

**Electronic supplementary information (ESI)**

**Influence of Ca-doping in layered perovskite PrBaCo<sub>2</sub>O<sub>5+δ</sub> on phase transition  
and cathodic performance of a solid oxide fuel cell**

Chaehyun Lim<sup>1</sup>, Areum Jun<sup>1</sup>, Hongil Jo<sup>2</sup>, Kang Min Ok<sup>2</sup>, Jeeyoung Shin<sup>3</sup>, Young-Wan Ju<sup>1\*</sup>,  
Guntae Kim<sup>1\*</sup>

<sup>1</sup> *Department of Energy Engineering, Ulsan National Institute of Science and Technology  
(UNIST), Ulsan, 44919, Republic of Korea*

<sup>2</sup> *Department of Chemistry, Chung-Ang University, Seoul, 06974, Republic of Korea*

<sup>3</sup> *Department of Mechanical Engineering, Dong-Eui University, Busan, 47340, Republic of  
Korea*

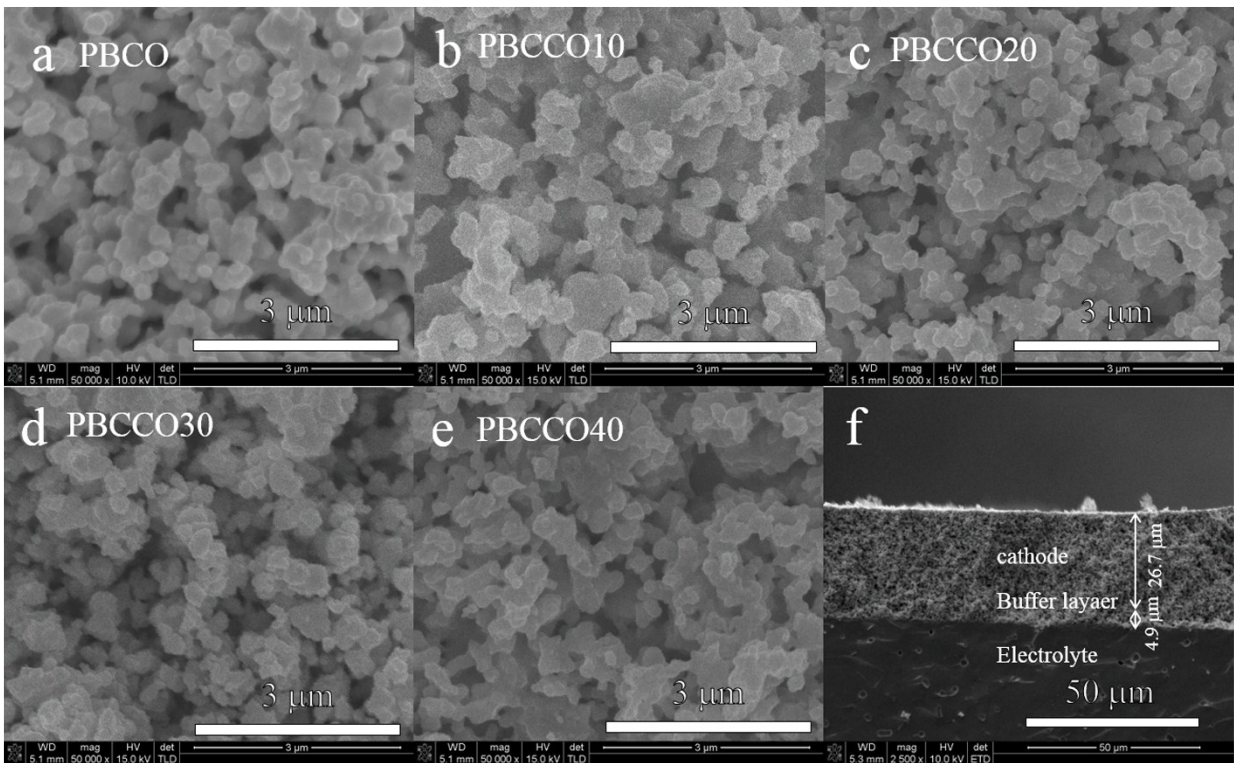
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\* *Corresponding author: E-mail: [ywju@unist.ac.kr](mailto:ywju@unist.ac.kr) (Y.W. Ju), [gtkim@unist.ac.kr](mailto:gtkim@unist.ac.kr) (G.T Kim)*

**Fig. S1.** Scanning electron microscope image of  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  composites, sintered at 973 K for 4 hours. (a)  $x = 0$ , (b)  $x = 0.1$ , (c)  $x = 0.2$ , (d)  $x = 0.3$ , (e)  $x = 0.4$  and (f) cross-sectional image of  $x = 0.3$

**Fig. S2.** *In situ* XRD patterns of  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  (a)  $x = 0$ , (b)  $x = 0.1$ , (c)  $x = 0.2$ , (d)  $x = 0.3$  and (e)  $x = 0.4$  in air from 303 to 1073 K.

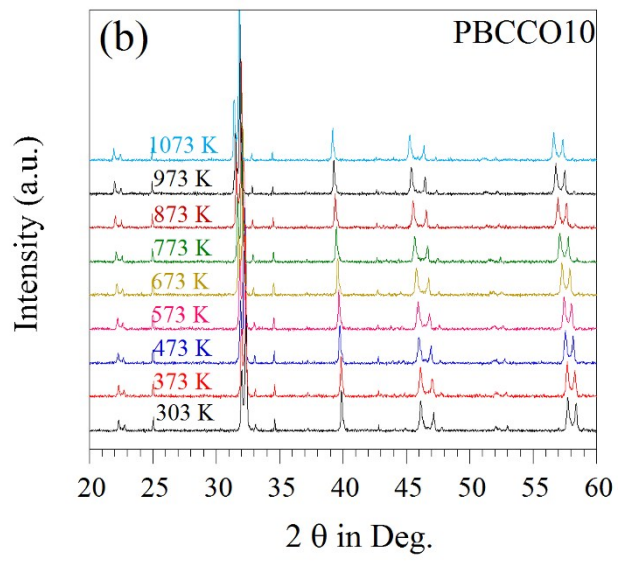
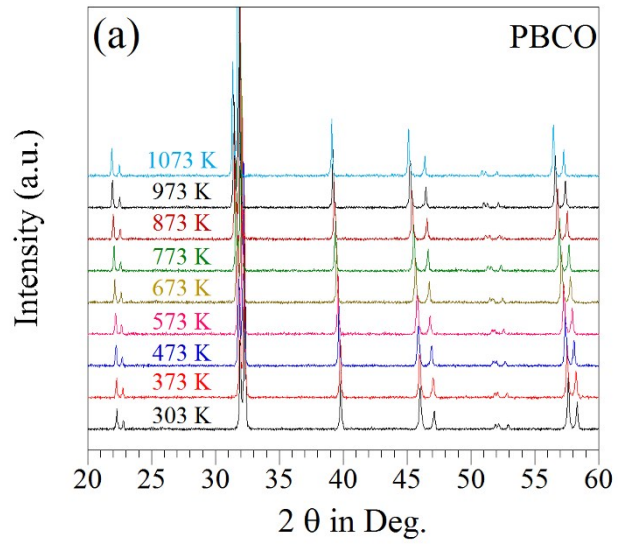
**Fig. S3.** X-ray diffraction patterns of  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  -  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (GDC) sintered at 1223 K for 4h.

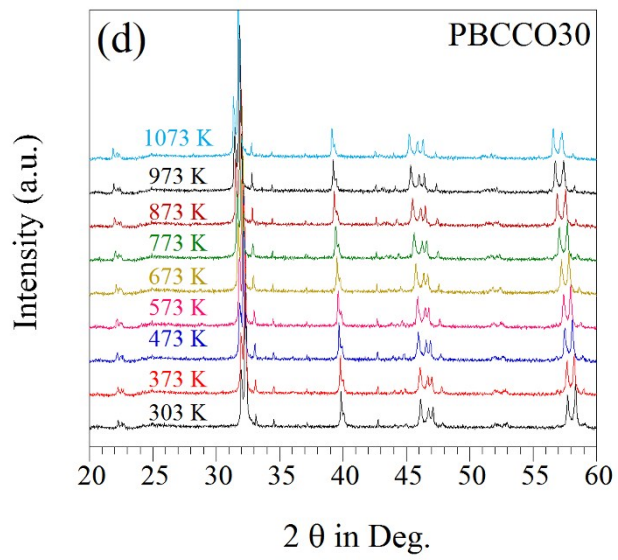
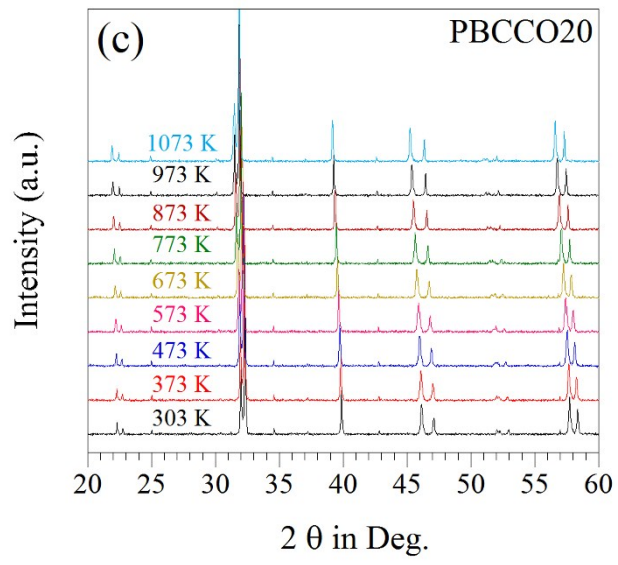


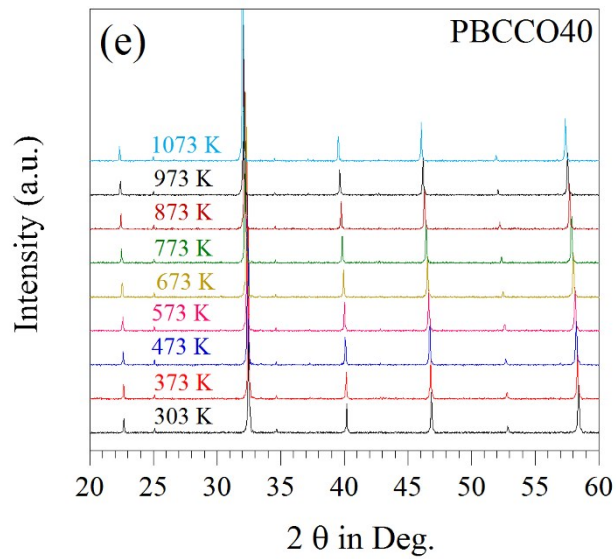
**Fig. S1.** Scanning electron microscope image of  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  composites, sintered at 973 K for 4 hours. (a)  $x = 0$ , (b)  $x = 0.1$ , (c)  $x = 0.2$ , (d)  $x = 0.3$ , (e)  $x = 0.4$  and (f) cross-sectional image of  $x = 0.3$

The microstructures of the  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  ( $x = 0, 0.1, 0.2, 0.3$  and  $0.4$ ) - GDC composites were investigated by a field emission scanning electron microscope (FE-SEM). The microstructure of the electrode is related with the surface area, electrochemical active sites, gas diffusion and electron transport.<sup>1,2</sup> These properties affect the fuel cell performance through the reaction kinetics, charge transport and mass transport processes. The microstructures of the porous  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  ( $x = 0, 0.1, 0.2, 0.3$  and  $0.4$ ) - GDC cathode are similar, and thus the substitution of

Ca for Ba and phase transition may not affect the electrochemical active site, which are related to the cell performance. Fig. S1 (f) shows a cross-sectional SEM image of  $\text{PrBa}_{0.7}\text{Ca}_{0.3}\text{Co}_2\text{O}_{5+\delta}$  - GDC/LDC/LSGM with an overview of the three layers, showing a thickness of about 25  $\mu\text{m}$  for the cathode and 5  $\mu\text{m}$  for the buffer layer. The interface between the cathode, buffer and electrolyte appears to be well-connected and the electrolyte and buffer layer are dense with no pores or cracks.

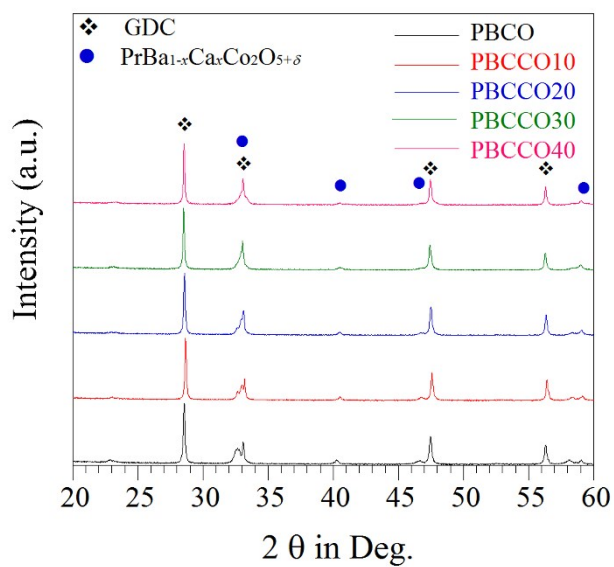






**Fig. S2.** *In situ* XRD patterns of  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  (a)  $x = 0$ , (b)  $x = 0.1$ , (c)  $x = 0.2$  and (d)  $x = 0.4$  in air from 303 to 1073 K.

Fig. S2 displays *in situ* XRD of the  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  ( $x = 0, 0.1, 0.2$  and  $0.4$ ) to confirm the thermal stability under the operating conditions (under ambient air and in a temperature range from 373 K to 1073 K). In the overall temperature range, it is confirmed that all samples can be considered thermally stable as determined from the absence of a significant phase change and impurities.



**Fig. S3.** X-ray diffraction patterns of  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  ( $x = 0, 0.1, 0.2, 0.3$  and  $0.4$ )- $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (GDC) sintered at 1223 K for 4h.

Generally, a phase reaction between the electrode and the electrolyte can result in the formation of an undesired insulating layer at the interface, which hinders the oxide-ionic and electronic transport.<sup>3</sup> Therefore, the chemical compatibility between  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  ( $x = 0, 0.1, 0.2, 0.3$  and  $0.4$ ) and GDC should be investigated as a preliminary study. Due to this reason, a reactivity test of the composite cathodes was conducted. Fig. 2 displays the XRD patterns of the  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  ( $x = 0, 0.1, 0.2, 0.3$  and  $0.4$ )-GDC composite obtained after heat treatment at 1223 K for 4 h. All the peaks can be attributed to both  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  and GDC, indicating that  $\text{PrBa}_{1-x}\text{Ca}_x\text{Co}_2\text{O}_{5+\delta}$  is chemically compatible with GDC under the given circumstances, even at temperature much higher than the IT-SOFC operating temperature ( $\sim 973$  K).