## Supporting information

Evaluation of Ba-deficient  $PrBa_{1-x}Fe_2O_{5+\delta}$  oxides as cathode materials for intermediate-

temperature solid oxide fuel cells

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**Figure S1.** Thermo-gravimetric analysis curves of  $PrBa_{1-x}Fe_2O_{5+\delta}$  (x = 0.00–0.10) oxides measured in air.



**Figure S2.** Electrical conductivity of  $PrBa_{1-x}Fe_2O_{5+\delta}$  (x = 0.00–0.10) oxides measured in air.

Figure S2 summarizes the electrical conductivities of the  $PrBa_{1-x}Fe_2O_{5+\delta}$  (x = 0.00–0.10) oxides in air at various temperatures. The oxygen ion conductivity of this kind of perovskite oxide has been reported to be much lower than the electron conductivity,<sup>1</sup> such that the electrical conductivity described herein can be assumed to represent the primarily electronic conductivity. As shown in this figure, all samples exhibit an initial increase in electrical conductivity from 300 °C to 425-450 °C, followed by a downward trend at higher temperatures, resulting from the thermally-induced lattice oxygen release and the formation of oxygen vacancies that hinders the mobility of electronic conduction carriers. Moreover, a downturn followed by an upturn is observed for the  $PrBa_{1-x}Fe_2O_{5+\delta}$  (x=0.00-0.05) oxides with higher levels of Ba deficiency at specific temperatures. Similar trend was observed in our previous work with the  $PrBa_{1-x}Co_2O_{5+\delta}$  (x = 0.00-0.08) system,<sup>2</sup> although different phenomena have been reported for other perovskites, such as  $La_{0.6}Sr_{0.4-x}Co_{0.2}Fe_{0.8}O_{3-\delta}$  (x =  $(0.0-0.2)^3$  and  $Ba_{1-x}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$  (x = 0.00-0.15)<sup>4</sup>. A monotonic decrease in electrical conductivity with increasing A-site cationic deficiency in the case of  $La_{0.6}Sr_{0.4-x}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (x = 0.0-0.2) oxides was observed by Kostogloudis and Ftikos,<sup>3</sup> who attributed this phenomenon to the formation of additional oxygen vacancies as the main charge compensation mechanism for Sr deficiency. The opposite trend was observed by Yang et al.<sup>4</sup> for the Ba<sub>1-x</sub>Co<sub>0.7</sub>Fe<sub>0.2</sub>Nb<sub>0.1</sub>O<sub>3-6</sub> (x = 0.00–0.15) oxides, and can be ascribed to the formation of holes as the main charge compensation mechanism for Ba deficiency. Generally, both additional holes and oxygen vacancies will form simultaneously in the mixed ion-electron conducting perovskites at higher A-site cationic deficiencies as charge compensation mechanisms, both of which adversely affect the electrical conductivity. The down and upturns observed in the electrical conductivity of the PrBa<sub>1-x</sub>Fe<sub>2</sub>O<sub>5+6</sub> (x = 0.00–0.05) series, which is similar to our previously reported results for the corresponding cobalt-based double-perovskites PrBa<sub>1-x</sub>Co<sub>2</sub>O<sub>5+6</sub> (x = 0.00–0.08),<sup>2</sup> is thus related to changes in the main charge (x=0.10) will result in a slightly decrease in electrical conductivity. This properly rated to the increase of impurity Pr<sub>6</sub>O<sub>11</sub> phases as which exhibits much lower electrical conductivity, typically 6.77×10<sup>-2</sup> S cm<sup>-1</sup> at 400 °C<sup>5</sup>, comparing to the PrBa<sub>1-x</sub>Fe<sub>2</sub>O<sub>5+6</sub> oxides.



Figure S3. Thermal expansion curves of  $PrBa_{1-x}Fe_2O_{5+\delta}$  (x = 0.00–0.10) oxides measured in air.



Figure S4. Thermal expansion curves of commercial Pr<sub>6</sub>O<sub>11</sub> oxide measured in air.

**Table S1.** Average thermal expansion coefficient of  $Pr_6O_{11}$  oxide at various temperature ranges.

Temperature (°C)	30-470	490-715	740-900	30-900
TEC×10 <sup>-6</sup> (°C <sup>-1</sup> )	12.0	26.0	14.3	22.3

Figure S3 presents the thermal expansion curves of  $PrBa_{1-x}Fe_2O_{5+\delta}$  (x=0.00-0.10) oxides that characterized by a dilatometer (Netzsch DIL 402PC) with a heating rate of 2 °C min<sup>-1</sup> from 30–900 °C. As depicted in this picture, excepted for an obviously decrease in the average TEC values of the  $PrBa_{1-x}Fe_2O_{5+\delta}$  oxides with Ba-deficient increase from 0.00 to 0.03, a gradually increase in TEC values were observed with further increase in x (x=0.05-0.10). To explore the possible reasons contribute to this phenomenon, the thermal expansion behavior of  $Pr_6O_{11}$  oxide (99.9% metals basis, Aladdin Industrial Inc.) was measured. The obtained data were plotted in Figure S4 and the derived average TEC values were listed in Table S1. Relatively high average TEC values,  $22.3 \times 10^{-6}$  °C<sup>-1</sup>, were obtained for the  $Pr_6O_{11}$  oxide in the temperature range of 30-900 °C which is much higher than that of  $PrBa_{1-x}Fe_2O_{5+\delta}$ oxides. As the concentration of  $Pr_6O_{11}$  phase increase with x increase from 0.05-0.10, it is reasonable to attribute the increase in TEC value of  $PrBa_{1-x}Fe_2O_{5+\delta}$  (x=0.05-0.10) oxides to the formation of additional  $Pr_6O_{11}$  phase.



Figure S5 Impedance spectra of  $PrBa_{1-x}Fe_2O_{5+\delta}/GDC/PrBa_{1-x}Fe_2O_{5+\delta}$  symmetrical cells

measured at 650  $^{\circ}\mathrm{C}$  (a) and 700  $^{\circ}\mathrm{C}$  (b) in air.

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