

High performance of protonic solid oxide fuel cell with $\text{BaCo}_{0.7}\text{Fe}_{0.22}\text{Sc}_{0.08}\text{O}_{3-\delta}$ electrode

Wei He^a, Rong-hua Yuan^a, Fei-fei Dong^b, Xue-lian Wu^{c}, Meng Ni^{a,*}*

^a Building Energy Research Group, Department of Building and Real Estate, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong 999077, China

^b School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou Higher Education Mega Center, Guangzhou 510006, China

^c Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong 999077, China

* Corresponding authors. Tel.: +852 2766 4152; fax: +852 2764 5131

Email: xuelianwu-2@my.cityu.edu.hk (Xuelian Wu)

meng.ni@polyu.edu.hk (Meng Ni)

Abstract

Solid oxide fuel cells (SOFCs) have attracted tremendous attention for their combination of environmental power generation and fuel flexibility. Proton conducting SOFCs (P-SOFCs) demonstrate advantages over oxygen-ion conducting SOFCs, such as less activation energies on ionic transport and higher fuel utilization efficiency. Central to the devices is a suitable cathode with high catalytic activity. Herein, a cubic perovskite $\text{BaCo}_{0.7}\text{Fe}_{0.22}\text{Sc}_{0.08}\text{O}_{3-\delta}$ (BCFSc) has been applied as the cathode in proton-conducting solid state fuel cell (SOFC) with $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) electrolyte. Peak power densities of 760, 591, 452 and 318 mW cm^{-2} are obtained at 650, 600, 550 and 500 °C with humidified hydrogen as the fuel and air as the oxidant. A low polarization resistance of $0.05 \Omega \text{ cm}^2$ under open circuit at 650°C is observed.

Key words: Proton-conducting solid oxide fuel cell, cathode, high performance, low polarization resistance

1 Introduction

Considering the high energy conversion efficiency and great fuel flexibility in production of electricity directly from fuel oxidation reaction, solid oxide fuel cells (SOFCs) have much potential in commercial application[1, 2]. In the field of SOFCs, it is of great interest to reduce the operation temperature, because low temperature can bring plenty of advantages, such as the higher chemical and structural stability, more sealing materials selection, short start-up time and so on[3, 4].

Recently, proton conducting SOFCs (P-SOFCs) operating at the intermediate temperature have attracted much attention[5-7]. Compared with oxygen-ion conducting SOFCs, P-SOFCs exhibit less activation energies on ionic transport (H^+)[8, 9]. Besides, the water forms in the cathode side, which avoids the dilution of fuel in oxygen-ion conducting SOFCs[10]. Many efforts have been made to develop a proper proton conductor[7, 11, 12]. Among all the electrolyte materials, the $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) exhibited high proton conductivity and stability under operation condition[13]. Therefore, the central to the P-SOFC at reduced temperature is the suitable cathode with high catalytic activity. Due to the generation of water in the cathode side, the requirements for cathode in P-SOFC is more restrict than that in oxygen-ion SOFCs[14], and the performance of the intermediate temperature P-SOFC is strongly determined by the cathode, especially the interface of the cathode and interface, because the polarization resistance increases rapidly with decreasing temperature[15].

The mixed ionic and electronic conductor (MIEC) cathodes with good oxygen transport and surface exchange properties have been applied in P-SOFCs, and show excellent performances, especially the perovskite cathode with cobalt element[16-18]. It was reported that the oxygen diffusion in some cathode in P-SOFC was the limit reaction in the dry and wet oxidizing atmospheres[19, 20]. $\text{BaCo}_{0.7}\text{Fe}_{0.22}\text{Sc}_{0.08}\text{O}_{3-\delta}$ (BCFSc) is a mixed oxygen-ion and electron conductor (MIEC), and has been applied in oxygen-ion SOFC recently[21]. The BCFSc exhibited excellent electro-catalytic activity in oxygen reduction reaction due to its high cubic symmetry structure and fast oxygen bulk diffusion rate and oxygen surface exchange kinetics, e.g., polarization resistance of $0.03 \Omega \text{ cm}^2$ in symmetric cell and peak power density of 1446 mW cm^{-2} in single cell at $600 \text{ }^\circ\text{C}$. Thus, the BCFSc with high electrocatalytic activity is considered to be a promising candidate material for P-SOFC cathode. In this study, the BCFSc was applied as the cathode in P-SOFC. A power density of 760 mW cm^{-2} was obtained at $650 \text{ }^\circ\text{C}$, meanwhile, a low polarization resistance of $0.05 \Omega \text{ cm}^2$ was observed under open circuit condition.

2 Experimental section

2.1. Powder preparation

BCFSc powder was synthesized by a sol-gel in combination with combustion method. A water solution with stoichiometric ratio Ba, Co, Fe and Sc nitrate was first prepared, then Ethylenediaminetetraacetic acid and citric acid were added into the solution as the complexing agents and the extra acid was neutralized by $\text{NH}_3 \cdot \text{H}_2\text{O}$ to keep pH at ~ 7 . A gel was obtained after stirring with heating, subsequently the gel was pre-fired at $250 \text{ }^\circ\text{C}$, and

self-combustion occurred to form solid precursor. The precursor was finally calcined at 850 °C for 2 h to form the BCFS_c powders. The BZCY and BaCo_{0.7}Fe_{0.3}O_{3-δ} (BCF) powders were produced by the same method.

2.2 Cell fabrication

The symmetrical cells with a BCFS_c|BZCY|BCFS_c configuration were fabricated by dry pressing employing spray-painting method. Dense BZCY substrates were prepared through dry pressing with subsequent calcination at 1450 °C for 5 h. BCFS_c powder was dispersed with glycol, ethylene glycol, and isopropyl alcohol to form a suspension through ball milling. The resulting electrode slurries were sprayed onto both surfaces of the BZCY disks and subsequently fired at 950 °C for 0.5 h in air to form the symmetrical cells. Silver paste was then applied onto the electrode surface as the current collector. The single cell was fabricated by the similar method. Mixed powders consisting of BZCY + NiO + Polyvinyl butyral (weight ratio 4:6:0.8) were pressed and then sintered at 800 °C for 2 h to produce an anode substrate. An electrolyte suspension containing 10 wt. % BZCY was sprayed on the anode substrate. After drying in air at room temperature, this substrate was co-fired at 1450 °C for 5 h, a half fuel with dense BZCY electrolyte film formed. The BCFS_c cathode was coated on the electrolyte surface using the similar spray-painting method in symmetric cell and calcination temperature was 950 °C. The effective area of the cathode was about 0.48 cm².

2.3 Characterization and cell testing

The structure of the powder was indexed by X-ray diffraction (XRD, Rigaku Smartlab). The microstructures for single cell were characterized by a scanning electron

microscope (SEM, JEOL 6490). The performance of fuel cell was examined by homemade testing system from 500 to 650 °C, with humidified H₂ (50 mL min⁻¹) as the fuel and air as the oxidant. The electrochemical impedance spectra were measured by a Solartron 1260A frequency response analyzer with a Solartron 1287 potentiostat under open-circuit from 0.1 Hz to 10⁶ Hz with AC amplitude of 10 mV.

3 Results and discussion

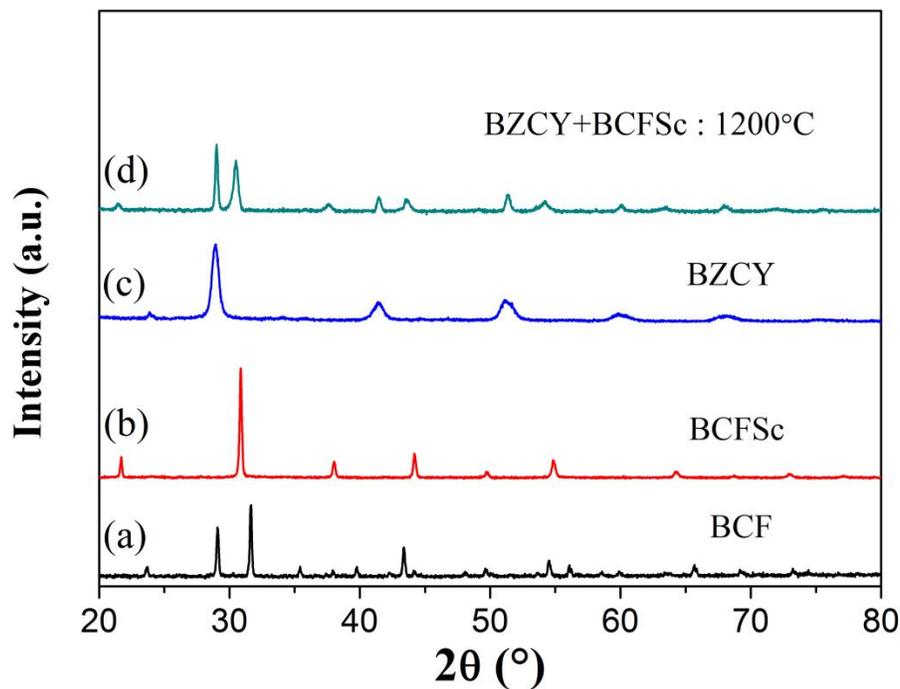


Fig. 1 XRD patterns of oxides (a) BCF, (b) BCFSr, (c) BZCY, (d) mixed BCFSr and BZCY powders with weight ratio of 1:1 after annealing at 1200 °C for 5 h.

Fig. 1 presents the XRD patterns of BCF, BCFSr, BZCY and mixed BCFSr-BZCY powders. The Sr doing stabilizes the structure of BCF and the BCFSr shows a cubic perovskite structure. It is noted that there are only peaks corresponding to the BZCY and

BCFSc in the mixture of BCFSC and BZCY powders after annealing, indicating that BCFSc is compatible with BZCY.

The area-specific resistances (ASRs) of the electrode in symmetrical cell are shown in Fig. S1. The values in wet air are 0.13, 0.57 and 2.32 $\Omega \text{ cm}^2$ at 700, 600 and 500 $^{\circ}\text{C}$, which are lower than the case in dry air. According to the analyst in Ref.[16], the introduction of water may facilitate the process of non-charge transfer such as adsorption–desorption and diffusion of oxygen. It is noted that the apparent activation energies (E_a) of the PBFSc in wet air and dry air are about 90.0 kJ mol^{-1} and 92.2 kJ mol^{-1} , lower than the 120.3 kJ mol^{-1} of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ cathode in air[18]. Low apparent activation energy indicates less chemical barrier for oxygen reduction, which results in a low ASR value[22].

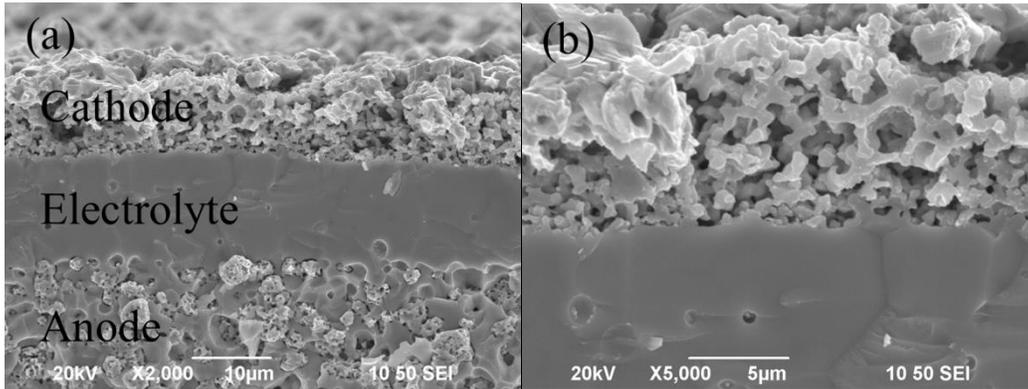


Fig. 2 SEM image of the single cell (a) cross section view, (b) close-up image of the interface of cathode and electrolyte.

To investigate the BCFSc as the cathode for P-SOFC, an anode-supported fuel cell (BCFSc|BZCY|NiO-BZCY) was fabricated. Fig. 2(a) is the microstructure of the single cell after testing from the cross sectional view. The densified electrolyte with thickness of

~ 10 μm indicates that spray-painting is an effective way to fabricate the thin film for electrolyte. The thickness of the porous cathode is also ~ 10 μm and no crack is found at the interface between the cathode and the electrolyte from Fig. 2(b), which is expected to enhance the compatibility and the stability of the cathode-electrolyte interface.

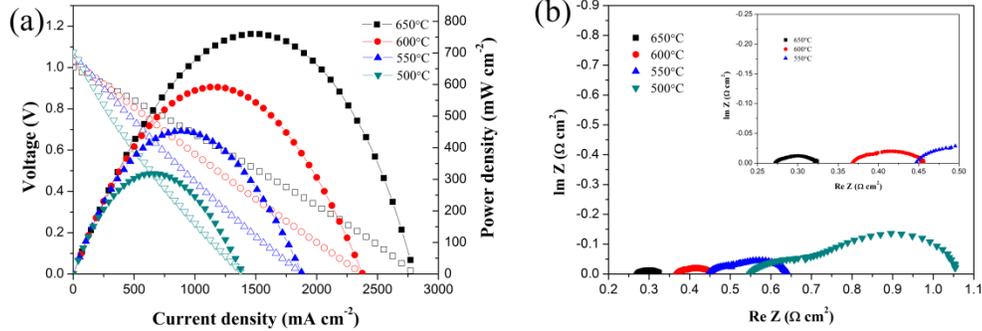


Fig. 3 Electrochemical performance of single cell (a) current density dependence of voltages and power densities for anode-supported cell at different temperatures, (b) impedance spectra of the testing single cell at open circuit condition.

Fig. 3(a) displays the I - V and I - P curves measured from 500 to 650 $^{\circ}\text{C}$ with humidified hydrogen (3% H_2O) as the fuel and ambient air as the oxidant. The open circuit voltages (OCVs) are observed to be from 1.07 V to 1.00 V, and maximum power densities of 760, 591, 452 and 318 mW cm^{-2} are obtained at 650, 600, 550 and 500 $^{\circ}\text{C}$. The table 1 shows a performance comparison of PBFSc and several other cobalt-containing cathodes using the same electrolyte of BZCY. The BCFSc exhibits a higher performance, which may be related to the low polarization resistances shown in Fig. 3(b).

Cathode	Electrolyte thickness (μm)	Peak power density (mW cm^{-2})	Ref
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PBFSc	10	760 (650 °C)	This study
NbBaCo ₂ O _{5+δ}	10	438 (700 °C)	[17]
Ag-Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	35	595 (750 °C)	[18]
PrBaCo ₂ O _{5+δ}	10	545 (700 °C)	[23]
Ba _{0.9} Co _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	20	300 (700 °C)	[24]
BZCY-PrBa _{0.5} Sr _{0.5} Co ₂ O _{5+δ}	15	522 (700 °C)	[25]
Y _{0.25} Bi _{0.75} O _{1.5} -La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ}	20	167 (550 °C)	[26]
BZCY-Sm _{0.5} Sr _{0.5} CoO _{3-δ}	20	650 (700 °C)	[27]
BZCY-Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	20	418 (700 °C)	[28]

Table 1 Summary of the performance data for our cell with literature reports

Fig. 3b exhibits the single cell resistances under operation condition. The intercept with the real axis at high frequency is the ohmic resistance of the cell (R_o), and the low frequency intercept means the total resistance of cell (R_{total}). The difference between the high and low frequency intercept presents the total interfacial polarization resistance (R_p) of the cell, which contains the cathode-electrolyte and anode-electrolyte interfacial resistances. As expected, all the estimated resistances decrease with increasing temperature as shown in Fig. S2. R_o of the single cell are 0.27, 0.37, 0.45 and 0.55 $\Omega \text{ cm}^2$ and R_p are measured as 0.05, 0.09, 0.20, 0.49 $\Omega \text{ cm}^2$ at 650, 600, 550, 500 °C respectively. It is noted that the polarization resistances are much lower than some other cobalt containing cathode in P-SOFC. At 600 °C, the R_p of this cell is about 0.1 - 0.7 times that of cells with cathode of PrBaCo₂O_{5+δ}, [23] Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} - BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} [28] and NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ}, [29] i.e., 0.92, 0.6, and 0.128 $\Omega \text{ cm}^2$. The low polarization resistance of PBFSc may be due to its fast oxygen diffusion and surface exchange kinetics, which is related to its symmetrical structure and high catalytic activity of Co/Fe cations [21]. The limit to the performance of the cell is the ohmic resistance, which mainly originates from the electrolyte. Therefore, the future research will be focused on decreasing the ohmic resistance to improve the performance of the P-SOFC. The stability of the cell is of importance. The short-term stability test is shown in Fig. S3. Under current density of 400

mA cm⁻² at 550 °C, the voltage of ~0.75 V is obtained without observable degradation, indicating a relative stability of the cathode.

4 Conclusions

A perovskite BCFS_c was applied in P-SOFC and the properties were investigated. The anode-supported cell exhibited an excellent performance with humidified hydrogen as the fuel and air as the oxidant. Peak powder density of 760 mW cm⁻² was obtained at 650 °C. And meanwhile the low polarization resistance of 0.05 Ω cm² was observed under open-circuit. The cathode also demonstrated relative stability in the duality test. The results indicate that BCFS_c is an excellent cathode candidate for P-SOFC at intermediate temperature.

Acknowledgements

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Captions

Fig. 1. XRD patterns of oxides (a) BCF, (b) BCFSc, (c) BZCY, (d) mixed BCFSc and BZCY powders with weight ratio of 1:1 after annealing at 1200 °C for 5 h.

Fig. 2. SEM image of the single cell (a) cross section view, (b) close-up image of the interface of cathode and electrolyte.

Fig. 3. Electrochemical performance of single cell (a) current density dependence of voltages and power densities for anode-supported cell at different temperatures, (b) impedance spectra of the testing single cell at open circuit condition.

Supplementary materials

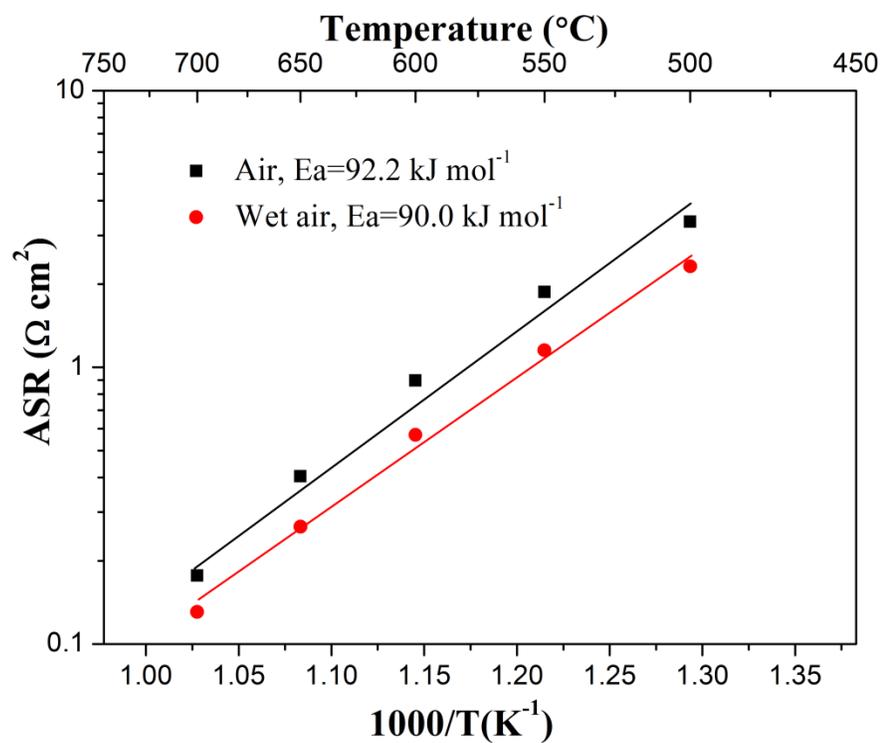


Fig. S1 Arrhenius plots of the area specific resistances for BCFSc cathode between 500 and 700 $^{\circ}\text{C}$.

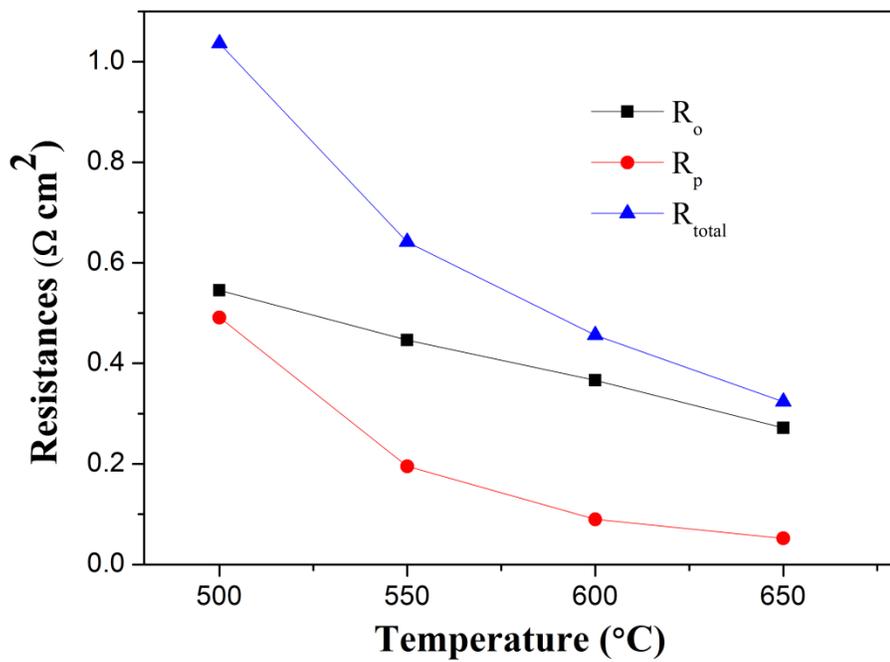


Fig. S2 The resistances of the single cell as a function of the temperature.

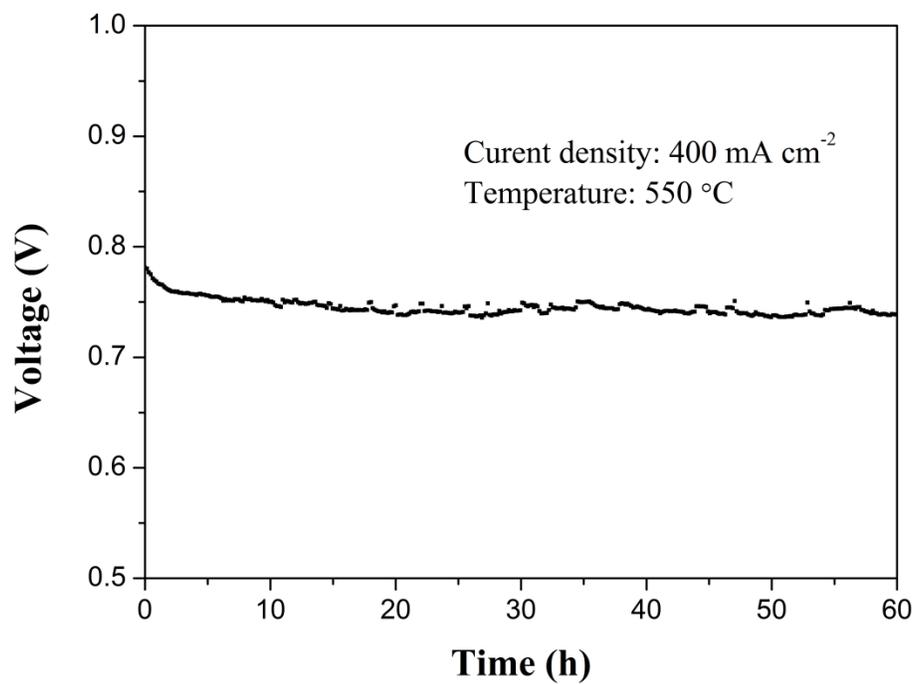


Fig. S3 Short-term stability of the single cell under a constant current density of 400 mA cm⁻² at 550 °C.