Electrocatalytic performances of $LaNi_{1−x}Mg_xO_3$ perovskite oxides as bi-functional catalysts for lithium air batteries

Zhenzhen Du [a], Peng Yang [a], Long Wang [b], Yuhao Lu [b], J.B. Goodenough [b], Jian Zhang [a], Dawei Zhang [a,b,c,∗]

[a] School of Chemical Engineering, Hefei University of Technology, Hefei 230009, PR China
[b] Texas Materials Institute, The University of Texas at Austin, 1 University Station, C2201, Austin, TX 78712, USA
[c] CAS Key Laboratory of Materials for Energy Conversion, Hefei 230026, PR China

HIGHLIGHTS

- $LaNi_{1−x}Mg_xO_3$ is used for bi-functional air electrode in Li−air batteries.
- $LaNi_{1−x}Mg_xO_3$ has higher Ni^{3+}/Ni^{2+} ratio and will absorb hydroxyl on the surface.
- Higher initial capacities of $LaNi_{1−x}Mg_xO_3$ in Li−air batteries are reported.

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ABSTRACT

Mg-doped perovskite oxides $LaNi_{1−x}Mg_xO_3$ ($x = 0, 0.08, 0.15$) electrocatalysts are synthesized by a sol−gel method using citric acid as complex agent and ethylene glycol as thickening agent. The intrinsic oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) activity of as-prepared perovskite oxides in aqueous electrolyte are examined on a rotating disk electrode (RDE) set up. Li−air primary batteries on the basis of Mg-doped perovskite oxides $LaNi_{1−x}Mg_xO_3$ ($x = 0, 0.08, 0.15$) and nonaqueous electrolyte are also fabricated and tested. In terms of the ORR current densities and OER current densities, the performance is enhanced in the order of $LaNiO_3$, $LaNi_{0.92}Mg_{0.08}O_3$ and $LaNi_{0.85}Mg_{0.15}O_3$. Most notably, partially substituting nickel with magnesium suppresses formation of Ni^{2+} and ensures high concentration of both OER and ORR reaction energy favorable Ni^{3+} ($e_g = 1$) on the surface of perovskite catalysts. Nonaqueous Li−air primary battery using $LaNi_{0.92}Mg_{0.08}O_3$ and $LaNi_{0.85}Mg_{0.15}O_3$ as the cathode catalysts exhibit improved performances compared with $LaNiO_3$ catalyst, which are consistent with the ORR current densities.

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1. Introduction

Li−air batteries have recently raised widespread concerns because of their significantly higher theoretical specific energy density (5200 Wh kg^{-1} based on full utilization of a lithium anode including the mass of oxygen) than Li ion batteries, low cost, and environ-mentally friendly operation [1,2]. Nonetheless, these batteries with non-aqueous electrolyte have considerable challenges. According to some researchers [3−5], in non-aqueous rechargeable Li−air batteries, the principal electrode reactions are thought to be:

$$2Li + 0.5O_2 \leftrightarrow Li_2O \tag{1}$$

$$2Li + O_2 \leftrightarrow Li_2O_2 \tag{2}$$

Charge and discharge reactions need to be catalyzed to reduce kinetic losses because of breaking and forming of the O−O bond on discharge and charge, respectively [6−8]. The group of Yang Shao-horn has developed platinum−gold nanoparticles exhibiting bi-functional catalytic activity for rechargeable Li−air battery [9]. Thapa et al. [10,11] have reported mesoporous Pd/MnO_2 with a charging potential of 3.6 V and a reversible capacity of ca. 545 mAh $g^{-1}_{catalyst}$ observed at 0.025 mA cm^{-2}. Platinum nanoparticle−graphene hybrids have also been successfully synthesized severed as cathode catalysts for Li−air battery [12]. However, the limited availability and high cost of the noble
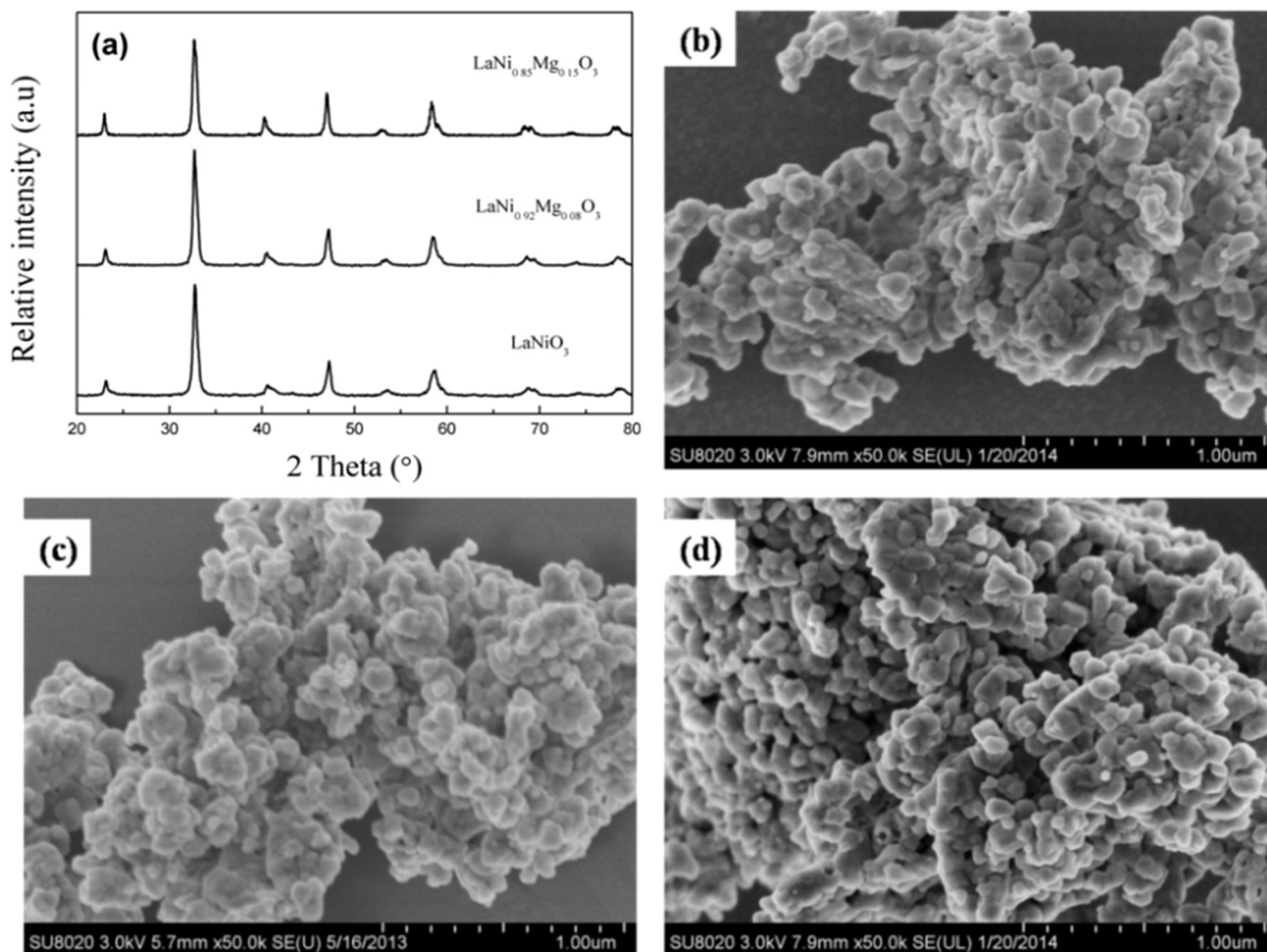
Fig. 1. (a) XRD patterns of $LaNi_{1-x}Mg_xO_3$ (x = 0, 0.08, 0.15) perovskite oxides. SEM images of (b) $LaNiO_3$, (c) $LaNi_{0.92}Mg_{0.08}O_3$, (d) $LaNi_{0.85}Mg_{0.15}O_3$.

metal-based bi-functional catalysts prevent their large-scale applications in the Li–air batteries. Therefore it is extremely significant to develop cost-effective, corrosion-resistant, and highly active bi-functional catalysts for both ORR and OER kinetics in Li–air batteries.

Perovskite materials have been widely used as catalysts for fuel cells and metal–air batteries owing to their defective structures, excellent oxygen mobility and low cost. $LaNiO_3$ is considered to have excellent both ORR and OER catalytic performance because that Ni^{3+} at B site in the perovskite structure has single electron-filled e_g orbit, and therefore, provides the favorable bond energy of M(B site)–O bond for ORR and OER. However, presence of Ni^{2+} in $LaNiO_3$ results in $e_g > 1$, decreases its ORR catalytic activity. In the light of tuning the strength of Ni–O bond covalency to sustain good catalytic performance, both B-site and/or A-site doping on $LaNiO_3$ has been demonstrated to be beneficial. The improved OER activities of perovskites are related to the high covalency of transition metal-oxygen bonds [13]. Suntivich and co-workers have recently reported that $LaNiO_3$ catalysts show comparable performances to platinum nanoparticles in actual fuel cell cathodes [14], which arises our interest in studying the catalytic property of partially substituting Ni with other cations.

Herein, we demonstrated the feasibility of improved electrocatalytic activities of $LaNi_{1-x}Mg_xO_3$ catalysts using the thin-film RDE technique [14,15], and Li–air batteries with such perovskites as cathode catalysts of non-aqueous electrolyte were also investigated.

2. Experimental section

2.1. Synthesis of materials

Perovskite oxide nanoparticles were synthesized by the sol–gel method. Briefly, desired amounts of $La(NO_3)_3 \cdot xH_2O$, $Mg(NO_3)_2 \cdot 4H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Sinopharm, reagent grade) were dissolved in deionized water, respectively. Subsequently, these metal nitrates were gradually added to a mixture of citric acid $(HOC(COOH)(CH_2COOH)_2, \geq 99.5\%)$ and ethylene glycol $(HOCH_2CH_2OH, 99.8\%)$ under stirring conditions at 60 °C. The molar ratios

Table 1
Binding energies obtained by XPS.

Catalyst	La $3d_{5/2}$	Ni $2p_{3/2}$	Mg 1s	O 1s
$LaNiO_3$	834.7	854.5	–	528.16
		856.0		529.29
				531.0
				532.02
$LaNi_{0.92}Mg_{0.08}O_3$	834.7	854.7	1302.7	528.4
		856.0	1304.3	529.3
				531.02
				532.02
$LaNi_{0.85}Mg_{0.15}O_3$	834.6	854.6	1302.3	528.1
		855.9	1304.3	529.3
				531.0
				532.01