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Electronic Supplementary Material

CO_2-promoted hydrogen production in a protonic ceramic electrolysis cell

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Experimental

Materials synthesis

The $BaCe_{0.3}Zr_{0.5}Dy_{0.2}O_{3-\delta}$ (BCZDy) powder material was prepared by a citrate-nitrate combustion route, using $Ba(NO_3)_2$, $Ce(NO_3)_3{\cdot}6H_2O$, $Dy(NO_3)_3{\cdot}5H_2O$, $ZrO(NO_3)_2$ as initial components with purity not less than 99.5%. They were taken in the strictly required amounts and dissolved in distilled water until complete salts dissolution. The obtained solution was heated at 80 °C and then citric acid was added in a mole amount exceeding by 2 times a total metal cations amount. A pH value of the solution around 7.0 was regulated by adding ammonia water. The resulting solution was heat-treated at 250 °C until self-ignition and producing a high disperse brown powder. The latter was calcined at 700 °C (1 h) to remove organic substances, pre-synthesized at 1050 °C (5 h) to reach material crystallization and synthesized at 1150 °C (5 h) to obtain the single-phase product; each temperature treatment was accompanied by powder milling. To ensure good densification behavior of the electrolyte and to suppress the refractory nature of Zr^{4+}, a sintering additive of CuO was added in a small amount (0.5 wt%) after citric acid dissolution.

The $Nd_{1.95}Ba_{0.05}NiO_{4+\delta}$ (NBN) powder material was prepared using a similar method, differing only by temperature treatments: 700 °C (1 h), 900 °C (3 h) and 1100 °C (5 h) for calcination, pre-synthesis and synthesis steps, respectively.

Materials characterization

The synthesized materials were analyzed by the X-ray diffraction (XRD) method. The data were obtained using the Rigaku Co. Ltd. D/MAX-2200 diffractometer [S1] under the following conditions: CuK_α radiation, within $20 \le 2\theta,^\circ \le 80$ range, with a $2^\circ\ min^{-1}$ scan rate and a 0.02° scan step. The XRD analysis was performed for the individual materials, for the BCZDy/NBN powder mixture to confirm chemical compatibility and BCZDy treated at 700 °C (5 h) by air passed through the boiling water and 100% CO_2 to check chemical stability in the aggressive media.

The images of morphology of the electrochemical cell's cross-section were obtained using scanning electron microscopy (SEM) method, a microscope TESCAN MIRA 3 LMU [S1].

The PCEC fabrication and characterisation

The protonic ceramic electrolysis cell (PCEC) was fabricated using a tape calendering method [S2], which is based on the co-rolling of the films consisted of the corresponding (BCZDy, NiO–BCZDy) powders in a special organic binder. Then the co-rolled films were treated at 900 °C (slow heating and cooling) to burn the carbon and organic components and then sintered at 1450 °C (5 h) to form the half-cell. To produce the single PCEC, the NBN–BCZDy slurry (7:3 wt ratio) was painted onto the electrolyte surface of the half-cell and sintered at 1100 °C for 1 h. No electrocatalytic methods (exsolution, infiltration) were used to improve the activity of the oxygen electrode.

The PCEC's performance was analyzed at 700 °C varying gas compositions at the both cathode and anode sides. The air with different water vapor partial pressure values (pH_2O = 0.01, 0.03,

0.1, 0.2 and 0.3 atm) was used as an oxidizing atmosphere, while wet hydrogen with different carbon dioxide partial pressure (pCO_2 = 0, 0.5, 0.7, 0.8 and 0.9 atm, pH_2O = 0.03 atm) was used as a reducing atmosphere. The pH_2O level was regulated by passing the gases through a bubbler heated at a specified temperature to reach desirable saturation. The pCO_2 level was regulated by mixing the H_2 and CO_2 fluxes, taking into account their flow rates. The flow rates of oxidizing and reducing gases were equal to 30 and 100 ml min^{-1}, respectively.

The electrochemical characterization was performed by means of a potentiostat/galvanostat Amel M2550 (Italy) and a FRA box MaterialsM Instruments (Italy). Volt-ampere curves were recorded within an applied voltage range from open circuit voltage (OCV) to 1.6 V and a step of 0.025 mV. Impedance spectra were obtained at three bias voltages (1.0, 1.3 and 1.6 V) in a frequency range of 10^{-1}–10^5 Hz and amplitude signal of 15–20 mV. The impedance data were analyzed by the means of equivalent circuit models (Zview software) and distribution of relaxation times (DRT) method [S3].

Tables

Table S1 Comparison of PCECs' performance: h is the thickness, T is the temperature, R_t, R_o and R_p are the total, ohmic and polarization resistances at open circuit voltage mode (i = 0 A cm^2) or *thermoneutral voltage mode (bias is equal ~1.3 V), i is the current density at U = 1.3 V, $i_{eff.}$* is the effective current density of PCECs based on the electrolytes with thickness reduced to 10 μm.

Electrolyte		Anode composition	Gas composition		T, °C	R_t, Ω cm^2	R_o, Ω cm^2	R_p, Ω cm^2	i, mA cm^2	$i_{eff.}$, mA cm^2	Ref.
Composition	h, μm		Anode	Cathode							
BCZDy	50	NBN–BCZDy (7:3)	30%H_2O/air	3%H_2O/H_2	700	0.67*	0.50*	0.17*	542	1345	This work
BCZDy	50	NBN–BCZDy (7:3)	30%H_2O/air	3%H_2O/(50H_2+50CO_2)	700	0.64*	0.49*	0.15*	628	1620	This work
BCZY0.3	20	SSC–BCZY0.3 (7:3)	30%H_2O/air	H_2	700	0.93*	0.52*	0.41*	380	530	[S4]
BCZYZ	75	LSMC–BCZYZ (65:35)	3%H_2O/N_2	5%H_2/Ar	700	0.89*	0.71*	0.18*	993	3200	[S5]
BCZYZ	60	F–BCZYZ (65:35)	3%H_2O/H_2	100%CO_2	614	-	-	-	315	-	[S6]
BZY	15	LSCF–BZY	3%H_2O/air	4%H_2/Ar	700	-	-	-	207	-	[S7]
BCZY0.1	15	$La_{1.2}Sr_{0.8}NiO_{4+\delta}$	20%H_2O/air	3%H_2O/H_2	700	0.49	0.22	0.27	1370	1610	[S8]
BCZY0.1	15	SEFC–BCZY0.1 (95:5)	10%H_2O/air	3%H_2O/H_2	700	0.45	0.33	0.12	1050	1390	[S9]

Electrolyte abbreviations: BCZDy = $BaCe_{0.3}Zr_{0.5}Dy_{0.2}O_{3-\delta}$, BCZY0.3 = $BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$, BCZYZ = $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$, BZY = $BaZr_{0.8}Y_{0.2}O_{3-\delta}$, BCZY0.1 = $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$.

Electrode abbreviations: NBN = $Nd_{1.95}Ba_{0.05}NiO_{4+\delta}$, SSC = $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$, LSMC = $(La_{0.75}Sr_{0.25})_{0.95}Mn_{0.5}Cr_{0.5}O_{3-\delta}$, F = Fe_2O_3, LSCF = $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, SEFC = $SrEu_2Fe_{1.8}Co_{0.2}O_{7+\delta}$.

* Since the listed data were obtained for PCECs with different design and materials, their performance can be compared estimating the $i_{eff.}$ values for the cells with the same electrolyte thickness. These values were calculated on the base of the following assumptions: (i) the electrolyte thickness is reduced to 10 μm, (ii) current density is inversely proportional to R_t, (iii) R_p does not change with varying the electrolyte thickness, and (iv) h and R_O values are decreased by the same magnitude, which follows from the constant conductivity level of the electrolyte membranes ($\sigma = h/R_O$). The highest $i_{eff.}$ for the cell studied in ref. [S5] can be associated with either an overestimated current density or a high error in the assumptions drawn.

Table S2 Equilibrium concentration of gas components[†] at 700 °C depending on the initial gas mixture composition supplied to the cathode side.

Partial pressures in initial gas mixture, atm			**Equilibrium partial pressures, atm**			
pH_2O	**pH_2**	**pCO_2**	**pH_2O**	**pH_2**	**pCO_2**	**pCO**
0.03	0.97	-	0.03	0.97	-	-
0.03	0.485	0.485	0.235*	0.280	0.280	0.205
0.03	0.291	0.679	0.205	0.116	0.504	0.175
0.03	0.194	0.776	0.166	0.058	0.640	0.136
0.03	0.097	0.873	0.109	0.018	0.794	0.079

The highest pH_2O value is marked by *.

[†] The equilibrium partial pressures of components were calculated according to law of mass action for the water gas shift reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

and its equilibrium constant at 973.15 K.

Figures

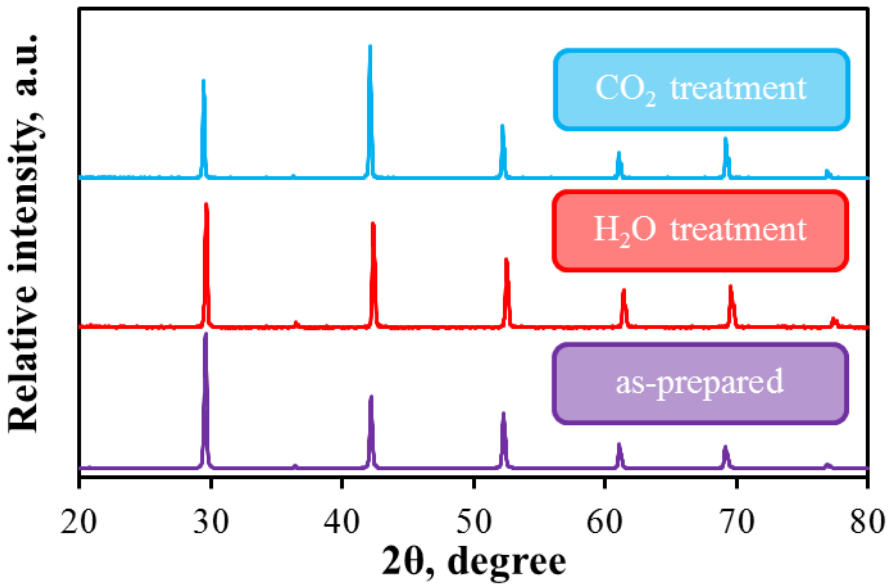

Fig. S1 XRD patterns for the as-sintered $BaCe_{0.3}Zr_{0.5}Dy_{0.2}O_{3-\delta}$ sample and ones treated by ~100% H_2O and 100% CO_2 at 700 °C for 5 h.

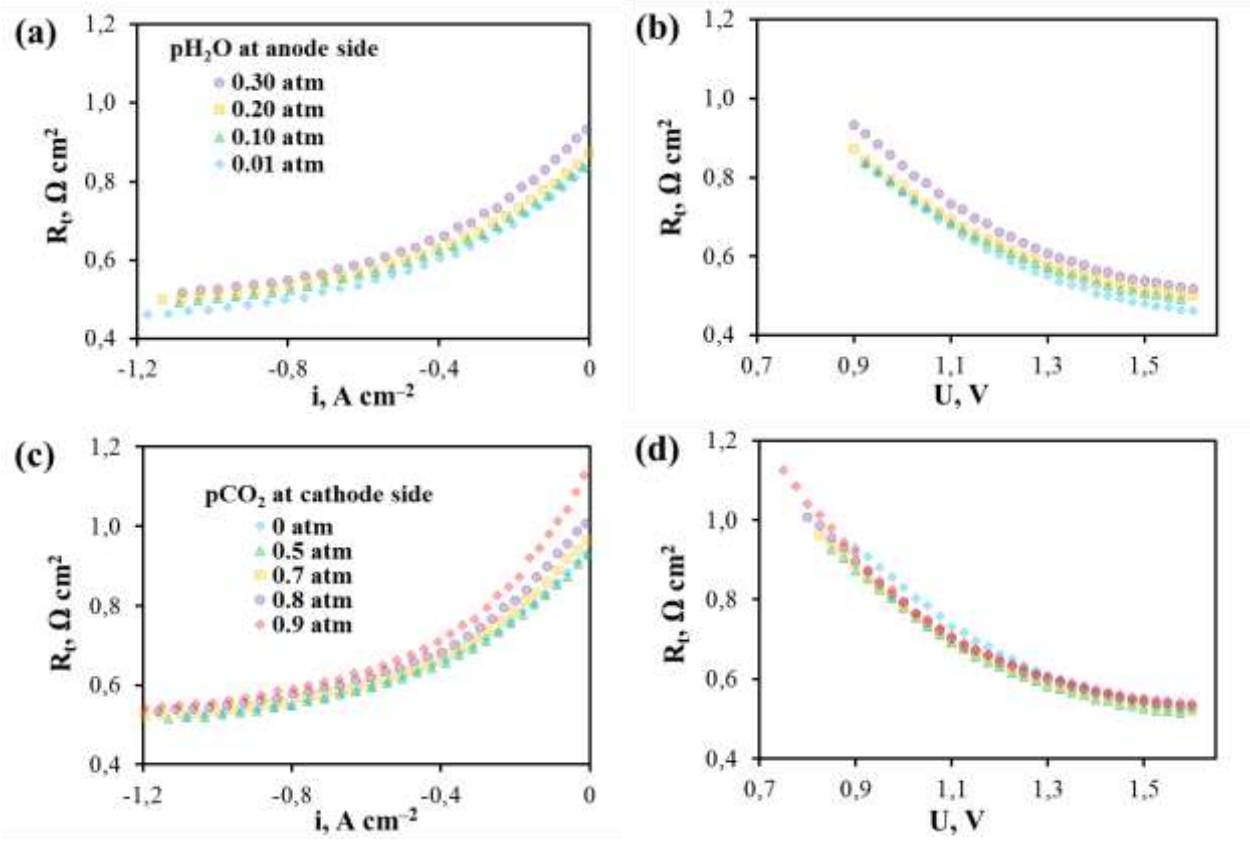

Fig. S2 Performance of the developed PCEC at 700 °C in term of its total cell resistance (R_t) as a function of current density (a,c) or applied voltage (b,d) at different pH_2O at the anode side (a,b) and pCO_2 at the cathode side (c,d). The R_t values were calculated on the base of the differential forms of volt-ampere dependences.

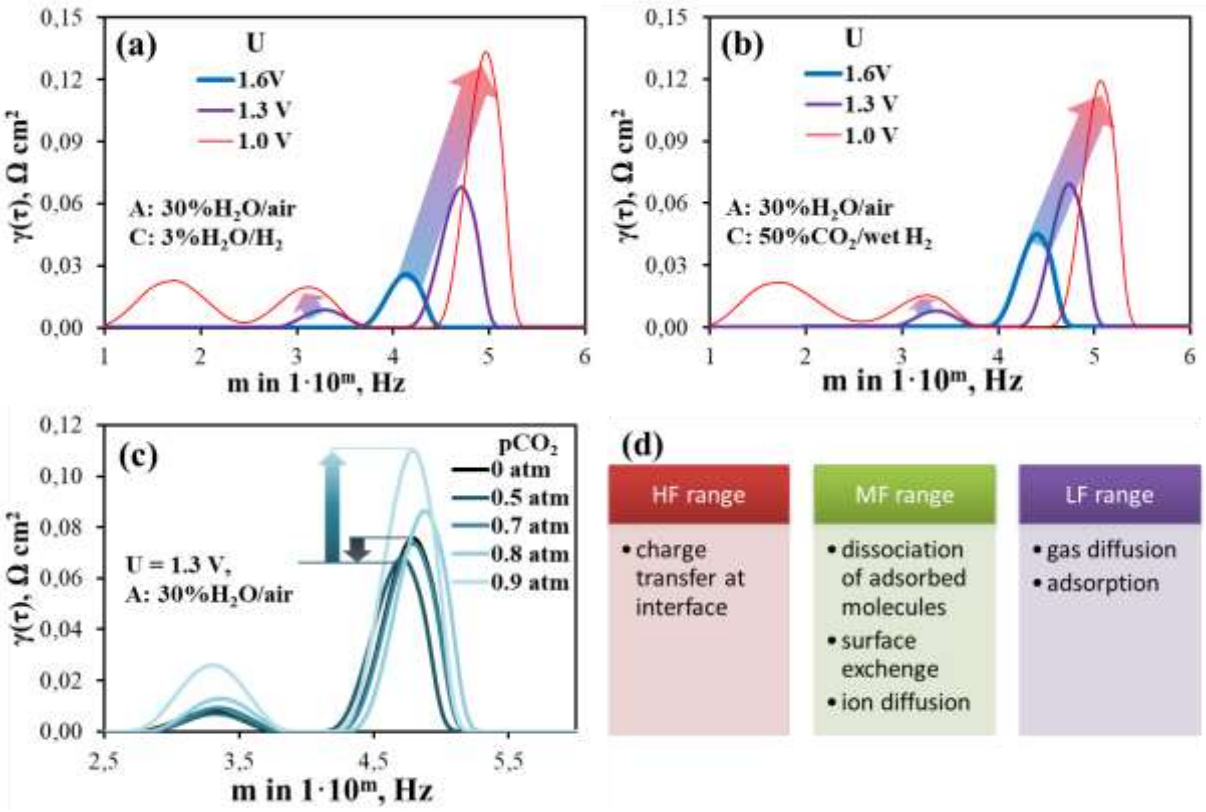

Fig. S3 DRT analysis of EIS data (a–c). The description is similar with **Fig. 3**; (d) the frequency ranges (high, medium and low) and corresponding electrode processes.[S10–S12]

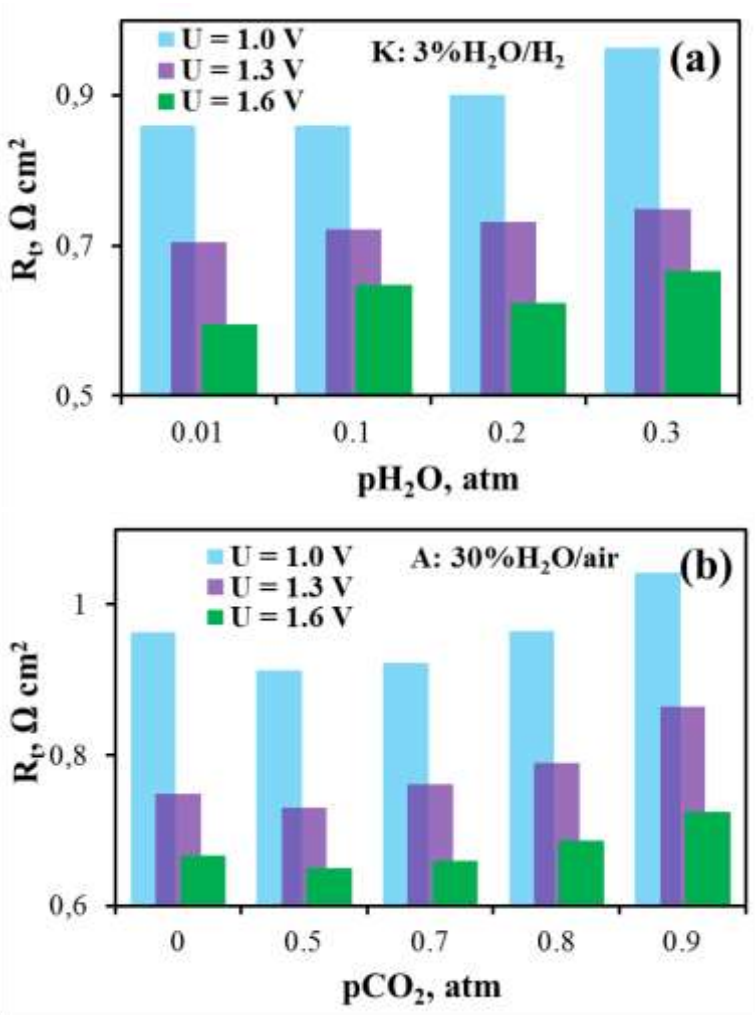

Fig. S4 Total resistance of the NBN–BCZDy|BCZDy|Ni–BCZDy electrolysis cell at 700 °C and the different bias depending on pH_2O at the anode side (a) and pCO_2 at the cathode side (b).

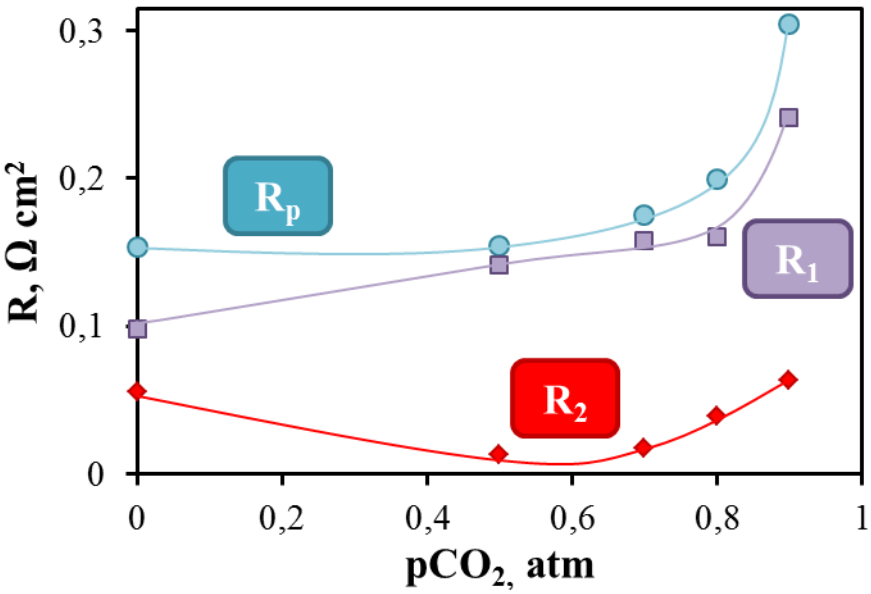

Fig. S5 Total polarization resistances of the electrodes and its high frequency (R_1) and medium frequency (R_2) components as a function of pCO_2 at the cathode side under the bias of 1.3 V. Lines are indicated for convenience of data perception.

References

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