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Electrical conductivity and cell performance of $La_{0.3}Sr_{0.7}Ti_{1-x}Cr_xO_{3-\delta}$ perovskite oxides used as anode and interconnect material for SOFCs

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ABSTRACT

The anode materials $La_{0.3}Sr_{0.7}Ti_{1-x}Cr_xO_{3-\delta}$ (LSTC, x = 0, 0.1, 0.2) with cubic structure were prepared via solid state reaction route. The influence of Cr content on the properties of LSTC as anode and interconnect materials for solid oxide fuel cells (SOFCs) was investigated. The Cr-doping decreased the lattice parameter while increased the sinterability of LSTC materials. The total electrical conductivity decreased with Cr doping level, from 230 S cm^{-1} for x = 0 to 53 S cm^{-1} for x = 0.2. The total electrical conductivity exhibited good stability and recoverability in alternative atmospheres of air and 5% H_2/Ar, showing excellent redox stability. The cell testing showed that the anode performance of LSTC was enhanced somewhat by Cr doping. The present results indicated that the prepared $La_{0.3}Sr_{0.7}Ti_{1-x}Cr_xO_{3-\delta}$ can be potential anode and interconnect materials for SOFCs.

1. Introduction

Solid oxide fuel cells (SOFCs) are promising energy generation devices converting chemical energy of fuel directly into electrical energy, which are characterized by high efficiency, reliability, modularity, fuel adaptability, and very low levels of SO_x and NO_x emissions [1–4]. Ni/YSZ cermet is the state-of-the-art anode material for SOFCs. It has high electronic conductivity, reasonable ionic conductivity and high catalytic activity for hydrogen oxidation. However, it tends to degrade with the direct use of hydrocarbon fuels due to the fatal problems including carbon deposition and sulphur poisoning [5–7]. Consequently, much effort has been devoted to developing new anode materials that can be operated with hydrocarbon fuels. Alternative cermets (copper cermet anode) [8–12] and mixed ionic–electronic conductors (MIECs, perovskite-, cubic fluorite-, pyrochlore-, spinel- and tungsten bronze-related structures) [12] have been proposed as anode materials. MIEC anode can not only exhibit improved resistance against carbon deposition and sulphur poisoning, but also effectively extend the three phase boundary (TPB) of anode [13]. As a result, the use of MIEC anode will promote the electrode reaction and improve the cell performance.

Among the perovskite anode materials for SOFCs, La-substituted $SrTiO_3$ (LST) has been widely investigated due to its high electronic conductivity in reducing atmospheres and good dimensional and chemical stability upon redox cycling [14–17]. However, all LST materials show very poor

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electro-catalytic performance [18]. Replacing the titanium on the B-site with other dopants has the possibility to alter the catalytic properties as well as the conductivity [19]. Manganese, cobalt, iron, gallium and scandium as dopants for LST were investigated, and the redox properties and the conductivity of the compounds are both strongly influenced by the choice of dopant [19]. The redox stability of the anode is a critical factor that affects the durability of the SOFC stacks. Some works have been attempted to improve the redox stability of LST [20–22].

Considering that $LaCrO_3$ is a good interconnect material for SOFC stacking [23], which has a good structural stability in a wide range of oxygen partial pressure, and Cr^{3+} ion has a similar ionic radius with Ti^{4+}, in this study, the Cr element was selected to partially substitute for Ti ions with the aim of improving the redox stability of LST. The influences of Cr content on the structural characteristics, electrical conductivity, redox behaviour, and cell performance were investigated. Its possibility as anode materials and interconnect materials was evaluated.

2. Experimental

The $La_{0.3}Sr_{0.7}Ti_{1-x}Cr_xO_{3-\delta}$ (LSTC, $x = 0$, 0.1, 0.2) powders were prepared via traditional solid-state reaction method by using high purity La_2O_3 (99.9%, Sinopharm Chemical Reagent Co. Ltd), $SrCO_3$ (AR, Sinopharm Chemical Reagent Co. Ltd), Cr_2O_3 (99.999%, Sinopharm Chemical Reagent Co. Ltd) and TiO_2 (AR, containing rutile and anatase, Sinopharm Chemical Reagent Co. Ltd) as raw materials. Stoichiometric amount of the raw materials were ball-milled (planetary ball mill, QM-3SP2, Nanjing NanDa instrument Plant) for 2 h in ethanol and then dried in an oven at 80 °C. After drying, the resultant powders were ground and calcined in 5% H_2/Ar at 1300 °C for 10 h to obtain the single phase materials. The calcined powders were pressed into pellets (diameter 19 mm, thickness 0.5 mm) and rectangular bars (42 mm × 7 mm × 3 mm), respectively, under a pressure of 150 MPa with appropriate amount of polyvinyl alcohol (PVA, 1 wt.%) as binder, followed by sintering at 1500 °C for 10 h in 5% H_2/Ar to get dense samples.

The phases and crystal structure of the samples were identified by X-ray diffraction (XRD, Rigaku D/max-A) with Cu Kα radiation. The scanning electron microscope (SEM, LEO-1450) was used to observe the microstructure of the sintered pellets and cells.

The total electrical conductivity of the samples was measured with standard four terminal DC method in 5% H_2/Ar in the temperature range of 100–900 °C. All the conductivity data were measured every 50 °C after holding at each temperature to equilibrate until no change was observed. In order to examine the redox stability of LSTC, the electrical conductivity was measured alternatively in air and 5% H_2/Ar. The conductivity as a function of oxygen partial pressure ($p(O_2)$) was also measured from 10^{-14} to 10^{-19} atm at 800 °C. The $p(O_2)$ was adjusted by bubbling 5% H_2/Ar gas through a water saturator, which was installed outside the furnace and had the temperature varying from room temperature to 100 °C.

To examine the chemical compatibility of LSTC with electrolyte YSZ, the 1300 °C-prepared LSTC powder, that already has a pure cubic perovskite structure and will be used as the anode powder in cell evaluation, was mixed uniformly with YSZ powder in the weight ratio of 1:1, and then pressed and calcined at 1350 °C for 10 h in air. The calcined pellet was crushed and examined by XRD to identify the phase purity.

The cell performance of the LSTC as anode for solid oxide fuel cells was tested with the configuration of LSTC/YSZ|YSZ|LSM/YSZ. The densed 8% YSZ electrolyte (~ 400 μm in thickness) was obtained by pressing the commercial Tosoh YSZ powder (TZ-8Y, Tosoh Corporation) into disks with a diameter of 19 mm and then sintering at 1400 °C for 4 h. The anode slurry were prepared by mixing the LSTC compounds with 25 wt.% YSZ and α-terpineol and ethyl cellulose homogeneously. The formed slurry was screen-printed onto the dense YSZ electrolyte (active area 0.502 cm^2), followed by sintering at 1350 °C for 4 h. The commonly used LSM ($La_{0.7}Sr_{0.3}MnO_3$)/YSZ with 50 wt.% YSZ and 50 wt.% LSM were applied as cathode by screen-printing and firing at 1200 °C for 2 h. Ag paste was used as the current collector, which was pasted on both sides of the calcined cell and fired at 600 °C for 0.5 h. Then the obtained cells were sealed on an alumina tube using a ceramic-based material (Cerama-bond 552-VFG, Aremco). The humidified H_2 was feed as fuel to the anode with a flow rate of 40 ml min^{-1} and the ambient air as oxidant.

3. Results and discussion

3.1. XRD and SEM

All the sintered samples $La_{0.3}Sr_{0.7}Ti_{1-x}Cr_xO_{3-\delta}$ ($x = 0$, 0.1, 0.2) were green in colour except for the sample with $x = 0$, which was gray. As shown in Fig. 1, all the XRD diffraction peaks of the synthesized samples can be well indexed with cubic structure. With Rietveld refinement on the XRD patterns by Jade 5.0 software, the lattice parameters of three samples were derived. The calculated lattice parameters as a function of Cr content are presented in Fig. 2. The lattice parameter of $La_{0.3}Sr_{0.7}Ti_{1-x}Cr_xO_{3-\delta}$ decreased linearly with Cr content,

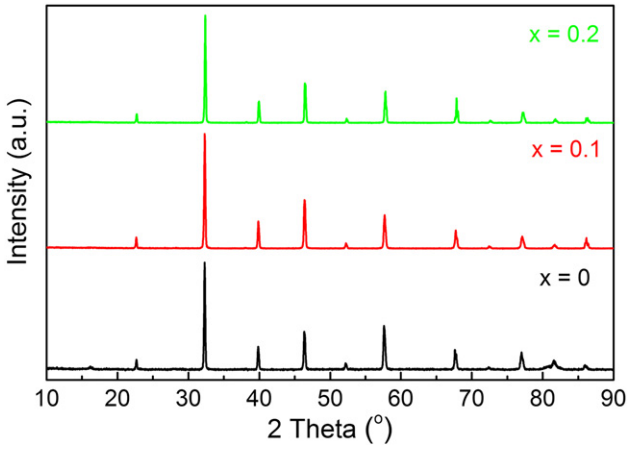

Fig. 1 – XRD patterns of $La_{0.3}Sr_{0.7}Ti_{1-x}Cr_xO_{3-\delta}$ ($x = 0$, 0.1, 0.2) sintered at 1500 °C for 10 h in 5% H_2/Ar.