

Co-Doped LaMnO₃ Perovskite Structure Nanoparticles as a Bifunctional Electrocatalysts for Oxygen Reduction/Evolution Reactions



Shaik Mahammad Rafi, Yong Min Kwon, An Seop Lim

Abstract: Current paper, we have examined lanthanum manganese cobalt (LaMn_{1-x}Co_xO₃) perovskite nanoparticles synthesized by utilizing the sol-gel process and following calcinated at 450 °C for 1h and 900 °C for 7h, respectively. The fabricated alloys show single-phase perovskite structure is an order of LaMn_{1-x}Co_xO₃ (x = 0, 0.2, 0.4, 0.6, 0.8, 1). The synthesized LaMn_{1-x}Co_xO₃ perovskite oxide nanoparticles have the crystal structure, and powder morphology properties were investigated by X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM), respectively. The perovskite structure has been shown to be particularly effective for the catalytic reactions of ORR and OER in alkaline medium. The merged valance transition metal oxides are bifunctional electrocatalysts which give rise to potential candidates, the electrochemical functioning of the LaMn_{1-x}Co_xO₃ catalyst was entirely investigated. All compounds of ORR polarization curves show that the four-electron pathway, which results in Koutecky-Levich is compatible with these perovskite structures. Current work, we describe B-site extend adding of Co ratio into perovskite structure is an appropriate strategy to increase ORR and OER electrocatalytic performance for application in metal-air batteries.

Keywords: Perovskite Structure, Electrochemical Functioning, Bifunctional Electrocatalysts, Metal-air Batteries.

I. INTRODUCTION

Electronic devices have been developing rapidly, which results in increasing demand for high energy/ power density sources. There is also a capable intension to promote electric vehicles by introducing batteries to overcome their dependence on fuel and reduce tailpipe emissions [1]. At this point, many researchers have been studied rechargeable metal-air battery and it has been considered as one of the much-encouraging energy sources for electric vehicles owing to few attractive benefits, like high power density, low-priced, and environmentally friendly. However, the improvement of rechargeable metal-air batteries is mainly controlled by two inactive procedures, especially, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics of oxygen electrocatalysts [2].

The air cathode designed for the oxygen reduction reaction catalysts (ORRC), gas diffusion layer, and current collector which gives the importance for metal-air batteries [3].

Currently, palladium (Pd) and platinum (Pt) are the mainly utilized favorable electrocatalysts for ORR, there is less activity towards OER. RuO₂ and IrO₂ are considered as the good OER electrocatalyst however show incomplete ORR activity [4]. Therefore, in terms of ORR activities, several non-metallic catalysts have been developed, similar compounds like MnO₂-based catalysts, carbon-based materials, also other transition metal oxides. Among these applicants as perovskite oxides have to be attractive cost-wise, high activity, and environmentally friendly, which gains the interest from science and technology [5]. Transition metal oxides have benefits such as good catalytic activity, controllable conductivity, as well as low cost for ORR and OER [6]. In various bifunctional electrocatalysts, La-based perovskite structure is represented by a chemical formula ABO₃, which is composed of several oxides. Where A-cation is usually rare-earth elements or alkaline earth elements and B-cation are transition metal elements [7].

The application of perovskite structure as oxygen electrocatalysts was initially described in the year of 1970s. Whereas, La-based perovskite structure, as a bifunctional electrocatalyst for ORR and OER which are attracted to more consideration and has developed one of the hot subjects in the electrocatalysis area [8]. In this current work, LaMn_{1-x}Co_xO₃ perovskite structure nanoparticles were synthesized by the sol-gel process. In metal-air batteries and fuel cells, LaMnO₃ is one of the most commonly used catalysts for ORR/OER [9]. LaMnO₃ based materials consist of electrical properties and very attractive electrocatalysts owing to their high electronic conductivity and good ionic conductivity [10]. Literature reports described that LaMnO₃ has good oxygen mobility and defective cation deficient lattice which shows excellent oxygen reduction reaction (ORR) catalytic activity [11].

The A-site defect perovskite structure is unstable because the vacant lanthanum locations have a high amount in the crystal structure. The perovskite materials have A-site defects which can change the B-site defects [12]. The catalytic reaction caused by the reduction of primary transition metals like Co, Mn, Fe forms the B-site cation. The combining of double dissimilar elements at the B-site guide to synergetic effect with improving electrocatalytic activity. The transition metal has properties of oxidoreduction, and high oxygen mobility associated with the perovskite oxides activity [13]. Through the air cathode application, there has been a special involvement of research on La-based perovskite structure (LaMO₃, M = Mn, Co, Fe).

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In the current work, we have generalized our research in-depth for lanthanum-based perovskite oxide nanoparticles in sol-gel synthesis and their characterization of electrocatalytic activities for ORR and OER reactions.

II. EXPERIMENTAL SECTION

A. Materials

Lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O, 99+%, Aldrich), manganese (II) nitrate tetrahydrate (Mn(NO₃)₂·4H₂O, 98%, Alfa Aesar), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 97.7%, Alfa Aesar), citric acid anhydrous (C₆H₈O₇, 99.5+%, Alfa Aesar), potassium hydroxide (KOH, 85%, Alfa Aesar). All chemicals were used as shown without further treatment.

B. Synthesis of LaMn_{1-x}Co_xO₃ Nanoparticles

The preparation of La-based nanoparticles, in an order of [LaMn_{1-x}Co_xO₃] (x = 0, 0.2, 0.4, 0.6, 0.8, 1) were synthesized by the sol-gel process. Lanthanum, manganese, cobalt nitrate compounds, and citric acid. Metal nitrates and citric acid having a molar ratio of 1: 2 has fixed. Afterward, the whole combined compound solution was kept at 80 °C temperature and mixed with a magnetic stirrer. Until to get the brown gel to continue this stirring process. Afterward, these prepared composition samples can be located in a heated furnace at the temperature of 200 °C to become amorphous precursor, later the desiccated powder has been shifted to a crucible and calcinated at 450 °C for 1 h and 900 °C for 7 h. The collected powders were LaMnO₃, LaMn_{0.8}Co_{0.2}O₃, LaMn_{0.6}Co_{0.4}O₃, LaMn_{0.4}Co_{0.6}O₃, LaMn_{0.2}Co_{0.8}O₃, and LaCoO₃.

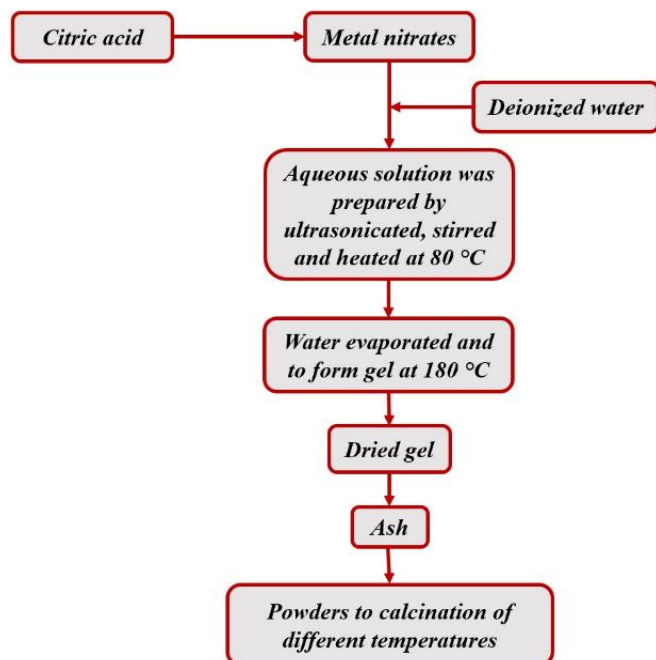


Figure 1. The preparation of the LaMn_{1-x}Co_xO₃ by the sol-gel process.

C. Characterization Techniques

a. X-ray diffractometer (XRD)

The crystal structure of LaMn_{1-x}Co_xO₃ perovskite structure nanoparticles was investigated by XRD

(wavelength $\lambda = 1.54 \text{ \AA}$, Rigaku Cu K α radiation) technique within 10° to 80° is the range of 2 θ .

b. Field Emission Scanning Electron Microscopy (FESEM)

The morphology, elemental distribution, and average particle size of LaMn_{1-x}Co_xO₃ perovskite structure nanoparticles are examined by FESEM (SIGMA 500, ZEISS) and elemental mapping analysis was investigated by EDS (Bruker, XFlash 6130).

c. Electrochemical Measurements

The synthesized LaMn_{1-x}Co_xO₃ perovskite structure nanoparticles for ORR and OER electrocatalytic performance, the rotating ring disk electrode (RRDE) technique was examined by using the electrochemical measurements which are attached to the workstation (BAS Inc.). An electrochemical cell that consists of a saturated three-electrode test system of an RRDE which consists of a graphite rod, glassy carbon (GC) substrate of a diameter 6.0 mm, 3.0 mm and saturated calomel electrode (SCE). The role of these three-electrode system plays as a counter, working, and reference electrodes. Aqueous KOH solution of a ratio 0.1 M is used as the electrolyte. To build a homogeneous ink by using prepared catalyst ink solution consist a mixture of Vulcan-XC72 carbon (2 mg) and LaMn_{1-x}Co_xO₃ perovskite structure (2 mg) were diffused in 1 mL of ethyl alcohol and combined with 0.15 mL of Nafion® solution. On a clean polishing cloth (R&B Inc.) RRDE GC disk electrode was cleaned initially with a 0.05 μm alumina abrasive suspension (R&B Inc.) frequently cleaned with DI water, later kept in the oven to dry. After the preparation of homogeneous ink in ultrasonication for 1h, the glassy carbon electrode is coated with 0.36 μL of catalyst ink. In RRDE experiments, the electrolyte has been saturated with the purging of high purity oxygen gas (99.99%) for 30 minutes. By using a CHI electrochemical workstation, the polarization curves for the LaMn_{1-x}Co_xO₃ of ORR was tested at 500, 1000, 1500, 2000, and 2500 rpm rotational speed, and the 1500 rpm rotational speed for oxygen evolution reaction (OER) with a scan rate is 0.005 V s⁻¹. The frequency range of the electrochemical resistivity measurements is carried out between 0.1 Hz to 100 kHz with a voltage bias of 5 mV amplitude. The overall reaction mechanism of ORR is to understand through the electron transfer number (n) by using the equation of Koutecky-Levich: [7]

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_d} = \frac{1}{nFkC_{O_2}} + \frac{1}{0.62nFD_{O_2}^{2/3}\omega^{1/2}\nu^{-1/6}C_{O_2}} \quad (1)$$

Where J is the current density, J_k is the kinetic current density, J_d is the diffusion-limiting current density, n is the electron number, F is the Faraday constant, k is the ORR rate constant, C_{O_2} is the oxygen concentration ($1.14 \times 10^{-6} \text{ mol cm}^{-3}$),

D_{O_2} is the oxygen diffusion coefficient ($1.73 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ω is the rotation rate of the electrode (rad/s), v is the

III. RESULTS AND DISCUSSION

The phase and crystal structure of the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ perovskite structure nanoparticles calcinated at 450°C for 1 h and 900°C for 7 h were characterized by using XRD, as shown in Fig. 2(a). All compounds demonstrated the single-phase cubic crystal structure, which confirmed from hygienic LaMnO_3 JCPDS-ICDD file no: 073-8342. No specific peak of lanthanum oxide or manganese oxide was detected, no effect is shown in the phase structure with the difference of La/Mn molar ratio. We detected that there is a clear peak shift towards a higher 2θ angle (right shift) with extend adding of Co ratio into LaMnO_3 like (0, 0.2, 0.4, 0.6, 0.8, 1).

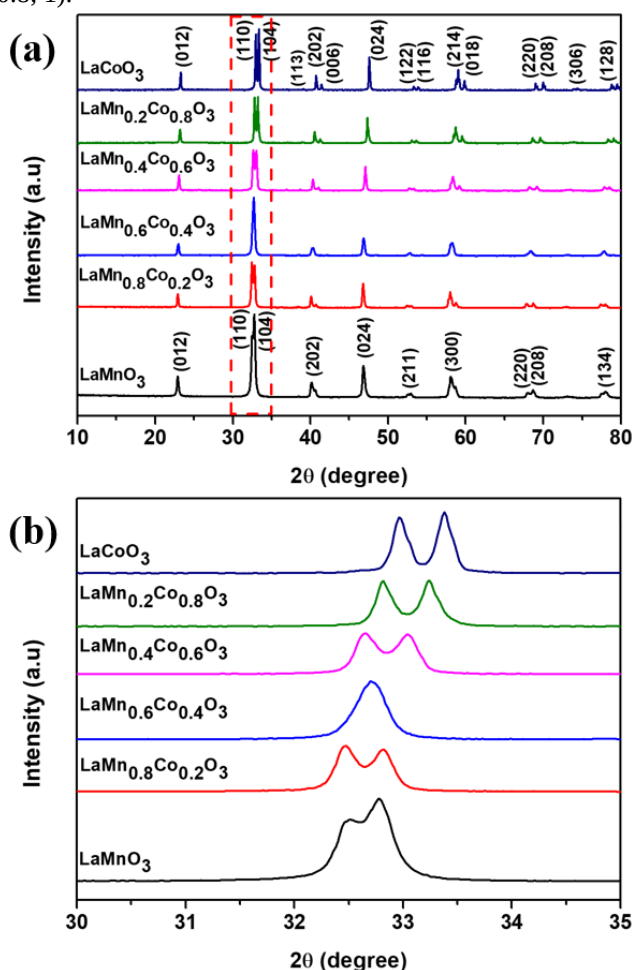


Figure 2. XRD sample of the (a) $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ upon 10° to 80° is the range of 2θ , (b) magnified XRD peak between 30° and 35° .

The $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ perovskite structure nanoparticles of surface morphology were characterized by using FESEM as shown in Fig. 3(a-b). The identical single or double layers of the particle size are few hundreds of nanometers. For example, the ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) compounds showing a particle size of 451 nm, 156.26 nm, 133.96 nm, 256.8 nm, 320.06 nm, and 350.13 nm. The particles have shown unsystematic structures and uneven distribution. The change in the particle sizes is probably associated with the sequence of changes in perovskite. The elemental mapping

electrolyte kinetic viscosity ($0.01 \text{ cm}^2 \text{ s}^{-1}$).

is shown in Fig. 3(g) of perovskite structure $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ under the FESEM method which presents the 1:1 atomic ratio for La: M (Mn, Co) catalysts. The chemical components in the perovskite structure are distributed regularly.

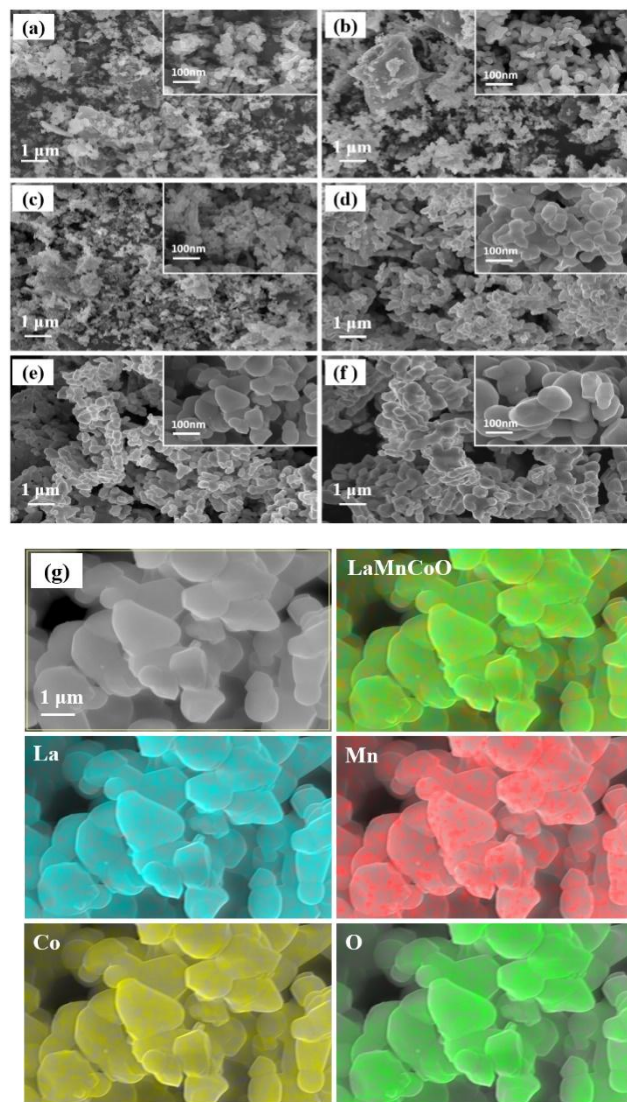


Figure 3. FESEM morphologies of (a) LaMnO_3 , (b) $\text{LaMn}_{0.8}\text{Co}_{0.2}\text{O}_3$, (c) $\text{LaMn}_{0.6}\text{Co}_{0.4}\text{O}_3$, (d) $\text{LaMn}_{0.4}\text{Co}_{0.6}\text{O}_3$, (e) $\text{LaMn}_{0.2}\text{Co}_{0.8}\text{O}_3$, and (f) LaCoO_3 (the high resolution images are shown in the top right in sets), (g) $\text{LaMn}_{0.2}\text{Co}_{0.8}\text{O}_3$ elemental mapping analysis.

In sequence to analyze the catalytic activities of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ perovskite structure nanoparticles for ORR and OER reactions. The RRDE measurements have been investigated through the linear sweep voltammetry (LSV) in oxygen saturated 0.1 M KOH electrolyte at different speed of rotations like 500, 1000, 1500, 2000, and 2500 rpm. $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ perovskite structure nanoparticle's current density is shown in Fig. 4(a), all samples of ORR current densities are with a scan rate is 0.005 V s^{-1} at 2500 rpm speed of rotation in -1.0 V to 0.0 V vs.

SCE is the potential range. The highest diffusion-limited current density is indicating to LaMn_{0.2}Co_{0.8}O₃ that reduces in the order of LaCoO₃ > LaMn_{0.8}Co_{0.2}O₃ > LaMn_{0.4}Co_{0.6}O₃ > LaMn_{0.6}Co_{0.4}O₃ > LaMnO₃. The initial potential of all samples is approximately -0.30 V. The OER activities for the designs are set to estimate their implementation as a bifunctional oxygen electrocatalyst. The OER activity was recorded through the LSV curves is shown in Fig. 4(b), at the rotation speed of 2500 rpm OER has explained each electrocatalyst in the potential region between 0.0 V to 1.0 V vs. SCE. At 0.60 V the kinetics of

LaMn_{0.2}Co_{0.8}O₃ is suddenly growing. LaMn_{0.2}Co_{0.8}O₃ is showing highest current density in oxygen evolution reaction and reduces in the order of LaCoO₃ > LaMn_{0.6}Co_{0.4}O₃ > LaMn_{0.8}Co_{0.2}O₃ > LaMn_{0.4}Co_{0.6}O₃ > LaMnO₃. The ORR current density of LaMn_{0.2}Co_{0.8}O₃ is recorded through the LSV curves on RRDE at different speed of rotations as 500 to 2500 rpm is shown in Fig. 4(c) with the rotational speed increases, the current density increases as the dissolved oxygen is rapidly transported to the electrode surface.

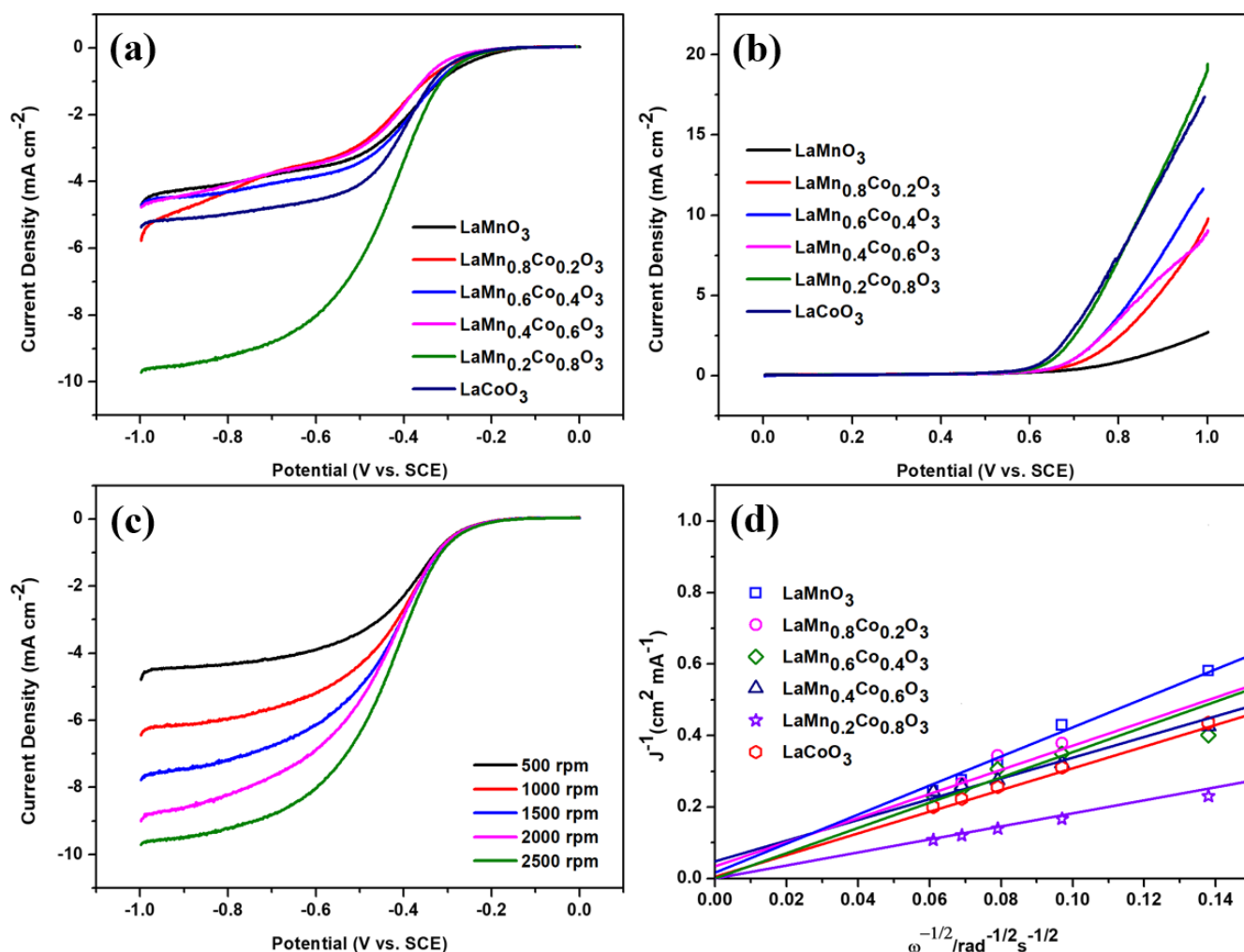


Figure 4. (a) The ORR polarization curves in Linear Sweep Voltammetry (LSV) test at 2500 rpm, (b) The potential range of OER current densities is from 0.0 V to 1.0 V, (c) ORR polarization curves of LaMn_{0.2}Co_{0.8}O₃ at different speed of rotations as 500 to 2500 rpm (d) ORR polarization curves of Koutecky-Levich analysis at -0.80 V.

The ORR kinetics of the electrocatalysts processes and more quantitative analysis by LaMn_{1-x}Co_xO₃ perovskite structure, we have calculated the Koutecky-Levich plots at -0.80 V vs. SCE through the LSV test derive from ORR polarization curves is shown in Fig. 4(d). By using Eq. (1) the electron transfer number (n) has been studied through the incline of the Koutecky-Levich analysis for LaMn_{1-x}Co_xO₃ is shown in Fig. 4(d) which are 3.8, 4.1, 4.0, 4.1, 4.4, and 4.1 respectively. The theoretical value (4.0) is very close to each sample of ORR in alkaline medium. A certain quantity of Co doping can forward the ORR procedure from

a 2-electron dominated pathway in the electrolyte medium (O₂ to HO₂⁻) is the reducing of the 4-electron dominated pathway from O₂ to OH⁻.

IV. CONCLUSIONS

In this study, by using the sol-gel process the LaMn_{1-x}Co_xO₃ was synthesized, which reduces the certain amount of the Mn ratio and increments the certain amount of the Co ratio.

The observation outcomes specify the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ demonstrated the single-phase perovskite cubic crystal structure, indicating higher 2θ angle have clear peak shift with extend adding of Co ratio like ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) into LaMnO_3 , and the identical single or double layers of the particle size is showing few hundreds of nanometers. The ORR and OER curves of electrochemical tests were investigated by using all synthesized perovskite structure in 0.1 M KOH electrolyte. $\text{LaMn}_{0.2}\text{Co}_{0.8}\text{O}_3$ is shown the highest diffusion-limiting current density for ORR based on the LSV curves. The OER has explained each electrocatalyst in the potential region between 0.0 V to 1.0 V vs. SCE. At 0.60 V the kinetics of $\text{LaMn}_{0.2}\text{Co}_{0.8}\text{O}_3$ is suddenly growing. Similarly, all compounds of ORR polarization curves show that the four-electron pathway corresponds to the Koutecky-Levich results. In metal-air batteries, for air cathode, the low-cost electrocatalyst is provided by Co-doped LaMnO_3 .

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