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Full Length Article

$La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ layered perovskite as an efficient bifunctional electrocatalyst for rechargeable zinc-air batteries

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A R T I C L E I N F O

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A B S T R A C T

In this work, a novel $La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ with a layered perovskite structure was synthesized by the sol-gel method and characterized by the X-ray diffraction (XRD), scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). Catalytic activities of $La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) were systematically investigated by the rotating disk electrode (RDE) technique in alkaline media. Compared to $La_2NiO_{4+\delta}$, $La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ demonstrated more active for ORR in terms of the higher limiting current density ($-4.05\,mA\cdot cm^{-2}$) and higher half-wave potential (0.568 V vs. RHE) at 1600 rpm. Zinc-air batteries using $La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ as the catalyst exhibited the higher peak power density ($60\,mW\cdot cm^{-2}$), the lower discharge-charge voltage gap (1.26 V) after 100 cycles and good discharge-charge cycling stability than that of $La_2NiO_{4+\delta}$.

1. Introduction

With the rapid depletion of fossil energy resources and the enhancement of environmental protection consciousness, renewable energy storage and conversion technology have attracted much attention [1,2]. Metal-air batteries (e.g., zinc-air, aluminum-air, magnesium-air and lithium-air, etc.) as a potential candidate for future energy application have attracted a great attention as good candidates in energy field due to their low cost, high energy density and environmentally friendly operation [3–6]. However, the commercialization of rechargeable zinc-air batteries must overcome many obstacles, such as the sluggish kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) as well as the poor cycling stability [7–10]. Pt, IrO_2 and RuO_2 are well-known ORR/OER catalysts with high activity. However, their large-scale application is restricted due to the scarcity, high cost and poor stability [11]. Therefore, much effort has devoted to explore high active and more economic catalysts [12,13]. Recently, mixed valence transition metal oxides attracted much attention due to their low cost, abundance and acceptable catalytic activity towards ORR and OER [14–17].

Some recent studies reported “layered” perovskite oxides ($A_2BO_{4+\delta}$) with K_2NiF_4-type structure described as stacked perovskite (ABO_3) layer alternating with rock-salt (AO) layer along the *c* direction maybe possess acceptable activities for ORR and OER [3,18]. Yu et al. systematically studied the ORR and OER performance of Ruddlesden-Popper type $La_{n+1}Ni_nO_{3n+1}$ (n = 1, 2, 3 and ∞) and determined the beneficial effect from the elongated Ni—O bonds and rock-salt layer towards ORR [19]. Similarly, a recent study suggested that easily removable oxygen in the Ruddlesden-Popper-type $LaSr_3Fe_3O_{10}$ “layered” perovskite facilitates the redox reaction of the transition metal, thereby lead to enhanced ORR and OER activity [18]. Wang et al. prepared carbon-coating functionalized $La_{0.6}Sr_{1.4}MnO_{4+\delta}$ layered perovskite oxide, which showed high ORR activities in alkaline media even comparable to commercial Pt/C catalyst [20]. The strategy of doping was a simple and efficient way to tune the bifunctional catalytic activities [5,21–23]. Jung et al. investigated the catalytic properties of $La_2NiO_{4+\delta}$ doped with Sr^{2+} towards ORR and OER, which displayed enhanced ORR and OER activities due the increasing Ni oxidation state and the higher surface coverage of hydroxide species, respectively [24]. Calcium-doped lanthanum nickelate layered perovskite $(La_{0.613}Ca_{0.387})_2NiO_{3.562}$ also revealed high OER activity [25]. Moreover, $LaNiO_3$ has been widely studied as a potential candidate bifunctional catalyst due to favorable chemical stability and high conductivity of ions and electrons [26–28]. Sunarso et al. systematically studied the ORR activity of $LaNiO_3$ and $LaNi_{0.5}Co_{0.5}O_3$ perovskite, which indicated that substituting half of the nickel with cobalt translates the ORR to a more positive onset potential [29].

Hence, the strategy by doping of Sr on La site and Co on Ni site of

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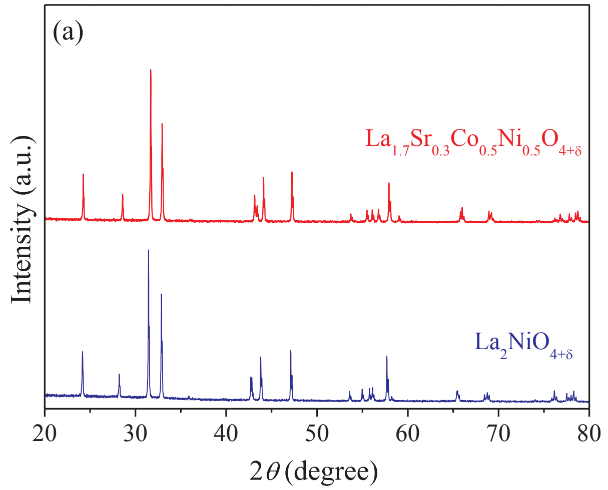

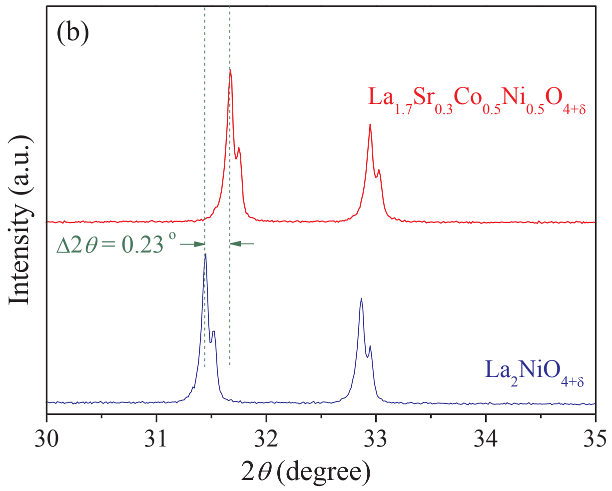

Fig. 1. XRD patterns of $La_2NiO_{4+\delta}$ and $La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ (a) and their magnified diffraction peaks (b).

$La_2NiO_{4+\delta}$ could be an efficient way to modify the catalytic activities for ORR and OER of $La_2NiO_{4+\delta}$. In this study, $La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ powder was prepared by the facile sol-gel method. The chemical and physical characterization was carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Both ORR and OER activities of $La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ were investigated in alkaline medium using a rotating disk electrode system. Furthermore, electrochemical performances of $La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ bifunctional catalyst were evaluated as the air electrode under realistic operating conditions using home-made zinc-air batteries.

2. Experimental section

2.1. Synthesis of electrocatalysts

$La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ powder was prepared by the traditional sol-gel method. All reagents were analytical grade chemicals and used as received without any further purification. In a typical synthesis, the nitrates of the respective metals (La, Sr, Co and Ni) in the required stomichiometric amounts were dissolved in distilled water. Citric acid (CA) in a molar ratio of 1.5:1 (CA: total metal ions) was then added to the above homogenous solution as a chelating agent and fuel. The as-prepared solution was continuously stirred under the water bath at 80 °C to form the gel. The gel was dried at a constant temperature of 200 °C for 12 h to form the solid precursor. Then, the powder was calcined at 1250 °C for 10 h twice with intermediate grinding under the air atmosphere to afford the $La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ crystalline powder. The calcined powder was then ground with an agate mortar and pestle for 1 h and then filtered with a 300-mesh sieve. For comparisons, undoped $La_2NiO_{4+\delta}$ was prepared through similar procedures, which was calcined at 1100 °C for 4 h.

2.2. Characterization

The crystal structure of the as-prepared samples was determined by X-ray diffraction (XRD, Rigaku D/max2200, Japan) using Cu-Kα radiation (λ = 0.15418 nm). The morphology of samples was characterized by a field emission scanning electron microscope (SEM, HitachiSU800, Japan). The chemical composition was measured by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, Al Ka radiation, $h\nu$ = 1486.6 eV). The binding energy of peaks was compensated by referring to C 1s binding energy (284.6 eV).

2.3. Electrochemical measurements

Catalyst ink for the ORR and OER testing was prepared by mixing 5 mg catalyst, 5 mg of conductive carbon (Super P Li, TIMCAL), 50 μl of Nafion solution (5 wt%) and 500 μl of ethanol. The ink was agitated in

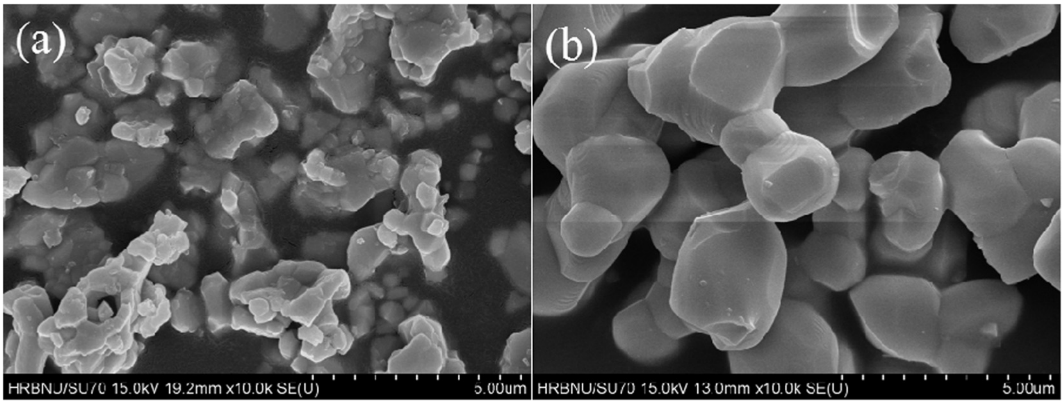

Fig. 2. SEM images of $La_2NiO_{4+\delta}$ (a) and $La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$ (b) samples.