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La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.79}M_{0.01}O_{3-δ} (M = Ni, Pd) perovskites synthesized by Citrate-EDTA method: Oxygen vacancies effect on electrochemical properties

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ABSTRACT

La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF08), La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.79}Ni_{0.01}O_{3-δ} (LSCF08-Ni) and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.79}Pd_{0.01}O_{3-δ} (LSCF08-Pd) perovskites were synthesized by Citrate-EDTA method, by using NiCl₂ or PdCl₂ as metal precursors, and their physicochemical properties were characterized by XRD, TGA, TPD and TPR. XRD data evidenced an expansion of the lattice parameters of LSCF08-Pd, while a contraction of the lattice occurred for LSCF08-Ni, with respect to the undoped LSCF, suggesting different oxygen vacancies content in the perovskite (confirmed by TGA) likely due to a different oxidation state of Ni and Pd species stabilized in the structure.

TEM analyses performed over LSCF08-Pd revealed the presence of metallic Pd nanoparticles well dispersed in the matrix that accounts for the increased reducibility of the Co and Fe species with respect to LSCF08-Ni and undoped perovskite. AC impedance measurements that were carried out on symmetric cells consisting of LSCF-based materials deposited onto Ce_{0.8}Gd_{0.2}O_{2-δ} (GDC) electrolyte proved the enhanced electrochemical performances of Ni/Pd doped LSCF.

The electrochemical characterization of LSCF08, LSCF08-Ni and LSCF08-Pd electrodes was completed by performing cyclic voltammetry experiments in the range of temperature 600–800 °C, varying the potential (U) between 0.3 V and –1 V, at scan rates in the range 1–50 mV s⁻¹ and working under flow of 0.7 vol % O₂ in He (30 ml/min).

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1. Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFCs) are promising energy converters for near future. For the moment, cell performance is still restricted by poor cathode kinetics resulting from low operation temperature, which must be overcome before their commercialization. Therefore, many efforts are made to search for novel cathode materials with high electro-oxygen reduction activity and stability.

Mixed ionic and electronic conductive (MIEC) La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ} (LSCF) perovskites, particularly La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF08) are promising cathodes for IT-SOFCs [1]. However, so far, its further application still demands improvement in electro-catalytic activity for oxygen reduction reaction (ORR) in the tem-

perature range of 500–800 °C. Some possible ways, such as controlling of microstructure or together with ionic conductor, e.g. GDC and SDC, to fabricate LSCF based composites have been investigated extensively [2].

The significant effect of metal promotion for LSCF cathode, by either surface modification or directly substitution has been confirmed by a large number of experiments [2]. It is evident that the syntheses approach is critical for such metal promoted LSCF cathodes. For instance, Sasaki et al. [3] reported even at a high Pt/LSCF ratio of 80/20, no evident promotion was found in LSCF-Pt cathode that synthesized by ball milling. However, as reported by Hwang et al. [4], a small amount of Pt impregnation (0.5 vol%) will reduce the cathode impedance of LSCF significantly. Such difference was possibly due to Pt partial substitution at LSCF external lattice in the case of impregnation which will weaken the resistance at Pt/LSCF interface and simultaneously inhibit agglomeration tendency of Pt particles at high temperature, indicating high fractional lattice-site interaction between metal and LSCF is

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needed in order to get better performance. The used metal species is another key factor that determines the final performance. Up to now, noble metals such as Pt [3,4], Ag [5–7] and Pd [8–10] are still preferred due to their intrinsic excellent catalytic capacities on oxygen surface exchange process. Nevertheless, recently, Huang et al. [11,12] reported a best performance by Cu infiltration among Cu, Ag and Pt added LSCF, implying the possible replacement of noble metals by more affordable ones.

Fundamental understanding in metal-promoted ORR process is still challenging, mainly due to the involved complicated steps in ORR that are hard to be studied experimentally. Recently, by using TGA coupled with TPR, Ozkan and co-workers confirmed experimentally the improvement in oxygen vacancies generation after Cu, Zn and Ni B-site substituted LSCF [13,14]. In good agreement with this, our DFT calculations on $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.75}\text{Fe}_{0.125}\text{Pd}_{0.125}\text{O}_{3-\delta}$ (LSCF0.25-Pd) and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_{3-\delta}$ (LSCF0.25) also verified a decrement in oxygen vacancy formation energy after Pd substitution. The obtained formation energy of Co–V_O–Pd type vacancy in LSCF0.25-Pd is 2.38 eV, which is lower than that of Co–V_O–Co in LSCF0.25. Those for Co–V_O–Co and Co–V_O–Fe in LSCF0.25-Pd are also reduced with respect to LSCF0.25 [15]. The increased oxygen vacancy amount influences ORR catalytic performance of LSCF directly via enlarge three-phase boundary (TPB) and enhance bulk diffusion as well. Besides, it is generally considered that the incorporation of a third metal ion at LSCF B-site would induce stronger redox ability and hence better catalytic properties for oxygen adsorption, dissociation and reduction [16,17]. Moreover, previous studies show that B-site substitution also contributes to the stability and influences the TEC value of LSCF based cathodes. For example, the calculated TEC of Cu substituted $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.1}\text{Fe}_{0.8}\text{Cu}_{0.1}\text{O}_{3-\delta}$, $12.2 \times 10^{-6} \text{ K}^{-1}$ is more beneficial for cathode use compared with that of Cu-free $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, $15.9 \times 10^{-6} \text{ K}^{-1}$ [18]. Nevertheless, deeper investigations need to be carried out in both theoretical and experimental fields in order to get specific mechanism of B-site substitute promotion.

Up to now, the most widely used approach for metal-promoted LSCF is impregnation. However, low substitute fraction and metal dispersion problem limit its further application. Few years ago, the synthesis of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.17}\text{Pd}_{0.03}\text{O}_{3-\delta}$ (LSCF02-Pd) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.77}\text{Pd}_{0.03}\text{O}_{3-\delta}$ (LSCF08-Pd) by sol-gel method using citrate as complexing agent was studied by some of us [19]. Preliminary results show that at this concentration, Pd was partially inserted into LSCF lattice in a fraction of 45% and 62% as Pd⁴⁺ and the rest Pd metal clusters of about 2 nm well dispersed on LSCF matrix surface, indicating sol-gel method as a new realizable approach for LSCF B-site substitution. Moreover, recently, in collaboration with Longo et al. we have clarified the fundamental role of Ni doping in the performance and electronic structure of LSCF cathodes with composition $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8-0.03}\text{Ni}_{0.03}\text{O}_{3-\delta}$ [20].

The interest in using Ni as B-site additional dopant for LSCF arises from the effect of Ni in the electronic structure of $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$, already investigated many years ago [21], where the cobalt spin state equilibrium was markedly affected by Ni, especially for low content. The microstructure, reducibility and magnetic properties of $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ perovskites have been recently addressed by other authors [22,23]. In such studies [22,23] the molar content of Ni was ranging between 0.1 and 0.5 or between 0.3 and 0.7, while the entire range of composition from Ni0.01 to Ni0.9 was examined only in the first report [21]. Therefore, in our opinion LSC and LSCF perovskites doped with very low Ni content are worthy to be investigated in more details.

Interestingly, in the group of Longo [20] some of us have proved by “in situ” XANES experiments carried out under air flow in the range of RT – 950 °C that the B-site Ni dopant (0.03), added by one pot sol-gel method, stabilizes the oxygen vacancies in LSCF08 and delays their formation. Moreover, by carrying out X-ray Raman

scattering spectroscopy to study the O K-edge, it was concluded that Ni helps to retain the hybridization between the O 2p and TM 3d orbital, which hinders the modification of the TM–O6 octahedron. It is worth noting that no promoting effect of Ni was observed for the sample prepared by wetness impregnation of Ni over the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8-0.03}\text{Ni}_{0.03}\text{O}_{3-\delta}$.

Based on these findings, in the present work we considered worthy of investigation lowering the metal (Ni, Pd) content with respect to the previous investigations [19,20,22,23] and study the influence of the synthesis conditions (such as Ni and Pd precursors, EDTA effect). Accordingly, Ni and Pd doped perovskites with composition, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.79}\text{M}_{0.01}\text{O}_{3-\delta}$, were prepared by Citrate-EDTA sol-gel method, then, physical chemical characterizations were carried out by X-ray diffraction (XRD), Thermogravimetric analysis (TGA), Temperature programmed desorption (TPD), Temperature program reduction (TPR), X-ray photoelectron spectroscopy (XPS), Transmission Electron Microscopy (TEM). The electrochemical performances of the LSCF and Ni, Pd doped perovskites were investigated by Electrochemical impedance spectroscopy (EIS) and Cyclic Voltammetry (CV) experiments.

2. Experiments

2.1. Preparation

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.79}\text{M}_{0.01}\text{O}_{3-\delta}$ (M equal to Ni and Pd), labelled respectively as LSCF08, LSCF08-Ni and LSCF08-Pd, were synthesized by citrate-EDTA method according with the literature [24], starting from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or PdCl_2 solution (5 wt % in 10 wt% HCl), as precursors. In a typical synthesis the precursors were dissolved in deionized water and then added to EDTA–citric acid–NH₄OH solution under stirring (mole ratio of EDTA: citric acid: total metal ions = 1:2.0:1). After adjusting the pH around 9 by using concentrated NH₄OH, the resulting solution was concentrated under oil bath at 80 °C followed by treatment in oven at 120 °C overnight. Based on our previous investigation on Ni doped LSCF [20], the so obtained samples were calcined at 1100 °C 2 h (heating rate of 2 °C/min). Such temperature is appropriate for the crystallization of the perovskite phase, avoiding dramatic sintering of crystallites and loss of porosity for O₂ permeability.

Elemental analysis of the so-prepared samples was determined by atomic absorption spectroscopy using a Perkin-Elmer Analyst 100 (AAS) after microwave disintegration of the samples (100 mg) in presence of pure nitric acid in a microwave mineralizator Magnum Ertec. The real composition also in terms of Ni and Pd corresponded to the nominal content within ±5%.

2.2. X-Ray diffraction (XRD)

XRD measurements on the starting powders were carried out with a Bruker D5000 vertical goniometer equipped with Cu anode (K α radiation $\lambda = 1.5418 \text{ \AA}$) and a graphite monochromator. A proportional counter and a 0.05° step size in 2 θ were used. The integration time was 5 s per step and the diffraction patterns were recorded in the range of 20° < 2 θ < 80°.

The crystal structure of the samples was established by using the Inorganic Crystal Structure Database (ICSD)–FIZ Karlsruhe and the POWDER CELL 2.4 software for full profile analysis and calculation of structural parameters.

2.3. Thermogravimetric analyses (TGA)

TGA in air were performed with a TGA/DSC1 STAR system Mettler Toledo. The samples (~10 mg) were pretreated in air

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