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Electronic Supplementary Information

A Highly Active, CO₂-tolerant Electrode for Oxygen Reduction Reaction

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Experimental details

Preparation of $PrBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$ (PBCC) powder

PBCC powder was fabricated by a citric nitrate solution combustion method. Stoichiometric amounts of high-purity praseodymium nitrate hydrate, barium nitrate hydrate, calcium nitrate hydrate, and cobalt nitrate hydrate (all from Alfa Aesar) were dissolved in DI water to form a solution of $PrBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$. A stoichiometric amount of citric acid was added as a complexing agent and the fuel for subsequent self-combustion. The powder was then fired at 1000 °C for 2 h.

Fabrication and characterization of pulsed laser deposition (PLD) model thin films:

To avoid the complication introduced by the surface microstruture, thin films prepared by PLD were used as a model system instead of porous electrode. PBCC thin film (100 nm) was grown on 8 mol% Y_2O_3 -doped ZrO₂ (YSZ) (001) single crystal substrate. The PLD growth were carried out at 700 °C under oxygen pressure of 10 mTorr. A KrF excimer laser with a wavelength of 248 nm, energy of 400 mJ per pulse and a pulse frequency of 10 Hz was used for the deposition. The target substrate distance was set to be 7 cm. The films were cooled down to room temperature in 2 torr oxygen pressure with a cooling rate of 5 °C min⁻¹. A SDC buffer layer (~4 µm) was deposited between YSZ and PBCC to avoid the undesired chemical reactions.

Fabrication of symmetrical cells and single cells:

SDC pellets were prepared by uniaxially pressing commercially available SDC powders (Fuelcell Materials, US) followed by sintering at 1450 °C for 5 h to achieve relative density of ~98%. BZCYYb powder was fabricated by a solid state reaction method. LSCF (Fuelcell Materials, US) or PBCC green tapes were prepared by tape-casting, which were then bound onto both sides of a

SDC electrolyte pellet using a slurry of SDC (function as buffer layer). The cells were then co-fired at 1080 °C for 2 h to form porous LSCF or PBCC electrodes (with an area of 0.316 cm²). The SDC powder was synthesized using a chemical co-precipitation process. The SDC powder was then dispersed in acetone with V-006A (Heraeus, US) as binder and ball-milled for 24 h to form a stable SDC slurry.

Tape-casted NiO/BZCYYb anode support was first fabricated and pre-fired at 1000 °C for 2 h. Then, a NiO/BZCYYb functional layer (~15 μ m) and a SDC electrolyte (~30 μ m) were sequentially deposited on the anode support by a particle suspension coating process followed by co-firing at 1400 °C for 5 h. PBCC cathode was screen-printed onto the surface of SDC electrolyte. The cells were then co-fired at 1000 °C for 2 h to form porous hybrid cathode (with an area of 0.316 cm²).

Characterization of Phase composition and Microstructure of Cathode:

Phase structure of PBCC was examined by X-ray diffraction (XRD, Panalytical Empyrean). The microstructure and morphology of the cells were examined using a scanning electron microscope (SEM, LEO 1530) or scanning transmission electron microscope (STEM, Hitachi HD-2700).

Electrochemical measurements:

The area specific resistances (*ASR*) of cathodes were measured in a two electrode symmetrical cell configuration using two pieces of Ag mesh as current collector (without Pt paste to avoid its possible contribution to catalytic activity) at 600-750 °C. Impedance spectra were acquired using a Solartron 1255 HF frequency response analyzer interfaced with an EG&G PAR potentiostat model 273A with an AC amplitude of 10 mV in the frequency range from 100 kHz to 0.1 Hz. The button cells were mounted on an alumina supporting tube for fuel cell testing at 600-750 °C, with

humidified hydrogen (3% H_2O) as the fuel and ambient air or air containing 1% CO_2 as the oxidant. The cell performance was monitored with an Arbin multi-channel electrochemical testing system.

In situ surface enhanced Raman spectroscopy (SERS)

Raman spectra were obtained using a Renishaw RM 1000 spectra-microscopy system (~2 µm spot size). An air-cooled Ar laser emitted at 514 nm was used for excitation of the Raman signal with a total power of 10 mW. For in situ Raman analysis, a customized Harrick environmental chamber was used to control the temperature, gas atmosphere, and electrical biases on model thin film electrodes. A quartz window sealed with BUNA O-ring allows the passage of excitation laser and Raman scattered photons. Lenses with focal lengths >8 mm were used to allow a sufficient distance between the lens and the sample surface. The stainless steel jacket of the chamber was cooled with running water. The Ag nanoparticles with a SiO₂ shell (abbr. Ag@SiO₂) were fabricated to provide enhanced Raman sensitivity at elevated temperatures. To form the Ag seeds, 0.75 g of polyvinyl pyrrolidone (PVP, $Mw = \sim 55000 \text{ g mol}^{-1}$) was fully dissolved in 3 mL of anhydrous ethylene glycol (EG, 99.8%) and then mixed with 0.25 g of AgNO₃. The resulting solution was kept at 120 °C for 1 h under vigorous stirring in which AgNO₃ was reduced to Ag nanoparticles. Afterward, 20 mL of ethanol was added to form homogeneous Ag colloidal suspension. Prior to the application of SiO₂ coating, 1 mL of concentrated NH₄OH was added into the Ag suspension to create a suitable basicity for SiO₂ growth. Then, 0.3 mL of tetraethyl orthosilicate (TEOS) was introduced into the suspension of Ag seeds to develop a uniform encapsulation of SiO₂ on Ag, after letting set for 1 hour. Afterward, Ag@SiO₂ core @ shell nanoparticles were extracted from the colloidal solution by repeated centrifugation at 6000 rpm with ethanol and D.I. water. After each centrifuge step, the supernatant liquid was decanted to remove excess organic precursors.

Computational details

Periodic density functional theory (DFT) calculations were performed by means of the Vienna ab initio simulation package (VASP)^{1,2} with the projector-augmented-wave (PAW) method³. Similar to the previous studies,⁴ all of calculations were carried out using the spin-polarization method with the Perdew-Burke-Ernzerhof (PBE)⁵ exchange-correlation functional since the concurrent optimization of two effective U parameters (Ueff) of two B-site cations could cause incorrect results. For the bulk structure optimization, La_{0.5}Sr_{0.5}Co_{0.5}Fe_{0.5}O₃ (LSCF; La₂Sr₂Co₂Fe₂O₁₂; Pnma) and PrBa_{0.75}Ca_{0.25}CoO₆ (PBCC; Pr₄Ba₃Ca₁Co₈O₂₄; P4/mmm) were used similar to the previous studies⁶. While Monkhorst-Pack meshes⁷ with the $(3 \times 3 \times 3)$ and $(3 \times 3 \times 1)$ were applied for bulk and surface calculations, respectively, a kinetic energy cutoff for a plane wave basis set of 415 eV was used. For the surface calculations, slabs were separated by a vacuum space of 10 Å to avoid any interactions between slabs. The adsorption energy (E_{ad}) of CO₂ on a surface was calculated by $E_{ad} = E[CO_2$ -surface] – (E[surface] + E[CO_2]), where E[CO_2-surface] and E[surface] are the predicted electronic energies for an adsorbed CO₂ species on a surface and its bare surface, respectively. E[CO₂] is that for gas-phase carbon dioxide. For the Raman activity simulations, DMol³ module^{8, 9} as implemented in the Materials Studio package was used with GGA-PBE exchange-correlation functional coupled with the double numerical polarization (DNP) 3.5 basis and the effective core potentials (ECP).



Figure S1 Temperature of surface exchange coefficient (a) and bulk diffusion coefficient (D) of PBCC (red ball) and LSCF (black ball)



Figure S2 XRD patterns of PBCC cathode (using SDC electrolyte) after testing with CO₂ concentration of 1% (green line), 5% (red line) and 10% (black line). It suggested that some impurities (most likely carbonate) were formed after testing with 10 % CO₂ for 208h, while little change can be detected after testing with 1%, consistent with previous electrochemical data.



Figure S3 Setup for single cell testing



Figure S4 Glancing angle incidence XRD of top surface of PBCC film (red line), indicating that the surface of PLD film is likely poly-crystalline.



Figure S5 (a) In situ SERS spectra of LSCF and PBCC pellet surface at 500 °C in atmosphere of pure O₂ or O₂ with 10% CO₂; (b) Intensity of carbonate peak of (~1060cm⁻¹) observed from LSCF and PBCC pellets surface.



Figure S6. The bulk structures of (a) LSCF $(La_{0.5}Sr_{0.5}Co_{0.5}Fe_{0.5}O_3)$ $(La_2Sr_2Co_2Fe_2O_{12}; Pnma)$ and (b) PBCC $(PrBa_{0.75}Ca_{0.25}CoO_{6.0})$ $(Pr_4Ba_3Ca_1Co_8O_{24}; P4/mmm)$ predicted at GGA-PBE. An orthorhombic type structure is used for LSCF, while a double-layered structure is for $Pr_4Ba_3Ca_1Co_8O_{24}$.



Figure S7. 2-D surface models of (a) CoO-terminated PBCC(010), LaSrO-terminated LSCF(010), and (c) CoFeO-terminated LSCF(010).



Figure S8. Cluster models for Raman activity simulations using DMol³ generated from CO_2 adsorption on LaSrO-terminated LSCF (010) as shown in Figure 6. To save the computational time, only the two top-most layers with the adsorbate CO_2 from the optimized structure of CO_2 adsorption on LaSrO-terminated LSCF(010) (see Figure 6) was applied by increasing its size. Only single-point energy calculations were carried out for predicting the Raman activity without any relaxation.



Figure S9. The bulk structure of SrCO₃ (*R*-3*C*; a = b = 5.1509, c = 17.6112) at GGA-PBE using VASP.



Figure S10. (a) Side view of LSCF(001). (b) CO_2 interaction with LaFeO-terminated LSCF(001) and (c) CO_2 interaction with SrCoO-terminated LSCF(001), and (d) the formation of SrCO₃-like layers on LSCF(001).

To examine the formation of SrCO₃-like layers, the La and Fe ions of the top-most LaFeO layer on LaFeO-terminated LSCF(001) (**Figure S10 b**) were replaced by Sr ions, and then one more Sr-CO₃ layer was added, followed by optimization. LaFeO-terminated LSCF(001) produces a carbonate species, while the SrCoO-terminated surface has molecular CO₂ adsorption. Similar to the LSCF(010) surface, the Sr-segregation effect from LSCF(001) (see **Figure S10 d**) also supports that the SrCO₃ formation may result in the growth of the SERS data at ~1,060 cm⁻¹.

No	Reaction	$\Delta H_R(kJ/mol)$	Remark
1	$SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$	985.6	LSCF
2	$FeO(s) + CO_2(g) \rightarrow FeCO_3(s)$	665.6	LSCF
3	$CoO(s) + CO_2(g) \rightarrow CoCO_3(s)$	631.5	LSCF, PBCC
4	$BaO(s) + CO_2(g) \rightarrow BaCO_3(s)$	941.7	PBCC
5	$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$	1028.6	PBCC

Supporting Information Table S1. Heat of reactions of the reactions of CO₂ and SrO, FeO, CoO, BaO, and CaO forming carbonates using thermodynamic data from Aspen Plus V8.8.

Supporting Information Table S2. Adsorption energies of CO_2 on LSCF and PBCC(010) surfaces using VASP.

Surface	Termination	Adsorption energy (eV)	*Surface energy (J/m ²)	Remark
LSCF(010)	LaSrO	-2.23		With one oxygen vacancy
LSCF(010)	LaSrO	-1.25	-1.03	
LSCF(010)	CoFeO	-0.88	-1.06	
PBCC(010)	CoO	-0.73		

*. Only the half of the top-most layers were relaxed for these surface energy calculations.

Supplementary Reference:

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