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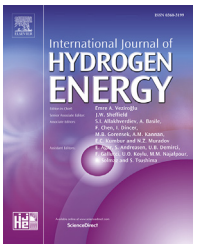

Alkaline metal doped strontium cobalt ferrite perovskites as cathodes for intermediate-temperature solid oxide fuel cells

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ABSTRACT

Perovskite oxides $Sr_{0.9}K_{0.1}Fe_xCo_{1-x}O_{3-\delta}$ (SKFCx, x = 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) are investigated as potential cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFCs) on $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) electrolyte. The cubic phase of the SKFCx oxides is demonstrated by x-ray diffraction. The SKFCx cathode shows good compatibility with the SDC electrolyte up to 900 °C. Among the investigated compositions, SKFC0.1 displays the highest electrical conductivity of 443–146 $S \cdot cm^{-1}$ from 350 °C to 800 °C in flow air. The area specific resistances (ASRs) of the SKFCx (x = 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) cathodes are 0.047, 0.058, 0.066, 0.101, 0.155 and 0.175 Ω cm^2 at 650 °C in air on an SDC electrolyte. Among the five tested cathodes, SKFC0.1 exhibits the lowest area specific resistances between 550 °C and 750 °C, when tested on its symmetric cell configuration of cathode|SDC|cathode. The thermally stabilized cubic perovskite structure of the SKFC0.1 powder is demonstrated by high-temperature XRD. The average linear thermal expansion coefficient α_L of SKFC0.1 is 18.9×10^{-6} K^{-1}. A peak power density of 1643 $mW \cdot cm^{-2}$ is achieved on SKFC0.1|SDC|Ni-SDC anode supported fuel cell at 650 °C. These features, and excellent electrocatalytic activity and good stability, indicate the potential of alkaline metal doped strontium cobalt ferrite perovskites are promising cathode materials for IT-SOFCs.

Introduction

Due to the high cell efficiency, zero pollution and low emission, solid oxide fuel cells (SOFCs) are receiving more and more attention [1–5]. However, the biggest problem is that the operating temperature (800–1000 °C) is so high that it cannot be commercialized. Reducing the working temperature of SOFC to intermediate temperature (IT) range (500–800 °C) is the best method to solve this problem [6–10]. Low operating temperature not only reduces the production costs but also

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expands the operating life. Unfortunately, new issues such as the cathode resistance increases would be brought when the temperature is decreased. Therefore, research and development of advanced cathode materials for SOFC is one of the key goals [11,12].

The most common cathode materials used for IT-SOFC are mixed ionic-electronic conducting (MIEC) perovskites with a formula of ABO_3 [13]. In intermediate temperature range, cobalt-containing perovskite cathodes exhibit the best electrocatalytic activity to oxygen reduction reaction (ORR), such as $SrCoO_{3-\delta}$ based perovskites [14–16]. $SrCoO_{3-\delta}$ based perovskite have many advantages, one of which is that the strontium in A-site of the perovskite acts as an acceptor and induces the formation of oxygen vacancies, Besides, the cobalt ions in B-site of perovskite promotes both the oxygen bulk diffusion and oxygen surface exchange. However, $SrCoO_{3-\delta}$ based perovskites also have some limitations and shortcomings such as the unstable structure and easy CO_2 poisoning. Partial doping cations for either A-site or B-site can overcome these defects [17].

Fe is one of the most common dopant elements in B-site because it can stabilize the cubic perovskite phase, such as LSCF and BSCF [18,19]. Unfortunately, when the B-site is substituted with Fe element, the electrical conductivity and the oxygen vacancies would be decreased [20–23]. In order to deal with this problem, it is necessary to introduce the A-site doping. The most commonly used A-site doping elements are rare-earth (RE), alkaline earth (AE) and alkaline metal (AM) elements. The RE elements such as La, and the AE elements such as Ba and the AM elements such as K and Na could be incorporated into the A-site of $SrCoO_{3-\delta}$-based oxide cathodes. According to the literature [24], more oxygen vacancies are created and the ionic conductivity is improved when substitute a small amount of Sr with K. Hou et al. [25] studied the partial substitution of Sr with K in the structure of $Sr_{0.9}K_{0.1}FeO_{3-\delta}$ (SKFO) based perovskite. They found that doping A-site with K has two major profits. One is that the perovskite tolerance factor (t) is increased because the ionic radius of Sr^{2+} (1.44 Å) is smaller than that of K^+ (1.64 Å), which can stabiles the crystal structure of perovskites. The other is that the doped K^+ would lead to better conductivity because it promotes the oxidization of Fe^{3+} to Fe^{4+}. However, the electrical conductivity of SKF is only 26 $S \cdot cm^{-1}$ in air at 800 °C and the peak power density is only 937 $mW \cdot cm^{-2}$ with pure H_2 as fuel at 850 °C.

Therefore, further study based on the SKFO should be conducted to obtain cathodes which suit for reduced operating temperature of SOFCs. In this work for the first time, we combine the merits of SCF and SKF to form a new series of perovskites $Sr_{0.9}K_{0.1}Fe_xCo_{1-x}O_{3-\delta}$ (SKFCx, x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) as potential cathodes for IT-SOFC. Effects of K and Co dopant on the phase structure, electrical conductivities, and chemical compatibility were measured. SKFC0.1 shows an area specific resistance value of 0.047 Ω cm^2 by symmetric cell tests and a peak power density of 1643 $mW \cdot cm^{-2}$ on SKFC0.1|SDC|Ni-SDC anode supported fuel cell at 650 °C, which demonstrate that the K and Co dopant has significant positive influences on electrochemical performance of materials.

Experimental

Material synthesis

EDTA-Citrate method (CEM) was used to synthesize $Sr_{0.9}K_{0.1}Fe_xCo_{1-x}O_{3-\delta}$ (SKFCx, x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) powders. Stoichiometric amounts of $Sr(NO_3)_2$ (99%), KNO_3 (99%), $Fe(NO_3)_3 \cdot 9H_2O$ (98.5%), and $Co(NO_3)_2 \cdot 6H_2O$ (99%) were dissolved in distilled water. Next, EDTA and citric acid was dissolved by ammonia followed adding to metal solution to form an aqueous mixed solution. And then the aqueous mixed solution was evaporated to become gelatum, which was then dried in oven at 250 °C for 5 h to obtain the precursor. Finally, the precursor was calcined at 900 °C for 5 h to become the required materials.

Cell fabrication

Symmetric cells with $Sr_{0.9}K_{0.1}Fe_xCo_{1-x}O_{3-\delta}$ |$Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)| $Sr_{0.9}K_{0.1}Fe_xCo_{1-x}O_{3-\delta}$ configuration were prepared for the electrochemical measurement. The SDC pellets were formed by dry pressing 0.35 g of SDC powders and sintering at 1350 °C for 5 h in air to get dense SDC electrolyte. To obtain the cathode slurry, the $Sr_{0.9}K_{0.1}Fe_xCo_{1-x}O_{3-\delta}$ powders were initially dispersed into a pre-mixed solution of glycerol, ethylene glycol and isopropyl alcohol, and then followed by planetary milling (Fritsch, Pulverisette 6) at 400 rpm for 0.5 h. The resultant slurry was symmetrically sprayed onto both sides of the SDC disks and then calcined at 900 °C for 2 h in air. Ag paste was painted on the surface of the symmetric cathodes and then dried as current collector.

A two layered (porous NiO-SDC anode| dense-thin-film SDC electrolyte) anode supported single cell was fabricated via dry pressing and co-sintering, and the NiO-SDC anode layer consists of 60 wt% NiO and 40 wt% SDC. The effective cathode area was 0.45 cm^2.

Characterizations

The phase structure of $Sr_{0.9}K_{0.1}Fe_xCo_{1-x}O_{3-\delta}$ samples were determined through a powder X-ray diffraction (XRD, Bruker D8 Advance) with Cu-K_α radiation (λ = 1.54056 Å).

The variation of crystal structures with temperature was characterized using the in situ high temperature XRD (HTXRD, Rigaku D/max 2500 V) technique and 2θ varying from 10 to 90° by steps of 10°. The dates were collected between room temperature and high temperature each 50 °C with a 10 °C min^{-1} heating rate, and the temperature was held for 20 min at each temperature step.

The chemical compatibility was examined by mixing the $Sr_{0.9}K_{0.1}Fe_xCo_{1-x}O_{3-\delta}$ with SDC powders at a weight ratio of 1:1 and calcination at 900 °C in air for 2 h.

The $Sr_{0.9}K_{0.1}Fe_{0.3}Co_{0.7}O_{3-\delta}$ powder was taken as a sample were characterized for their microstructure and size using a JEOL-JSM 6400F scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). The morphology of the cathode|electrolyte|anode cross section was obtained by SEM.

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