Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

$BaTb_{0.3}Fe_{0.7}O_{3-\delta}$: a new proton-conductor-derived cathode for proton-conducting solid oxide fuel cells

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Experimental section

$BaTb_{0.3}Fe_{0.7}O_{3-\delta}$ (BTF) and $BaZr_{0.3}Fe_{0.7}O_{3-\delta}$ (BZF) powders were synthesized by a wet chemical route, using metal nitrates as the starting materials. Citric acid was used as the complexing agent. The preparation details can be found in our previous studies.[1, 2] The powder was calcined at 1000 ^{o}C for 3 h to achieve pure phase. The phase purity of the powders was examined by using X-ray diffraction (XRD). The morphology and the elemental distributions of the BTF powder were observed by scanning transmission electron microscopy (STEM, JEM-2100F). To test the stability of the powders, BFT and BZF powders were placed in the furnace under the flowing CO_2 atmosphere. The concentration of the CO_2 gas was 20% and the rest was air. The samples were kept in the CO_2-containing atmosphere at 600 ^{o}C for 10 and then the phases of the BFT and BZF powders were examined by XRD. X-ray photoelectron spectroscopy (XPS) analysis for both BTF and BZF powders was carried out to explore the valence state of the cations. The diffusion and surface exchange ability of oxygen-ions and protons for BTF and BZF were investigated by using the electrical conductivity relaxation (ECR). Dense BTF and BZF bars were prepared and the testing atmosphere was changed from dry air to dry 50%O_2 or dry air to wet air to explore the oxygen (proton) diffusion coefficient and oxygen (proton) surface exchange coefficient for BTF and BZF.

To evaluate the performance of BTF as the cathode for proton-conducting solid oxide fuel cells (H-SOFCs), anode-supported $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BCZY) half-cells were fabricated by the conventional co-pressing and co-sintering method and the co-sintering temperature was set at 1300 ^{o}C and the details can be found in our previous

study.[3] The single-phase BTF cathode was deposited on the sintered BCZY electrolyte surface, followed by a co-firing procedure at 900 °C for 10 min in the microwave sintering furnace. Then, the cell was tested with H_2 as the fuel and static air as the oxidant. The identical half-cell with BZF as the cathode was also tested under the same condition for comparison. The electrochemical performance of the cell was recorded using an electrochemical workstation ((Squidstat Plus, Admiral Instruments). The morphologies of the tested cell were observed using a scanning electron microscopy (SEM, Phenom XL).

Density functional theory (DFT) calculations were carried out by using VASP (Vienna ab initio simulation package).[4, 5] All calculations were performed with a cutoff energy for the valence electrons of 500 eV, in a (4x4x4) gamma centered K-point mesh. The oxygen vacancy formation energies for BTF and BZF were calculated according to $E_{vo} = E_{defect} + \frac{1}{2}E_{O_2} - E_{perfect}$, where E_{vo} is the oxygen vacancy formation energy; E_{defect} is the total energy of defective bulk,; E_{O_2} is the energy of molecular oxygen; and $E_{perfect}$ is the total energy of the stoichiometric bulk. More details for the DFT calculations can be found elsewhere.[6]

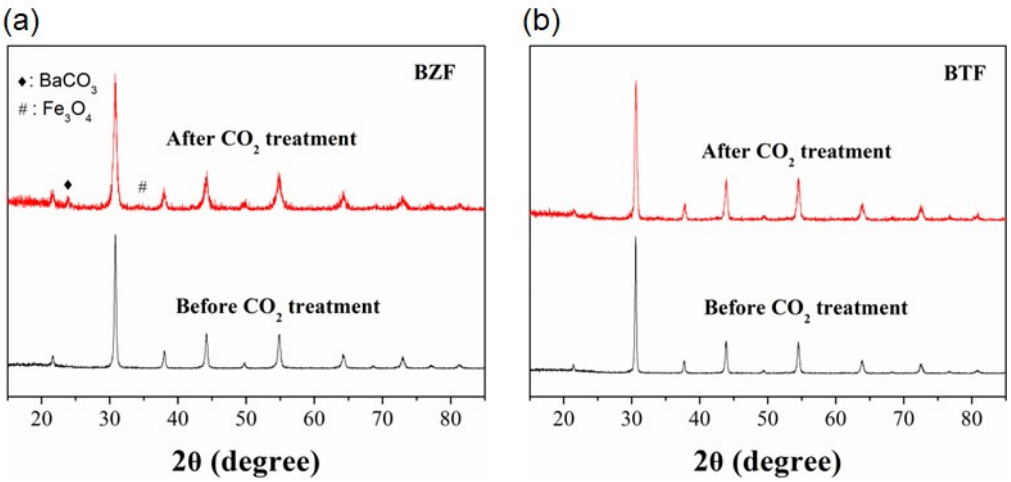

Figure S1. XRD patterns for (a) BZF and (b) BTF before and after the treatment in 20% CO_2 at 600 °C for 10 h.

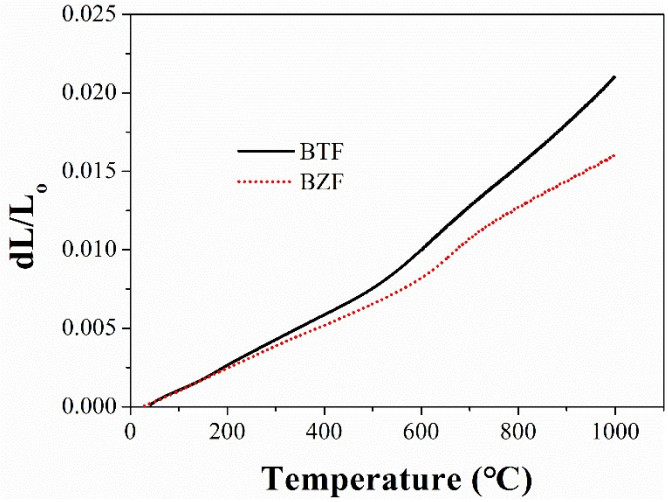

Figure 2. TEC curves for BZF and BTF.

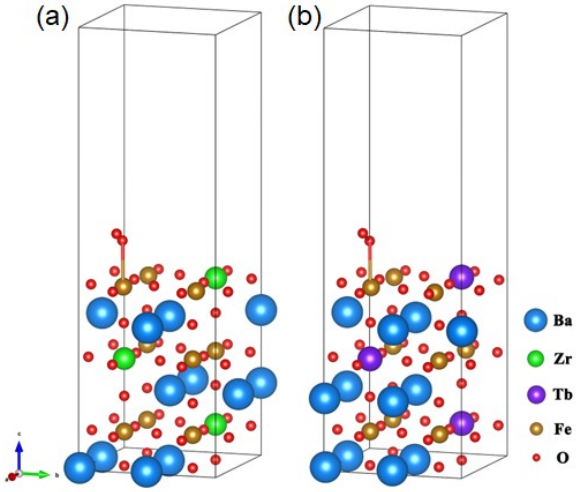

Figure 3. O_2 adsorption model for (a) BZF and (b) BTF.

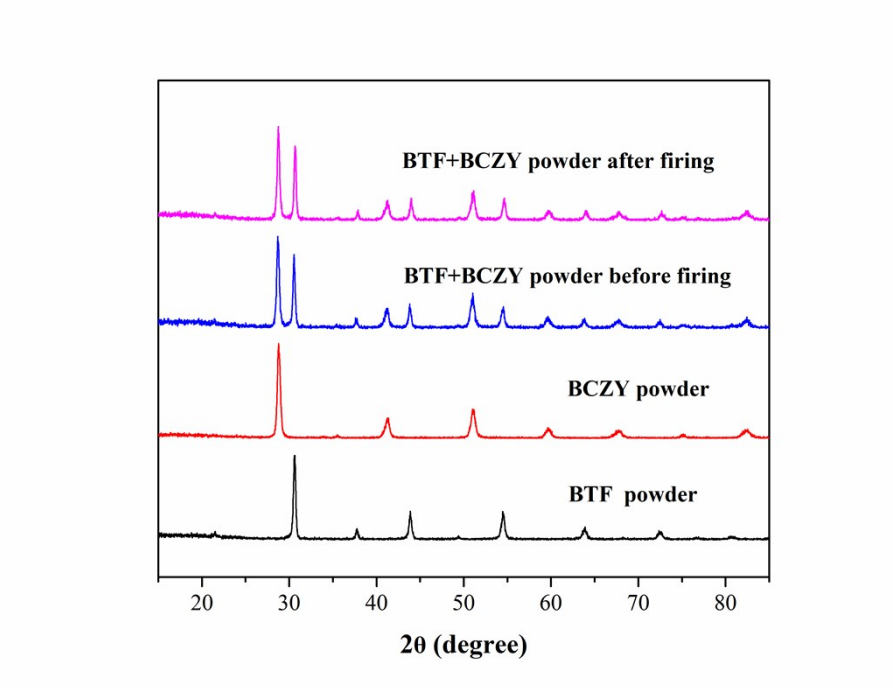

Figure 4. XRD patterns for BTF+BCZY composite powder before and after firing. The XRD patterns for BTF and BCZY are also added as the reference.

References

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