Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Proton Uptake Process in Double Perovskite Triple Ionic-Electronic Conducting Oxides for Protonic Ceramic Cells

Seunghyeok Im, Muhammet Ali Berk, Sungeun Yang, Byung-Kook Kim, Kyung Joong Yoon, Ji-Won Son, Jong-Ho Lee* and Ho-Il Ji*

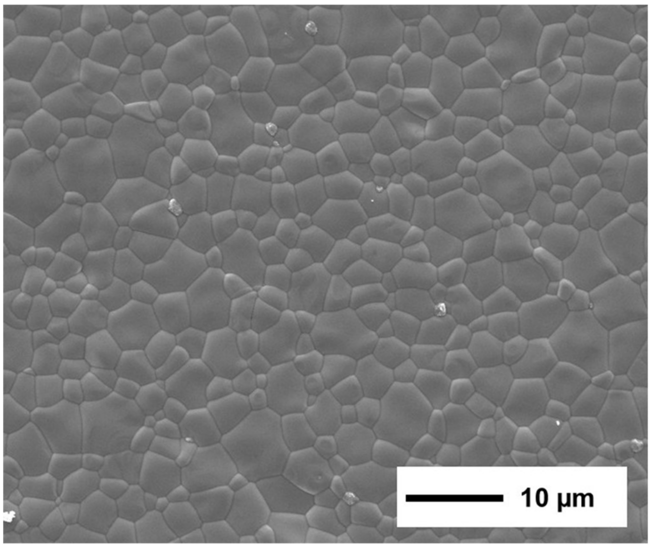

Figure S1 Surface microstructure of PBSCF bulk after sintering at 1150ºC.

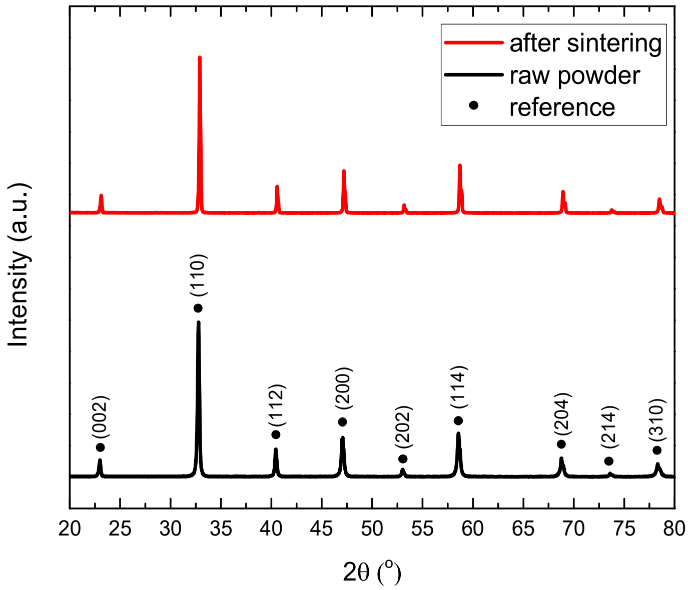

Figure S2 X-ray diffraction pattern of as-received $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ (PBSCF) powder (red line) and PBSCF bulk after sintering at 1150ºC (black line). Black circle indicates PBSCF reference.

Dependency of normalized weight change ratio and conductivity change on degree of hydration (α)

Let us consider the arbitrary one-to-one functions of "degree of hydration (α)", *f*(α), *g*(α), and *h*(α), whose return values are all experimentally measurable but of different dependency on α as shown in Figure S3. To precisely extract "α" from the (experimentally obtained) value of function, it is essential to select the appropriate one among the available functions; *e.g.*, if α is expected to be close to 1, *h*(α) is more appropriate than *f*(α) and *g*(α). The investigating functions in this study are i) the ratio of weight change under D_2O to that under H_2O ($\Delta w_{\mathrm{D_2O}}/\Delta w_{\mathrm{H_2O}}$), Equation 5, and ii) the difference between conductivity under dry and H_2O ($\sigma_{\mathrm{dry}} - \sigma_{\mathrm{H_2O}}$), Equation 9. The normalized form of these functions exhibits the dependency on α as follows:

1) $\Delta w_{\mathrm{D_2O}}/\Delta w_{\mathrm{H_2O}}$

$$\frac{\left(\dfrac{\Delta w_{\mathrm{D_2O}}}{\Delta w_{\mathrm{H_2O}}}\right)(\alpha)-\left(\dfrac{\Delta w_{\mathrm{D_2O}}}{\Delta w_{\mathrm{H_2O}}}\right)_{\alpha=1}}{\left(\dfrac{\Delta w_{\mathrm{D_2O}}}{\Delta w_{\mathrm{H_2O}}}\right)_{\alpha=0}-\left(\dfrac{\Delta w_{\mathrm{D_2O}}}{\Delta w_{\mathrm{H_2O}}}\right)_{\alpha=1}}=\left(\frac{\dfrac{\alpha M_{\mathrm{D_2O}}+(1-\alpha)M_{\mathrm{D_2}}}{\alpha M_{\mathrm{H_2O}}+(1-\alpha)M_{\mathrm{H_2}}}-\dfrac{M_{\mathrm{D_2O}}}{M_{\mathrm{H_2O}}}}{\dfrac{M_{\mathrm{D_2}}}{M_{\mathrm{H_2}}}-\dfrac{M_{\mathrm{D_2O}}}{M_{\mathrm{H_2O}}}}\right) \quad \text{(S1)}$$

2) $\sigma_{\mathrm{dry}} - \sigma_{\mathrm{H_2O}}$

$$\frac{\sigma(\alpha)-\sigma_{\alpha=1}}{\sigma_{\alpha=0}-\sigma_{\alpha=1}}=\frac{(1-\alpha)M_{\mathrm{H_2}}}{\alpha M_{\mathrm{H_2O}}+(1-\alpha)M_{\mathrm{H_2}}}. \quad \text{(S2)}$$

Surprisingly, two expressions above are almost identical as shown in Figure S4. For the simplicity, $M_{\mathrm{D_2}}$ and $M_{\mathrm{D_2O}}$ in Equation S1 are substituted for $M_{\mathrm{H_2}}$ and $M_{\mathrm{H_2O}}$ using the correlations of $M_{\mathrm{D_2}} \approx 2M_{\mathrm{H_2}}$ and $9M_{\mathrm{D_2O}} \approx 10M_{\mathrm{H_2O}}$, respectively, the right term in Equation S1 will be identical to Equation S2:

$$\frac{\left(\frac{\Delta w_{D_2O}}{\Delta w_{H_2O}}\right)(\alpha)-\left(\frac{\Delta w_{D_2O}}{\Delta w_{H_2O}}\right)_{\alpha=1}}{\left(\frac{\Delta w_{D_2O}}{\Delta w_{H_2O}}\right)_{\alpha=0}-\left(\frac{\Delta w_{D_2O}}{\Delta w_{H_2O}}\right)_{\alpha=1}} \approx \frac{(1-\alpha)M_{H_2}}{\alpha M_{H_2O}+(1-\alpha)M_{H_2}}\ . \qquad \text{(S3)}$$

The result implies that both functions, $\Delta w_{D_2O}/\Delta w_{H_2O}$ and $\sigma_{dry}-\sigma_{H_2O}$, may induce relatively larger error in determination of α as α approaches to 1.

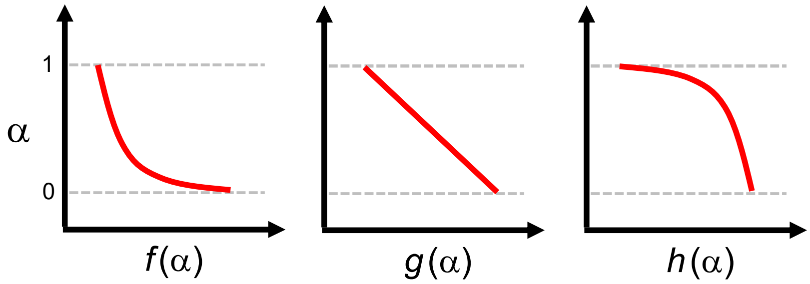

Figure S3 Schematic behavior of degree of hydration "α" vs. three arbitrary functions of α (g(α): linear dependency on α, f(α): convex under linear dependency, g(α): concave over linear dependency).

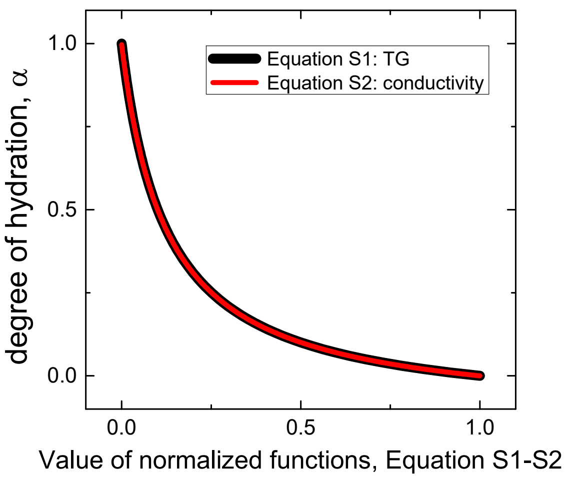

Figure S4 Correlation between "α" vs. normalized ratio of weight change (Equation S1; black curve) and normalized conductivity (Equation S2; red curve).