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## Study of oxygen reduction mechanism on Ag modified Sm<sub>1.8</sub>Ce<sub>0.2</sub>CuO<sub>4</sub> cathode for solid oxide fuel cell

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1 **Study of oxygen reduction mechanism on Ag modified**  
2 **Sm<sub>1.8</sub>Ce<sub>0.2</sub>CuO<sub>4</sub> cathode for solid oxide fuel cell**

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15 **ABSTRACT**

16 Different amount of metal silver particles are infiltrated into porous  $\text{Sm}_{1.8}\text{Ce}_{0.2}\text{CuO}_4$  (SCC)  
17 scaffold to form SCC–Ag composite cathodes. The chemical stability, microstructure  
18 evolution and electrochemical performance of the composite cathode are investigated using  
19 X-ray diffraction (XRD), scanning electron microscopy (SEM), and AC impedance  
20 spectroscopy respectively. The composite cathode exhibits enhanced chemical stability. The  
21 metal Ag remains un-reacted with SCC and  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (CGO) at 800 °C for 72 h. The  
22 polarization resistance of the composite cathode decreases with the addition of metal Ag. The  
23 optimum cathode SCC-Ag05 exhibits the lowest area specific resistance (ASR,  $0.43 \Omega \text{ cm}^2$ ) at  
24 700 °C in air. Investigation shows that metal Ag accelerates the charge transfer process in the  
25 composite cathode, and the rate limiting step for electrochemical oxygen reduction reaction  
26 (ORR) changes to oxygen dissociation and diffusion process.

27 *KEYWORDS: Solid oxide fuel cell; Silver infiltration; Composite cathode; Electrode reaction*

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## 30 **1 Introduction**

31 One of the research targets for SOFCs is lowering the operating temperature in order to  
32 increase the life-time of the cell/stack/module as well as to reduce the cost of the materials. So  
33 far, many studies have been focused on the development of new electrode and electrolyte  
34 materials toward low temperature operable SOFCs [1], [2], [3] and [4]. Layered perovskite  
35 oxides with  $K_2NiF_4$ -type structure were extensively studied in recent years, due to their  
36 promising transport and catalytic properties, thermochemical stability and compatibility with  
37 other cell components [5], [6], [7], [8], [9], [10], [11], [12], [13], [14] and [15]. Among these  
38 oxides,  $Ln_2CuO_4$  materials were found to exhibit excellent performance. For example, Li et  
39 al. reported that the ASR of the  $La_{1.7}Sr_{0.3}CuO_4$  cathode was as low as  $0.16 \Omega \text{ cm}^2$  at  $700 \text{ }^\circ\text{C}$   
40 [16]. We studied the electrochemical performance of  $Sm_{2-x}Ce_xCuO_4$  and the ASR of  
41  $Sm_{1.8}Ce_{0.2}CuO_4$  was found to be  $1.16 \Omega \text{ cm}^2$  at  $700 \text{ }^\circ\text{C}$  [17]. Further research on the oxygen  
42 reduction kinetics of these cuprate cathodes always found that the charge transfer reaction was  
43 the rate limiting step [16], [17], [18], [19] and [20]. Thus, enhancing the oxygen reduction  
44 activity of these cathode materials is crucial for the development of novel IT-SOFC cathode.

45

46 Studies proved that cathodes infiltrated with Palladium (Pd) and platinum (Pt) metal particles  
47 showed promising oxygen reduction activity, due to the substantially increase of the surface  
48 catalysis properties [21] and [22]. Ag is another attractive infiltrating candidate than those  
49 precious metals, due to its good catalytic activity, high electrical conductivity and relatively  
50 low cost. Numerous works have been performed on the Ag-added perovskite cathodes [23],  
51 [24], [25], [26] and [27], but less attention was paid to the  $K_2NiF_4$ -type material [28].

52

53 To continue our studies on  $\text{Sm}_{1.8}\text{Ce}_{0.2}\text{CuO}_4$  (referred as SCC in this paper) cathode materials,  
54 and to understand the effect of Ag doping on the electrode performance, SCC-Ag composite  
55 cathode was selected and the electrochemical property was studied compared with the bare  
56 SCC electrode. The mechanism of the oxygen reduction on the SCC-Ag composite cathode  
57 was investigated using electrochemical impedance spectroscopy (EIS) technique.

## 58 **2 Experimental**

59  $\text{Sm}_{1.8}\text{Ce}_{0.2}\text{CuO}_4$  powder was synthesized using the glycine-nitrate process (GNP). According  
60 to the formula, stoichiometric amount of metal nitrates were mixed in a beaker to form a  
61 solution, and then glycine (aminoacetic acid,  $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ ) was added into the nitrate  
62 solution at 1:2 M ratio of metal ions/glycine according to propellant chemistry. After drying  
63 and firing, the resultant powder was calcined in air at 1000 °C for 12 h. The  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$   
64 (CGO) powder (Rhodia Courbevoie, France) was pressed uniaxially at 220 MPa and sintered  
65 at 1400 °C for 10 h to form a densified pellet. In order to perform EIS measurement, a test  
66 cell with three electrodes configuration was constructed. The  $\text{Sm}_{1.8}\text{Ce}_{0.2}\text{CuO}_4$  powder was  
67 mixed with terpineol to form a slurry, and subsequently painted on one side of the CGO  
68 electrolyte pellet to form an electrode area of 0.5 cm<sup>2</sup>, used as working electrode (WE). The  
69 WE was first heated at 400 °C for 2 h to eliminate organic binders, followed by sintering at  
70 1000 °C for 4 h in air, with a heating/cooling rate of 3 °C min<sup>-1</sup>. Platinum paste was painted  
71 on the other side of the CGO pellet in symmetric configuration, and then sintered at 800 °C  
72 for 1 h in air, to form porous counter electrode (CE). A Pt wire was used as reference  
73 electrode (RE) and put on the same side of the working electrode. Silver nitrate solution was  
74 then infiltrated into the porous cathode. The detail of infiltration process was as follows: 0.05  
75 mol L<sup>-1</sup>  $\text{AgNO}_3$  solution was prepared by dissolving silver nitrate powders in mixture solution  
76 of distilled water and ethanol. Ethanol was added to reduce the surface tension on SCC

77 backbone. The ratio of ethanol to water is 1 to 1. The infiltration was carried out in a vacuum  
78 chamber by dripping the  $\text{AgNO}_3$  solution onto the SCC cathode area carefully using an  
79 injector and drying at  $80\text{ }^\circ\text{C}$ . The infiltrated cathode was then calcined at  $800\text{ }^\circ\text{C}$  for one hour.  
80 This infiltration step was repeated several times to obtain a suitable weight of Ag loaded on  
81 the SCC backbone. The obtained cathodes with different weight ratio of Ag were abbreviated  
82 as SCC-Ag02 for  $\text{Sm}_{1.8}\text{Ce}_{0.2}\text{CuO}_4$  with 2 wt.% Ag, SCC-Ag05 for  $\text{Sm}_{1.8}\text{Ce}_{0.2}\text{CuO}_4$  with 5  
83 wt.% Ag, and so on.

84

85 In order to check the chemical stability of SCC with CGO at high temperature, these two  
86 components were mixed thoroughly in 1:1 weight ratio, and heat-treated at  $1000\text{ }^\circ\text{C}$  for 4 h in  
87 air. Silver nitrate was then added to the mixture, and again heated up to  $800\text{ }^\circ\text{C}$  for 72 h to  
88 form SCC–CGO–Ag composite powders.

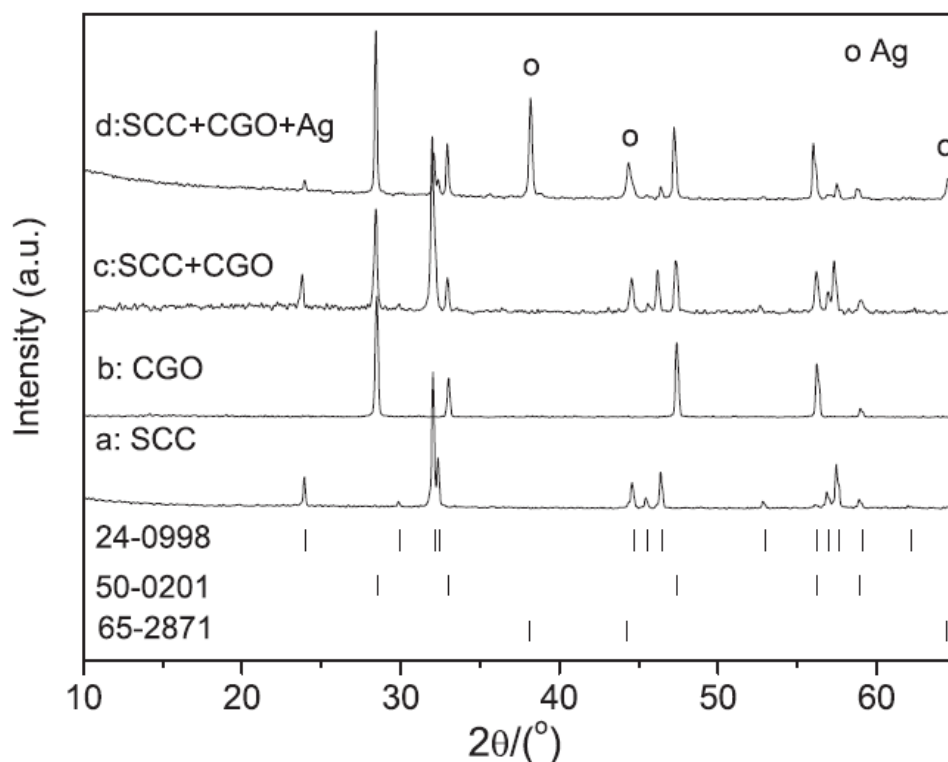
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90 The sample was characterized using X-ray diffraction instrument (Rigaku, D/MAX-3B) and  
91 scanning electron microscopy (SEM) (Hitachi, S-4700 FEG), respectively. The impedance  
92 spectra were recorded over the frequency range 1 MHz to 0.1 Hz using Autolab PGStat30.  
93 The measurements were performed at OCV as a function of temperature ( $550\text{--}700\text{ }^\circ\text{C}$ ) and  
94 oxygen partial pressure (in  $\text{N}_2/\text{O}_2$  mixed atmosphere).

### 95 **3 Results and discussion**

96 Phase purity of the prepared SCC and chemical compatibility of Ag metal with SCC and  
97 CGO were first investigated. Fig. 1 shows XRD patterns of the sintered SCC–CGO and SCC–  
98 CGO–Ag composite powders. The spectra of pure SCC and CGO materials are also presented  
99 in the same figure for comparison. The SCC powder made by GNP process crystallizes in  
100 body-centered tetragonal symmetry (Fig. 1(a)), consisting with  $\text{Sm}_2\text{CuO}_4$  structure (PDF card

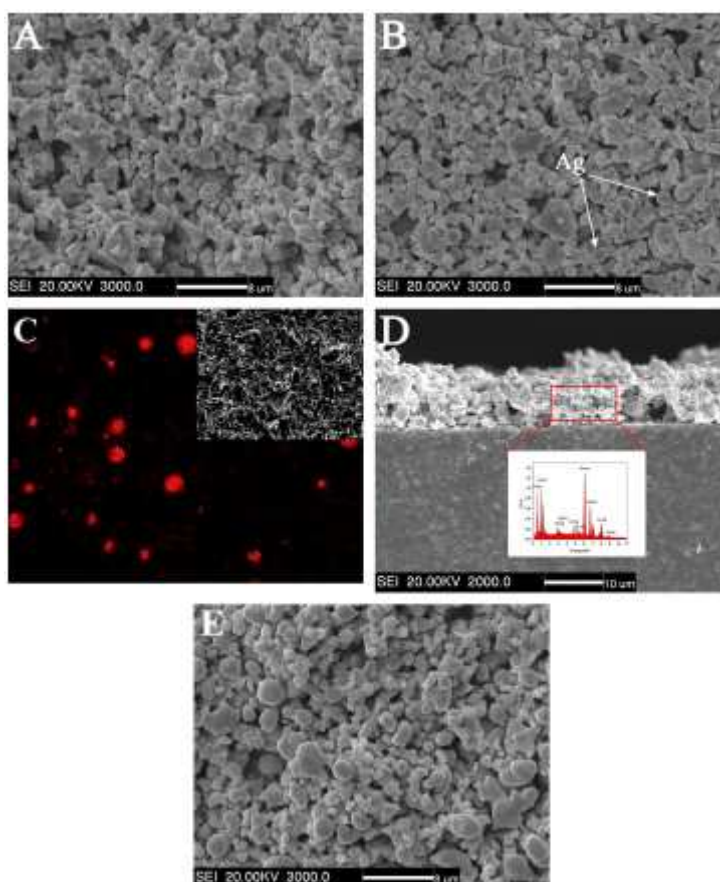
101 No. 24-0998). After sintered at 1000 °C for 4 h, SCC and CGO retained their own structures  
102 in the SCC–CGO mixture (Fig. 1(c)). When Ag was added and the composite cathode was  
103 then heated at 800 °C for prolonged 72 h, no additional peaks except those from metal Ag,  
104 SCC and CGO can be detected (Fig. 1(d)). This result indicates that Ag is highly chemical  
105 compatible with SCC and CGO materials.



106  
107 Fig. 1: XRD patterns of SCC, CGO, SCC–CGO and SCC–CGO–Ag powders.

108 The SEM images of SCC and SCC–Ag cathodes are comparably shown in Fig. 2. Obviously a  
109 fine microstructure with moderate porosity and well-necked particles is formed in the SCC  
110 cathode after firing at 1000 °C for 4 h (Fig. 2(A)). The impregnation of Ag does not change  
111 the microstructure adversely. Some round-shape particles are found in the SCC-Ag05 cathode  
112 after the infiltration of AgNO<sub>3</sub> and then firing at 800 °C for 1 h (Fig. 2(B)). The surface  
113 mapping result indicates that these round-shape particles are metallic Ag, which are dispersed  
114 uniformly on the surface of the cathode (Fig. 2(C)). The average particle size of Ag is about  
115 1–2 μm. The cross-sectional image of the SCC-Ag05 cathode and the CGO electrolyte is

116 presented in Fig. 2(D). Clearly the cathode and the electrolyte form good contact with each  
117 other. There is no delamination or cracking that can be observed at the electrode/electrolyte  
118 interface. The thickness of the electrode is about 15  $\mu\text{m}$  (Fig. 2(D)). The EDX result further  
119 supports that metal Ag is distributed in the SCC-Ag05 cathode (Fig. 2(D), inset). When the  
120 Ag loading increases to 10 wt.%, however, the glomeration and growth of Ag particles can be  
121 visualized (Fig. 2(E)). This aggregation results in less TPBs and thus can be suspected to increase  
122 the polarization resistance.

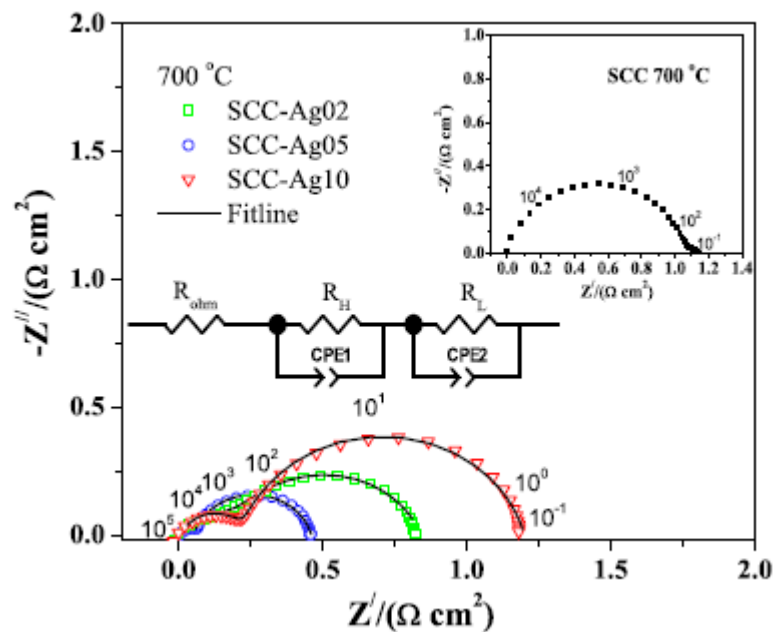


123  
124 Fig. 2: SEM micrographs of the cathodes: (A) SCC without Ag (1000  $^{\circ}\text{C}$ , surface), (B) SCC-  
125 Ag05 (800  $^{\circ}\text{C}$ , surface), (C) EDS elemental Mapping to show the spatial distribution of  
126 metallic Ag (red), inset shows the mapping area of SCC-Ag05 cathode: (D) SCC-Ag05 (800  
127  $^{\circ}\text{C}$ , cross-sectional image), inset is the EDX result of the cross-sectional part of SCC-Ag05  
128 cathode, (E) SCC with 10 wt.% Ag (800  $^{\circ}\text{C}$ , surface).



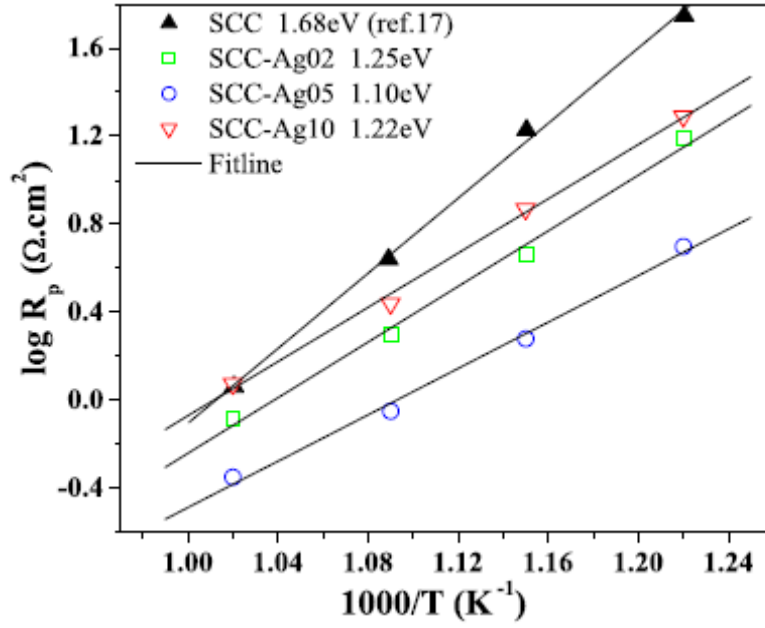
129 To explore the effects of Ag loading on polarization resistance, the impedance spectra of SCC  
130 cathode impregnated with different amounts of Ag were measured (Fig. 3). For all the  
131 cathodes, the impedance spectra can be separated into two arcs located in the high-frequency  
132 zone and the low-frequency zone respectively, implying two consecutive reaction processes  
133 related to oxygen reduction reaction (ORR) might take place. The overall size of the two arcs  
134 is primarily attributed to the cathode area specific resistance (ASR), which is widely used to  
135 describe the resistance terms related to electrode process. The Arrhenius plots of ASR are  
136 given in Fig. 4. Obviously the activation energy ( $E_a$ ) of SCC–Ag cathode is much smaller  
137 than SCC cathode. The ASR decreases with the Ag content, reaches a minimum at 5 wt.%  
138 Ag, and then increases again at 10 wt.% Ag. The variation of ASR with Ag contents can be  
139 understood, considering that the ORR process of the SCC electrode is likely promoted by the  
140 surface modification with silver. However, with the further increase of Ag content in the  
141 composite cathode, some surface of the SCC particles may be covered by the Ag metal, and  
142 the active sites for oxygen reduction reaction will be reduced. This deduction was proved by  
143 fitting the impedance spectra with an equivalent circuit (Fig. 3, inset) composed of two R-  
144 CPE elements in series to obtain the resistance of different processes. In this equivalent  
145 circuit,  $R_{ohm}$  represents the combination of electrolyte resistance, electrode ohmic resistance,  
146 lead resistance and contact resistance between cathode and Pt mesh current collector,  $R_H$  and  
147  $R_L$  are the polarization resistance ( $R_p$ ) corresponding to the high-frequency and low-frequency  
148 arc, respectively. The ASR is the sum of  $R_H$  and  $R_L$ . CPE is constant phase element whose  
149 value reflects the reaction mechanism of different electrode processes. The fitting results are  
150 presented in Fig. 5. It can be seen that  $R_H$  is much larger than  $R_L$  in SCC cathode. In a  
151 previous study, we proved that the reaction rate limiting step of SCC cathode was charge  
152 transfer reaction, which was characterized by the high frequency arc in the EIS spectrum [17].  
153 Compared to SCC electrode, the addition of Ag reduces dramatically the value of ASR and

154 the decrease is mainly attributed by the reduction of  $R_H$ . Arrhenius plots of the fitting results  
 155 for SCC–Ag composite cathode are given in Fig. 6. It is found that both  $R_H$  and  $R_L$  first  
 156 decreases with the addition of Ag, and then increases again when the Ag content is up to 10  
 157 wt.% in the SCC–Ag composite. The activation energy for  $R_H$  is in the range of 1.52–1.55 eV,  
 158 close to the activation energy of the oxygen surface exchange process in  $\text{La}_2\text{NiO}_{4+\delta}$  [5]. At the  
 159 same time, the low frequency arc becomes dominant in the impedance spectra (Fig. 3), and  
 160 the values of  $R_L$  are larger than these of  $R_H$  in the SCC–Ag composite cathodes (Fig. 6). The  
 161 activation energy for  $R_L$  is in the range of 0.96–1.16 eV, which is close to the dissociation and  
 162 diffusion activation energy of the adsorbed oxygen molecular on the cathode surface [29].  
 163 The contribution of Ag loading is further illustrated in the Bold plot (Fig. 7). The enhanced  
 164 charge transfer reaction can be seen by a dramatic decrease of the phase angle of the high  
 165 frequency peak in the Bold plot. This is clearly different from that of SCC cathode. According  
 166 to the fitting results, this difference indicates that the oxygen reduction mechanism has been  
 167 changed with the addition of Ag.



168

169 Fig. 3: Nyquist plot for SCC–Ag composite cathodes measured at 700 °C in air.

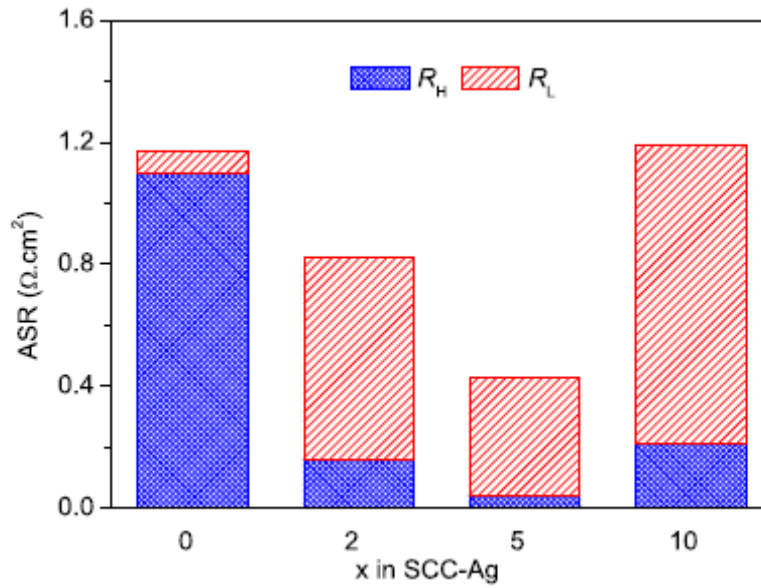


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171

Fig. 4: Temperature dependence of the polarization resistance  $R_p$  for various SCC-xAg composites measured in air.

172

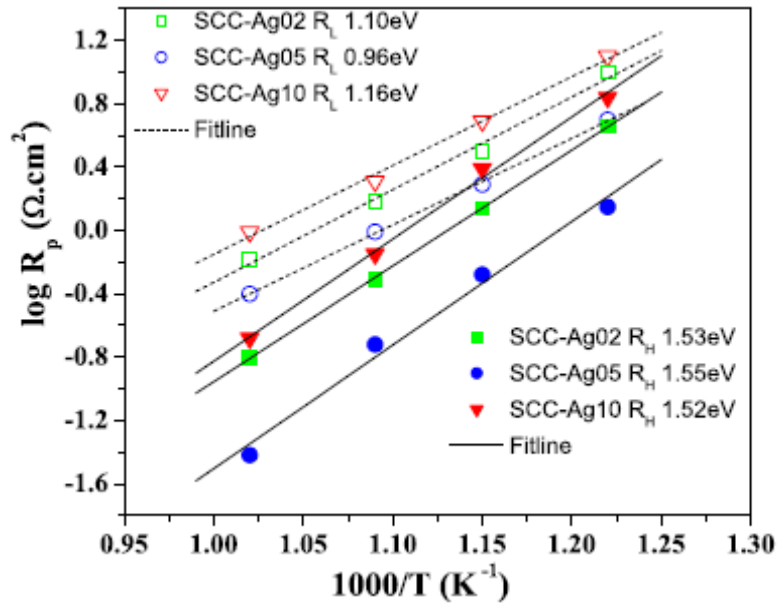


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Fig. 5: Comparative evolution of the polarization resistance ( $R_H$  and  $R_L$ ) with different amount of Ag in the SCC-Ag composite cathode.

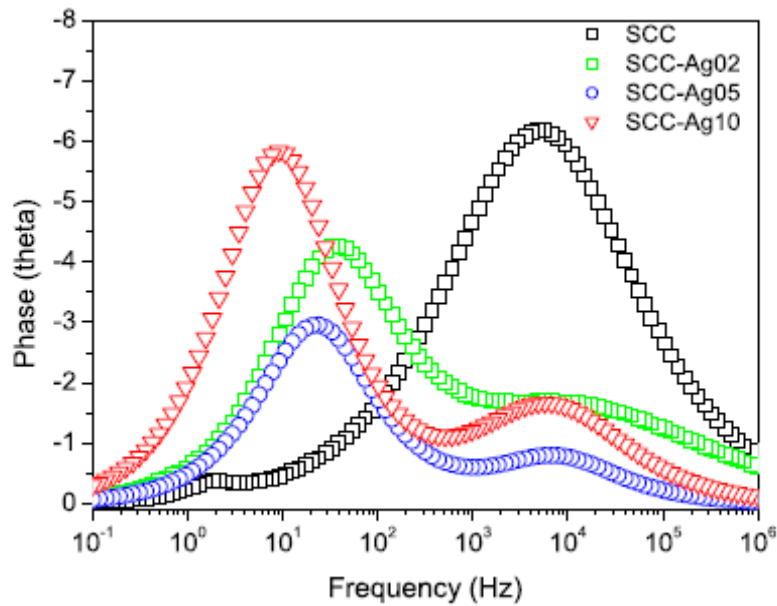
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176

177 Fig. 6: Temperature dependences of fitted high frequency resistances and low frequency

178 resistances of the SCC–Ag composite electrodes with different Ag content.



179

180 Fig. 7: Bode plot for SCC–Ag composite cathodes measured at 700 °C in air.

181 The electrochemical reaction mechanism of SCC–Ag composite cathode was studied as a

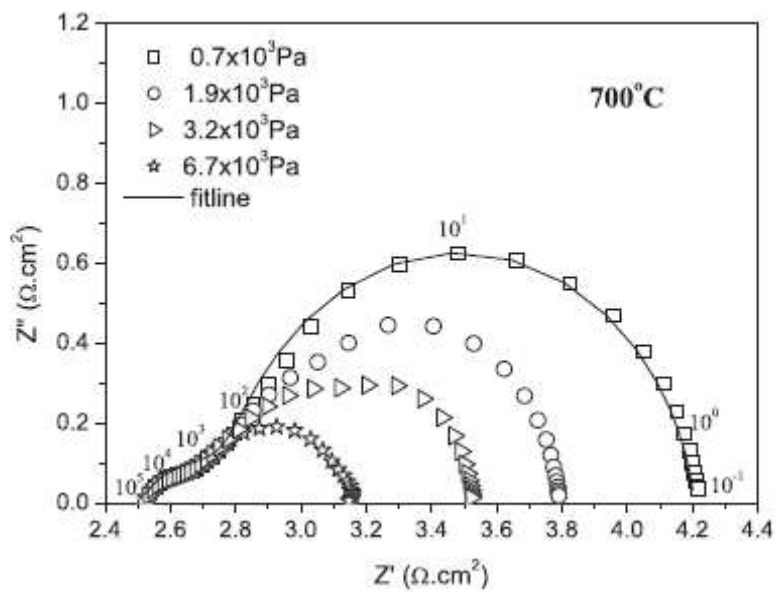
182 function of oxygen partial pressure. Fig. 8 shows the impedance spectra of SCC-Ag05

183 cathode measured at 700 °C under various oxygen partial pressures ( $P_{O_2}$ ). The polarization

184 resistance decreases with the increase of oxygen partial pressure, indicating an oxygen

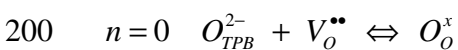
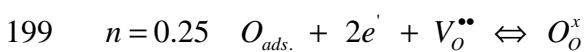
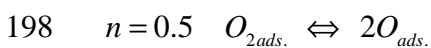
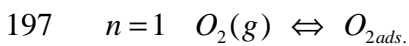
185 activity related electrochemical reaction that occurred on the composite cathode. By using the  
 186 same equivalent circuit presented in Fig. 3, the values of  $R_H$  and  $R_L$  under different oxygen  
 187 partial pressure can be calculated. It is found that the resistance of the high frequency arc ( $R_H$ )  
 188 is always much smaller than that of the low frequency one ( $R_L$ ). This means that the  $R_L$  related  
 189 process is the reaction rate limiting step. Generally, the polarization resistance ( $R_p$ ) varies  
 190 with the oxygen partial pressure according to the following equation:

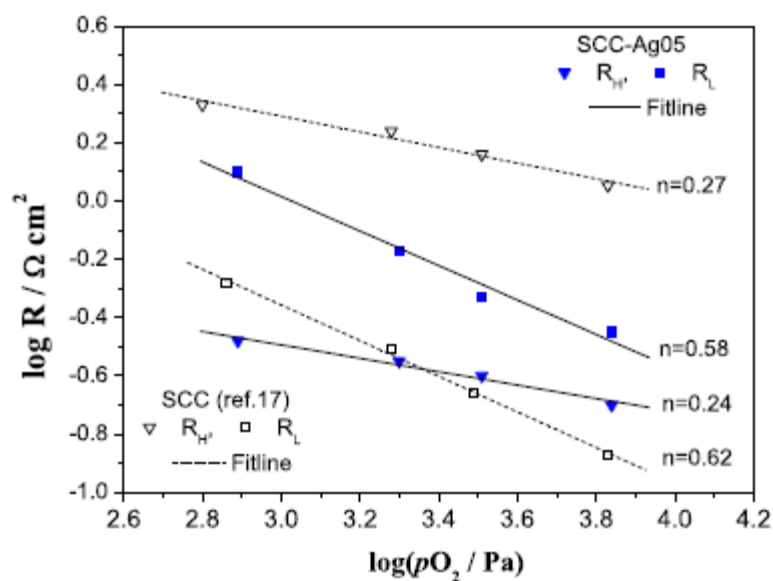
191 
$$R_p = R_p^0 \times (P_{O_2})^n$$



192  
 193 Fig. 8: Impedance spectra for the SCC-Ag05 cathode on CGO at 700 °C under various  
 194 oxygen partial pressures.

195 The value of  $n$  could give useful information about the type of species involved in the  
 196 reactions [30] and [31]:





201  
 202 Fig. 9: Dependence of polarization resistance on oxygen partial pressure for SCC-Ag05  
 203 composite cathode at 700 °C.

204 The dependence of polarization resistances ( $R_H$  and  $R_L$ , respectively) on oxygen partial was  
 205 presented in Fig. 9. It is found that the values of  $n$  corresponding to  $R_H$  and  $R_L$  are 0.24 and  
 206 0.58 respectively. In this case the high frequency arc is confirmed to be related to the charge  
 207 transfer process, and the low frequency arc is assigned to the dissociation and diffusion of  
 208 adsorbed oxygen. Compared to the results obtained in Fig. 8, it is clear that the  $R_L$  related  
 209 process is the major rate limiting step for SCC-Ag05 composite cathode in the whole range of  
 210 measurement oxygen partial pressure. However for SCC cathode, the  $n$  values of  $R_H$  and  $R_L$   
 211 are 0.27 and 0.62 respectively, and the value of  $R_H$  is always larger than  $R_L$ , which implied  
 212 that the charge transfer process on SCC cathode is the rate limiting step [17]. So it is clear that  
 213 when Ag was added in the electrode, a change of the rate limiting step from charge transfer  
 214 process to diffusion of the dissociative adsorbed oxygen was likely happened. As we  
 215 expected, Ag catalyst promotes the surface exchange process (charge transfer reaction) and  
 216 additionally, Ag particles can provide additional electron transport pathway through the  
 217 cathode surface due to its high electronic conductivity. Therefore, the oxygen reduction  
 218 reaction could be more effective at the boundary of Air/Ag/SCC than at Air/SCC, and

219 consequently the electrochemical performance is enhanced by the impregnation of Ag  
220 catalyst.

221 It should point out that the great reduce of  $R_H$  value is paid back by the simultaneous increase  
222 of  $R_L$  (Fig. 5). It is proposed that this simple infiltration method used may lead to the growth  
223 of micrometer size Ag particles, which will cover the SCC particle surface and block the  
224 oxygen diffusion channel in the cathode. So the microstructure of the cathode need to be  
225 further optimized.

#### 226 **4 Conclusion**

227 The  $\text{Sm}_{1.8}\text{Ce}_{0.2}\text{CuO}_4\text{-Ag}$  composite cathodes were prepared and their electrochemical  
228 properties were studied below 700 °C. The SCC-Ag05 composite exhibits improved catalytic  
229 activity for the oxygen reduction reaction compared to the  $\text{Sm}_{1.8}\text{Ce}_{0.2}\text{CuO}_4$  cathode, due to the  
230 increased electronic conductivity and electro-catalytic activity contributed by Ag particles.  
231 The lowest area specific resistance obtained at 700 °C in air is  $0.43 \Omega \text{ cm}^2$  for SCC-Ag05  
232 composite cathode. The addition of Ag in the SCC electrode changes the rate limiting step  
233 from charge transfer process to oxygen dissociation and diffusion process. However, further  
234 long-term stability investigation by operating over an extended period may be needed to  
235 verify the effect of Ag diffusion.

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239 Program for Science and Technology Project of Heilongjiang Province (WB10A204).

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