Supporting Information

Role of oxygen vacancies in water oxidation for perovskite cobalt oxide electrocatalysts: are more better?

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Materials Synthesis.

Polycrystalline powders of $PrBaCo_2O_{6-\delta}$ were synthesized by a sol-gel method. Stoichiometric amounts of $Pr(NO_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$, and $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in deionized water. Citric acid and ethylenediaminetetraacetic acid (EDTA) were then added as complexing agents. To ensure complete complexation, the pH value was adjusted to 6 using NH_4OH solution. The transparent solution was slowly evaporated at 100 ^oC to get a gel, which was decomposed at 400 ^oC for 10 h to form a solid precursor. The resulted precursor was sintered in air at 1000 ^oC for 10 h and then annealed in a pure nitrogen atmosphere at the 250 and 600 ^oC for 30 min to obtain $PrBaCo_2O_{6-\delta}$ samples with different oxygen vacancies.

Materials Characterizations

The phase purity and crystal structure of the samples were determined by X-ray diffraction (XRD) at room temperature on a Rigaku TTR-III diffractometer using Cu K_α radiation (λ = 1.54187 Å). The field emission scanning electron microscopy (SEM) images were obtained on a JEOL-2010 SEM. The high resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were performed on a JEOL JEM-ARM200F TEM at an acceleration voltage of 200 kV. X-ray photoelectron spectra (XPS) was recorded on an ESCALAB 250 X-ray photoelectron spectrometer with Al $K\alpha$ as the excitation source. The magnetic measurements were performed with a MPMS SQUID magnetometer. The temperature dependent resistivity was measured with a standard four-probe method on a Quantum Design physical property measurement system (PPMS). The nitrogen adsorption-desorption isotherms were conducted on a Micromeritics ASAP 2000 system at 77 K.

X-ray absorption measurements (XAS)

O *K*-edge XAS were measured at the beamline BL12B of National Synchrotron Radiation Laboratory (NSRL, Hefei) in the total electron yield mode by collecting the sample drain current under a vacuum better than 10^{-7} Pa. All spectra were normalized to the absorption background at the energy ranges both blow the adsorption edge and at ~ 560 eV. The Co 3d-O 2p hybridization could be estimated by the integrated intensities of the pre-edge peaks below 535 eV.

Electrochemical measurements

The electrochemical tests were performed at room temperature with a three-electrode on the CHI660E electrochemical station. Platinum wires and saturated Ag/AgCl were used as the counter and the reference electrodes, respectively. All potentials were referenced to the reversible hydrogen electrode (RHE) according to the Nernst equation: $E_{\mathrm{RHE}} = E_{\mathrm{Ag/AgCl}} + 0.059 \times \mathrm{pH} + 0.1976$. To prepare the working electrode, sample (3.7 mg), activated carbon (740 μg) and Nafion solution (5 wt%, 20 μL) were dispersed in 1 mL tetrahydrofuran (THF) with sonication for 30 min to form a homogenous ink. Then 5 μL ink was drop-casted onto a glassy carbon electrode of 3 mm in diameter (loading 0.25 mg cm^{-2}). Linear sweeping voltammograms were obtained at a scan rate of 5 mV s^{-1}. The potentials are *iR*-corrected to compensate for the effect of solution resistance, which were calculated by the following equation: $E_{iR\text{-corrected}} = E - iR$, where i is the current, and R is the uncompensated ohmic electrolyte resistance (~ 10 Ω) measured via high frequency ac impedance in O_2-saturated 1.0 M KOH. Electrochemical impedance spectroscopy (EIS) measurements were carried out at the potential of 1.6 V vs RHE with the frequency ranging from 100 KHz to 100 mHz under an AC voltage of 5 mV. Error bars represented s.d. from at least three independent measurements.

Iodometric titration test

Oxygen vacancies concentration (δ) of the samples was determined by iodometric titration method described elsewhere.[1] Typically, each sample (15 mg) was firstly dissolved in dilute hydrochloric acid (25 mL 1M HCl) containing potassium iodide (3 ml 2M KI), the corresponding reaction as follow: (1) $2Co^{3+} + 3I^- \rightarrow 2Co^{2+} + I_3^-$; (2) $Co^{4+} + 3I^- \rightarrow Co^{2+} + I_3^-$. Then, the generated I_3^- was titrated with 0.01M $Na_2S_2O_3$ according to the reation: (3) $I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$. The titrimetric end was indicated by starch /iodine indicator. In order to avoid the interference of atmospheric oxygen, we carried out all the experiments under nitrogen atmosphere. Oxygen vacancies concentration (δ) for the 250 and 600 °C annealing samples were determined to be about 0.25 and 0.50.

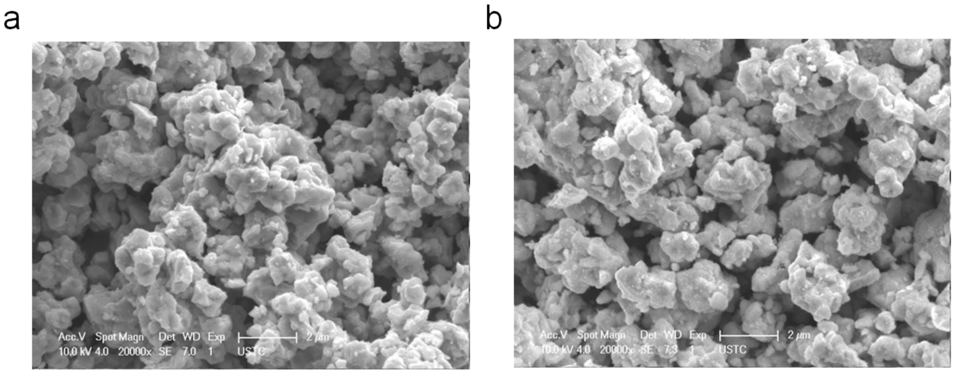

Fig. S1 SEM images of (a) $PrBaCo_2O_{5.75}$ and (b) $PrBaCo_2O_{5.5}$.

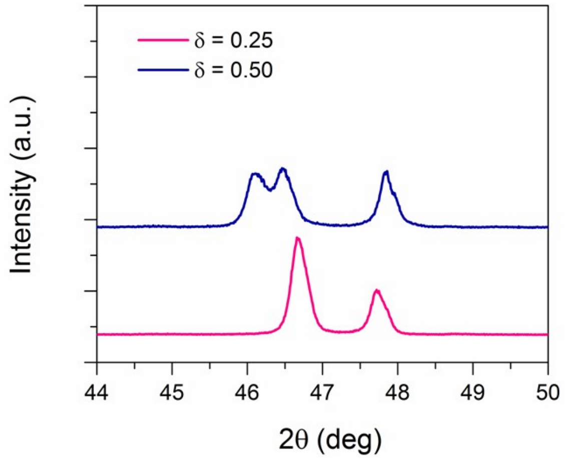

Fig. S2 PXRD patterns for $PrBaCo_2O_{6-\delta}$ in the range of 44 ° ~ 50°.

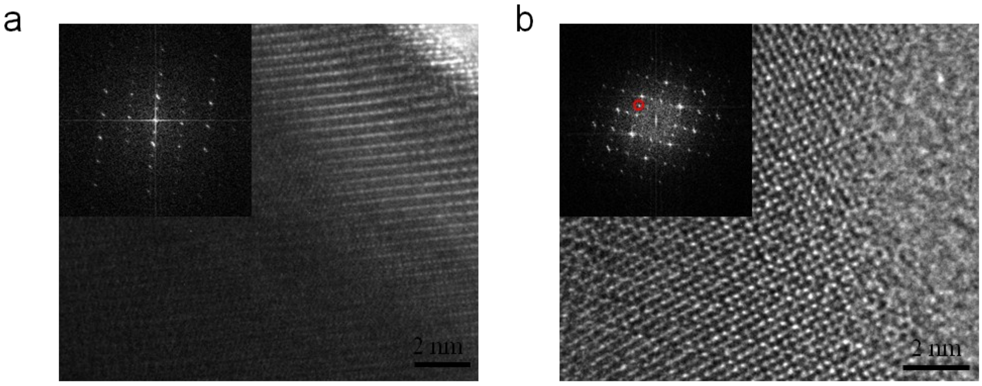

Fig. S3 High resolution TEM images for (a) $PrBaCo_2O_{5.75}$ and (b) $PrBaCo_2O_{5.5}$. The insets are the corresponding fast Fourier transforms (FFTs).

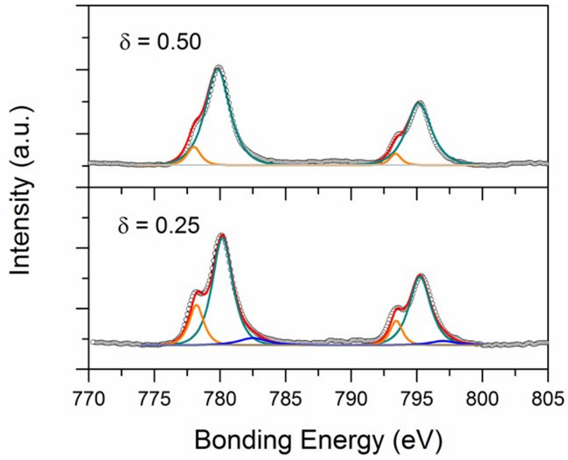

Fig. S4 XPS spectra of Co 2p/Ba 3d for $PrBaCo_2O_{6-\delta}$. The Co 2p/Ba 3d core level spectra are simultaneously deconvoluted due to the overlay between the Co 2p and Ba 3d peaks. For both the samples, the bonding energies at 780.0 eV and 795.2 eV are assigned to Ba $3d_{5/2}$ and Ba $3d_{3/2}$, respectively. The two fitted peaks for Co 2p are Co^{3+} (778.2 eV and 793.6 eV) and Co^{4+} (782.4 eV and 797.0 eV). Accordingly, the average cobalt oxidation state for both the 250 and 600 ^{o}C annealing samples are calculated to be about 3.25 and 3.00, respectively, in line with the results of iodometric titration analysis.

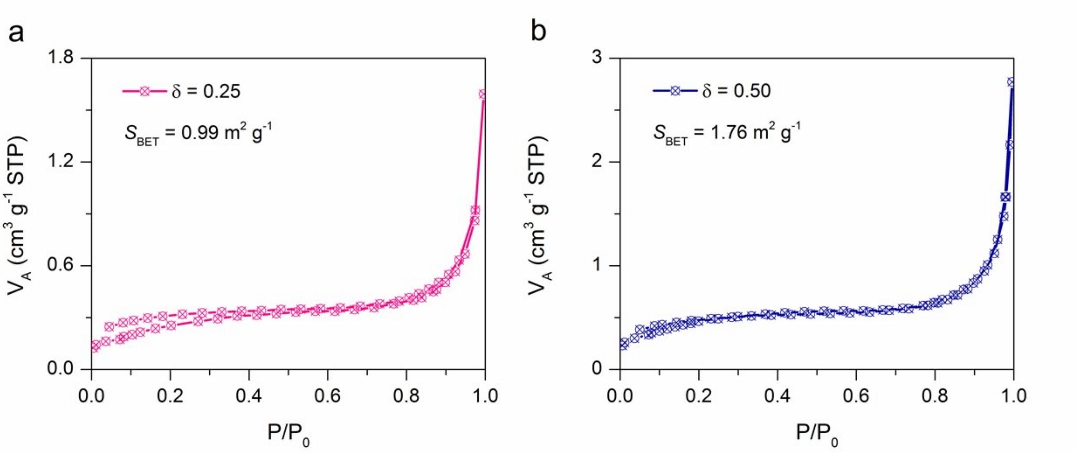

Fig. S5 Nitrogen adsorption-desorption isotherm curves for (a) $PrBaCo_2O_{5.75}$ and (b) $PrBaCo_2O_{5.5}$.

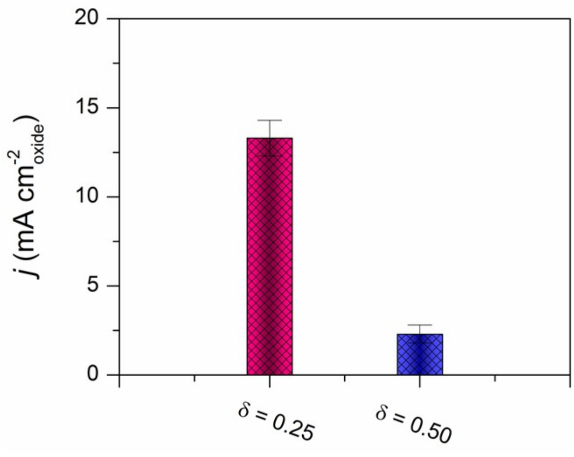

Fig. S6 Specific activities for $PrBaCo_2O_{6-\delta}$ normalized by the BET surface areas at $\eta = 0.42$ V.

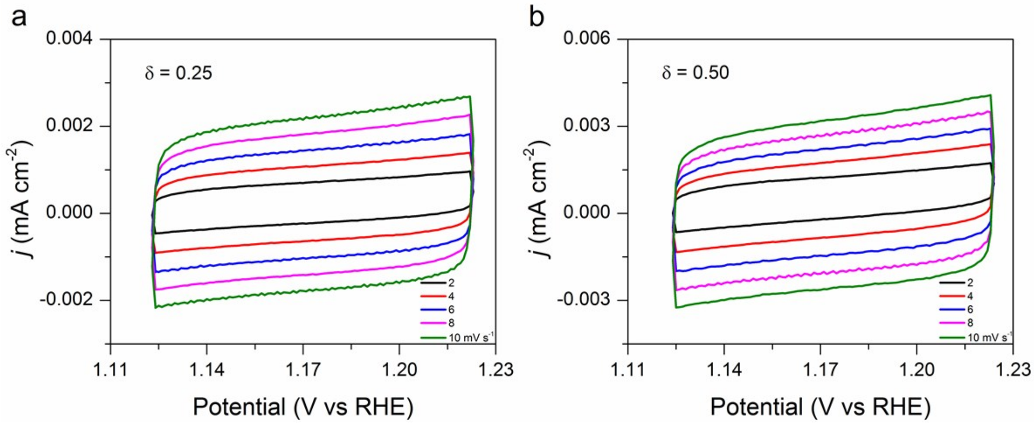

Fig. S7 Cyclic voltammetry curves for (a) $PrBaCo_2O_{5.75}$ and (b) $PrBaCo_2O_{5.5}$ measured in O_2-saturated 1.0 M KOH solution at scan rates from 2 to 10 mV s^{-1}.

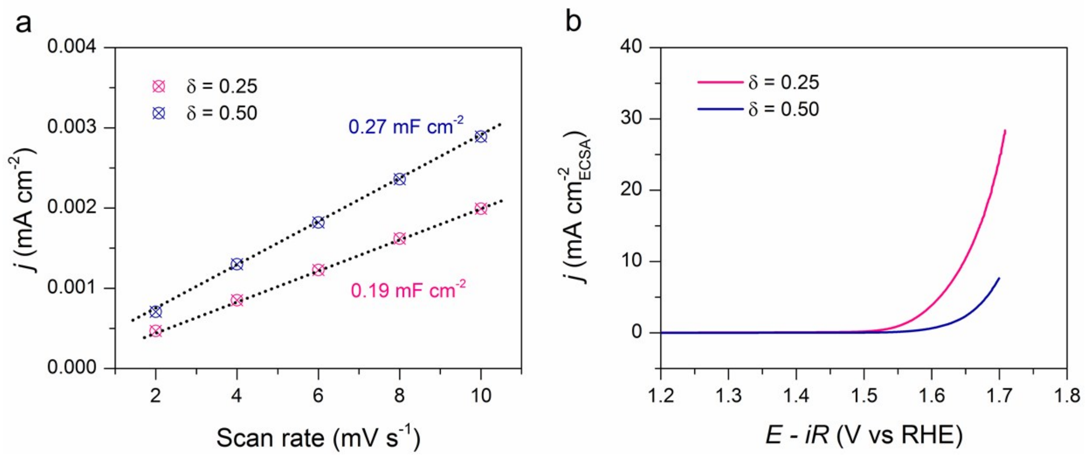

Fig. S8 (a) The capacitive current density for $PrBaCo_2O_{6-\delta}$ at 1.17 V vs RHE was plotted against scan rates. The linear slope that is the double-layer capacitance (C_{dl}) was used to estimate the electrochemically active surface areas (ECSAs). (b) OER specific activity for $PrBaCo_2O_{6-\delta}$ normalized by ECSAs.

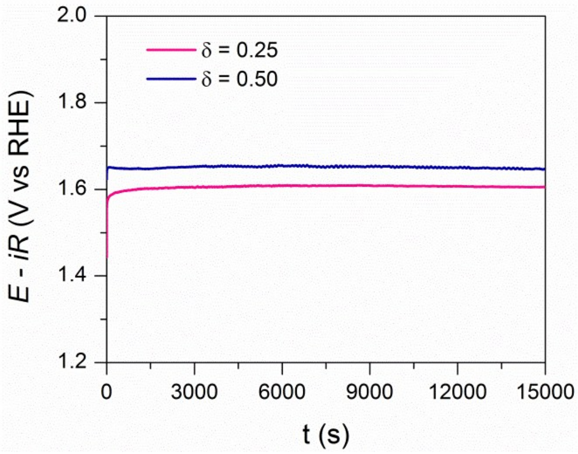

Fig. S9 Chronopotentiometric measurements for $PrBaCo_2O_{6-\delta}$ at a current density of 10 mA cm^{-2}.

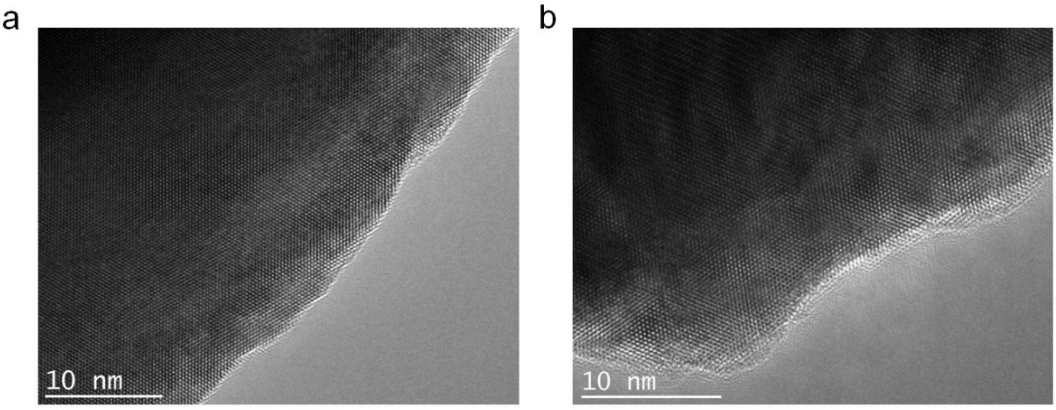

Fig. S10 HRTEM images for (a) $PrBaCo_2O_{5.75}$ and (b) $PrBaCo_2O_{5.5}$ after the OER test.

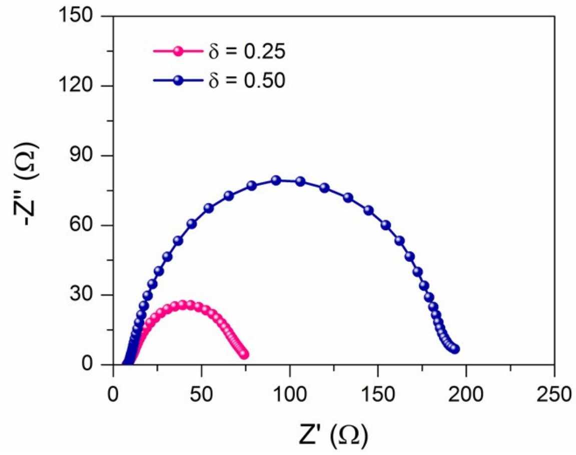

Fig. S11 Nyquist plots for $PrBaCo_2O_{6-\delta}$ at 1.6 V vs RHE.

Table S1. Lattice parameters *a*, *b*, and *c*, volume of the unit cell (*V*), and agreement factors *R* for $PrBaCo_2O_{5.75}$ and $PrBaCo_2O_{5.5}$ from the Rietveld refinements.

Smaples	**$PrBaCo_2O_{5.75}$**	**$PrBaCo_2O_{5.5}$**
Space group	*P4/mmm*	*Pmmm*
a (Å)	3.9005(8)	3.9066(8)
b (Å)	3.9005(8)	7.8737(5)
c (Å)	7.6389(1)	7.6049(4)
V (Å^3)	116.217(5)	233.922(1)
R_p (%)	14.6	13.2
R_{Bragg} (%)	5.2	8.1

References

(1) K. Conder, E. Pomjakushina, A. Soldatov and E. Mitberg, *Mater. Res. Bull.*, 2005, **40**, 257–263.