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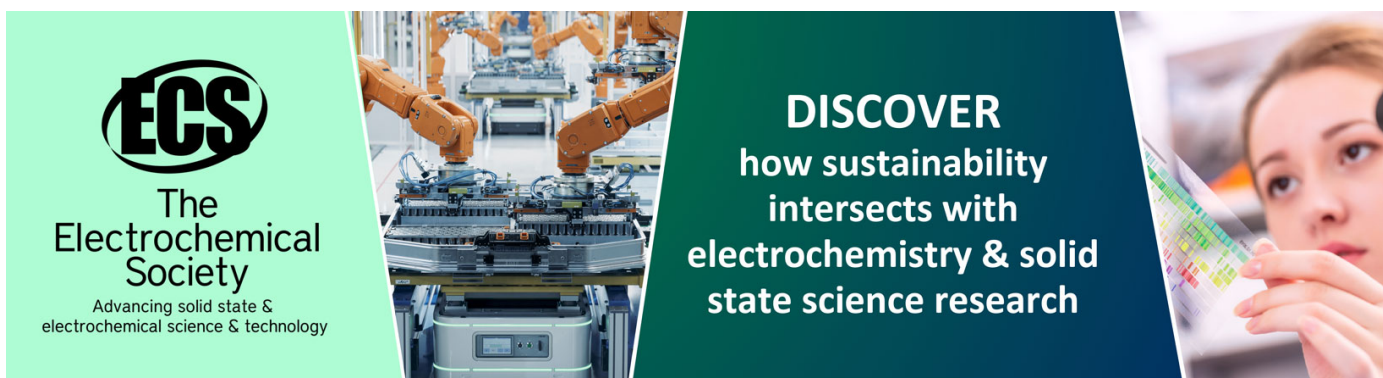
A new A-site-deficient Ti-doped SrCoO_{3-δ} perovskite cathode material for intermediate-temperature solid oxide fuel cells

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A new A-site-deficient Ti-doped $\text{SrCoO}_{3-\delta}$ perovskite cathode material for intermediate-temperature solid oxide fuel cells

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Abstract. To lower the operating temperatures of solid oxide fuel cells (SOFCs), A new A-site-deficient Ti-doped $\text{SrCoO}_{3-\delta}$ (SCT) are synthesized by a modified Pechini method and used as new highly active and stable cathode materials for intermediate-temperature SOFCs. The phase structure and electrical, thermal, and electrochemical properties of the SCT samples are evaluated. A phase transformation of $\text{SrCoO}_{3-\delta}$ from hexagonal to cubic perovskite structure occurred at room temperature by the substitution of Ti. A lower TEC value of the SCT oxide was observed with increasing the Ti doped content and A-site deficiency. NiO-SDC-supported single cells with various SCT as cathode materials were operated at intermediate temperatures using humidified H_2 as fuel and the static air as oxidant, respectively. Significant improved electrochemical performance for the A-site-deficient SCT sample was observed. An open-circuit potential of 0.83 V and the max power density of 745 mW cm^{-2} were achieved at 650 °C. The experimental results indicated that the A-site-deficient $\text{Sr}_{0.95}\text{Co}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ cubic perovskites are promising candidates as cathode materials for IT-SOFCs.

1. Introduction

As future solid-state energy conversion devices, solid oxide fuel cells (SOFCs) have gained great attention owing to its good fuel flexibility, low pollution, high conversion efficiency, and excellent system compatibility [1-4]. The main issues for the commercialization of SOFCs are high operating temperature (800-1000 °C), the resulting functional materials limitations, and operating complexities [5-7]. Decreasing the operation temperature to an intermediate-to-low temperature (400-700 °C), results in lower systems costs and performance degradation rates, as well as fast start-up and shutdown cycles [8, 9]. However, the oxygen reduction reaction (ORR) activities of cathode dramatically increase as the temperature decreased [1, 10-12]. Therefore, it is both important and necessary to develop the cathode materials with stable and high catalytic activity towards ORR for intermediate-temperature solid oxide fuel cells.

Comparing with conventional electronically-conducting $\text{La}_x\text{Sr}_{1-x}\text{MnO}_{3-\delta}$ (LSM) perovskite cathodes, mixed ionic and electronic conductors (MIECs) [3, 4, 9, 13] with the benefits of high catalytic activity and good conductivity can significantly extend the active sites of cathode from triple phase boundaries (TPBs) to the entire surface and bulk of the porous cathode, which can enhance the electrochemical performance for SOFCs [4, 7, 14-16]. As one of the MIECs with high catalytic activity, $\text{SrCoO}_{3-\delta}$ is a polymorph with three phase, orthorhombic brownmillerite phase (RT-653 °C), hexagonal phase (653-920 °C) and cubic perovskite phase (above 920 °C) [5, 8, 10, 12, 14-19]. Among



these three phase structures, the doped $\text{SrCoO}_{3-\delta}$ cubic perovskites exhibit the highest ORR activity and conductivity at intermediate temperatures [19]. However, the stability performance, the chemical and thermal compatibility with other components, and the CO_2 tolerance of doped $\text{SrCoO}_{3-\delta}$ have made it difficult to deal with the problems in SOFC devices [7, 8, 10, 12, 20].

Introducing the proper amount of A-site deficiencies into the lattice of perovskite can significantly enhance the electrochemical performance of SOFC cathode materials [21]. A-site deficiency in perovskites can form a large amount of oxygen vacancies, promote the ORR and facilitate oxygen ion diffusion within the cathode materials [22-28]. For example, A-site deficiency in LSM cathodes with higher chemical stability could result in a decrease in both electrode interfacial resistance and polarization loss [1]. A-site deficiency in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ (LSF) as well as $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) cathodes could significantly improve the electrochemical performance due to a lowering of the surface segregation of La and Sr [2, 22, 23]. A-site deficiency in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) can lead to a decrease in the thermal expansion coefficient (TEC), which makes the cathode more compatible with the electrolyte [28]. In addition, A-site deficient $\text{Sr}_{0.95}\text{Co}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ cathode with enhanced CO_2 resistivity not only shows high ORR activity at low temperatures, but also exhibits excellent stability and compatibility with electrolyte [21].

2. Experimental

2.1 Synthesis

The $\text{Sr}_{1-x}\text{Co}_{1-y}\text{Ti}_y\text{O}_{3-\delta}$ ($x=0, 0.05; y=0.05, 0.1$) oxides were synthesized via a modified pechini method. Commercial $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and n-butyl titanate, and citric acid were used as the raw materials. The exact concentration was confirmed through a chemical titration method. The molar ratio of citric acid and metal was 1.5:1. After the combustion process, the as-prepared cathode powders were calcined at 950°C for 3 h in air to obtain fine black phase-pure powders. $\text{SrCo}_{0.95}\text{Ti}_{0.05}\text{O}_{3-\delta}$, $\text{SrCo}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ and $\text{Sr}_{0.95}\text{Co}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ were named as SCT-1, SCT-2 and SCT-3, respectively. In addition, the $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) powders were synthesized by the same method with the raw materials $\text{Sm}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$ at a proper molar ratio (1.5:1) and then calcined at 700°C for 2 h.

2.2 Sample preparation

The synthesized SCT powders were pressed into bars ($40\text{ mm} \times 5\text{ mm} \times 2\text{ mm}$) with the pressure of 220 MPa followed by sintering at 1200°C for 5 h in air for the measurement of TEC and electrical conductivities. Anode-supported single cells of NiO-SDC/SDC/SCT-SDC (70 wt.% : 30 wt.%) were fabricated by a dry-pressing/co-sintering process. NiO + SDC + Starch mixture (60 wt.% : 40 wt.% : 20 wt.%) were pre-pressed at 200 MPa as substrates. Then the loose SDC powders were uniformly distributed onto the prepared anode substrates, co-pressed at 300 MPa and sintered finally at 1400°C for 5 h in air to form the dense electrolyte. The doped $\text{SrCoO}_{3-\delta}$ slurry was then painted on dense SDC membrane, and calcined in air at 1000°C for 3 h to form a tri-layer NiO-SDC | SDC | SCT-SDC cell. The active cathode area was 0.237 cm^2 .

3. Results and discussion

Fig. 1 shows the room-temperature XRD patterns of the SCT samples calcined at 950°C for 3 h in air. Obviously, there is a significant phase transformation between the undoped SrCoO_3 and $\text{SrCo}_{1-y}\text{Ti}_y\text{O}_{3-\delta}$ (SCT) samples, which show a hexagonal phase structure and a cubic perovskite structure, respectively [19, 20]. This means that the Ti dopant can stabilize the cubic perovskite phase at high temperature, even for the A-site deficient perovskite $\text{Sr}_{1-x}\text{Co}_{1-y}\text{Ti}_y\text{O}_{3-\delta}$ samples [4, 12, 15]. To obtain pure phases of A-site Sr^{2+} -deficient $\text{Sr}_{1-x}\text{Co}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ samples and determine the upper limit of Sr^{2+} -deficiency, different compositions, i.e. $\text{Sr}_{1-x}\text{Co}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ $x=0.05, 0.10$ and 0.13 were synthesized and characterized. The result indicates that the highest Sr^{2+} -deficiency content in SCT was 0.1, and higher content $x=0.13$ will generate some impurity phase.

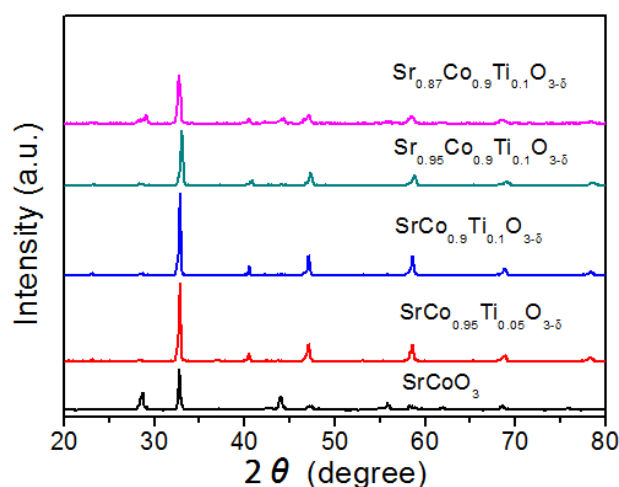


Fig. 1 Room temperature XRD patterns of the SCT samples calcined at 950°C for 3 h.

Recent studies [6, 10, 13, 19, 20] make a direct connection between the stability of SrCoO₃-based cathode and the valence of the doping cation, which means that variation in the oxygen nonstoichiometry, 3-δ, upon cation doping should directly relate to the cubic perovskite stability. Based on the simple point defect model expressed in Kröger-Vink notation [4, 9, 28], we can qualitatively investigate the influence of the A-site deficiency (Sr) and B-site doping (Ti) on the oxygen nonstoichiometry.

Fig. 2 shows the thermal expansion curves of the SCT samples between RT-1000 °C in air. The SCT samples show linear expansion during the operate temperatures. The SCT-1 sample shows an obvious shrink at approximately 900°C due to the amount of lattice oxygen escape at high temperature. However, the SCT-2 and SCT-3 samples do not exhibit the same phenomenon at 900°C due to Ti contents increased in the lattice reduced concentrations of oxygen vacancies. The average thermal expansion coefficient (TEC) of SCT-1, SCT-2 and SCT-3 are 21.5×10^{-6} , 18.2×10^{-6} and $17.2 \times 10^{-6} \text{ K}^{-1}$, respectively. Obviously both Ti doping and A-site deficiency cause a considerable reduction in the TEC value of SCT cathode, which is more promising for the thermal compatibility of cell components [2, 13].

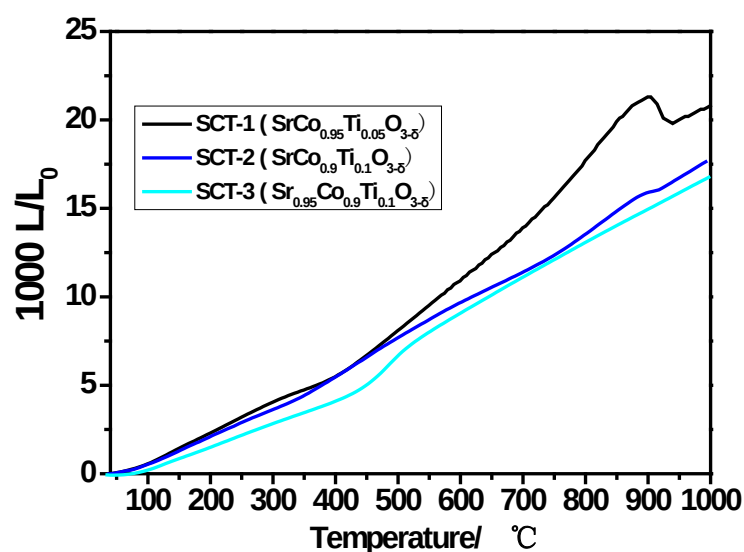


Fig. 2 The SCT samples thermal expansion curves tested at RT-1000°C in air.

Fig. 3 shows the electrical conductivities of SCT samples tested at 250-700 °C in air. The function of electrical conductivities dependence on the temperatures of all the samples increases first and followed by a decrease. This may be attributed to an increase in formation of small polar on hole conductors in competition with a decrease in the numbers of charge carriers due to charge compensation [8, 27]. The conductivity values of the samples achieved the max conductivities values of 282-478 S cm⁻¹ at 400 °C. The sample SCT-1 has the highest electrical conductivity about 478 S cm⁻¹ at 400 °C. And the electrical conductivity decreased with the substitution of Ti (SCT-2 or SCT-3). However, considering the higher stability of SrCoO_{3-δ} based cubic perovskites with higher Ti dopant, SrCo_{0.9}Ti_{0.1}O_{3-δ} cathode is more promising for SOFC with good long-time stability [20]. It can be seen from the Fig. 3 b and c, the A-site deficiency sample with the same Ti doped content had a lower electrical conductivity values at low temperature (250-550 °C) but a higher one at middle temperature (550-700 °C). The conductivity of all the SCT samples is greater than 200 S cm⁻² between 250 °C and 700 °C, which is acceptable for the application of cathodes for IT-SOFCs [2, 3].

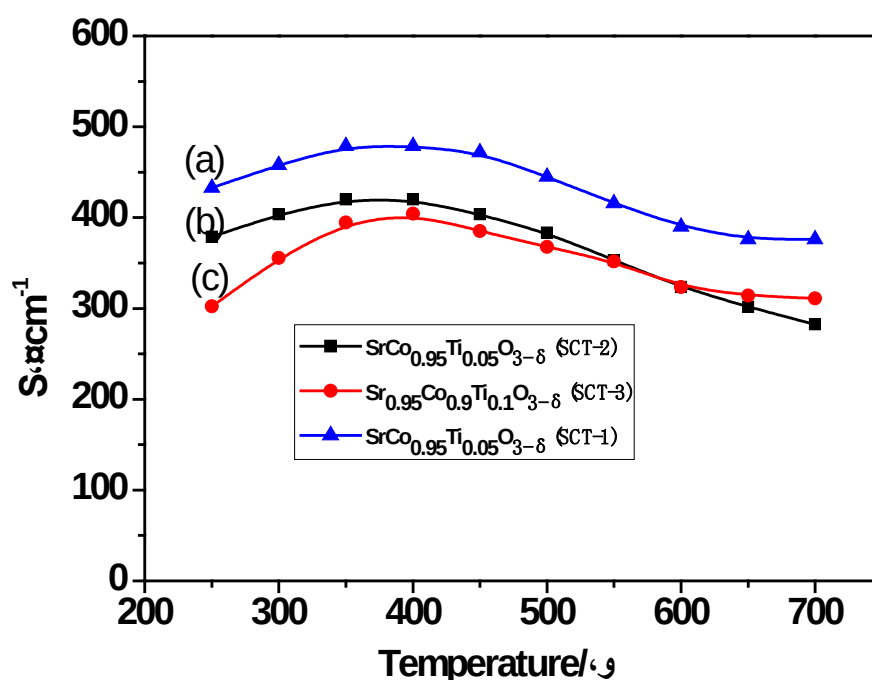


Fig. 3 Temperature dependence of the electrical conductivity of the SCT samples.

To evaluate the electrochemical performances, the single cells were fabricated with various SCT samples as cathode materials, these cells were tested at 450-650 °C. The current densities dependence of voltages and power densities curves are shown in Fig.4. The open circuit voltages (OCVs) at 650 °C were 0.85, 0.82 and 0.83 V for the NiO-SDC-supported single cells with SCT-1, SCT-2 and SCT-3 cathode, respectively. In addition, the cell voltage of each single cell decreased linearly with current densities. The maximum power densities at 650 °C were 721, 641 and 745 mW/cm² for the cells with SCT-1, SCT-2 and SCT-3 cathode, respectively.

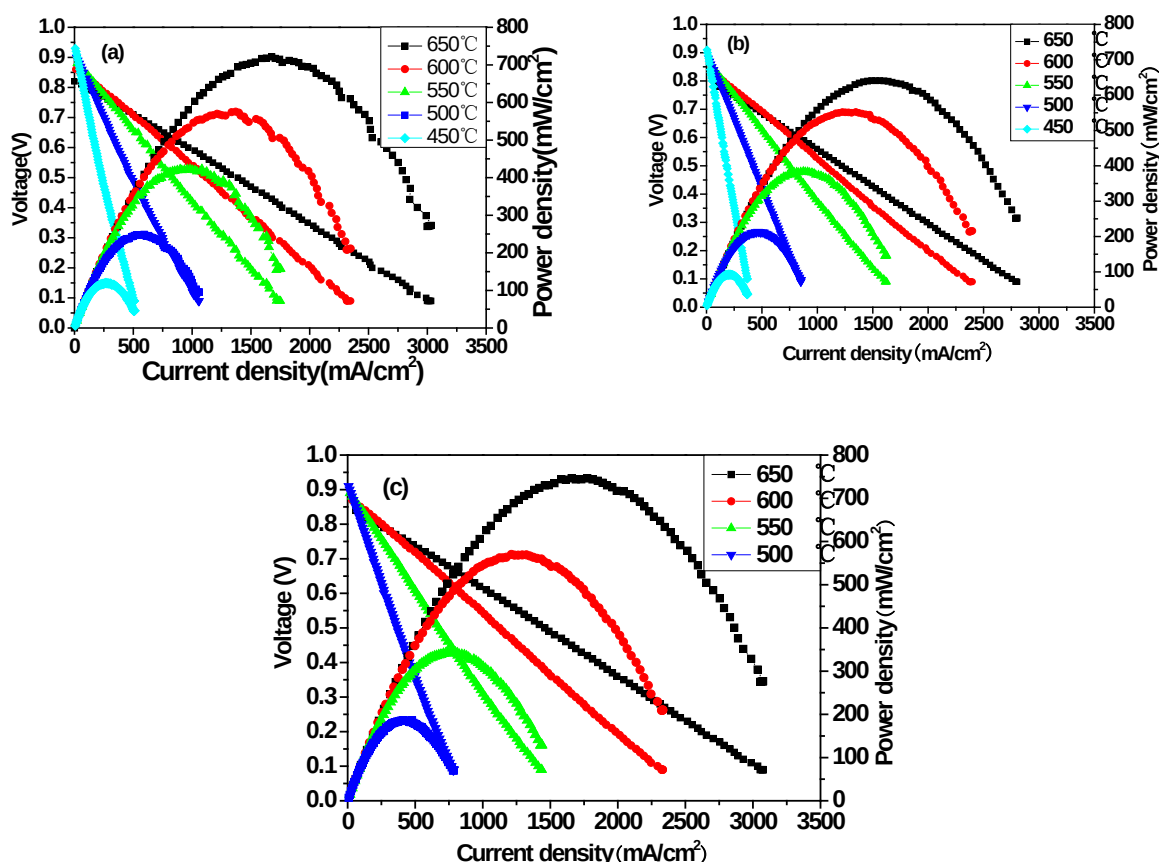


Fig. 4 Electrochemical performance data of the Ni-SDC-supported single cells were fabricated with different SCT cathodes (a: SCT-1, b: SCT-2, c: SCT-3).

Comparison with SCT-1 and SCT-2 as cathode materials, the power density of SOFCs decreased with the increasing of Ti content, which is agree with previous reports. The single cell with SCT-3 oxide cathode achieves a peak power density of 745 mW/cm², which is higher than that of any other with cathodes. Owing to the same fabrication technology and the same components of cells, the difference of output performance between several cells is attributed to the internal electrochemical properties of cathode materials. We can see from Fig.3 that the electrical conductivity of SCT-3 sample is lower than SCT-1. Hence, the higher performance could be attributing to the ionic conductivity in the cathode due to the A-site deficiency. This result demonstrates that Sr deficiency at the A site has a great effect on the properties of electrochemical performances.

4. Conclusion

The A-site deficiency and Ti-doping on B-site of SCT as cathode materials for IT-SOFC have been synthesized to enhance the performances. The cubic perovskite structure was obtained after the substitution of Ti. A lower TEC value of the SCT oxide was observed with increasing the Ti doped content and A-site deficiency. The highest content of Sr²⁺-deficiency of $S_{1-x}Co_{0.9}Ti_{0.1}$ was 0.1 which has no change on the perovskite structure. The A-site-deficient SCT-3 exhibits the lowest polarization resistance 0.029Ω cm² at 650 °C. Ni-SDC-supported single cells with various SCT as cathode materials were operated at intermediate temperatures using 97%H₂-3%H₂O as fuel and the static air as oxidant, respectively. Significant improved electrochemical performance for the A-site-deficient Sr_{0.95}Co_{0.9}Ti_{0.1}O_{3-δ} sample was observed. An open-circuit potential of 0.83 V and the max power density of 745 mW cm⁻² were achieved at 650 °C. The experimental results showed that the A-site-deficient Sr_{0.95}Co_{0.9}Ti_{0.1}O_{3-δ} cubic perovskites are promising candidates as cathode materials for IT-SOFCs.

Acknowledgments

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