Supporting Information (SI)

## Metal Ion Migration: A New Insight into the H<sup>+</sup>/O<sup>2–</sup> Dual-Ion Transport in Perovskite– Fluorite Composites

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**Figure S1.** EIS results of the pellets (BZCY1, YDC and BZCY1-YDC) tested under: (a) dry air, (b) dry H<sub>2</sub>, (c) wet air, and (d) wet H<sub>2</sub> at 200 °C.



**Figure S2.** Enlarged EIS images of (a) the perovskite samples tested under dry air, (b) YDC tested at dry air, (c) the perovskites tested at wet air, and (d) YDC immersed in wet air. All the results were tested at 450  $^{\circ}$ C.



**Figure S3.** EIS results of the pellets tested at 500 °C under different atmospheres: (a) BZCY at dry air, (b) YDC at dry air, (c) BZCY under wet air and (d) YDC at wet air.



**Figure S4.** EIS results of the samples tested at 550 °C under various atmospheres: (a) BZCY at dry air, (b) YDC at dry air, (c) BZCY at wet air and (d) YDC under wet air.



**Figure S5.** EIS results of the samples under: (a) dry air for BZCY, (b) dry air for YDC, (c) wet air for BZCY, and (d) wet air for YDC, at 600 °C.



**Figure S6.** EIS results of the ceramic pellets tested under different atmospheres: (a) BZCY under dry air, (b) YDC at dry air, (c) BZCY at wet air and (d) YDC under wet air, at 650 °C.



**Figure S7.** EIS results of the as-prepared pellets tested under: (a) dry air, (b) dry  $H_2$ , (c) wet air, (d) wet  $H_2$  at 500 °C.



**Figure S8.** EIS results of the ceramic pellets recorded under: (a) dry air, (b) dry  $H_2$ , (c) wet air, (d) wet  $H_2$ , at 600 °C.



Figure S9. EIS results of YDC ceramic membrane tested under pure H<sub>2</sub> at: (a) 450 °C, (b) 500 °C, (c) 550 °C, and (d) 600 °C.



**Figure S10.** SEM and EDS mapping images focusing on the cross-section of BZCY0.9-YDC.



**Figure S11.** SEM and elemental analysis results under the EDS mapping model focusing on the cross section of BZCY1.1-YDC.



**Figure S12.** TEM-EDS mapping of BZCY0.9-YDC. (a) The grain, and (b) EDS scanning result. EDS of (c) Ba, (d) Ce, (e) Y, (f) O. (g) HRTEM image of the grain, (h) enlarged image of the red square in (g), and (i) lattice-plane spacing scanning result.



**Figure S13** TEM-EDS mapping results of BZCY1.1-YDC: (a) the grain, (b) Ba, (c) Zr, (d) Ce, (e) O, and (f) Y.

Typical	YDC	BZCY0.9	BZCY1	BZCY1.1	BZCY0.9-	BZCY1-	BZCY1.1-
peaks					YDC	YDC	YDC
Fluorite	28.191°				28.289°	28.285°	28.289°
peak							
Perovskite		28.627°	28.536°	28.572°	28.569°	28.547°	28.573°
peak							

Table S1. A comparison between the diffraction values of the typical fluorite and perovskite peaks of different specimens.