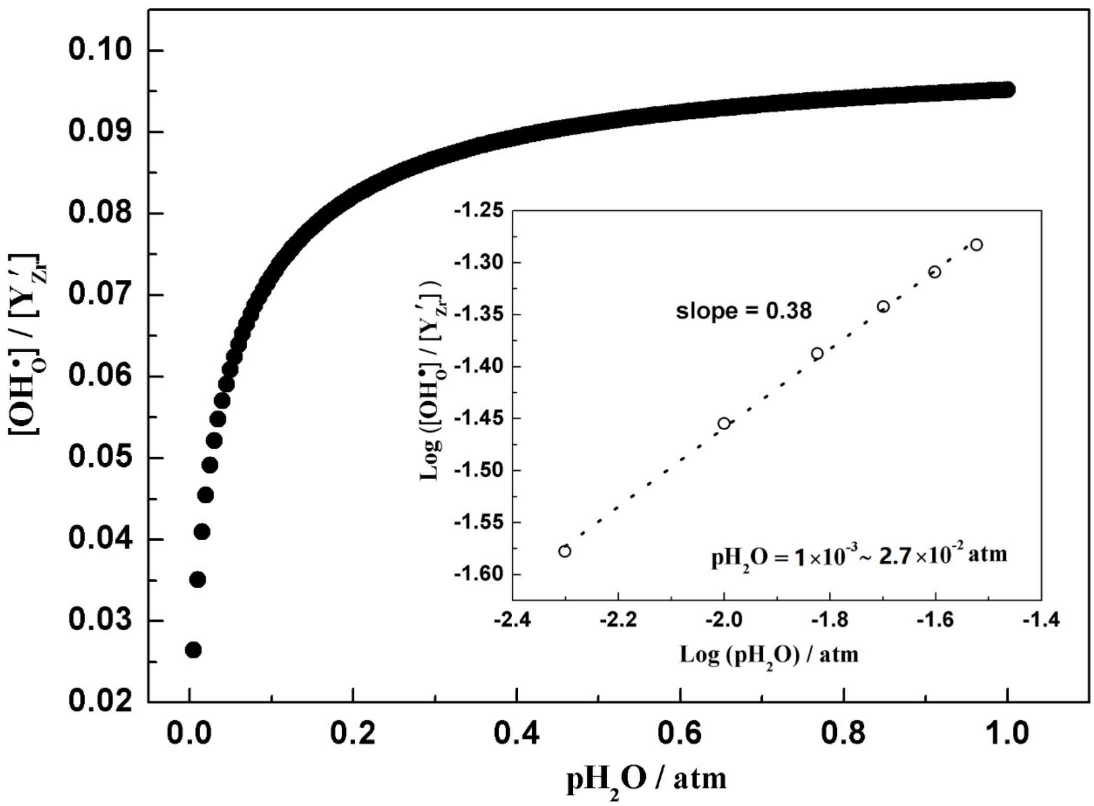

Figure S3. Normalized proton concentration ($OH_O^\bullet / Y_{Zr}^{'}$) in the bulk of the BZY10 material ($C_{H^+}^{bulk}$) as a function of pH_2O at 600°C in reducing atmosphere.