Electronic Supplementary Information

Surface Protonic Conduction in Porous Alkaline Earth Zirconate Perovskites $CaZrO_3$, $SrZrO_3$, and $BaZrO_3$

Jie Gu [1], Xinwei Sun [2], Lulu Jiang [1], Zihan Zhang [1], Truls Norby [1,2*], Donglin Han [1,3,4,5*]

[1] College of Energy, Soochow University, No 1 Shizi Street, Gusu District, Suzhou 215006, China

[2] Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Gaustadalléen 21, NO-0349 Oslo, Norway

[3] Provincial Key Laboratory for Advanced Carbon Materials and Wearable Energy Technologies, Soochow University, No 1 Shizi Street, Gusu District, Suzhou 215006, China

[4] Jiangsu Key Laboratory of Advanced Negative Carbon Technologies, Soochow University, Suzhou 215123, China

[5] Light Industry Institute of Electrochemical Power Sources, Shahu Science & Technology Innovation Park, Suzhou 215638, China

* Corresponding authors:

Truls Norby (truls.norby@kjemi.uio.no)

Donglin Han (dlhan@suda.edu.cn)

1. XRD analysis

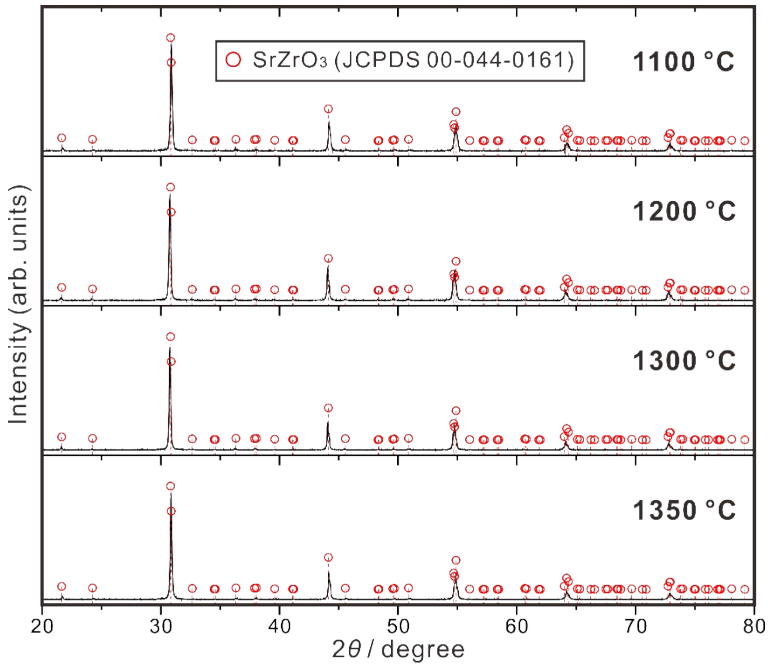

Fig. S1 Room temperature powder XRD patterns of $SrZrO_3$ sintered at 1100, 1200, 1300, and 1350 °C for 24 h in ambient air.

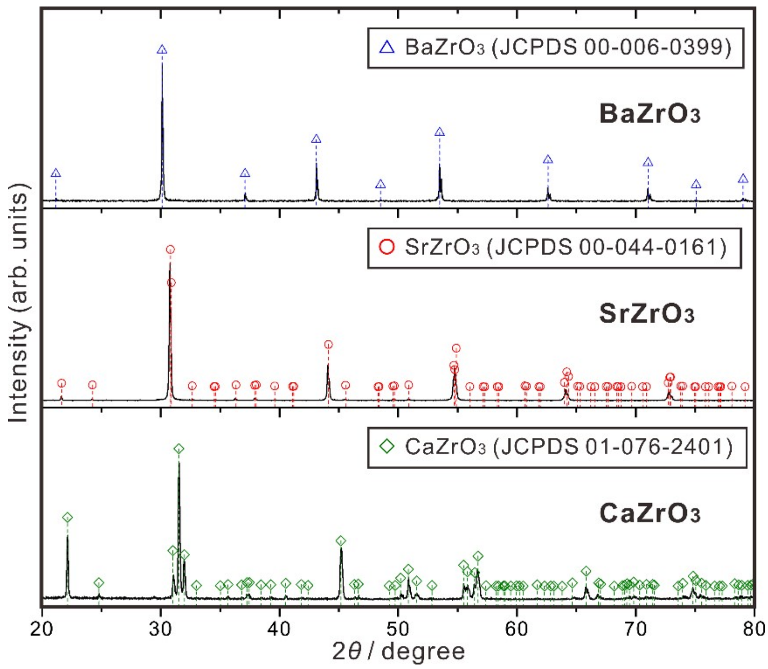

Fig. S2 Room temperature powder XRD patterns of $CaZrO_3$, $SrZrO_3$, and $BaZrO_3$ sintered at 1300 °C for 24 h in ambient air.

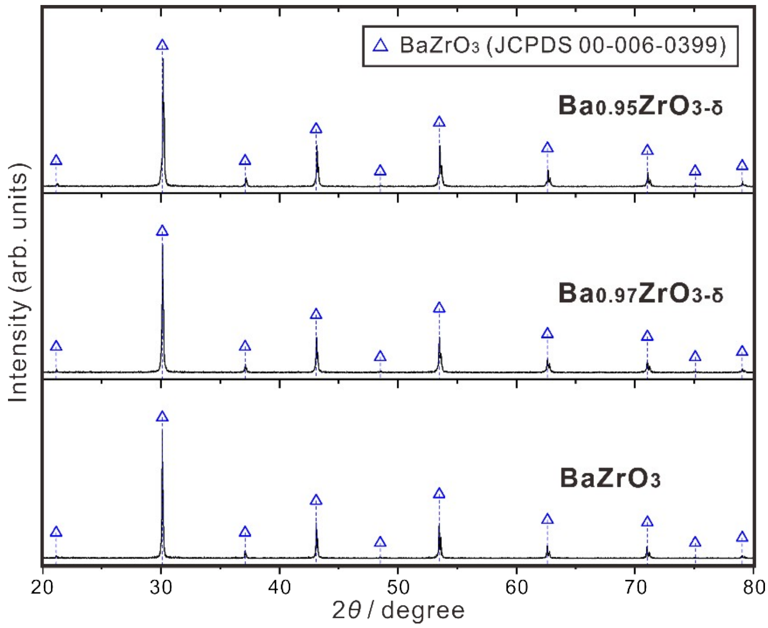

Fig. S3 Room temperature powder XRD patterns of $Ba_{0.95}ZrO_{3-\delta}$, $Ba_{0.97}ZrO_{3-\delta}$, and $BaZrO_3$ sintered at 1300 °C for 24 h in ambient air.

2. XPS analysis

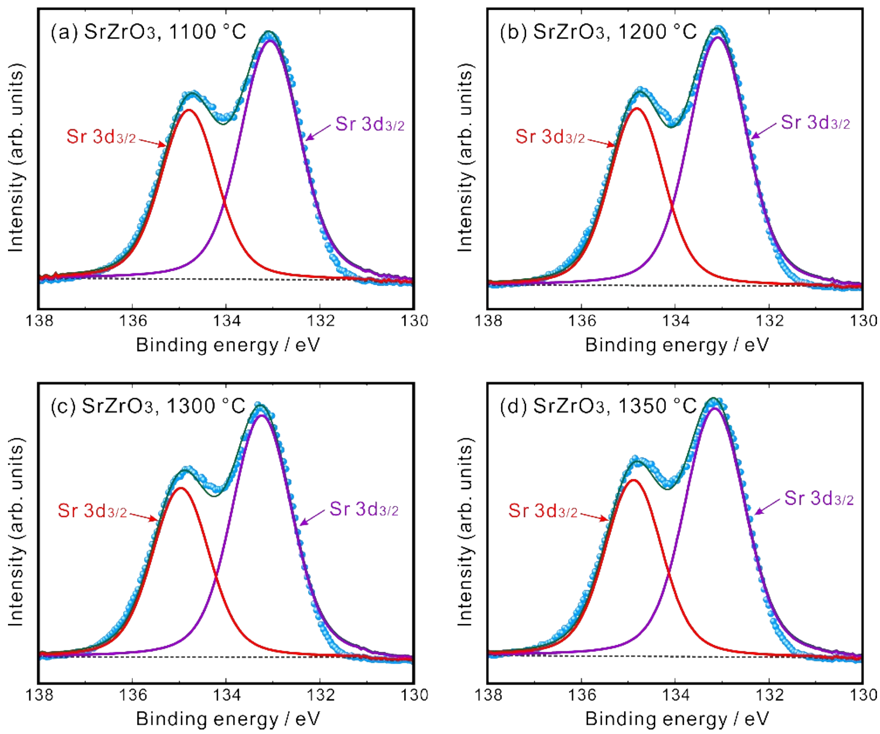

Fig. S4 Sr 3d XPS spectra of $SrZrO_3$ sintered at (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, and (d) 1350 °C in ambient air.

3. Conductivity

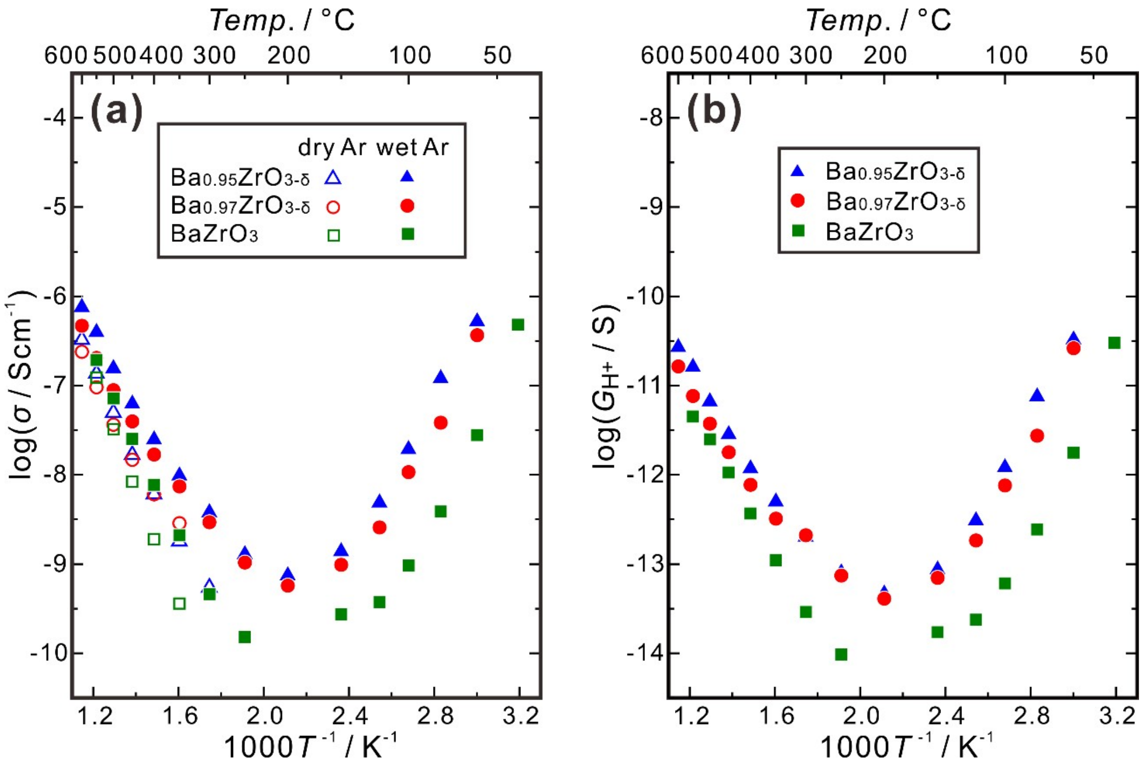

Fig. S5 (a) Total conductivities and (b) surface protonic conductance of the porous samples of $Ba_{0.95}ZrO_{3-\delta}$, $Ba_{0.97}ZrO_{3-\delta}$ and $BaZrO_3$ in dry and wet (p_{H_2O} = 0.04 atm) Ar atmospheres. All the samples were sintered at 1300 °C for 24 h in ambient air.

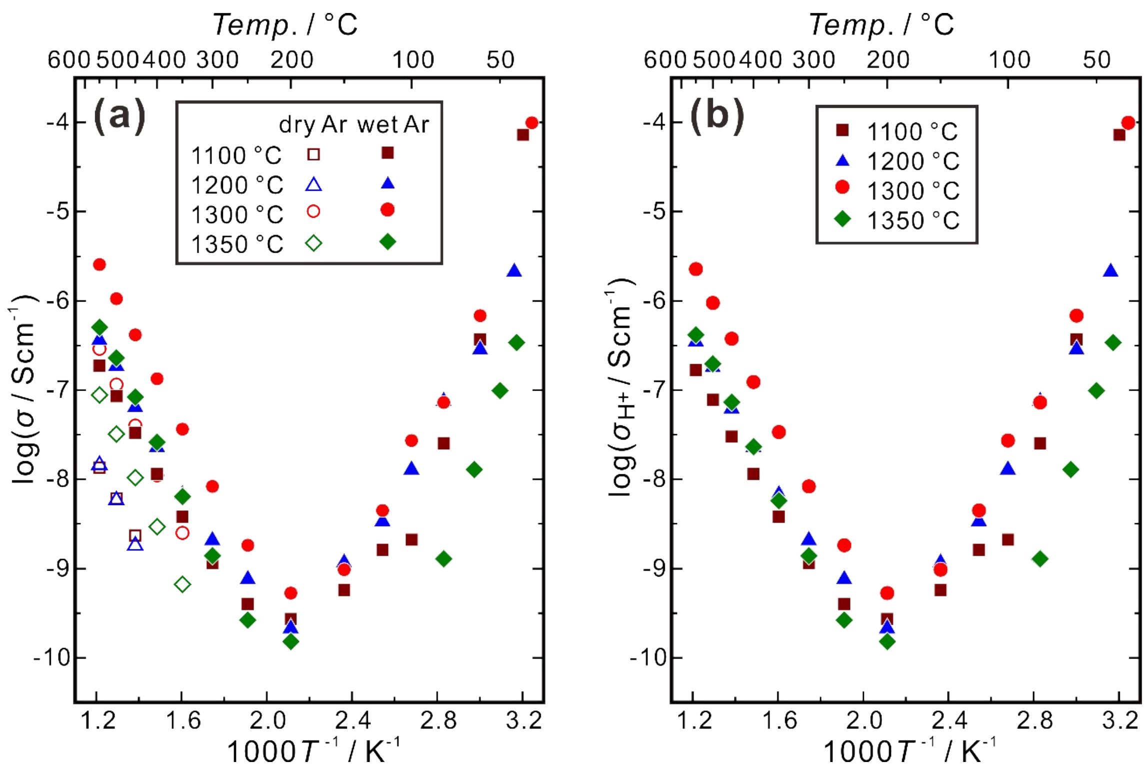

Fig. S6 (a) Total conductivities of $SrZrO_3$ (sintered at 1100, 1200, 1300 and 1350 °C) in dry and wet (p_{H_2O} = 0.04 atm) Ar atmospheres, and (b) surface protonic conductivity after subtraction of the dry conductivities.

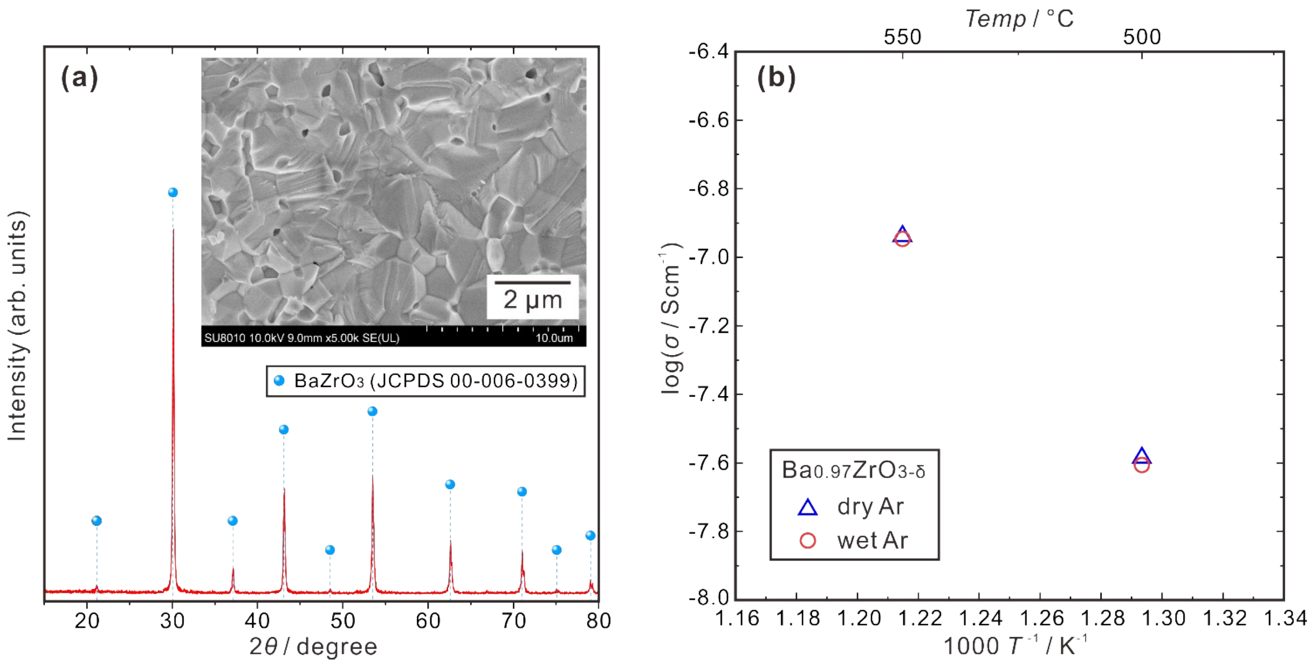

Fig. S7 (a) XRD pattern and SEM image, and (b) total conductivities measured in dry and wet (p_{H_2O} = 0.03 atm) of $Ba_{0.97}ZrO_{3-\delta}$ with relative density above 90% obtained by sintering at 1650 °C for 24 h. During the sintering process, the sample was covered with as-synthesized $Ba_{0.97}ZrO_{3-\delta}$ powder to prevent evaporation of BaO.

Table S1 Derived p_{H_2O} dependences and predicted preexponentials of surface protonic conductance within the chemisorbed water layer at p_{H_2O} = 1 and 0.04 atm according to four models of dissociation and transport in cases of low coverage (Sun *et al*., *Appl. Surf. Sci.*, 2023, **611**, 155590), for which molecular or dissociated chemisorption have the same parameters. Also included are predictions for full coverage, where there are no p_{H_2O} dependences, but differences between molecular or dissociated dominance. The predicted preexponentials are calculated based on a rough estimate of density of surface adsorption sites (i.e., terminating cations) and oxygen-oxygen distance for proton jumps that should be equally valid for perovskites as for binary oxides.

Model Parameter	cms-s cds-s	cms-sa cds-sa	cms-a cds-a	cma-a	cms-s	cds-s	cms-sa	cds-sa	cms-a	cds-a	cma-a
n in $G_{s,H^+0} \propto p_{H_2O}^n$	1/2	1	3/2	2	0 (full coverage)						
G^0_{s,H^+0} (SK), p_{H_2O} = 1 atm	2×10^{-6}	3×10^{-9}	3×10^{-12}	6×10^{-15}	1×10^{-3}	4×10^{-4}	1.5×10^{-3}	8×10^{-4}	1×10^{-3}	8×10^{-4}	1.5×10^{-3}
G_{s,H^+0} (SK), p_{H_2O} = 0.04 atm	4×10^{-7}	1×10^{-10}	4×10^{-13}	1×10^{-19}	1×10^{-3}	4×10^{-4}	1.5×10^{-3}	8×10^{-4}	1×10^{-3}	8×10^{-4}	1.5×10^{-3}

Table S2 Experimental preexponentials of surface protonic conductance within the chemisorbed water layer and the physisorbed layer at p_{H_2O} = 0.04 atm.

Conditions	Type of conduction	Sample Parameter	SZO-1100	SZO-1200	SZO-1300	SZO-1350	CZO-1300	BZ0-1300	$Ba_{0.97}ZrO_{3-\delta}$-1300	$Ba_{0.95}ZrO_{3-\delta}$-1300
High T, wet	chemisorbed	G_0 / SK	5×10^{-4}	2×10^{-3}	5×10^{-2}	2×10^{-2}	4×10^{-1}	6×10^{-4}	6×10^{-5}	2×10^{-3}
Low T, wet	1st physisorbed	G_0 / SK	10^{-21}				-	10^{-22}	10^{-21}	