

**Advancing the cathodic electrocatalysis via an in-situ generated dense active
interlayer based on CuO₅ pyramid structured Sm₂Ba_{1.33}Ce_{0.67}Cu₃O₉**

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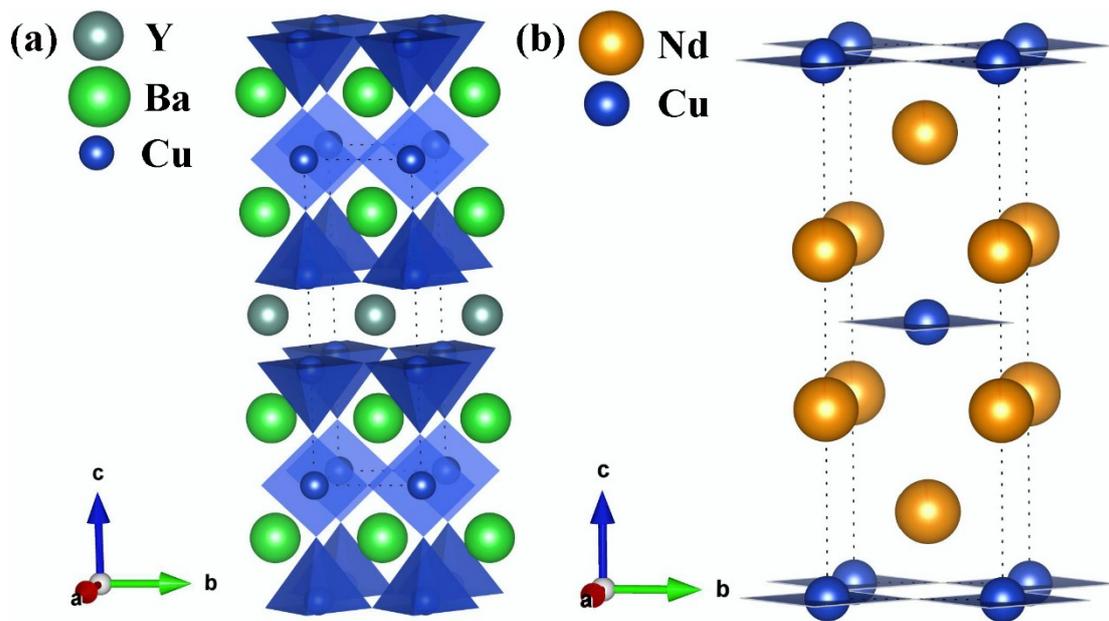


Figure S1 Crystal structure of (a) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and (b) Nd_2CuO_4 .

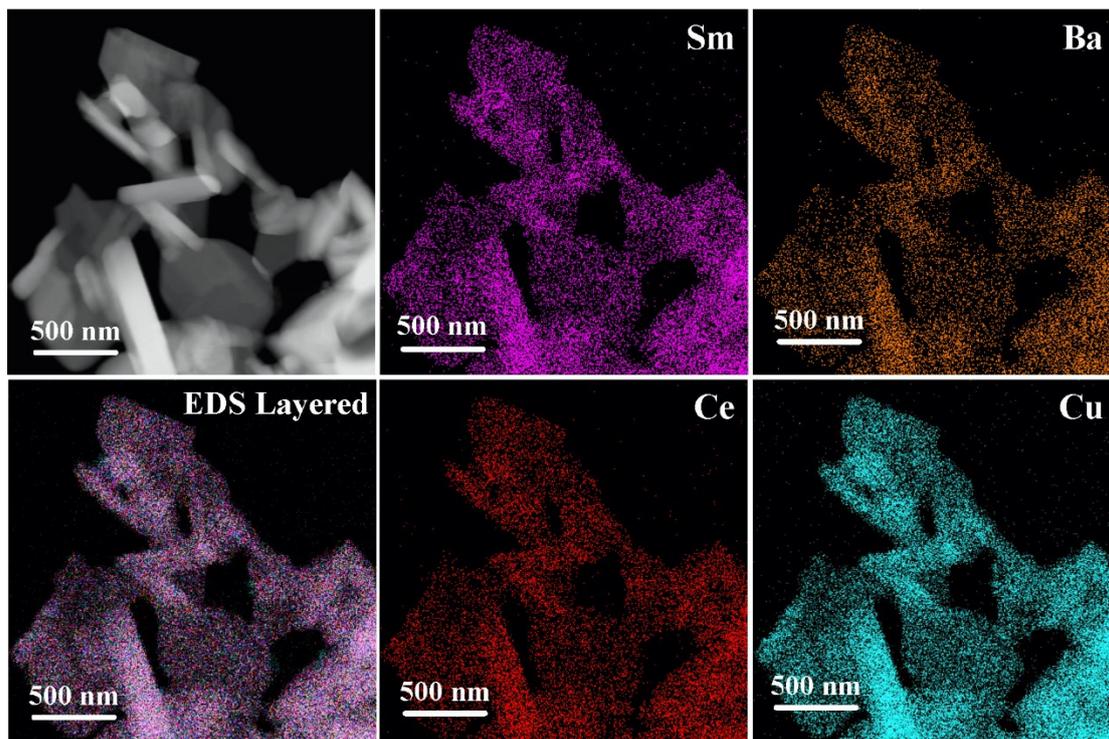


Figure S2 SBCC dark-field TEM image with the corresponding Energy dispersive X-ray spectroscopy (EDS) element mapping data of Sm, Ba, Ce and Cu, and the EDS layered element mapping.

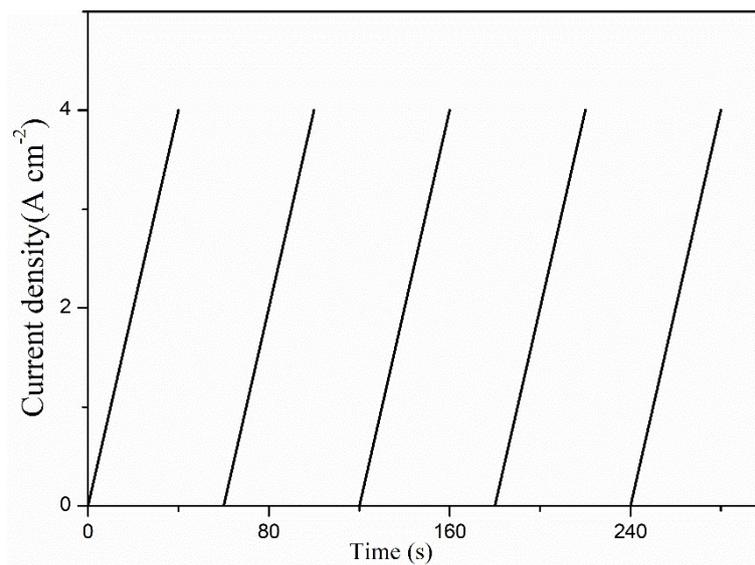


Figure S3 The relation of the linear sweeping current and the time during the LCS treatment.

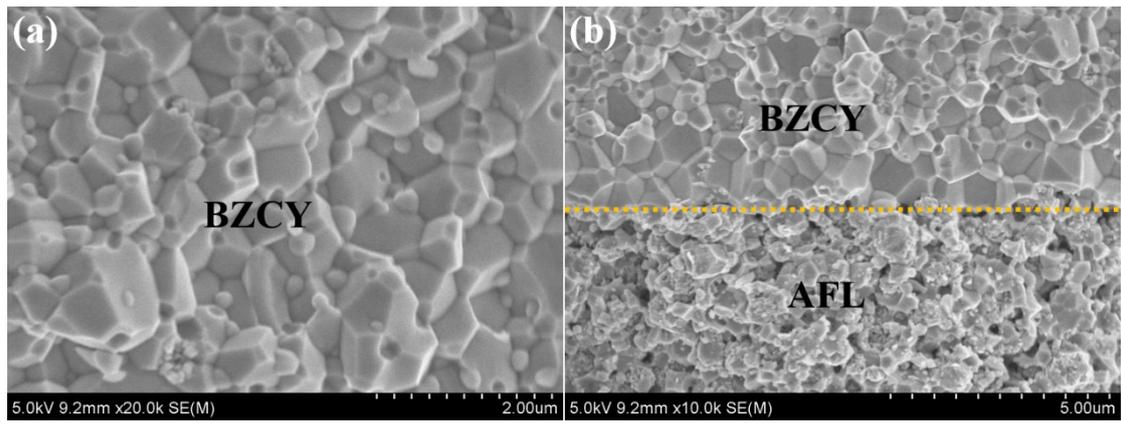


Figure S4 Cross-sectional SEM images of the (a) BZCY electrolyte layer and (b) the interface between the AFL and BZCY membrane after the cell testing.

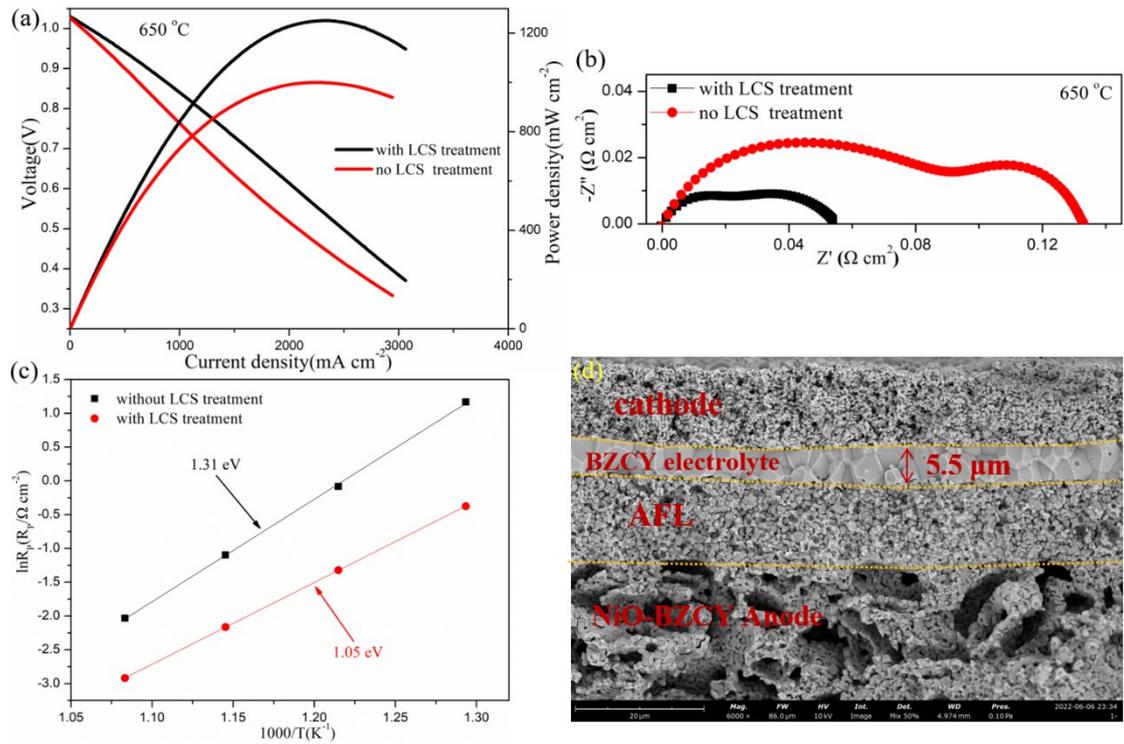


Figure S5 The comparison of (a) the typical V-I and P-I curves, (b) the EIS plots at 650 °C and (c) the corresponding Arrhenius plots of R_p for the single cells with and without LCS treatment; (d) Cross-sectional SEM images of the four-layered single cell without LCS treatment after testing.

Table S1 The PPD and R_p comparison of single cells with and without LCS treatment at 550-650 °C.

PPD (mW cm ⁻²) and R_p (Ω cm ²)	650 °C		600 °C		550 °C		500 °C	
	PPD	R_p	PPD	R_p	PPD	R_p	PPD	R_p
With LCS treatment	1252	0.054	905	0.115	636	0.267	418	0.687
No LCS treatment	1000	0.131	542	0.334	338	0.92	154	3.209

S1. Experimental Section

S1.1. Synthesis of powders

$\text{Sm}_2\text{Ba}_{1.33}\text{Ce}_{0.67}\text{Cu}_3\text{O}_9$ (SBCC) and $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) powders were synthesized via a citric acid-nitrate gel combustion process. Set SBCC as an example, Sm_2O_3 , BaCO_3 , $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ at a stoichiometric ratio were dissolved and citric acid as complexation agent with molar ratio of citric acid/metal at 1.5 was then added. The solution was heated under stirring to evaporate water until it changed into viscous gel and finally ignited to flame, resulting in atramentous ash. The crude materials for synthesis of white BZCY powders were BaCO_3 , $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. After combustion, the two as-prepared ash-like powders were calcined at 900 and 1000 °C for 3 h in air to obtain SBCC and BZCY powders, respectively.

S1.2. Fabrication of anode-supported single cells

The NiO-BZCY (65:35 weight ratio) composite powders for the anode substrate and anode functional layer (AFL) were also prepared by the one-step gel combustion process (Refer to part S1.1 in *Experimental Section*). The composite powders were calcined at 1000 °C for 3 h and then 20 wt.% starch was added as pore-creating materials to form adequate porosity in anode. The anode supported half cells with a tri-layered structure containing anode substrate, AFL (NiO-BZCY with no starch) and BZCY layer, were fabricated by a co-pressing method. Firstly, the NiO-BZCY (with starch) powders were pressed in a stainless steel module to form an anode substrate with a flat surface and a certain mechanical strength. Subsequently, the loose NiO-

BZCY (without starch) powders were added and evenly distributed onto the substrates. Then it was pressed together with the anode substrate to obtain the NiO-BZCY AFL. The BZCY layer was obtained by the same method with NiO-BZCY AFL and the thickness of the AFL and BZCY membrane could be controlled by varying the amount of powder used. Finally, the green half-cells were co-fired at 1300 °C for 5 h. SBCC was mixed thoroughly with a 10 wt.% ethylcellulose-terpineol binder to get the SBCC ink, which was then painted onto the dense BZCY electrolyte membrane and fired at 900 °C for 3 h in air to attain a porous cathode layer. Ag paste and wire were applied as a current collector and the conducting wire, respectively. The effective area of the cathode was 0.237 cm².

S1.3. Characterization, the electrochemical measurements and LCS procedures

Phase compositions of SBCC, BZCY powders and the dry mixed SBCC-BZCY compistes fired at 900, 1000 and 900 °C were identified by an X-ray diffractometer (Rigaku TTR-III) using CuK α radiation. The surface chemical states of the SBCC powders could be analyzed from the X-ray photoelectron spectroscopy (XPS) conducted on a Thermo ScientificTM K-Alpha^{TM+} spectrometer equipped with a monochromatic Al K α X-ray source (1486.6 eV) operating at 100 W. The transmission electron microscopy (TEM, JEOL 2100F) was utilized at an accelerating voltage of 200 kV to analyze the morphology and crystallinity. The microstructures of the cell components were investigated by a scanning electron microscopy (SEM, Hitachi S4800). The single cell was tested in a home-made testing system with static ambient air and humidified hydrogen (~3% H₂O) at a flow rate of 30 ml min⁻¹ as the oxidant

and fuel, respectively. The water vapor pressure about 0.03 atm was achieved by bubbling H₂ through water at about 25 °C. Before performing the cell electrochemical performance testing, the single cell was in-situ treated under the linear current sweeping (LCS) procedures from 0-4 A cm⁻² (amplitude) for 5 cycles (the time for one cycle is 40 s) at 700 °C, which is illustrated in Fig. S3. After the in-situ generation of cathode functional layer (CFI) at the electrolyte/cathode interface, the cell V-I and P-I curves were collected through an electrochemical workstation (Squidstat Plus, Admiral Instruments) using the Linear Sweep Voltammetry (LSV) mode based on a four-probe configuration at 500-700 °C. The electrochemical impedance spectra (EIS) were collected under open circuit conditions using the same electrochemical workstation with a frequency range of 0.1-1 MHz. The cell ohmic and polarization resistances under open circuit conditions were decided from the EIS.