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Electronic Supplementary Information

Enhanced stability of Zr-doped Ba(CeTb)$O_{3-\delta}$-Ni cermet membrane for hydrogen separation

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Experimental section

The $BaCe_{0.85}Tb_{0.05}Zr_{0.1}O_{3-\delta}$ (BCTZ) perovskite powder was prepared through the glycine-nitrate combustion process. $Ba(NO_3)_2$, $Ce(NO_3)_3$, $Tb(NO_3)_3$, $ZrO(NO_3)_2$ and glycine were used as the raw materials to form an aqueous solution in their appropriate stoichiometric ratios. The molar ratio of glycine: total metal ions was 2:1. After evaporation of excess water at 200 ^oC with stirring, the aqueous solution became a viscous liquid and further heating up to 400 ^oC caused the auto-combustion process, which produced the BCTZ precursor ash. The BCTZ powder with perovskite structure was obtained after calcining at 1000 ^oC for 5 h. The as-prepared BCTZ powder was also treated in Ar and 50% H_2-50% Ar atmosphere at 800 ^oC for 20 h. The Ni-BCTZ cermet membrane was synthesized by mixing the BCTZ oxide powder and the commercial metallic nickel powder in a weight ratio of 1:1 followed by sintering at 1400 ^oC for 10 h in Ar atmosphere.

X-ray diffraction (XRD, D8 Advance, Bruker-AXS, with Cu-Ka radiation) was used to determine the phase structure. Data sets were recorded in a step-scan mode in the 2θ range of 20 - 90^o with intervals of 0.02^o. The phase analysis was carried out using the database of Powder Diffraction File (PDF) of International Centre of Diffraction Data (ICDD). The lattice parameters were calculated through structure Rietveld refinement by the program TOPAS (Bruker, version of 4.2). The morphology of the fresh and spent Ni-BCTZ cermet membrane were characterized by scanning electron microscopy (SEM) at 2 keV and by energy dispersive X-ray spectroscopy (EDXS) at 15 keV using a Jeol-JSM-6700F. The element distribution in the grains of the cermet membrane was studied on the same electron microscope by EDXS with Oxford Instruments INCA-300 EDX spectrometer at 15 keV.

Thermogravimetric analysis was conducted to study the stability of the BCT and BCTZ powder in N_2 atmosphere with NETZSCH-STA449C apparatus. The samples were heated in N_2 atmosphere at a rate of 5°C/min before holding at 800°C for 30 min.

Hydrogen temperature-programmed reduction (H_2-TPR) was carried out in a U-type quartz tube reactor to identify the chemical reduction properties of all the samples. Sample powder was loaded in a U-type quartz tube and pretreated under a 10% H_2-90% Ar atmosphere at a flow rate of 20 ml/min for 30 min at room temperature. The temperature was then increased from room temperature to 800 ^{o}C at a ramp rate of 10 ^{o}C/min. The consumption of hydrogen was monitored by an in situ thermal conductivity detector (TCD) using a micromeritics-AutoChem II, Chemisorption Analyzer.

For the hydrogen permeation measurement, a disk-shaped dense Ni-BCTZ cermet membrane with 0.5 mm thickness was used. The ceramic sealant was used to seal the membrane with an alumina tube to form the permeation compartment. 30 ml/min of 50% H_2 diluted with He were used as feed gas and 60 ml/min of Ar was used as sweep gas. Composition of the permeated effluent gas was measured using an online coupled gas chromatograph (GC, Agilent 6890, Ar as carrier gas) with a thermal conductivity detector (TCD). The concentration of the helium in the sweep side due to the imperfect sealing at high temperatures was less than 0.1% during all the experiments.

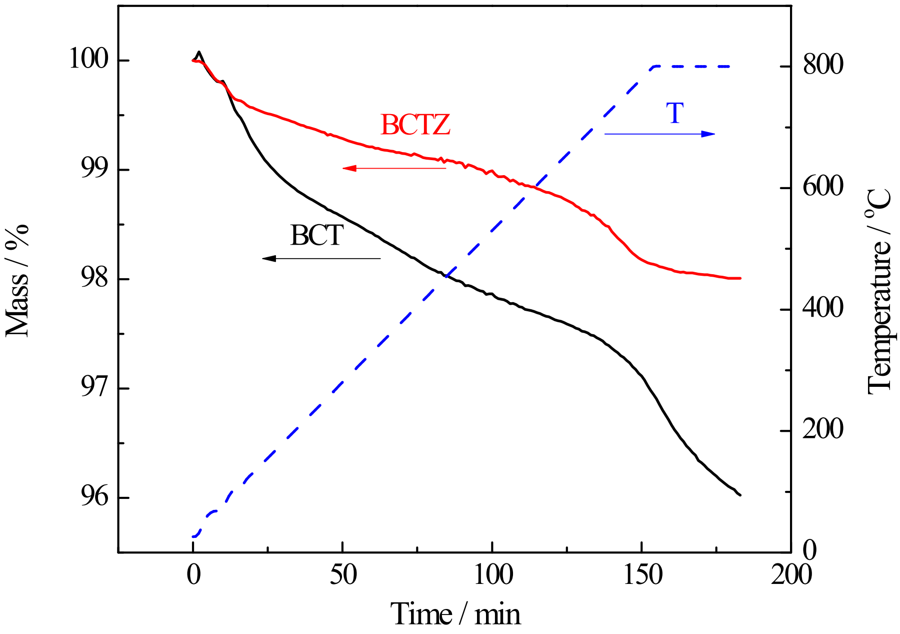

Figure S1. Thermo-gravimetric curves of BCT and BCTZ powder samples in N_2 atmosphere.

The mass of both BCT and BCTZ powder slightly decreased in the N_2 atmosphere as the temperature increased. The slight weight loss potentially resulted from dehydration and the release of oxygen from the perovskite oxides. It can be found that compared with BCT, the weight loss of BCTZ is more slight which indicates the better stability of the oxide.

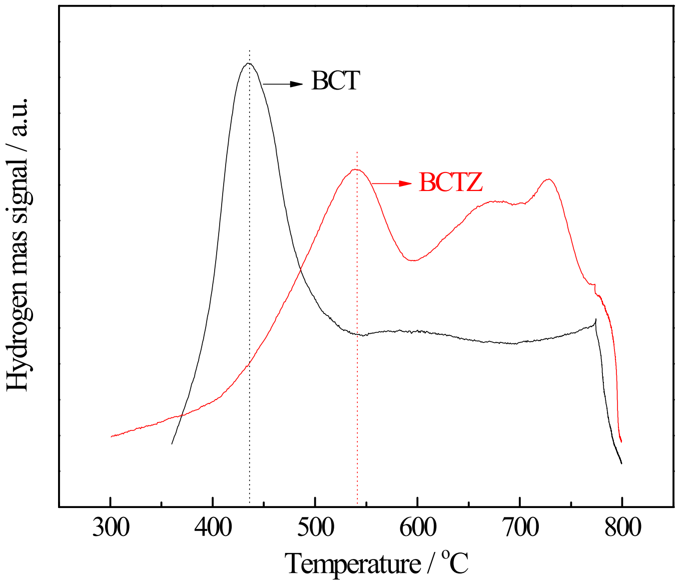

Figure S2. H_2-TPR profiles of BCT and BCTZ samples.

As shown in Figure S2, for the BCT sample, a big reduction peak can be observed at approximately 434 °C, which is related to the reduction of Ce^{4+} to Ce^{3+} in the lattice. Compared to BCT, the reduction peak of BCTZ sample has been moved to a higher temperature, the first reduction peak centered at 539 °C can be attributed to the surface Ce^{4+} reduction to Ce^{3+}, and the other broad peak located between 658 °C to 729 °C can be attributed to the bulk Ce^{4+} reduction to Ce^{3+}.[1,2] It can be found from the H_2-TPR results that Zr-doping makes the reduction peak appearing at higher temperature, which indicates that Zr-doping enhances the stability of BCT in the reducing atmosphere.

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[1] Y. Liu, R. Ran, S. Li, Y. Jiao, M. O. Tade, Z. Shao. Significant performance enhancement of yttrium-doped barium cerate proton conductor as electrolyte for solid oxide fuel cells through a Pd ingresse-egress approach. J. Power Sources 257 (2014) 308-318.

[2] C. Decarne, E. Abi-aad, B. G. Kostyuk, V. V. Lunin, A. Aboujais. Characterization of cerium and copper species in Cu-Ce-Al oxide systems by temperature programmed reduction and electron paramagnetic resonance. J. Mater. Sci. 39 (2004) 2349-2356.

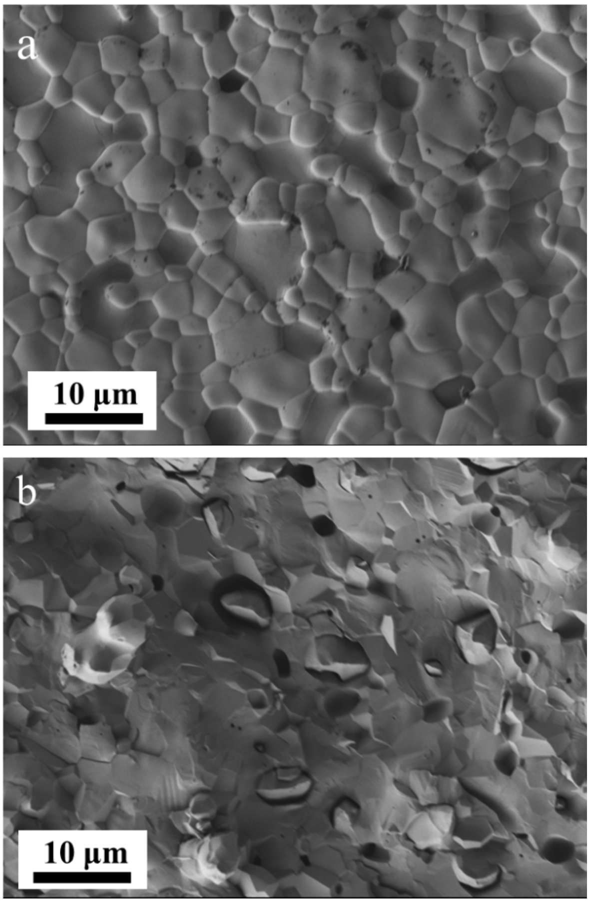


Figure S3. SEM micrographs of (a) the surface and (b) the bulk of the as-calcined Ni-BCTZ cermet membrane.

The SEM images of both the bulk and surface of the Ni-BCTZ cermet membrane (see Figure S3) indicates that it becomes a dense membrane after sintering at 1400 ^{o}C for 10 h. It can also be found that the grain size of Ni particles (around 3-7 µm) is a little bigger than that of BCTZ particles (about 2-5 µm). The EDXS elemental distribution (Figure S4c, d and g, h) of both the surface and bulk of the Ni-BCTZ membrane shows the homogeneous distribution of the Ni and the perovskite BCTZ oxide phase, which demonstrates that the metallic nickel and the BCTZ oxide are well mixed. A good homogeneity of the cermet membrane is important for its hydrogen transportation because it guarantees the formation of a percolation network of the two individual phases for both electron and proton transport.

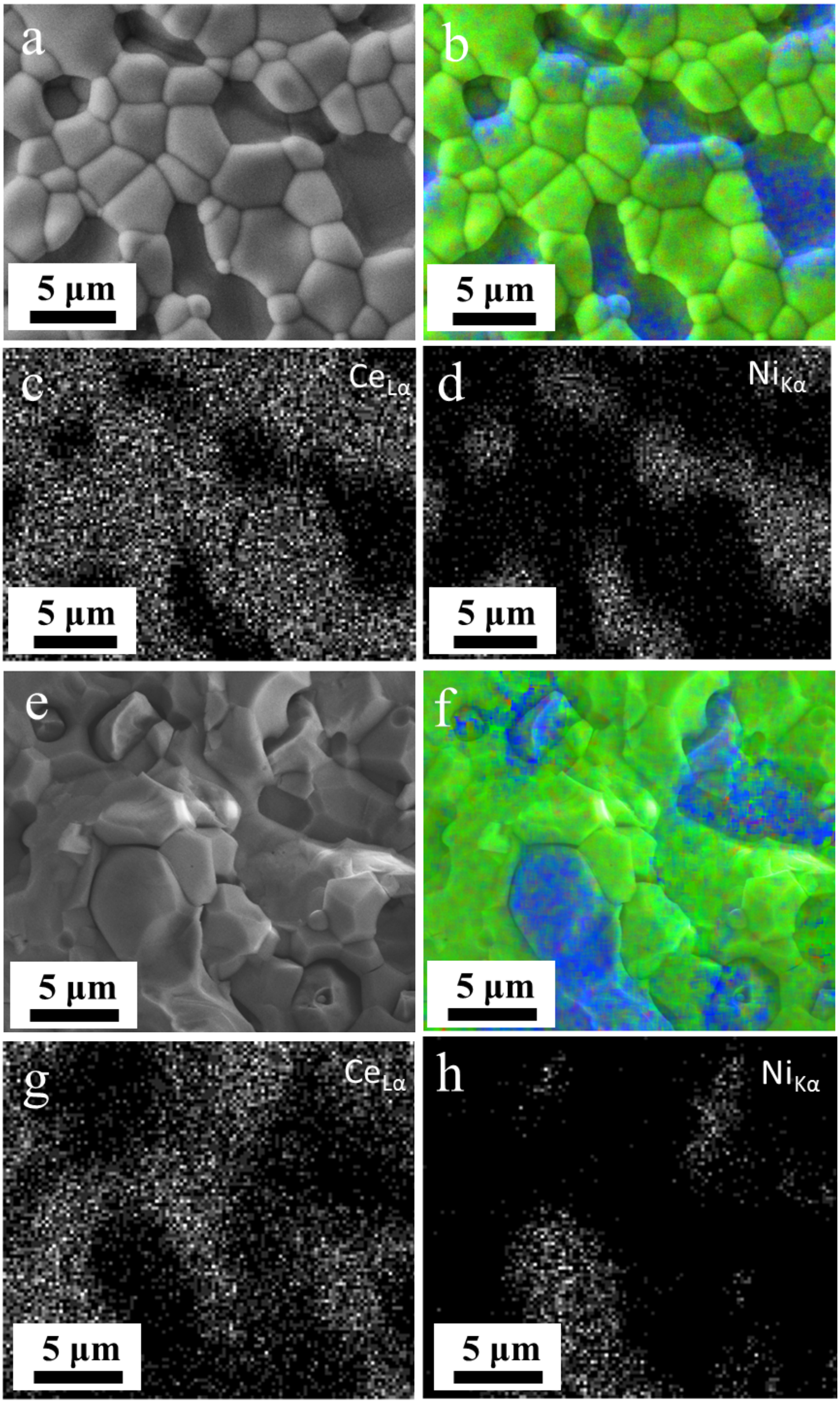


Figure S4. SEM and EDXS elemental distributions of Ce and Ni in (a-d) the surface and (e-h) the bulk of the as-calcined Ni-BCTZ cermet membrane. Blue: metallic Ni phase; green: perovskite oxide phase.

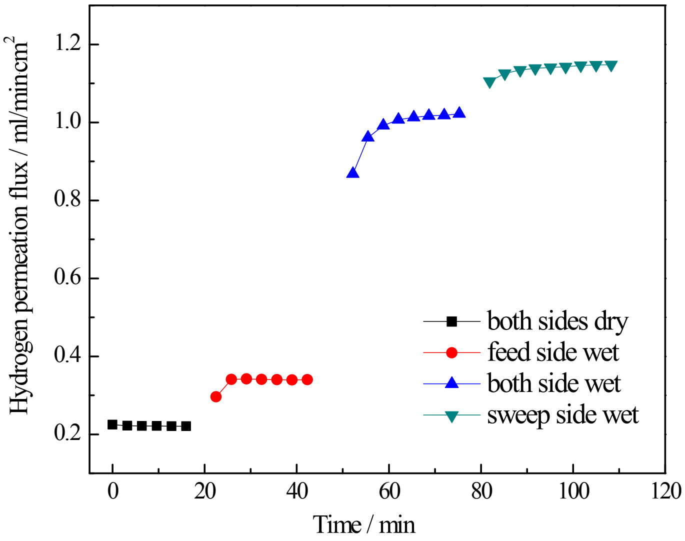


Figure S5. Hydrogen permeation flux variation resulted from the humidity on the feed and sweep sides at 1000 ^{o}C. P_{H2O}=0.03atm.

The hydrogen permeation flux through the Ni-BCTZ cermet membrane is measured as a function of temperature under four different humid conditions as shown in Figures S5 and S6. The hydrogen permeation flux is only 0.22 ml/min·cm^2 when both sides are dry at 1000 ^{o}C, while it increases to 0.34 ml/min·cm^2 when 0.03 atm steam is added to the feed side, which increases the protonic conductivity. This effect can be ascribed to the hydration of the membrane that allows the formation of two protonated oxygen atoms (lattice or interstitial oxygen), which are the essential charge carriers involved in hydrogen transport. The hydrogen permeation flux can even jump over 1 ml/min·cm^2 when 0.03 atm steam is introduced to the sweep side. However, in this case some part of the hydrogen comes from the thermal water splitting.

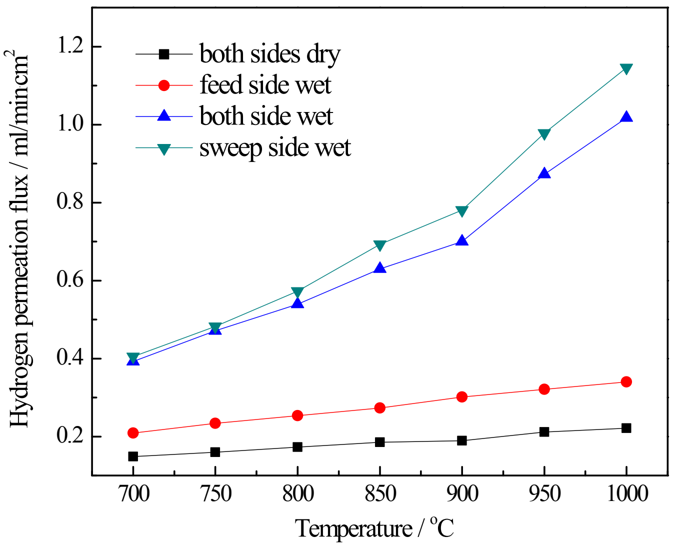


Figure S6. Hydrogen permeation flux as a function of the temperature under four humid conditions. P_{H2O}=0.03atm.

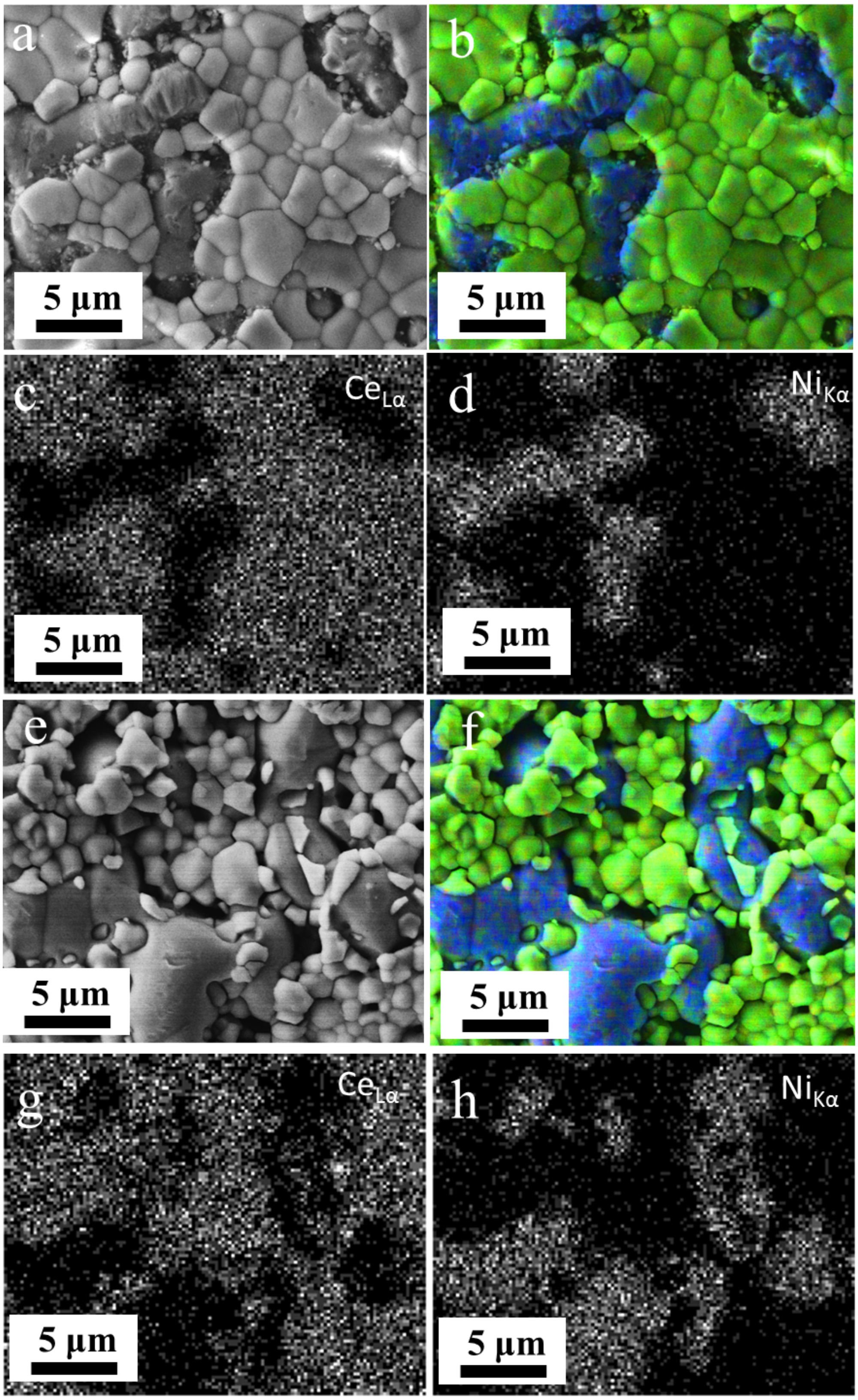
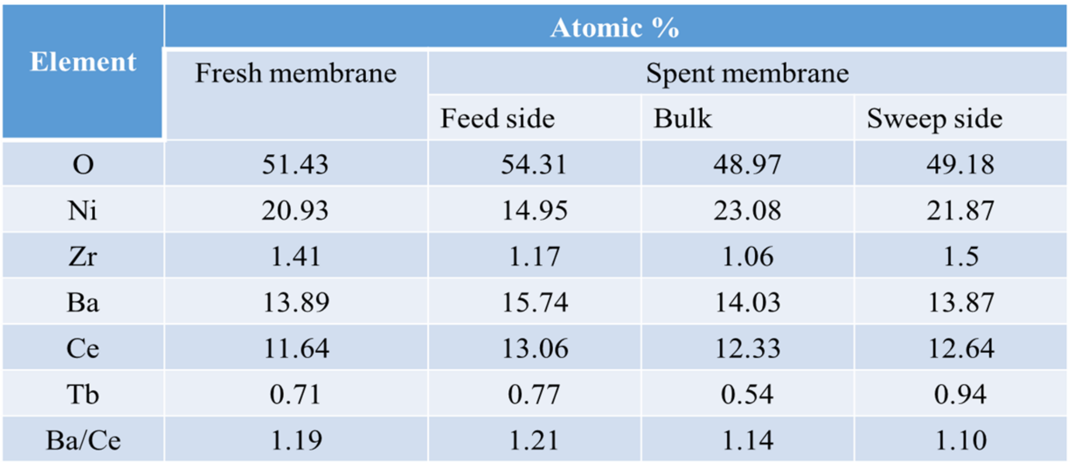


Figure S7. SEM and EDXS elemental distributions of Ce and Ni in the surfaces of the spent Ni-BCTZ cermet membrane after 100 h hydrogen permeation, (a-d) the surface of the feed side; (e-h) the surface of the sweep side. Blue: metallic Ni phase; green: perovskite oxide phase.



Element	Atomic %			
	Fresh membrane	Spent membrane		
		Feed side	Bulk	Sweep side
O	51.43	54.31	48.97	49.18
Ni	20.93	14.95	23.08	21.87
Zr	1.41	1.17	1.06	1.5
Ba	13.89	15.74	14.03	13.87
Ce	11.64	13.06	12.33	12.64
Tb	0.71	0.77	0.54	0.94
Ba/Ce	1.19	1.21	1.14	1.10

Table S1. EDXS results on both surfaces and bulk of the spent and fresh Ni-BCTZ membrane.

The EDXS data of the spent Ni-BCTZ membrane after the long term operation is shown in Table S1. For better comparison, the EDXS results for the fresh membrane has also been given. The ratio of Ba/Ce of the fresh membrane is 1.19, which is close to the theoretical value of 1.18. After the long term hydrogen separation, there is only small change on the Ba/Ce ratio in the spent membrane, which illustrates the good stability of Ni-BCTZ membrane.

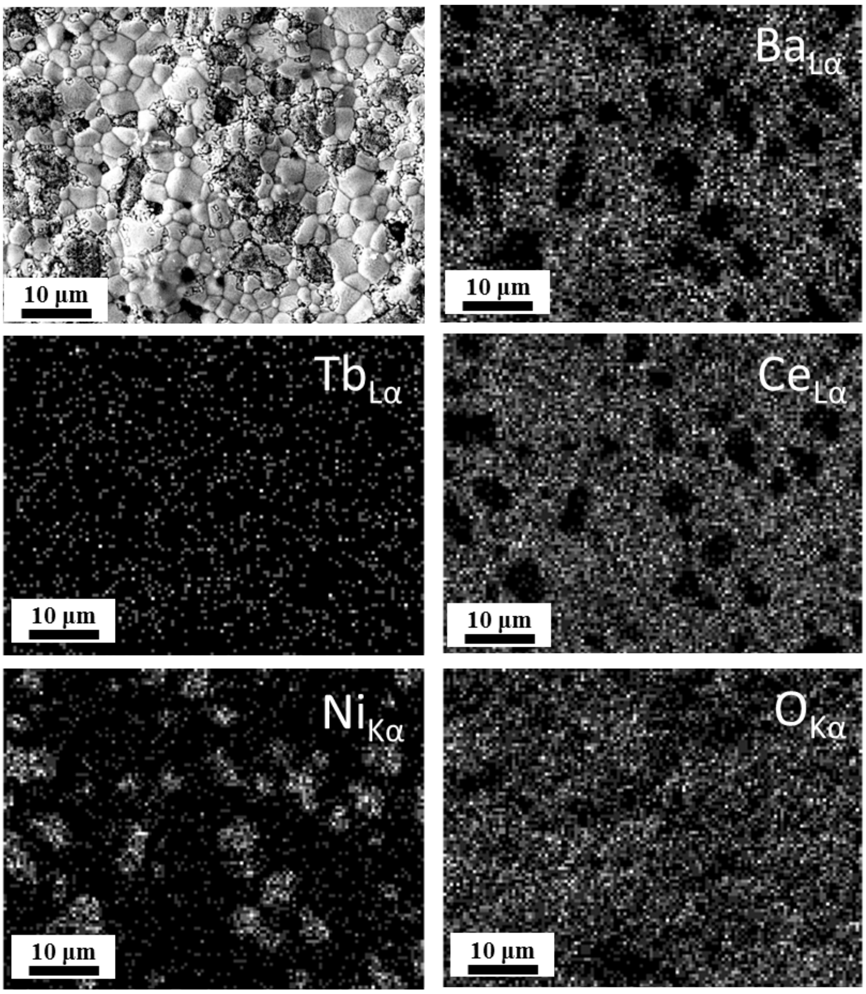


Figure S8. SEM and EDXS elemental distributions on the feed side surface of the spent Ni-BCT cermet membrane.

As shown in Figure S8, although the feed side surface of the spent Ni-BCT membrane still seems to be dense, but there are some coralloid porous structure covered on the surface, especially near the Ni part. On the contrary, it cannot be found on the feed side surface of the spent Ni-BCTZ membrane as shown in Figure S7. For the other side (sweep side) of the spent membrane, it looks like the original intact grain cracked to be many small particles shown in Figure S9, which may attributed to the big change of the lattice cell volume of BCT during the reduction and oxidation processes. Compared with Ni-BCT, the situation of Ni-BCTZ is much better due to the Zr-doping, which restrains the lattice cell expansion in reducing atmosphere and enhanced the phase structure stability.

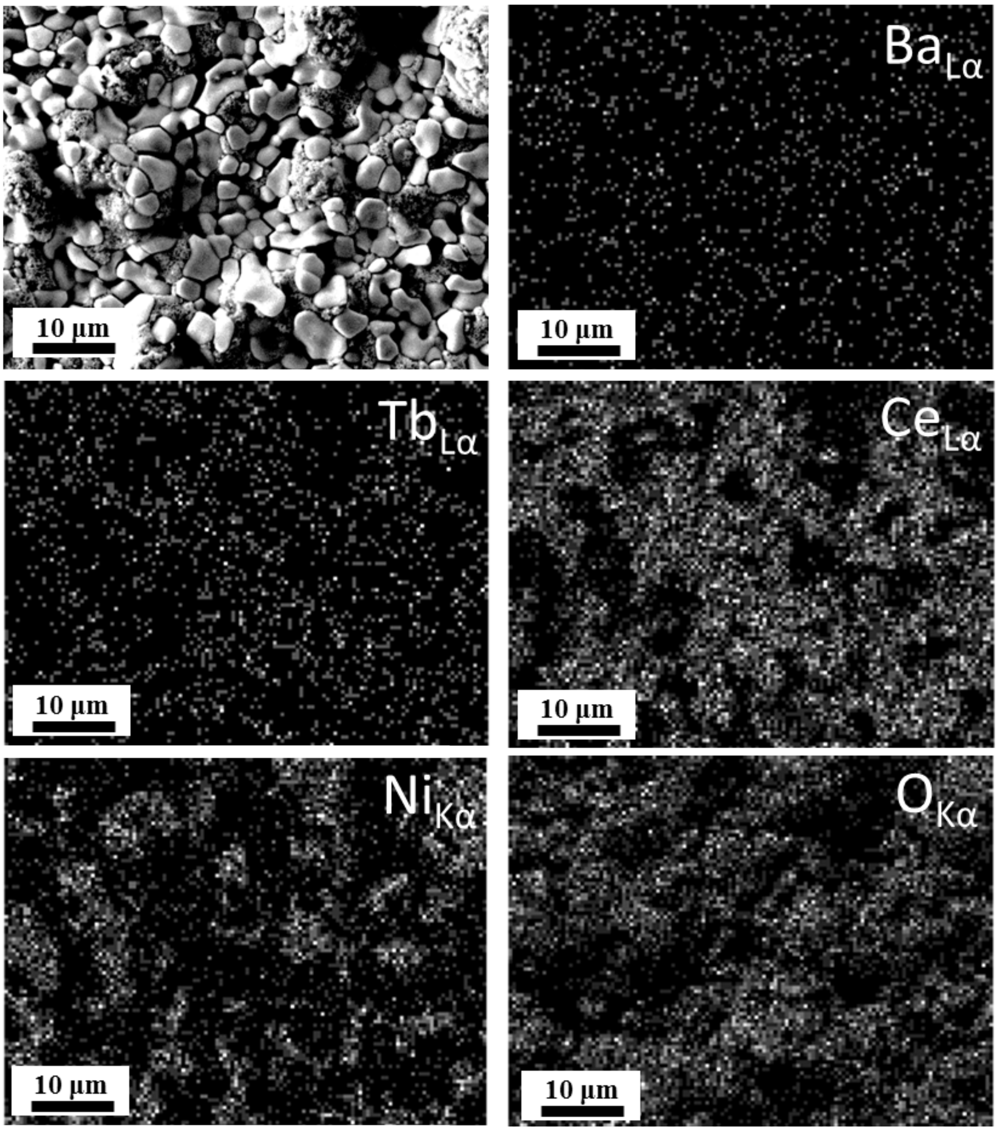
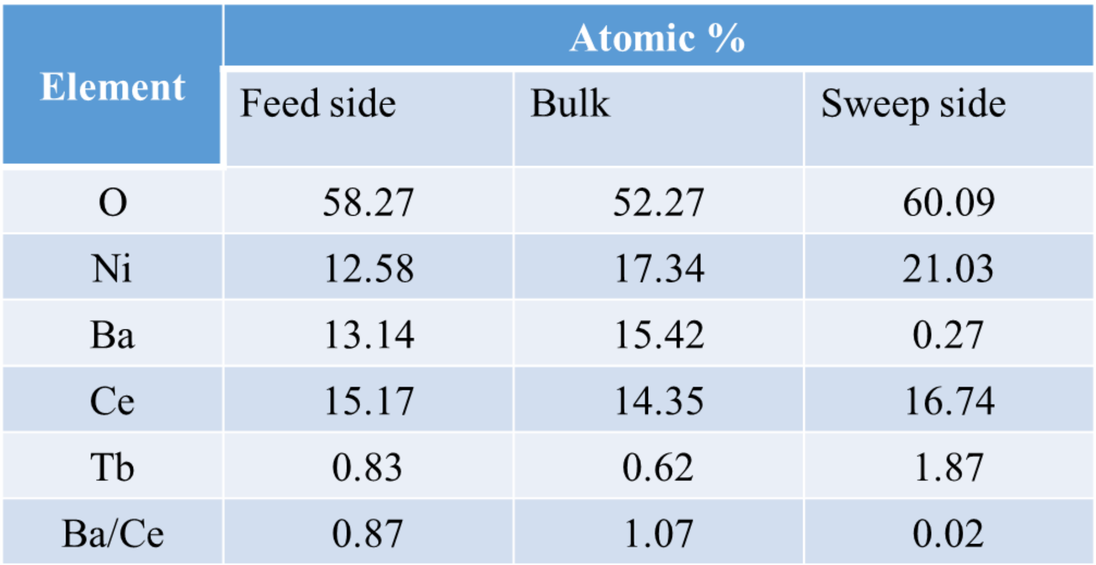


Figure S9. SEM and EDXS elemental distributions on the sweep side surface of the spent Ni-BCT cermet membrane.



Element	Atomic %		
	Feed side	Bulk	Sweep side
O	58.27	52.27	60.09
Ni	12.58	17.34	21.03
Ba	13.14	15.42	0.27
Ce	15.17	14.35	16.74
Tb	0.83	0.62	1.87
Ba/Ce	0.87	1.07	0.02

Table S2. EDXS results on both surfaces and bulk of the spent Ni-BCT membrane.

Table S2 shows the EDXS data of the spent Ni-BCT membrane. In the bulk part, the Ba/Ce ratio is 1.07, which is close to the theoretical value of 1.05. But on the feed side surface, Ce content is higher than Ba content. On the sweep side, there is little Ba can be detected unexpectedly. Combined with the XRD result of the spent Ni-BCT shown in Figure S10, it is obvious that the impurity peak of CeO_2 appears, which is in accordance with the result of Meng's work.[6] In order to check the Ba-lacked layer on the sweep surface, the SEM image and EDXS elemental distributions on the cross section near the sweep side of the spent Ni-BCT membrane are shown in Figure S11. It can be found that a layer with a thickness of around 13 μm connected to the sweep surface, which is really Ba-lacked compared with that in the membrane bulk. It can be resulted from the elements (such as Ce and Tb) migration from the bulk in the reducing atmosphere.

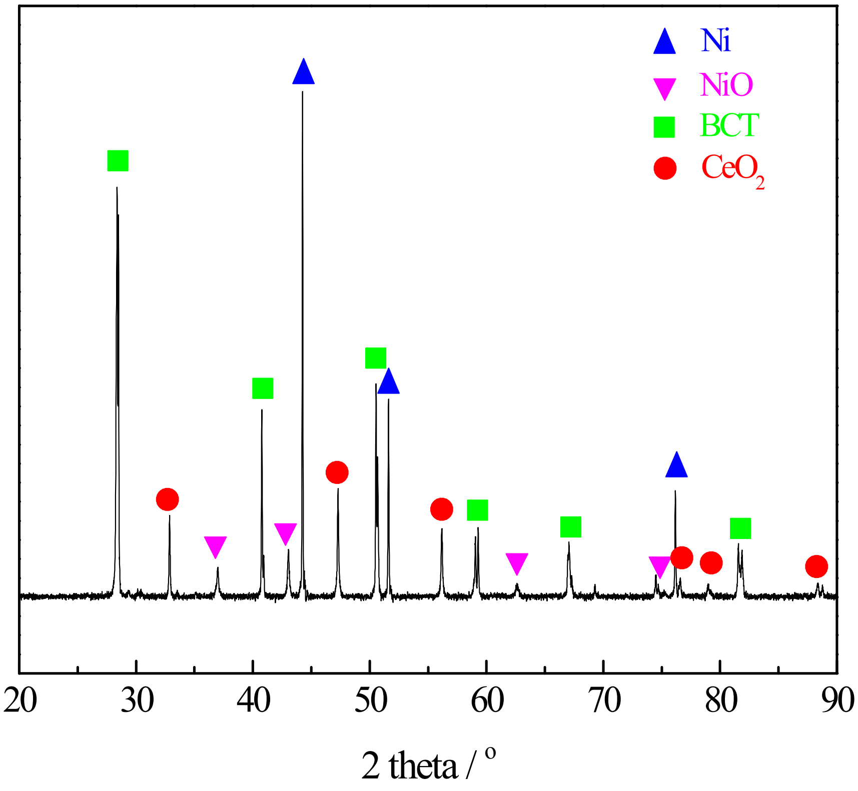


Figure S10. X-ray diffraction pattern of the spent Ni-BCT membrane.

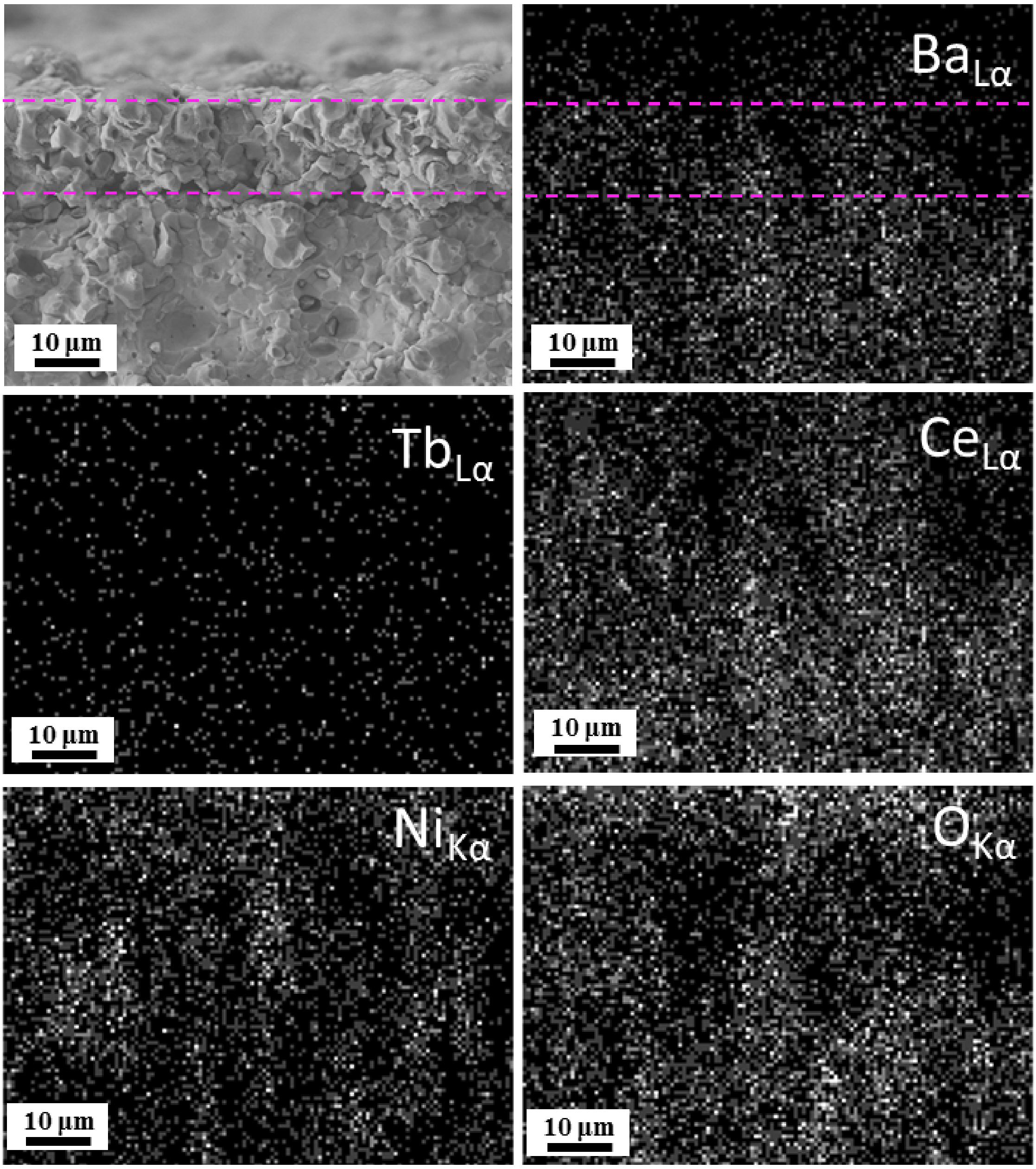


Figure S11. SEM and EDXS elemental distributions on the cross section near the sweep side of the spent Ni-BCT cermet membrane.

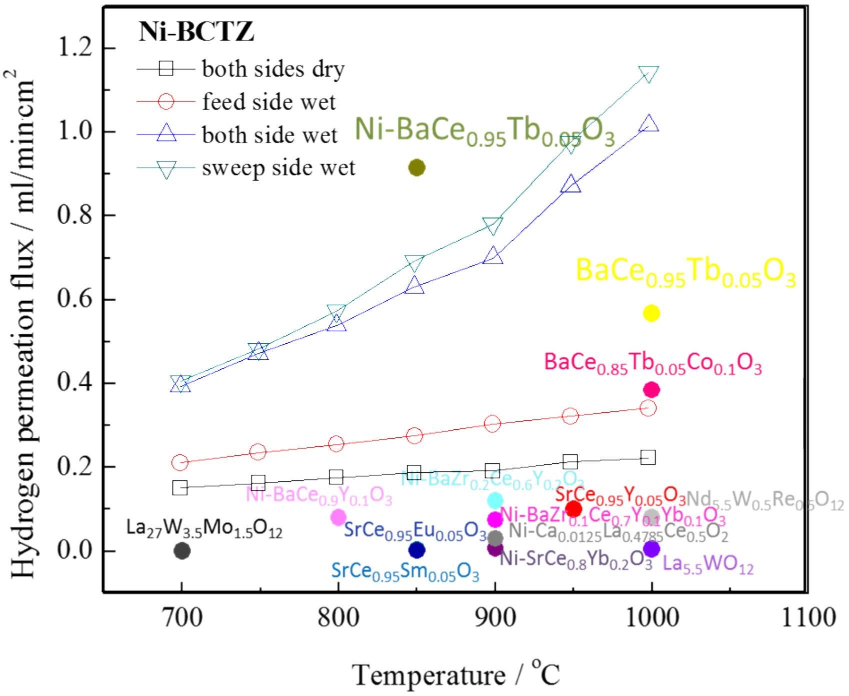


Figure S12. The hydrogen permeation fluxes through various proton conductive membranes at different temperatures.[3-4]

One important thing should be emphasized that among numerous proton conductive oxides for hydrogen separation, there are only a few materials which exhibit both good stability and nice permeation flux. As shown in Figure S12, for different kind of materials, including the perovskite, tungstate, and cermet dual phase materials, most of the proton conductive membrane exhibit the hydrogen permeation fluxes below 0.1 ml/min·cm^2 even at 1000 °C. Compared with these materials, the hydrogen permeation fluxes through the Ni-BCTZ membrane in our work are far above this level, which indicate its attractive hydrogen permeability. On the other hand, from the point of stability, although the fluxes through some

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[3] S. Zhan, X. Zhu, B. Ji,W. Wang, X. Zhang, J. Wang, W. Yang, L. Lin. Preparation and hydrogen permeation of $SrCe_{0.95}Y_{0.05}O_3$ asymmetrical membranes. Journal of Membrane Science 340 (2009) 241–248.

[4] S. Fang, L. Bi, L. Yan, W. Sun, C. Chen, W. Liu. CO_2-Resistant Hydrogen Permeation Membranes Based on Doped Ceria and Nickel. J. Phys. Chem. C 2010, 114, 10986–10991.

Tb-containing membrane, such as $BaCe_{0.95}Tb_{0.05}O_3$, $BaCe_{0.85}Tb_{0.05}Co_{0.1}O_3$, Ni-$BaCe_{0.85}Tb_{0.05}O_3$, are higher than that through Ni-BCTZ, but their fluxes cannot keep steady for more than several hours.[5,6,10] To the contrary, Ni-BCTZ membrane can be operated steadily for over 100 h in both dry and wet reducing conditions. Therefore, in consideration of both hydrogen permeability and stability, Ni-BCTZ is really a promising material candidate for hydrogen separation.