

学 位 論 文 の 要 旨

専 攻	安全システム工学 専攻	ふりがな 氏 名	しよけいてい ぱいるざ XIAOKAITI PAIRUZHA
学位論文題目	Development of perovskite-type electrode materials for solid oxide fuel cells (固体酸化物型燃料電池電極用ペロブスカイト型酸化物材料に関する研究)		
<p>学位論文要旨</p> <p>A solid oxide fuel cell (SOFC) is a promising energy device that can produce electricity by converting of chemical energy directly with high efficiency. However, its high operating temperature (usually>1000 °C) is the main barrier in this technology since high temperature will lead to a slow start-up/shut-down procedure, poor thermal stability, poor fuel cell durability, as well as high material cost. Decreasing the operating temperature down to the temperature range of 900- 750 °C is an effectively solution to these problems, but it makes the oxygen reduction kinetics in the electrolyte and electrodes weaken. Therefore, maintaining the oxygen reduction kinetics at lower temperatures is one of the main challenges in this field. Meanwhile, the hydrocarbon fuels are easily cracked on the anode, resulting in carbon deposition, which will decrease the activity, and finally reducing the cell performance. Thus, development of coking-resistance electrode materials with high electroactivity is also important for the SOFCs. In this dissertation, Fe-Co-based perovskite oxides with high activity as well as stability were developed as the electrodes for the SOFCs. The effects of various doping elements at different position on the ABO₃ unit perovskite on the performance of oxygen reduction reaction (ORR) were investigated. Moreover, in order to solve the possible coke formation and/or sulfur poisoning on the surface of the anode, these perovskite oxides were used as the symmetrical electrode materials to fabricate symmetrical SOFCs (SSOFCs), in which the same material is used as both anode and cathode so that the deactivated anode can be regenerated by sequentially using the anode as a cathode. It includes 6 Chapters.</p> <p>Firstly, by doping larger-radius element of niobium (Nb) at B-site, perovskite materials of Pr_{0.4}Sr_{0.6}(Co_{0.3}Fe_{0.6})_{1-x}Nb_xO_{3-δ} (PSCFN_x, x=0, 0.05, 0.1 and 0.2) were firstly synthesized as the cathode materials for solid oxide fuel cells (SOFCs) using a solid state reaction method. The effect of Nb doping amount on the lattice structure, oxygen desorption and electrochemical properties of PSCFN_x at different calcination temperatures were investigated. It is found that this material family had a perfectly cubic structure based on the Pm-3m space group whose lattice size increased with x, and found that the materials were thermally stable after calcination and showed desirable chemical compatibility with the La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ} electrolyte in the condition of calcination at 1250 °C for 8 h under an air atmosphere. The optimum x value of 0.1 was found for the PSCFN_x cathode materials, which had the minimum polarization resistance value of 0.018 Ωcm² at 900 °C. As shown in Figure 1(a), the single cell with the PSCFN_{0.1} cathode delivered a power density of 0.731 Wcm⁻² at 900°C with the humidified H₂ (~3% H₂O) as the fuel and ambient air as the oxidant, which indicates that PSCFN_{0.1} should be a promising cathode material for the SOFCs.</p>			

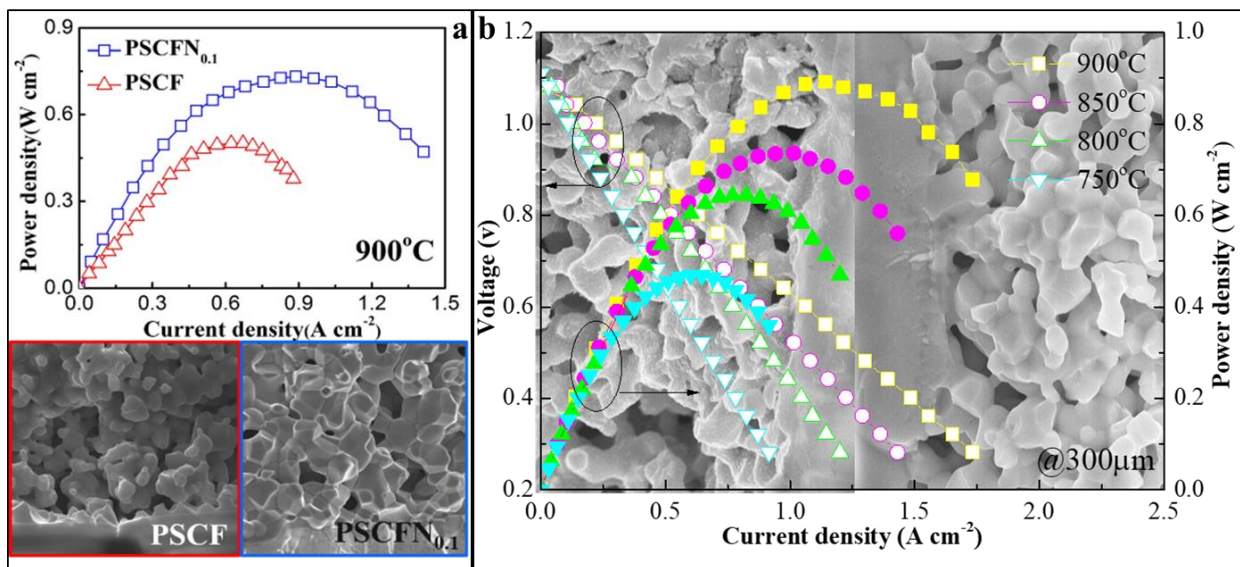


Figure 1 (a) power density of PSCF and PSCFN_{0.1} at 900 °C and cathode side SEM images.
(b) PSCF_{0.6}N power density at temperature 750-900 °C with 300 μm thickness LSGM.

Secondly, Sr_{0.9}Co_{0.3}Fe_{0.7}O_{3+δ} was doped by cerium via the solid state reaction method to enhance the electrochemical activity. The obtained novel cathode materials (Ce_{0.1}Sr_{0.9})_xCo_{0.3}Fe_{0.7}O_{3-δ} ((CS)_xCF) were confirmed to have a Pm-3m cubic perovskite structure when x was in the range of 0.90-1.10 based on X-ray diffraction (XRD) analysis. A-site deficiency was generated as x<1.0 but A-site excess(x>1.0) resulted in impurity phases. The generation of A-site deficiency was confirmed based on X-ray photoelectron (XPS) and O₂-TPD measurements. As a result, the SOFCs with (CS)_{0.9}CF cathode showed the maximum power density of 0.571 Wcm⁻² at 800 °C and the maximum conductivity of 109.6 Scm⁻¹ at 500 °C.

Thirdly, Pr_{0.4}Sr_{0.6}Co_{0.9-x}Fe_xNb_{0.1}O_{3-δ} (PSCF_xN) (x=0, 0.2, 0.4, 0.6 and 0.9) oxides were evaluated as the symmetric electrode materials for SOFCs. Effects of stoichiometric amounts of iron (Fe) and cobalt (Co) on electrical conductivity, thermal expansion and electrochemical properties were investigated. Both the thermal expansion coefficient (TEC) and conductivity decreased with the increase in Fe amount. With higher Fe content, more Fe⁴⁺ species were reduced to Fe³⁺, generating more oxygen vacancies. This effectively promoted the oxygen incorporation kinetics, and lowered the polarization resistance (Rp). As a result, the PSCF_{0.6}N exhibited the lowest polarization resistance of 0.028 Ω cm² at 900 °C and the highest electrical conductivity of 258.90 Scm⁻¹ at 650 °C among all the prepared PSCF_xN materials. Meanwhile, with the doping of Fe, the TEC decreased near to the electrolyte's TEC value, and the TECs of PSCN, PSCF_{0.6}N and LSGM (electrolyte) were 17.39, 11.79 and 10.01 ×10⁻⁶, respectively, in air. As such, the peak power densities of the electrolyte supported symmetric SOFCs with different electrolyte thicknesses of 500, 400 and 300 μm were 0.642, 0.713 and 0.891 Wcm⁻², respectively(Figure 1 (b)), indicating that the PSCF_{0.6}N material should be a promising electrode material for the symmetric SOFCs.