

A HIERARCHICAL HYBRID ELECTRODE FOR RAPID OXYGEN REDUCTION REACTION BELOW 800 °C

by

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The 3-D backbones with ionic conductivity are first built by sintering $Ce_{0.8}Sm_{0.2}O_{1.9}$ silks, then $Ca_3Co_2O_6$ nanoparticles as electrocatalyst are filled in by infiltrating ionic solution, as a result, a hybrid electrode with hierarchical structure is constructed as the cathode of solid oxide fuel cells. Compared with the single-phase $Ca_3Co_2O_6$ bulk cathode and common $Ca_3Co_2O_6$ - $Ce_{0.8}Sm_{0.2}O_{1.9}$ composite one, this hybrid electrode is very active for oxygen reduction reaction. At 800 °C, area specific resistance with this cathode is reduced to 0.062 Ωcm^2 , and power density peak with the electrolyte-supported single-cell is promoted to 760 mW/cm². The superior catalytical activity is attributed to the enlarged area for surface oxygen exchange kinetics and enhanced ionic transport behaviour.

Key words: solid-oxide fuel cells, cathode, fiber, oxygen reduction reaction, area specific resistance

Introduction

Sizeable impedance in solid oxide fuel cells (SOFC) arises from the catalytic cathode on which oxygen reduction reaction (ORR) is sluggish due to the hard splitting of molecular oxygen, fig. 1. Especially at the reduced operating temperatures, the cathode even becomes the main cause of polarization losses resulted from the sharply degraded activity [1-3]. So it is quite important to develop the active electro-catalysts with well-balanced physicochemical properties and to construct the appropriate electrode architectures as well.

Recently, a promising cathode material was explored to a great length by our team, and this interesting material is the hexagonal $Ca_3Co_2O_6$ (CCO) compound which shows the relatively low thermal expansion coefficient [4]. However, our subsequent investigation reveals that this material also poses the great challenges. Firstly, its ionic transport or its electronic conductivity is unreliable due to its hexagonal stacking nature of atomic arrays. Secondly, working as conventional bulk cathode constructed from the screen-printing common catalyst-containing slurry and subsequent sintering treatment, its apparent catalytic activity is barely satisfactory compared with those common cubic or quasi-cubic ABO_3 -type counterparts, such as $(La,Sr)CoO_{3-\delta}$, $Ba_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3-\delta}$, et al [5-8].

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To overcome these drawbacks with CCO cathode, great effort has been devoted in our previous work and consequently the CCO's electrochemical performance is partially improved by ion doping or by making composite with other cobalt-contained perovskites [9-11]. Especially, to improve the oxygen-ion transport property, fast ion-conductor $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) is introduced, and accordingly a binary composite $\text{Ca}_3\text{Co}_2\text{O}_6\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (CCO-SDC) is developed

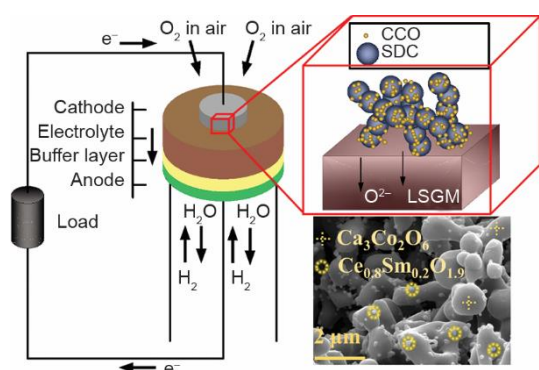


Figure 1. Components of SOFC and structure of common CCO-SDC composite cathode

by one-pot preparation [11]. However, thus prepared composite cathode presents no intentional structure which rarely conforms to the principle of efficient ORR. Firstly, in this composite structure as shown in fig. 1, SDC phase particles are too fine, and so there is insufficient bulk to form a percolating ionic conducting network. Secondly, CCO phase particles are too coarse to contribute insufficient catalytic area for surface oxygen exchange kinetics instead.

To reverse that situation and to make their morphologies quite opposite, *i. e.* to make the SDC backbones much larger and to reduce CCO particles infinitely finer, herein we report a hybrid electrode with hierarchical

structure as the new cathode materials of SOFC so that more marginal performance can be further gained from CCO. In this structure, high speed 3-D SDC backbones for oxygen-ion transport is first built by sintering the annealed SDC silks, and CCO nanoparticles with high specific surface are then filled in by ion-infiltration. This hybrid electrode bears much favorable catalytic activity for rapid ORR. Not confined to this function in SOFC, the designed hybrid electrode structure can also be readily applicable to other energy and environmental fields, including catalytic converters, oxygen-separation membranes, and batteries.

Experimental

Cells fabrication

As the preliminary materials, single-phase CCO powders and CCO-SDC common composite in optimized molar ratio of 1:1 are synthesized one after another according to our previous work [11]. Single-phase SDC powders and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ (LSGM) dense electrolyte discs are prepared by the sol-gel route and solid reaction respectively, as described elsewhere [12]. The SDC fibers are annealed from SDC silks at 700 °C for 5 hours in air, which are prepared by electrospinning 0.4 N $\text{Ce}_{0.8}\text{Sm}_{0.2}(\text{NO}_3)_{3.8}$ ethanol solution with 10 wt.% polyvinyl-pyrrolidone (PVP), as sketched in fig. 2.

Button-sized single cells are fabricated, fig. 1, in which three types of cathode with different structures are successively constructed. These cathodes are the hierarchical hybrid, common composite and conventional single-phase ones, labeled as CCO@SDC, CCO-SDC, CCO, respectively. To construct CCO@SDC cathode, 3-D SDC backbones are firstly built on LSGM discs (~230 μm thick) by sintering (at 1200 °C for 2 hours in air) the annealed SDC silks, and CCO nanoparticles are then filled in by repeatedly infiltrating 0.1 N $3\text{Ca}(\text{NO}_3)_2 \cdot 2\text{C}_4\text{H}_6\text{CoO}_4 \cdot 10\text{C}_6\text{H}_8\text{O}_7$ (citric acid) solution into SDC backbones under capillary force

and subsequent annealing at 960 °C for 5 hours in air. Common CCO-SDC composite and conventional CCO single-phase cathodes are constructed as our previous work [11]. The anode (~30 μm thick) is constructed before cathode by screen-printing the NiO-SDC slurry onto the SDC buffer layer and subsequently baking at 1250 °C for 4 h, whereas SDC buffer layer (~10 μm thick) is prepared by screen-printing SDC slurry onto LSGM disc and sintering at 1300 °C for 2 hours in air.

Characterization and performance

Phase species are distinguished by X-ray powder diffraction (XRD, PANalytical B. V.: Empyrean) in Bragg-Brentano geometry with Cu-Kα radiation. Diffraction patterns are collected in the 2θ range of 10–80° with the scan rate of 5° per minute. Microstructural morphologies are observed by SEM, (FEI: Sirion 200) and TEM (FEI: Tecnai G2 F30).

Electrochemical impedance spectroscopy (EIS) with symmetric cells in configuration of cathode|LSGM|cathode is tested under open-circuit conditions by advanced electrochemical system (Princeton Applied Research: PARSTAT 2273). In EIS test, a sinusoidal disturbance signal with 10 mV amplitude is applied and the frequency is modulated from 100 kHz to 10 mHz, and software ZsimpWin is used to construct the equivalent circuit model and to fit the EIS data based on the least-squares method. Current-Voltage (*I*-*V*) curve is measured on the button-sized single cells in configuration of anode|SDC|LSGM|cathode to demonstrate the power density output and polarization extent.

Results and discussion

Figure 3 is the morphology of SDC fibers before they are applied to build 3-D cathode backbones on LSGM electrolyte discs. As shown in figs. 3(a) and 3(b), uniform and smooth SDC silks are achieved from electrospinning, and they are around 500 nm in diameter. Even after these silks are annealed and shrank greatly after cubic phase formation, the filamentous shape is still quite preserved and annealed SDC silks are turned to around 200–300 nm in diameter, as exhibited in fig. 3(c). By probing with TEM in fig. 3(d), the annealed SDC silks are found much dense and solid, and this structure is much preferred because only in this case ionic transport is consecutive after molecular oxygens are reduced to oxygen ions.

The annealed SDC silks are further built on LSGM discs by sintering the pasted SDC fibers,

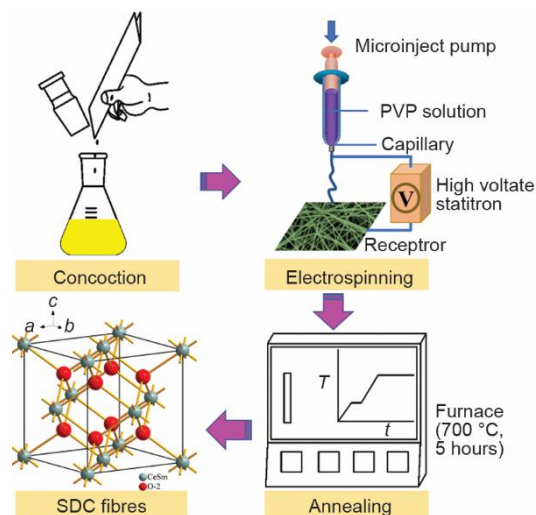


Figure 2. Preparation route for SDC fibers

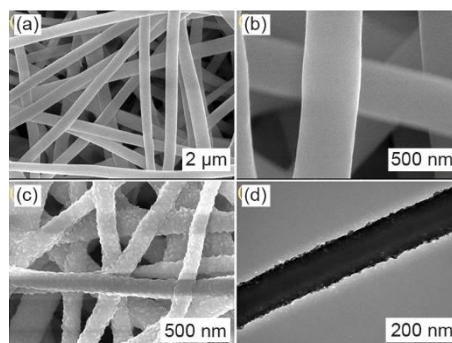


Figure 3. Morphology of SDC fibers; (a, b) SEM for fresh silks from electrospinning, (c) SEM for annealed silks, (d) TEM for annealed silks

and thus 3-D backbones are constructed as fig. 4(a), firmly connected with LSGM electrolyte and greatly inherited the precursors' fibrous morphology. By comparison with common backbone built from plain SDC particles in fig. 4(b), 3-D backbones bear more favored 3-D interconnected pores, which necessarily facilitate subsequent CCO infiltration and are capable of loading more flexible amount of CCO nanoparticles. Figure 4(c) shows the hierarchical structure of CCO@SDC hybrid after infiltration of CCO into the 3-D SDC backbones. Electrocatalyst nanoparticles are very fine and large specific surface for surface oxygen exchange is generated. Meanwhile, the gaseous diffusion paths are also maintained as the unoccupied voids. By XRD identification in which the X-rays are shed directly onto the intact cathode layer, the 3-D backbones are highly compatible with the CCO, and there is no phase reaction between them, as has been well demonstrated in our preceding work [11]. No impurity phases are involved in, and LSGM diffraction peaks come from the electrolyte substrate.

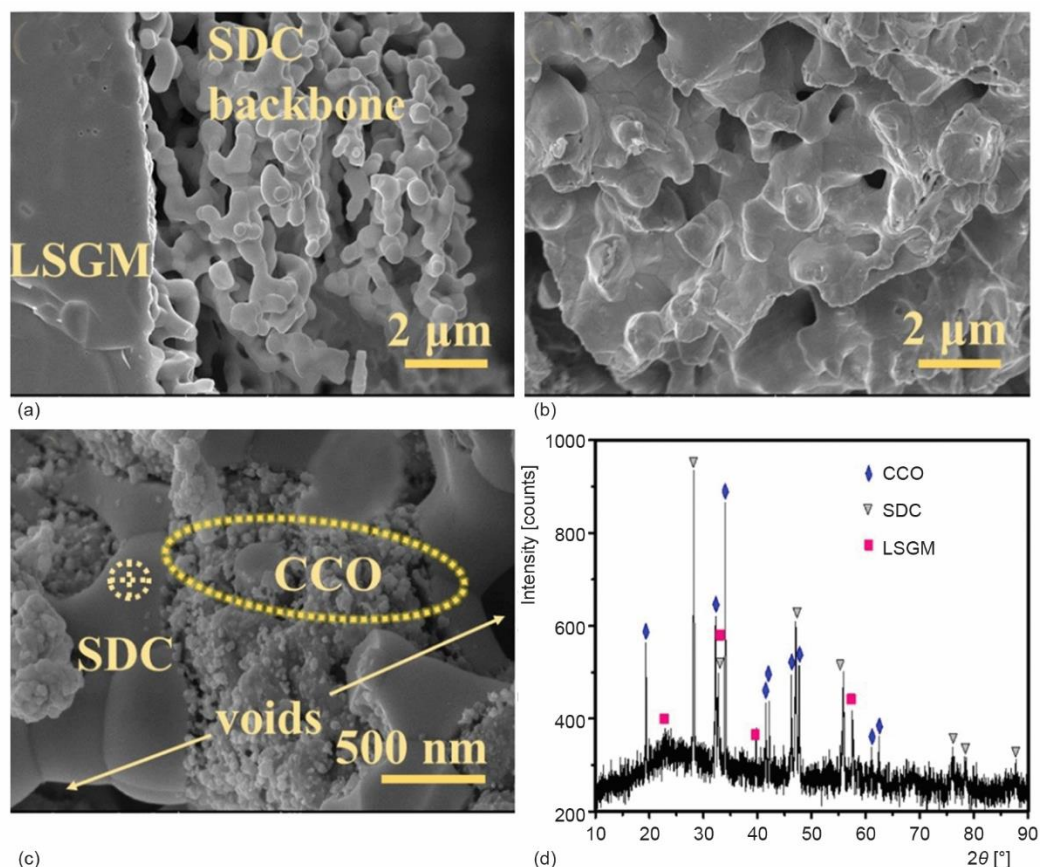


Figure 4. Structure analysis; (a) sectional SEM for SDC backbones from sintering the annealed SDC silks, (b) sectional SEM for SDC backbones from sintering the common SDC powders, (c, d) sectional SEM for CCO@SDC cathode and the corresponding XRD spectrum

Kinetics of ORR is investigated by EIS with symmetrical cathode|LSGM|cathode cells in air, and the corresponding Nyquist plots at 800 °C are shown in fig. 5(a). On the whole, all Nyquist plots comprise two overlapped capacitance arcs arising from different relaxation processes, which means that ORR is primarily governed by two different electrode

processes [13]. Therefore, equivalent circuit model of $LR_{ohm}(Q_1R_1)(Q_2R_2)$ is used to fit the spectra if response of inductive part at high frequencies is included in, and this inductive part is frequently resulted from larger perturbation amplitude which induces large magnetic fields [14]. In this model, R_{ohm} is the ohmic resistance from the electrolyte, electrode, and lead; Q_1 and Q_2 are constant phase elements. The high-frequency resistance is associated with the charge-transfer process, R_1 , while the one at low frequency is ascribed to the oxygen surface process, R_2 , including oxygen adsorption-desorption of oxygen, oxygen dissociation, and surface diffusion of intermediate oxygen species [15]. The detailed fitting data are listed in tab. 1, and the fitted results agree well with the experimental measurement, and so the kinetics explanation of electrode process based on equivalent circuit is well grounded. Particularly, the length between real axes intercepts of capacitance arcs (also R_1+R_2) stands for the total cathode polarization resistance, commonly normalized as area specific resistance (ASR), and less ASR corresponds to higher electro-catalytic activity. It is evident that electrochemical activity of CCO@SDC cathode is greatly promoted in contrast with the common CCO-SDC composite and the conventional single-phase bulk CCO cathode. For example, ASR is only $0.062 \Omega \text{ cm}^2$ for CCO@SDC as compared sharply with the $0.12 \Omega \text{ cm}^2$ for CCO-SDC and the $0.28 \Omega \text{ cm}^2$ for CCO. The temperature-dependence of ASR is linearly regressed to extract the thermal-activated energies, E_a , shown in fig. 5(b). Remarkably, CCO@SDC cathode exhibits a very low E_a values of 89.4 kJ/mol for the ORR (equivalent to 0.89 eV), much less than other two types of cathode. More significantly, both ASR and E_a of CCO@SDC cathode under comparable conditions are smaller than those of most promising ABO_3 -based cathodes, as concluded in tab. 2.

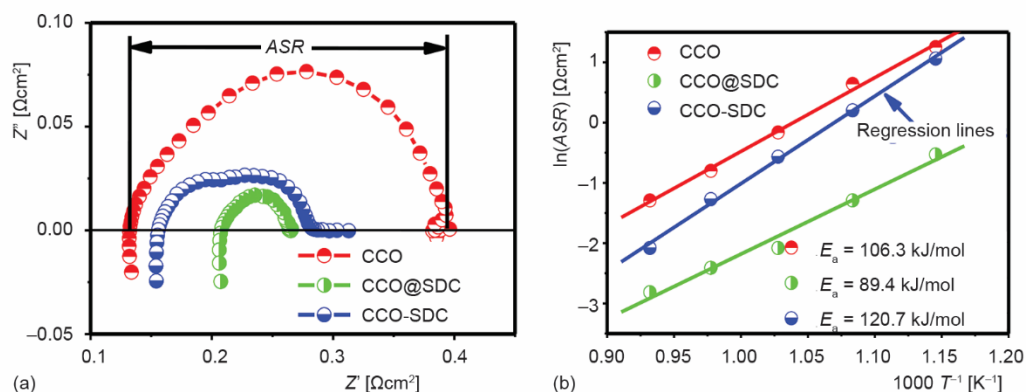


Figure 5. The EIS with different symmetrical cathodes, (a) Nyquist plots at 800°C , (b) Arrhenius plots of temperature-dependent ASR of the electrodes and calculated active energy, E_a

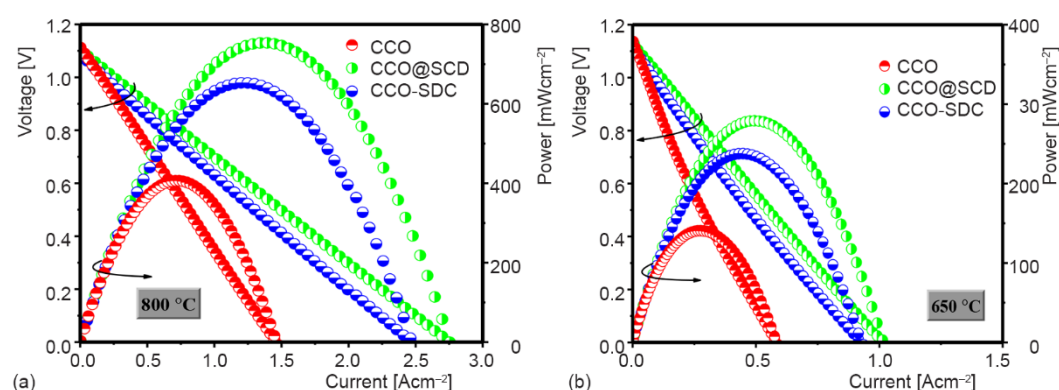
Figure 6 compares the output performance of LSGM-electrolyte-supported single-cells with different cathodes. All open circuit voltages (OVC) of cells reach to high above 1.12 V , and the nearly linear I - V plots imply that substantial portion of the driving power is applied by the thick LSGM electrolyte. Even so, power density peaks for the cell with CCO@SDC cathode still reach to 760 mW/cm^2 , 280 mW/cm^2 at 800°C , 650°C , respectively, much higher than 650 mW/cm^2 and 240 mW/cm^2 of cell with CCO-SDC cathode, further higher than 406 mW/cm^2 and 140 mW/cm^2 of cell with CCO cathode. This performance rank agrees well with that concluded from comparison of their ASR.

Table 1. Fitted results of EIS by $LR_{ohm}(Q_1R_1)(Q_2R_2)$ equivalent circuit with different symmetric electrodes at 800 °C

Elements	CCO	CCO-SDC	CCO@SDC
L [H]	$3.316 \cdot 10^{-8}$	$4.451 \cdot 10^{-8}$	$4.139 \cdot 10^{-8}$
R_{ohm} [Ω]	subtracted	subtracted	subtracted
Q_1 [$Ss^{-n}cm^{-2}$]	0.1066	0.5373	0.1368
Freq power n with Q_1	0.8546	0.7131	0.8537
R_1 [Ωcm^2]	0.1586	0.0817	0.02056
Q_2 [$Ss^{-n}cm^{-2}$]	$7.539 \cdot 10^{-2}$	$2.599 \cdot 10^{-2}$	0.2168
Freq power n with Q_2	0.7048	0.8658	0.5823
R_2 [Ωcm^2]	0.0999	0.0435	0.0398

Table 2. The ASR and E_a values of CCO@SDC against typical ABO₃-based cathodes on the same platform of LSGM electrolyte

Cathode	Temperatures [°C]	ASR [Ωcm^2]	E_a [eV]	Reference
$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}-Gd_{0.2}Ce_{0.8}O_{1.9}$	800	0.11	0.66	[8]
$SrCo_{0.9}Mo_{0.1}O_{3-\delta}$	750	0.13	1.05	[16]
$Sr_{0.7}Y_{0.3}CoO_{2.65-\delta}$	800	0.11	1.46	[17]
$PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$	800	0.07	/	[18]
CCO@SDC	800	0.062	0.89	this work
	750	0.09		

**Figure 6.** Current-dependent cell-voltage and power with different types of cathode at (a) 800 °C and (b) 650 °C

Conclusion

We demonstrate that CCO@SDC hierarchical hybrid is a quite promising high-performance cathode for SOFC operating below 800 °C. At 800 °C, the power density peak is around 760 mW/cm² for the LSGM-electrolyte-supported single-cell built with the CCO@SDC cathode, and ASR for this cathode is as low as 0.062 Ωcm^2 , showing the fast ki-

netics for ORR. Meanwhile, this cathode also exhibits much favorably low active energy for ORR. We believe that much marginal performance of CCO is still left behind this novel electrode architecture because many substructures are far from being optimized, such as concentration of CCO nanoparticles, trunk size and pore distribution of SDC backbones, thickness of overall cathode layer, etc. The macromolecular electrospinning [19-21] and the bubble electrospinning [22-24] provide additional approach to fabrication of SDC fibers.

Acknowledgment

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