# Supporting information

# **Experimental details**

Synthesis of Pr<sub>0.5</sub>Ba<sub>0.5</sub>MnO<sub>3-6</sub>. Original PBM powders were synthesized by a complexing process with ethylene diamine tetraacetic acid (EDTA) and citric acid (CA). Stoichiometric amounts (molar ratio) of corresponding salts, i.e.,  $Pr(NO_3)_3 \bullet 6H_2O(AR)$ ,  $Ba(NO_3)_2(AR)$ , and  $Mn(CH_3COO)_2 \bullet 4H_2O(AR)$ , were mixed thoroughly in deionized water, followed by adding CA and EDTA as the complexing agents for the metal ions. The molar ratio of CA, EDTA and total metal ions was 2:1:1. The pH of the solution was controlled to  $\sim 6$  by mixing NH<sub>3</sub> aqueous solution to guarantee full complexation. The solution was heated continuously at 80 °C to allow water evaporation until the gelation. The gel was pretreated at 250 °C for 5 h to fully remove water and form black solid precursors which were then heated to 1100 °C at the heating rate of 5 °C min<sup>-1</sup>, and sintered at this temperature for 10 h in ambient air. Synthesis of  $PrBaMn_2O_{5+\delta}$ . The A-site ordered H-PBM was obtained by annealing PBM in reducing H<sub>2</sub> at 800 °C for 15 h.

**Preparation of carbon-supported catalyst inks.** Vulcan Carbon XC-72 was used as the conducting support for the perovskite oxides. Catalysts with various mass ratio of perovskite oxide to carbon were prepared, i.e. 1:3, 1:1, and 3:1. A typical catalyst ink consists of 10 mg of catalyst (perovskite oxide and carbon), 0.1 mL Nafion solution

(perfluorinated resin solution, 5 wt.%, Sigma Aldrich), and 1.9 mL ethanol. Finally the mixture was treated ultrasonically for 30 min.

### **Basic characterizations**

The morphology and structure characterizations of both PBM and H-PBM were carried out by transmission electron microscopy (TEM) and by high-resolution TEM (HRTEM) (JEM-2010F). Specimens for TEM and HRTEM characterizations were prepared by dispersing a suspension in ethanol on a carbon-coated copper grid. Energy dispersive X-ray spectroscopy (EDS) equipped with the TEM was conducted in order to record the atomic ratio of prepared materials. The structure and crystal phase analysis were carried out by powder X-ray diffractometer (PXRD, Empyrean PANalytical) using Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) at 40 kV and 40 mA. The surface elemental compositions and the change of oxidation state of transition metal ion were examined by X-ray photoelectron spectroscopy (XPS, PHI 5600) using Al monochromatic ray at 350 W. Average oxidation state of transition metal ion (Mn ion) in the sample was determined by iodometric titration. Thermogravimetric analysis (TGA) was conducted (TA Instruments Q500) with a heating rate of 10 °C min<sup>-1</sup> in flowing air.

#### **Electrochemical characterization**

A three-electrode cell configuration with a rotating ring disk electrode device (RRDE-

3A, ALS Co., Ltd.) was utilized to evaluate electrochemical performance. The rotating working electrode substrate was a glassy carbon disk with an area of 0.126 cm<sup>2</sup>. A platinum wire (with a radius of 0.25 mm) was employed as the counter electrode, with a reference electrode of Ag/AgCl. 10 µL of the homogeneously dispersed solution (~0.4 mg cm<sup>-2</sup>) was then loaded to the polished glassy carbon electrode, and dried by air. Commercial Pt/C (20 wt.%) and RuO<sub>2</sub> catalysts (Sigma Aldrich) with identical loading were also evaluated for comparison. KOH solution (0.1 M) was prepared as the electrolyte for both ORR/OER measurements. Linear sweeping voltammetry (LSV) was controlled using an ALS2325E, ALS Co., Ltd. potentiostat. To decompose the  $H_2O_2$ , the potential offset on the ring electrode was selected to be 0.4 V when ORR currents were measured. OER currents were obtained by taking an average between positive and negative scans at a scan rate of 5 mV  $s^{-1}$ , and ORR currents were recorded from 1 to 0.3 V vs. RHE (negative scan) at a scan rate of 5 mV s<sup>-1</sup>. The OER current densities were also corrected by subtracting the electrolyte resistance.

# **Figures and tables**



Fig. S1 TEM characterization: (a) TEM image, (b) High-resolution TEM image, and (c) corresponding fast-Fourier transformed pattern for PBM; (d) TEM image, (e) High-resolution TEM image, and (f) corresponding fast-Fourier transformed pattern for H-PBM.



Fig. S2 TEM-EDS of (a) PBM and (b) H-PBM

(3)
Table S1 Atomic contents obtained from EDS for PBM and H-PBM

	PBM	H-PBM
Mn	29.54 %	29.59 %
Ba	15.57 %	13.98 %
Pr	16.03 %	14.37 %



Fig. S3 XPS characterization: (a) Survey spectra for PBM and H-PBM; (b) high-resolution scan of the Mn 2p core level spectra.



Fig. S4 TG analysis of PBM and H-PBM in air from RT to 800 °C. From the curve it is observed that the mass weight of H-PBM is increased with the increase of temperature, which can be attributed to the introduction of gaseous oxygen to the lattice.

(6)



Fig. S5 The potential conversion between Ag/AgCl and RHE. The RHE correction is conducted in 0.1M KOH solution. Pt wire and Ag/AgCl performed as the working

electrode and reference electrode, respectively. The CV curve was scanned at the rate of 1 mV s<sup>-1</sup>. From the average potential of two intersection points where the current curve crosses "zero", we can obtain:

$$E(RHE)=E(Ag/AgCl)+1.07V$$



Fig. S6 ORR activities for (a) PBM/C and (b) H-PBM/C with different mass ratios (1:3, 1:1 and 3:1). For all the catalysts, the mass loadings are the same, i.e.,  $\sim 0.4$  mg cm<sup>-2</sup>. The scan rate is 5 mV s<sup>-1</sup>.



Fig. S7  $N_2$  adsorption-desorption isotherm curves for (a) PBM and (c) H-PBM;

Corresponding pore size distribution for (b) PBM and (d) H-PBM.

(8)



Fig. S8 RRDE measurement for (a) PBM/C and (c) H-PBM/C (mass ratio = 1 : 3); The corresponding electron transfer number (black line) and peroxide concentration (blue line) are shown in panel (b) and (d).



Fig. S9 ORR and OER stabilities of (a, b) PBM/C and (c, d) H-PBM/C in 0.1 M KOH for over 1000 cycles. Cycles are scanned at the rate of 0.2 V s<sup>-1</sup> and the LSV are swept at 0.005 V s<sup>-1</sup>. <sup>1</sup>

## **References:**

1 Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat Mater*, 2011, **10**, 780-786.

(10)