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Supporting information

Triggering interfacial activity of traditional $La_{0.5}Sr_{0.5}MnO_3$ cathode with Co-doping for proton-conducting solid oxide fuel cells

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Experimental section

$La_{0.5}Sr_{0.5}MnO_3$ (LSM) and $La_{0.5}Sr_{0.5}Mn_{0.9}Co_{0.1}O_{3-\delta}$ (LSMCo) powders were prepared by a traditional wet chemical method.[1-2] Thermal treatment of 1000 °C for 3 h was applied for LSM and LSMCo powders to reach a pure phase. The phase purity of the powders was examined X-ray diffraction (XRD). High-resolution transmission electron microscopy (HR-TEM, JEM-2100F) coupled with the energy-dispersive X-ray spectroscopy (EDS) was used to measure the samples' morphologies and the elemental distributions. The stability of the LSMCo powder was examined in both CO_2 and H_2O-containing conditions. Regarding the stability test against CO_2, the LSMCo powder was treated in the CO_2-containing condition with the CO_2 concentration of 10%, and the high-temperature in-situ XRD was employed to record the phase composition of the LSMCo powder under the CO_2 condition. The chemical stability of the LSMCo in the steam condition was carried out by treating the LSMCo powder in a 30% H_2O -containing atmosphere at 700 °C and the ex-situ XRD was employed to compare the phase composition of the powder before and after the steam treatment.

To compare the performance of LSM and LSMCo cathodes in H-SOFCs, half-cells using the $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BCZY) electrolyte and NiO-BCZY anode were prepared. The proton conductor $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY) was used as the proton-conducting phase in the composite cathode. Then different cathodes, including LSM, LSMCo, LSM-BZY, and LSMCo-BZY, were deposited on the surface of the sintered BCZY electrolyte to form the H-SOFC using the LSM single-phase cathode, LSMCo single-phase cathode, LSM-BZY composite cathode, and LSMCo-BZY composite cathode. The cathode slurry was consisted of the cathode powder, terpineol and ethyl cellulose in a weight ratio of 10 : 10 : 1. The complete cells were co-sintered in a microwave sintering furnace at 900 ^{o}C for 10 min. The chemical compatibility between LSMCo and BZY was examined by using the in-situ XRD to study the phase composition of LSMCo-BZY mixed powder from room temperature to 1000 ^{o}C. All these assembled cells were tested in the fuel cell working condition using H_2 as the fuel and static air as the oxidant. The electrochemical performance of the cells was recorded with an electrochemical workstation (Squidstat Plus, Admiral Instrument).

Theoretical calculations were carried out by using the density functional theory (DFT) method [3-5] with the VASP (Vienna ab initio simulation package) software.[6, 7] All calculations were performed with a cutoff energy for the valence electrons of 500 eV, in a (4x4x4) gamma centered K-point mesh. The calculations were made to compare the oxygen vacancy formation energy, hydration energy, and proton migration energy between LSM and LSMCo. The interfacial properties were calculated by constructing the structure of LSM/BZY and LSMCo/BZY. The calculation details can be found in previous studies.[8-10]

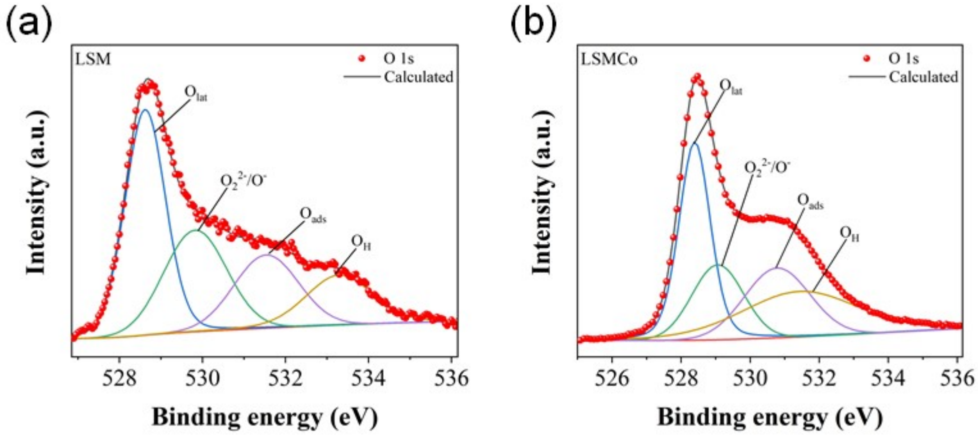

Figure S1. XPS O 1sspectra for (a) LSM and (b) LSMCo.

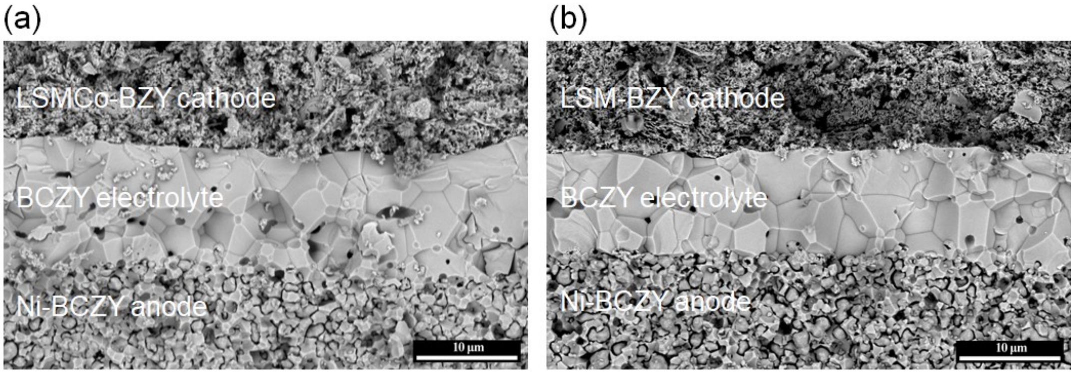

Figure S2. Cross-sectional view for the H-SOFC using (a) LSMCo-BZY composite cathode and (b) LSM-BZY composite cathode.

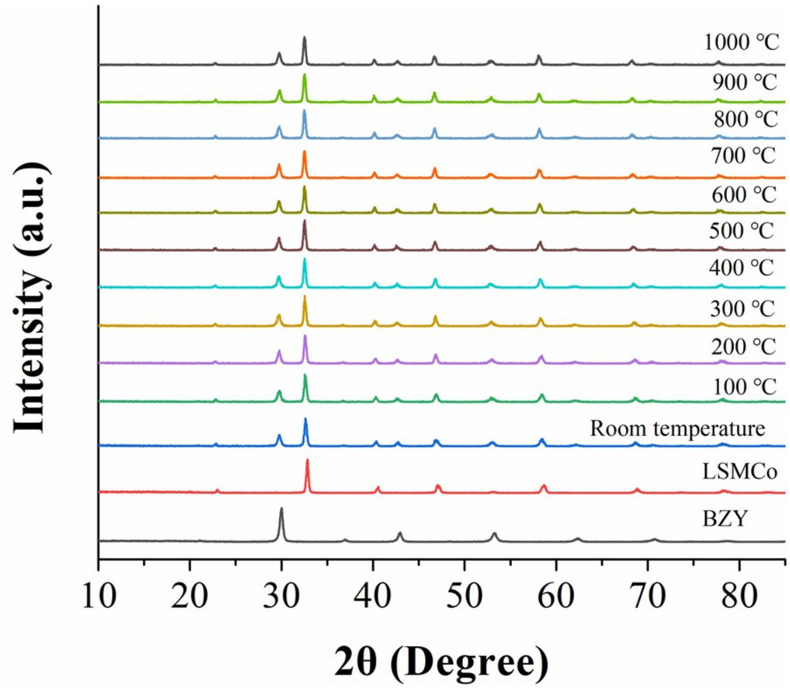

Figure S3. XRD patterns for the BZY-LSMCo composite powder measured by the in-situ XRD at different temperatures. The XRD patterns of the synthesized BZY and LSMCo are added as the reference.

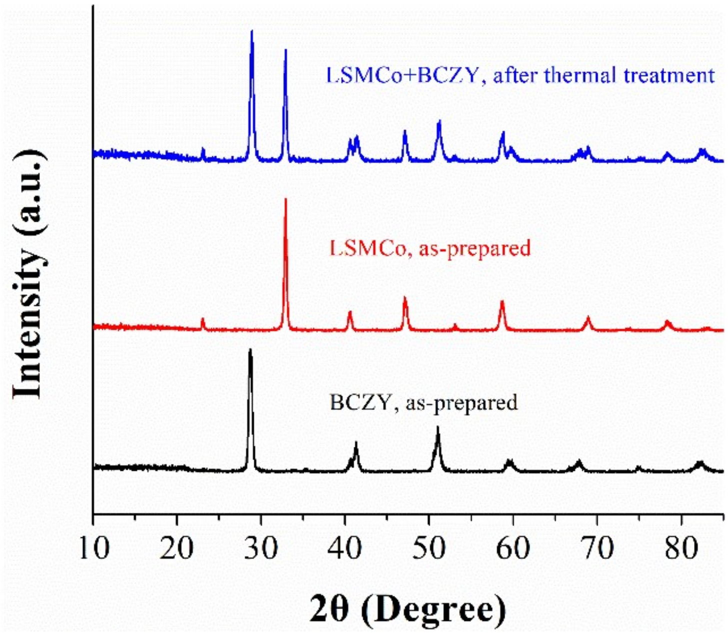

Figure S4. XRD patterns for the as-prepared BCZY and LSMCo powders and for the LSMCo+BCZY composite powder after co-firing in a microwave sintering furnace at 900 ^{o}C.

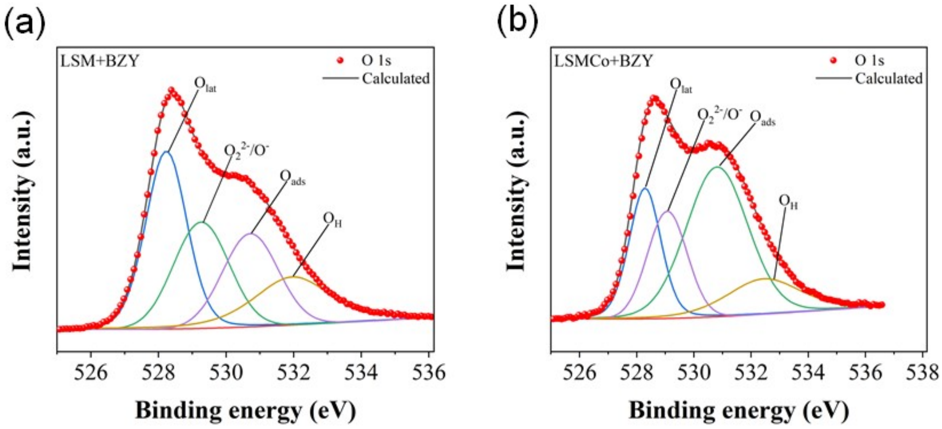

Figure S5. XPS O 1sspectra for (a) LSM+BZY composite cathode and (b) LSMCo+BZY composite cathode.

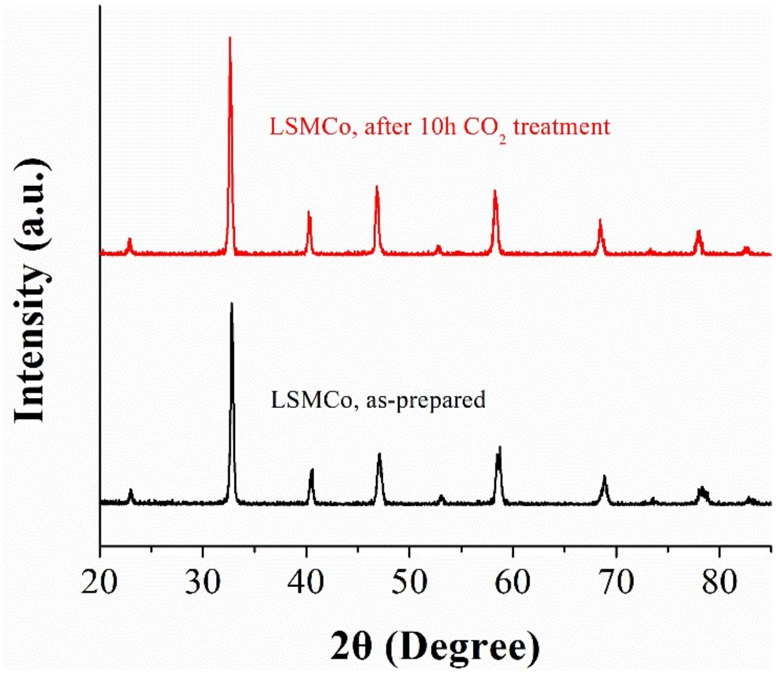

Figure S6. XRD patterns for the as-prepared LSMCo powder and for the LSMCo powder after the treatment in 10% CO_2 condition at 700 °C for 10 h.

References

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