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Tuning the high temperature properties of PrSrCoO₄ cathode with Cu²⁺ dopant for intermediate temperature solid oxide fuel cells

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Abstract

PrSrCo_{1-x}Cu_xO_{4+δ} ($x = 0.0, 0.1, 0.3, 0.5$) are synthesized by solid-state reaction method. The effects of Cu²⁺ doping on electrical conductivity, thermal expansion, oxygen diffusion properties and oxygen reduction reaction (ORR) activity are investigated. PrSrCo_{1-x}Cu_xO_{4+δ} oxides crystallize in a single-phase tetragonal structure with *I4/mmm* space group. Partial substitution Co³⁺ by Cu²⁺ results the increase of electrical conductivity and decrease of thermal expansion coefficient. Introducing Cu²⁺ promotes the formation of interstitial oxygen, accelerates the kinetics of oxygen transport, and significantly improves the electrocatalytic activity of

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1 ORR. The lowest area specific resistance (ASR) value of $0.08 \Omega \text{ cm}^2$ is obtained for
2 the $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ cathode at 700°C in air. The ORR mechanism study
3 demonstrates that Cu-doping (30 %) promotes the charge transfer process. The
4 reaction rate control step on $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ cathode is the dissociation and surface
5 diffusion process of adsorbed molecular oxygen.

6 **Keywords:** solid oxide fuel cells (SOFCs); K_2NiF_4 structure; cathode material;
7 electrochemical properties

9 1. Introduction

10 The A_2BO_4 oxides with K_2NiF_4 -type structure have been considered as promising
11 cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs), due
12 to their high oxygen diffusion and exchange coefficients, good electronic conductivity,
13 suitable thermal expansion coefficient (TEC) for typical electrolytes and excellent
14 electrocatalytic activity towards oxygen reduction reaction (ORR) [1-4]. A_2BO_4
15 oxides can be considered as a superstructure that composed by perovskite layer
16 (ABO_3) and rock salt layer (AO) alternatively overlapped along c-axis direction. Due
17 to the insertion character of rock salt layer, these materials exhibit special structural
18 flexibility: they can withstand reducing conditions via loss of oxygen, usually from
19 equatorial planes, and accommodate excess interstitial oxygen under oxidizing
20 conditions [5]. Studies have proved that the presence of rock salt block in T-phase
21 A_2BO_4 favors the high oxygen mobility in the bulk material [6]. Compared to the
22 traditional ABO_3 perovskite oxides, these A_2BO_4 materials show relatively large

1 oxygen ion conductivity and promising electrode performance. Therefore, Nickelate
 2 and copper based A_2BO_4 oxides with mixed ionic-electronic conducting (MIEC)
 3 properties have been thoroughly evaluated as cathode materials for IT-SOFCs [7-20].
 4 In contrast to the wealth of data accumulated on nickelate and copper oxides, few
 5 studies have been reported to date on the structure and electrochemical catalytic
 6 activity of cobalt-based A_2BO_4 oxides. An early study in 2005 by Munnings et al.
 7 found that the oxygen diffusion coefficient (D^*) and oxygen exchange coefficient (k^*)
 8 of $La_2CoO_{4+\delta}$ were even higher than that of $La_2NiO_{4+\delta}$ at $T < 700\text{ }^\circ\text{C}$ [21]. Wang and
 9 Nie reported that Ln_2CoO_4 ($Ln=Pr$ and Sm) could be applied as cathodes for SOFC
 10 via studying their thermal stability and conductive properties [22]. The
 11 electrochemical properties of Co-based A_2BO_4 materials can be further optimized by
 12 doping aliovalent elements in A and/or B site. For instance, the transport properties of
 13 Sr^{2+} doped $La_{2-x}Sr_xCoO_{4\pm\delta}$ have been systematically investigated [23]. In another
 14 study, the effects of Sb doping on the cathode property of $LaSrCo_{1-x}Sb_xO_4$ was
 15 reported by Wang et al [24]. Recently, Cao Y et al. evaluated the cathode performance
 16 of $Pr_{2-x}Sr_xCoO_{4+\delta}$ materials. They found that $Pr_{0.8}Sr_{1.2}CoO_{4+\delta}$ had the minimum
 17 polarization resistance of $0.29\text{ }\Omega\cdot\text{cm}^2$ at $700\text{ }^\circ\text{C}$ [25]. It was reported that ABO_3
 18 perovskite with Cu^{2+} at B site always exhibited low TECs [26, 27], whereas Pr based
 19 perovskite oxides are known to exhibit high electrochemical activity, due to the redox
 20 cycles of Pr^{3+} cations in the lattice [28-30]. In this study, Cu^{2+} doped
 21 $PrSrCo_{1-x}Cu_xO_{4+\delta}$ are synthesized and the effects of Cu^{2+} substitution on the crystal

1 structure, high-temperature electrical conductivity, thermal expansion behavior and
2 the electrochemical properties of the compounds are investigated. We propose the
3 $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ material, which combine the merits of both Cu^{2+} dopants and Pr^{3+}
4 cations, would be potential cathode candidate for IT-SOFCs.

5 **2. Experimental**

6 **2.1 Materials synthesis**

7 $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ ($x = 0.0, 0.1, 0.3, 0.5$) oxides are synthesized by traditional
8 solid-state reaction method. The reactants are Pr_6O_{11} , SrCO_3 , Co_3O_4 and CuO . All of
9 these materials are high purity (99.99, Aladdin industrial corporation, China), and
10 used as received. According to the chemical formula, stoichiometric amount of above
11 mentioned materials are mixed with ethanol in a planetary ball-mill for 1 h. Then the
12 obtained mixtures are pressed into pellets under 100 MPa and reacted at 1000 °C for
13 12 h in air. The obtained pellets are ground, tableted and reacted again at 1000 °C for
14 additional 12 h. This operation is repeated three times until the target products are
15 obtained. For thermal expansion coefficient (TEC) and electrical conductivity
16 measurements, the product powders are pressed under 100 MPa and then sintered at
17 1050 °C for 12 h in air, to form rectangular bars with dimensions 15 mm × 3 mm × 1
18 mm. The relative bulk densities of the rectangular bars are over 95% of the theoretical
19 values that measured by Archimedes method (Sartorius balance with a density kit).

20 **2.2 Cell fabrication**

21 $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) powder was obtained from Ningbo SuoFuRen Energy Co. Ltd.

(China). The GDC powders are pressed uniaxially at 220 MPa and then sintered at 1400°C for 10 h to form dense pellet with 10 mm in diameter and 0.8mm in thickness. The cathode ink is prepared by mixing 100 mg $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ powders with 4 mL terpineol containing 4% ethyl cellulose. The symmetric cell $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}/\text{GDC}/\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ is fabricated by painting the cathode ink on both sides of GDC pellet in symmetric configuration. The effective cathode area is 0.25 cm². The cells are initially heated at 500 °C for 0.5 h to eliminate the organic binders, and then followed by calcinations at 950 °C for 3 h with a heating/cooling rate of 5 °C min⁻¹. The electrolyte-supported single cell Ni-GDC|GDC| $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ is prepared for full cell performance test. NiO-GDC anode ink (NiO:GDC = 60:40 wt.%) is firstly painted on one side of GDC pellet, followed by heat-treatment at 1250 °C for 4 h in air to form anode with surface area of 0.25 cm². $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ cathode is then prepared on the other side of GDC pellet in symmetrical configuration.

2.3 Characterization

The phase purity and chemical compatibility of $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ with GDC are characterized by powder X-ray diffraction method (XRD, Bruker AXS D8). The measurements are conducted at 40 kV and 40 mA using Cu $K\alpha$ radiation. The diffraction data is collected in the 2θ range of 20°-75° with scanning speed 8°/min. The unit cell parameters are analyzed by LeBail refinement method with the Fullprof package. In the refinement procedure, the 6-coefficients polynomial function and Pseudo-Voigt function are selected to fit the background and peak shape, respectively.

1 TG measurements are performed from 25 °C to 900 °C in air, with the heating rate of
2 10 °C/min using Setaram Setsys 16/18 thermoanalyser. The thermal expansion
3 behavior of the sample is monitored in air from 100 °C to 800 °C with the heating rate
4 of 5 °C/min (Setaram Setsys 16/18 dilatometer).

5 X-ray photoelectron spectroscopy (XPS) is recorded to study the surface oxygen
6 species of the material. The measurement is performed using a Kratos Axis Ultra Dld
7 photoelectron spectrometer equipped with Al K α (1486.6 eV) radiation source. The
8 microstructure of the symmetrical cell is recorded using field-emission scanning
9 electron microscope (FE-SEM, S-4800, Hitachi).

10 The electrical conductivity and electrical conductivity relaxation (ECR) of the
11 specimens are measured by standard four-probe DC method. The conductivities are
12 measured in the temperature range of 100-800 °C in air. The ECR measurements are
13 performed at 650°C, 700°C and 750°C. In order to obtain the transient curve at each
14 temperature, the oxygen partial pressure of the measurement atmosphere is switched
15 rapidly from 20% to 2%.

16 The EIS diagrams are collected with electrochemical workstation (AUTOLAB,
17 PGStat 30) under open circuit voltage (OCV). The applied frequency is ranged from
18 1MHz to 0.01Hz, and the signal amplitude is 50 mV. The measurements are
19 performed as a function of temperature (500 °C-700 °C) and oxygen partial pressure
20 that controlled by N₂ (99.999%)/O₂ (99.999%) mixed atmosphere.

21 The power output performance of the electrolyte-supported single cell is tested with

1 the device of ProboStat30. Humidified H_2 (97% H_2 /3% H_2O) is fed to the anode
2 chamber at a flow rate of 50 ml min^{-1} , while the cathode is exposed to ambient air. Ag
3 meshes are used as current collectors for both anode and cathode sides.

4 **3. Results and discussions**

5 3.1 Phase identification

6 The XRD patterns of $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ are shown in Figure 1a. All the patterns are
7 similar to the reported PrSrCoO_4 material [31], indicating the sample is crystallized in
8 single-phase K_2NiF_4 -type structure with SG $I4/mmm$. The refinement results of the
9 unit cell parameters are listed in Table 1. It is observed that the cell parameter c
10 increases steadily with Cu^{2+} doping. This observation can be understood, considering
11 the Jahn-Teller effect of Cu^{2+} with electronic configuration of d^9 . Cu^{2+} cations tend to
12 form square planar coordination. In this sense, the apical Cu–O distance is much
13 longer than that of equatorial Cu–O distance in $[\text{CuO}_6]$ octahedron. In addition, more
14 interstitial oxygen is generated in the rock-salt layer with Cu^{2+} doping, which also
15 causes the expansion of c -axis. The similar conclusions have been drawn in the other
16 Cu^{2+} doped Ln_2NiO_4 materials [32-35]. On the other hand, the cell parameters a (b)
17 decrease first and then increase again with the Cu^{2+} doping, with an inflection point at
18 $x = 0.3$. In order to maintain the charge neutrality requirement, Cu^{2+} doping leads to
19 the partial oxidation of Co^{3+} to Co^{4+} . According to the valence bond theory, the
20 cobalt-oxygen bond is strengthened and the bond length along $a(b)$ -axis direction
21 decreases with the Cu^{2+} doping. At the same time, we should also consider the size

1 effects of doped Cu^{2+} (the radius of Cu^{2+} (72 pm) is larger than that of Co^{3+} (63 pm)
2 and Co^{4+} (53 pm)). Therefore, the variation of cell parameters a (b) for
3 $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ oxides seems to be a competitive results of the doped amount of

4
5 Fig. 1. Experimental (black continuous line) and calculated (red line) XRD patterns,
6 and their difference (green line at the bottom) for $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$. Blue vertical bar
7 indicate the position of Bragg peaks of the phases contained in the sample (a),
8 Mixture of $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ with GDC after annealed at 1000 °C for 24 h in air (b).

9 **Table 1**

10 Cell parameters of $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ ($x = 0.0, 0.1, 0.3, 0.5$).

	a/b (Å)	c (Å)	V (Å ³)	Space group	R_p (%)	R_{wp} (%)	χ^2
$\text{PrSrCoO}_{4+\delta}$							2.40
	3.792(3)	12.460(3)	179.19	$I4/mmm$	6.59	8.74	
$\text{PrSrCo}_{0.9}\text{Cu}_{0.1}\text{O}_{4+\delta}$							1.36
	3.790(2)	12.461(3)	179.01	$I4/mmm$	4.01	5.58	
$\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$							1.36
	3.781(3)	12.478(7)	178.39	$I4/mmm$	6.25	7.96	
$\text{PrSrCo}_{0.5}\text{Cu}_{0.5}\text{O}_{4+\delta}$							1.7
	3.787(6)	12.519(5)	179.55	$I4/mmm$	5.69	6.73	
							1

11 Cu^{2+} and the valence state of Co ions. To assess the possible reaction between

1 PrSrCo_{0.7}Cu_{0.3}O_{4+δ} and GDC electrolyte, the two oxide powders are mixed in weight
2 ratio of 1:1, and then sintered at 1000 °C for 24 h in air. The XRD patterns of the
3 sintered mixtures are shown in Fig. 1b. No additional peaks indicating new phase
4 formation are detected from the patterns of the mixture. It is concluded that
5 PrSrCo_{0.7}Cu_{0.3}O_{4+δ} is chemically compatible with GDC below 1000 °C.

6 3.2 X-ray photoelectron spectroscopy analysis and Oxygen non-stoichiometry in 7 PrSrCo_{1-x}Cu_xO_{4+δ}

8 To identify the surface properties of PrSrCo_{1-x}Cu_xO_{4+δ} ($x = 0.0, 0.1, 0.3, 0.5$) oxides,
9 the chemical states of elemental Co, Cu, and O are measured by X-ray photoelectron
10 spectroscopy (XPS) and normalized with C 1s peak at 284.6 eV. The strontium ions
11 and copper ions exhibit mono-oxidation state as Sr²⁺ and Cu²⁺ in PrSrCo_{1-x}Cu_xO_{4+δ},
12 while Pr and Co cations display mixed valance states. The Co 2p XPS spectra and the
13 fitting curves are presented in Figure 2a. The peaks at 779.5 and 794.3 eV can be
14 assigned to Co³⁺ 2p_{3/2} and 2p_{1/2}, whereas the other set of peaks with binding energies
15 of 780.8 and 795.5 eV represent Co⁴⁺ 2p_{3/2} and 2p_{1/2}, respectively [36,37].

16 The Pr 3d XPS spectra and the fitting curves are presented in Figure 2b. The peaks
17 with binding energy at 927.9/933.0 eV and 948.4/953.6 eV originate from Pr³⁺ 3d_{5/2}
18 and 3d_{3/2}, and the doublet peaks located at 931.0 eV and 952.3 eV can be assigned to
19 Pr⁴⁺ 3d_{5/2} and 3d_{3/2}, respectively [37,38]. The fitting results indicate that Pr³⁺ coexists
20 with Pr⁴⁺ in these samples.

21 From the XPS analysis, the percentage contributions of different valence states are

1 calculated and the average valences of Pr and Co ions are tabulated in Table 2.

2
3 Fig. 2. XPS spectra and fitting lines of Co 2p (a), Pr 3d (b) in $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$
4 samples at room temperature.

5 **Table 2**

6 Contents of non-stoichiometric oxygen (δ), average valences of Pr ($m+$) and Co ($n+$)
7 ions in $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ oxides.

x	Pr ^{m+}	Co ⁿ⁺	δ
0.0	3.04	3.00	0.02
0.1	3.11	3.06	0.03
0.3	3.26	3.23	0.06
0.5	3.42	3.49	0.08

8 Quantitative analysis of O content for each sample is carried out according to the XPS
9 spectra and the results are also listed in Table 2. The oxygen contents for all of the
10 as-prepared samples are found to be slightly above 4.0, indicating the existence of
11 interstitial oxygen in the material. The average valences of Pr and Co increase steadily

1 with the substitution of Cu from $x = 0.1$ to $x = 0.5$, and the overstoichiometric oxygen
2 content (δ) increases from 0.02 to 0.08.

3 Since oxygen species on the cathode surface play a key role for oxygen reduction
4 reaction, the O1s XPS spectra of $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ are further analyzed, and the
5 fitting results are presented in Figure 3. The peak around 528.5 ± 0.4 eV corresponds to
6 the lattice oxygen ($\text{O}_{\text{lattice}}$) associating to the redox properties of metal ions [24, 39-43].
7 The broad peak centered around 531.2 ± 0.3 eV can be assigned to the absorbed
8 oxygen species (O_{abs}) on surface [38-43].

9
10 Fig. 3. O 1s core-level spectra and fitting lines of $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ at room
11 temperature.

12 Table 3 summarizes the area percentage of different kinds of oxygen species in
13 $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$. Obviously, the amount of chemisorbed oxygen increases with the

1 value of x , implying the improved ORR catalytic activity of Cu^{2+} doped materials.

2 **Table3**

3 The fitting results of O 1s XPS spectra for $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$.

$\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$	$\text{O}_{\text{lattice}}$		O_{abs}	
	Position(eV)	Area(%)	Position(eV)	Area(%)
$x = 0.0$	528.9	14.9	531.3	85.1
$x = 0.1$	528.1	8.7	530.9	91.3
$x = 0.3$	528.2	8.0	531.0	92.0
$x = 0.5$	528.7	3.6	531.4	96.4

4 3.3 Surface oxygen exchange and Electrical conductivity relaxation

5 It is known that the lattice oxygen in the perovskite oxides can be released at high
6 temperatures and leads to changes of the point defects. To get this knowledge, the
7 thermogravimetric analysis (TGA) is performed on $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ samples (Figure
8 4a). The measurement is carried out within two consecutive thermo-cycles in between
9 room temperature up to 900 °C with a ramp of 10 °C min⁻¹ each cycle, and the data of
10 the second cycle is recorded. The corresponding oxygen non-stoichiometry as a
11 function of temperature is determined from the weight change of the sample,
12 assuming the initial oxygen content is obtained from the XPS analysis (Figure 4b). All
13 the samples show weight loss at temperatures above ~ 400 °C, due to the
14 thermal-driven release of interstitial oxygen from the lattice, accompanied by the
15 reduction of Co ions. It can be observed that the weight loss of the samples with $x =$

0.0 and 0.1 are very small, while it becomes significant for the samples with $x = 0.3$ and 0.5. In addition, the Cu^{2+} doped materials exhibit reversible behavior of oxygen lose and uptake throughout the heating/cooling cycles.

Fig. 4. (a) Thermogravimetric curves of $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ ($x = 0.0 \sim 0.5$); (b) corresponding oxygen non-stoichiometry plots as function of temperatures.

For $\text{PrSrCoO}_{4+\delta}$ however, the weight could not reach to its initial value after the thermo-cycle. This behavior suggests that the oxygen exchange process between the oxides and gaseous oxygen is promoted for the Cu^{2+} doped samples. This can be reasonably interpreted. Firstly, Cu^{2+} doping promotes the oxygen surface adsorption ability of the $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ oxides (as that proved from the O1s XPS results). Secondly, the interstitial oxygen concentration (δ) increases with the increase of Cu^{2+} doping concentration (table 2). Diffusion of interstitial oxygen may enhance oxygen reduction reaction occurring on the cathode in the intermediate temperature range. [44-47].

Fig. 5 shows the typical normalized conductivity relaxation transient curves for $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$. The values of D_{chem} and k_{chem} are obtained from fitting the

1 normalized conductivities to the appropriate solution of Fick's second law (inset, Fig.
2 5). The D_{chem} and k_{chem} values obtained at 750°C in this study are $1.39 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$
3 and $1.28 \times 10^{-2} \text{ cm s}^{-1}$ respectively. For comparison, the D_{chem} value of $5.5 \times 10^{-4} \text{ cm}^2$
4 s^{-1} and k_{chem} of $2.1 \times 10^{-2} \text{ cm s}^{-1}$ at 750 °C were reported by Saher et al. for $\text{Pr}_2\text{NiO}_{4+\delta}$
5 [48]. Li et al. measured a D_{chem} and k_{chem} values of $3.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $1.6 \times 10^{-3} \text{ cm}$
6 s^{-1} at 750 °C for $\text{La}_2\text{NiO}_{4+\delta}$ [49]. It can be seen that oxygen transport properties of
7 $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ is comparable to those cathode materials with excellent ORR
8 activity reported in the literatures.

9
10 Fig. 5. Normalized conductivity transients measured on $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ cathode
11 material at different temperatures.

12 3.4 Electrical conductivity

13 Fig. 6 presents the conductivity of $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ as a function of temperature in
14 air. All the materials show gradual increase of the conductivity with the measuring
15 temperature. It is observed that the conductivity of Cu^{2+} doped materials are always
16 higher than $\text{PrSrCoO}_{4+\delta}$, and it increases further with the Cu^{2+} doping concentration.

1 The conductivity values of all samples exceed 100 S cm^{-1} at 700°C , meeting the
 2 requirement of the SOFC cathode materials.

3
 4 Fig. 6. Temperature dependencies of electrical conductivity of $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ ($x =$
 5 $0.0 \sim 0.5$) in air at different temperatures.

6 3.5 Electrocatalytic activity

7 In order to investigate the electrochemical properties, symmetrical cells are
 8 constructed with $\text{PrSrCo}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ electrode and GDC electrolyte. Fig.7 shows the
 9 surface and cross-section SEM images of $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ cathode on GDC
 10 electrolyte that sintered at 950°C for 3 hours. Clearly $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ adheres

11
 12 Fig.7. SEM images of the $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ electrode sintered at 950°C for 3 h (a:

1 surface; b: cross section).

2 tightly on the dense GDC electrolyte, to form a porous cathode with thickness ~ 22

3 μm and no obvious delamination can be observed. This result is due to the similar

4 TEC value of $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ ($13.6 \times 10^{-6} \text{ }^\circ\text{C}$) and GDC electrolyte ($13.1 \times 10^{-6} \text{ }^\circ\text{C}$)

5 (inset figure 7b). It is also observed that the TEC value has been greatly reduced in

6 the Cu^{2+} doped material.

7 Fig. 8a shows the impedance spectra of $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ cathode measured at

8 different temperatures. Obviously depressed arcs with irregular shape are observed at

9 the measurement temperatures. The polarization resistance (R_p) is obtained from the

10 difference between low frequency intersection and high frequency one with Z' axis. It

11 is observed that R_p decreases rapidly with the increase of measurement temperature,

12 showing a thermoactivated ORR reaction. Fig. 8b shows the Arrhenius plot of R_p as a

13 function of temperature. The R_p value of 0.46, 0.14, 0.08 and $0.18 \text{ } \Omega \text{ cm}^2$ are

14 obtained at $700 \text{ }^\circ\text{C}$ for $x = 0.0, 0.1, 0.3$ and 0.5 , respectively. It can be seen that Cu^{2+}

15 doping significantly improves the catalytic performance of the electrode. This may be

16 because the incorporation of copper ions increases the interstitial oxygen

17 concentration in the material, which improves the oxygen ion transport performance.

18 The activation energy of ORR is obtained from the slope of the Arrhenius plot, and

19 the results are listed in Fig. 8b. Compared to the pristine $\text{PrSrCoO}_{4+\delta}$, the activation

20 energy of Cu^{2+} doped cathode is significantly reduced, suggesting that the oxygen

21 reduction mechanism on the copper-doped electrode is different from that of

1 PrSrCoO_{4+δ}.

2

3 Fig. 8. (a) Nyquist plots of PrSrCo_{0.7}Cu_{0.3}O_{4+δ} cathode measured at different
 4 temperatures in air. In order to show clearly the change of R_p with temperature, the
 5 resistance contribution of electrolyte and lead wires have been removed from the plot;
 6 (b) Polarization resistance plotted versus inverse temperature for PrSrCo_{1-x}Cu_xO_{4+δ} (x
 7 = 0.0, 0.1, 0.3, 0.5) cathodes.

8 In order to further understand the rate control step of the oxygen reduction (ORR) on
 9 different electrodes, the impedance spectra of PrSrCoO_{4+δ} and PrSrCo_{0.7}Cu_{0.3}O_{4+δ} are
 10 collected at 700 °C under different oxygen partial pressures, and fitted with equivalent
 11 circuit R_{ohm}-(R_H-CPE)-(R_L-CPE) (Fig.9a and Fig.10a). Here R_{ohm} is the resistant
 12 contribution of GDC electrolyte and lead wires, R_H and R_L represent the polarization
 13 resistances of high frequency arc and low frequency arc related electrode processes.
 14 The electrochemical reaction mechanism on the cathode is studied by plotting R_H and
 15 R_L as a function of oxygen partial pressure (P_{O₂}), respectively (Fig.9b and Fig.10b). It
 16 is known that the variation of R_p vs P_{O₂} can be well described by the following
 17 expression: R_p = R_p⁰ × (P_{O₂})ⁿ

1 The n values give information about the species involved in the electrode reactions
 2 [50-52]

3 $n = 1 \quad O_2(g) \rightarrow O_{2,ads}$ (Adsorption of O_2 onto the cathode surface)

4 $n = 1/2 \quad O_{2,ads} \rightarrow 2O_{ads}$ (Dissociation of molecular adsorbed oxygen into atom
 5 adsorbed oxygen on cathode surface)

6 $n = 3/8 \quad O_{TPB} + e^- \rightarrow O_{TPB}^-$ } (Reduction reaction of atom adsorbed oxygen
 7 $n = 1/8 \quad O_{TPB}^- + e^- \rightarrow O_{TPB}^{2-}$ } into adsorbed oxygen ion at TPBs)

8 $n = 0 \quad O_{TPB}^{2-} + V_O^{\bullet\bullet} \rightarrow O_O^x$ (The ionic oxygen transfers from the TPB to the
 9 electrolyte)

10 Obviously, $PrSrCoO_{4+\delta}$ and $PrSrCo_{0.7}Cu_{0.3}O_{4+\delta}$ cathodes exhibit different reaction
 11 order (n). For $PrSrCoO_{4+\delta}$ cathode, the value of n is about 0.04 for R_H , which can be
 12 ascribed to the step of oxygen ions transfer through the electrode and
 13 electrode/electrolyte interface. The n value of low frequency arc is about 0.34, which
 14 is close to 3/8. Therefore, the low frequency arc is confirmed to be related to the

15
 16 Fig. 9. (a) Impedance plots of the $PrSrCoO_{4+\delta}$ electrode with different morphologies
 17 measured at $700^\circ C$ in air; (b) Logarithm plot of polarization resistance vs oxygen

1 partial pressure.

2

3 Fig. 10. (a) Impedance spectra for the $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ cathode on GDC at 700 °C
4 under various oxygen partial pressures; (b) Logarithm plot of polarization resistance
5 vs oxygen partial pressure.

6 charge transfer process. In the whole range of the oxygen partial pressure that
7 measured, the value of R_L is always larger than that of R_H , which means that the
8 charge transfer process on $\text{PrSrCoO}_{4+\delta}$ cathode is the rate-limiting step. In the case of
9 $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ cathode, however the magnitude of n for high frequency arc is
10 close to 1/2, which suggests this process relates to the dissociation of the adsorbed
11 molecular oxygen and surface diffusion. In addition, the n value of low frequency arc
12 is about 1.0, suggesting a diffusion process of gas oxygen inside the porous cathode.
13 The larger resistance value of R_H than that of R_L under various oxygen partial
14 pressures means that the reaction rate-limiting step on $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ cathode is
15 the dissociation and surface diffusion of the adsorbed molecular oxygen. In summary,
16 we found that Cu^{2+} doping in $\text{PrSrCoO}_{4+\delta}$ cathode changes the oxygen reduction
17 mechanism from the charge transfer process to the dissociation of adsorbed molecular

oxygen and surface diffusion process.

Fig.11 presents the I-V and I-P curves of the electrolyte support single cell with the configuration of Ni-GDC|GDC|PrSrCo_{0.7}Cu_{0.3}O_{4+δ}. The single cell exhibits the maximum power density of 327 mW cm⁻² at 700 °C. This value is much higher than that of 201 mW cm⁻² for (Pr_{0.9}La_{0.1})₂Ni_{0.74}Cu_{0.21}Ga_{0.05}O_{4+δ} cathode [53] and 298 mW cm⁻² for Pr₂NiO₄ cathode [54] at 700 °C reported in the literatures with similar cell configuration. Accordingly, the oxygen exchange capacity and electrocatalytic performance of PrSrCoO₄ cathode are successfully improved by Cu²⁺ doping strategy.

PrSrCo_{0.7}Cu_{0.3}O_{4+δ} is proved to be a potential cathode material for IT-SOFCs.

Fig. 11. Cell voltage and power density as a function of current density for electrolyte-supported cells Ni-GDC/GDC/ PrSrCo_{0.7}Cu_{0.3}O_{4+δ} with humidified H₂ as fuel and ambient air as oxidant.

4. Conclusions

PrSrCo_{1-x}Cu_xO_{4+δ} ($x = 0.0, 0.1, 0.3, 0.5$) materials were synthesized by solid-state reaction method. The results show that PrSrCo_{1-x}Cu_xO_{4+δ} has good chemical and

1 thermal compatibility with GDC electrolyte. Copper doping increases the interstitial
2 oxygen concentration and improves the electrochemical performance of the material.
3 $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ cathode exhibits the lowest polarization resistance of $0.08 \Omega \text{ cm}^2$
4 at 700°C , and the rate determining step (RDS) of $\text{PrSrCo}_{0.7}\text{Cu}_{0.3}\text{O}_{4+\delta}$ cathode is
5 dissociation of the adsorbed molecular oxygen and surface diffusion process.

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9

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