

## 아연-공기전지용 페로브스카이트 산화물 촉매의 산소환원반응 특성

선호정<sup>1</sup> · 조명연<sup>1</sup> · 안정철<sup>4</sup> · 엄승욱<sup>5</sup> · 박경세<sup>2</sup> · 심중표<sup>3†</sup>

<sup>1</sup>군산대학교 신소재공학과, <sup>2</sup>군산대학교 화학과, <sup>3</sup>군산대학교 나노화학공학과

<sup>4</sup>포항산업과학연구원 탄소소재연구실, <sup>5</sup>한국전기연구원 전지연구센터

### Characterization of LaCoO<sub>3</sub> Perovskite Catalyst for Oxygen Reduction Reaction in Zn-air Rechargeable Batteries

HO-JUNG SUN<sup>1</sup>, MYUNG-YEON CHO<sup>1</sup>, JUNG-CHUL AN<sup>4</sup>, SEUNGWOOK EOM<sup>5</sup>,  
GYUNGSE PARK<sup>2</sup>, JOONGPYO SHIM<sup>3†</sup>

<sup>1</sup>Department of Material Science & Engineering Kunsan National University, Jeonbuk, 573-701, Korea

<sup>2</sup>Department of Chemistry Kunsan National University, Jeonbuk, 573-701, Korea

<sup>3</sup>Department of Nano & Chemical Engineering, Kunsan National University, Jeonbuk, 573-701, Korea

<sup>4</sup>Carbon Materials Research Group, Research Institute of Industrial Science & Technology,  
Pohang, Gyeongbuk, 790-330, Korea

<sup>5</sup>Battery Research Center Korea Electrotechnology Research Institute, Changewon, Gyeongnam, 641-120, Korea

**Abstract** >> LaCoO<sub>3</sub> powders synthesized by Pechini process were pulverized by planetary ball-milling to decrease particle size and characterized as a catalyst in alkaline solution for oxygen reduction and evolution reaction (ORR & OER). The changes of physical properties, such as particle size distribution, surface area and electric conductivity, were analyzed as a function of ball-milling time. Also, the variations of the crystal structure and surface morphology of ball-milled powders were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The electrochemically catalytic activities of the intrinsic LaCoO<sub>3</sub> powders decreased with increasing ball-milling time, but their electrochemical performance as an electrode improved by the increase of the surface area of the powder.

**Key words** : Zn-air battery(아연공기전지), Cathode(양극), Perovskite(페로브스카이트), LaCoO<sub>3</sub>, Oxygen reduction(산소환원), Oxygen evolution(산소발생)

## 1. Introduction

Rechargeable batteries with high energy density and lower cost are needed to apply to many electrical devices, from portable electronics to electrical vehicles. Since

1980's, lithium secondary batteries have shown significantly higher performance than other secondary batteries such as lead-acid and nickel-metal hydride batteries<sup>1,2)</sup>. However, they should overcome several disadvantages for the application to electric vehicles; two of them are safety and cost. To solve these problems, considerable efforts have been focused on the development of new type batteries, zinc-air rechargeable batteries (ZARB). Although

<sup>†</sup> Corresponding author : jpshim@kunsan.ac.kr

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ZARB have received much attention due to its low cost, high stability, non-explosion and environmental benignity<sup>3)</sup>, they have not shown any advantages because their poor cycleability, high solubility of zinc compounds and low rate of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) of air electrode. Thus, as one of key points, increasing ORR and OER in the air electrode as a bi-functional electrode is important to enhance the performance of zinc-air rechargeable batteries.

Platinum (Pt) has been well known to be the best catalyst for the ORR, but it has moderate activity for OER<sup>4)</sup>. Ruthenium (Ru) and iridium (Ir) oxides showed higher activity than Pt for the OER, but they are not as active as Pt for the ORR<sup>5)</sup>. Manganese oxide materials had been studied much for the catalyst of the air electrode because of low cost<sup>6-8)</sup>. They have good catalytic activity for the ORR but did not show high activity for the OER as it did for ORR<sup>9)</sup>. The catalytic activities of lanthanum cobaltate perovskite ( $\text{LaCoO}_3$ ) and related compounds have also received much attention because of relatively high catalytic activity for ORR & OER, and low cost synthetic process<sup>10-12)</sup>.

Air electrode consists of active materials as a catalyst, carbon black as a conductive additive, and a polymeric binder. For the activity for ORR & OER, the chemical composition and surface area of the catalyst are very important in the bi-functional electrode. Conventionally,  $\text{LaCoO}_3$  has been synthesized by Pechini process which can produce the particles of sub micron size or lower. In this work, we synthesized  $\text{LaCoO}_3$  perovskite by Pechini process and pulverized powders mechanically by the planetary ball-milling to decrease particle size. The electrochemical catalytic activities of  $\text{LaCoO}_3$  powders with different particle sizes for ORR & OER were characterized in alkaline electrolyte.

## 2. Experimental

$\text{LaCoO}_3$  perovskite was synthesized by Pechini process<sup>13)</sup> by reacting  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , citric acid and ethylene glycol (Aldrich Co.). Metal nitrates were firstly dissolved in water, and citric acid as chelating agent and ethylene glycol as polymerizing agent were added with continuous stirring. The solution was heated at 60°C until it became gel. The obtained gel was dried at 120°C for 12h, and calcined at 900°C for 5h.  $\text{LaCoO}_3$  powder was pulverized by the planetary ball-milling with zirconia balls (diameter 5mm) in ethanol at a rotational speed of 600rpm using a planetary mono mill (Fritsch, pulverisette 6). The crystal structure and surface morphology of the obtained  $\text{LaCoO}_3$  powders were characterized by X-ray diffractometer (XRD, PANalytical, EMPYREAN) and field emission-scanning electron microscopy (FE-SEM, Hitachi, S-4800), respectively. Particle size distribution (Sympatec GmbH, Nanophox) and BET surface area (ATI, Quadrasorb SI-Kr) were measured to characterize the effect of ball-milling. For conductivity measurement, the powder was pelletized at 5 ton of pressure after mixing with 20 weight % of the polymer binder (Polyvinylidene fluoride, PVdF, Aldrich Co.). The conductivity of the pellet was measured by 4-point probe method using conductive meter (Changmin Tech, CMT-SR-100N).

Porous and bifunctional electrode was prepared by the following process.  $\text{LaCoO}_3$  powders were mixed with carbon black (Vulcan XC-72, Cabot) as the conductive agent and PTFE as the binder in ethylene glycol. PTFE emulsion (60% dispersion, DuPont) was used. Small amount of the surfactant was added to protect the agglomeration of particles. The mixture was stirred for 30 min to make slurry. And then it was cast on Al foil

using Dr. blade and dried at 120°C for 6 hours. The cast sheet as the catalytic layer was transferred to a wet-proofed carbon paper (AvCarb P50, Ballard) as a gas diffusion layer by hot-press at 250°C. It was treated at 350°C for 30min to remove the surfactant<sup>14)</sup>.

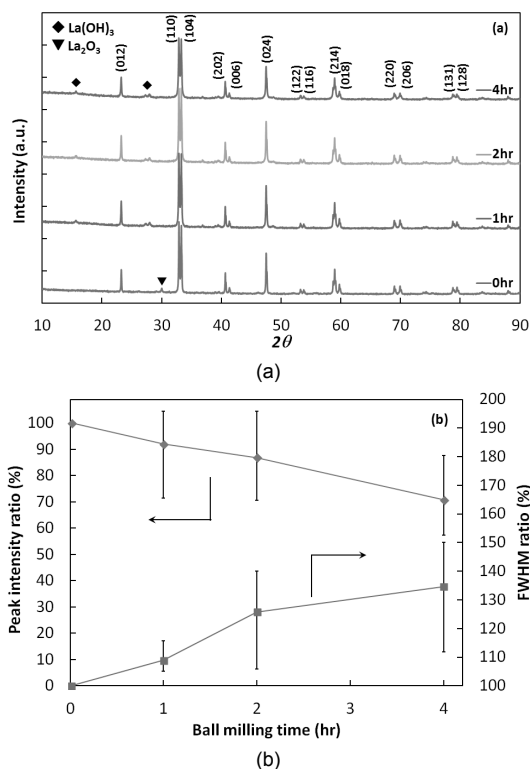
The electrode was electrochemically characterized for ORR and OER in 8M KOH solution at three electrode systems. The size of working electrode was 1cm<sup>2</sup>, which was cut with round shape. Counter and reference electrodes were Pt mesh and Zn wire with 1mm diameter, respectively. The electrochemical analysis was conducted at room temperature. In three electrode systems, the catalytic layer made contact with KOH solution, and the gas diffusion layer (carbon paper) exposed to the air. Cell potential by a linear sweep potential method was scanned between 0.8 and 2.5V vs. Zn/Zn<sup>2+</sup>, which was assigned to -0.413 and 1.287V vs. SHE (standard hydrogen electrode)<sup>15)</sup>.

### 3. Results and discussion

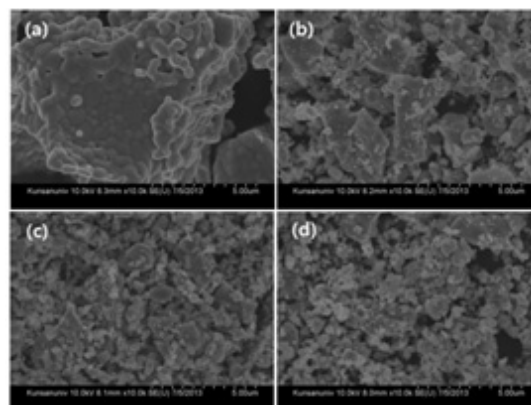
Fig. 1(a) shows the X-ray diffraction patterns of LaCoO<sub>3</sub> powders. These patterns confirmed that the crystal structure of LaCoO<sub>3</sub> was not damaged by the ball milling<sup>16)</sup>. Untreated LaCoO<sub>3</sub> had tiny amount of impurity for La<sub>2</sub>O<sub>3</sub> (Joint Committee on Powder Diffraction Standards (JCPDS) file number 05-0602) and it was disappeared in the ball-milled samples. However, other impurity, La(OH)<sub>3</sub> (JCPDS file number 36-1481), was produced. Fig. 1(b) shows peak intensity and FWHM (full width at half maximum) ratio for (110) plane compared to untreated sample. Peak intensity decreased and FWHM increased with increasing the ball milling time, and those results may be caused by the reduction of crystallinity by ball milling.

Fig. 2 shows SEM images of untreated and the

ball-milled LaCoO<sub>3</sub> powders. Untreated powder has particles (more than 10μm size) agglomerated with small grain (ca. 1.0μm). After the ball milling, the particle size



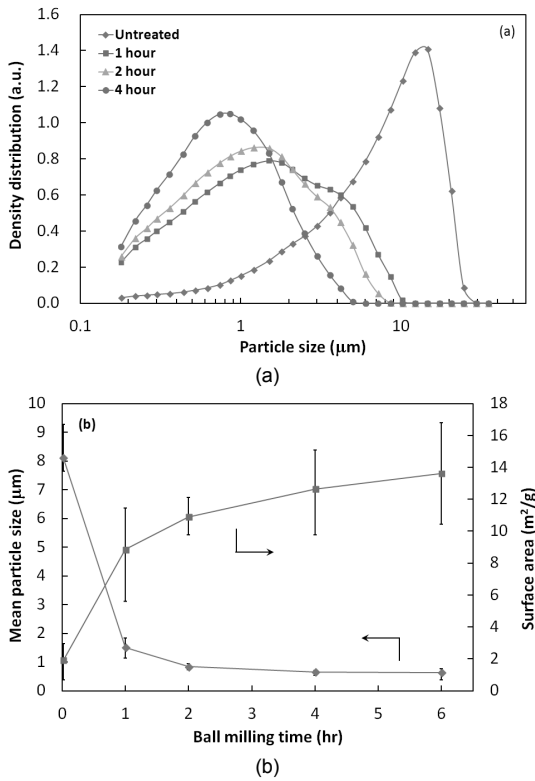
**Fig. 1** XRD patterns (a), and peak intensity & FWHM ratios (b) for (110) plane of untreated and ball-milled LaCoO<sub>3</sub> powders. Peak intensity and FWHM ratios of ball-milled samples in comparison to untreated one



**Fig. 2** SEM imaged of ball-milled LaCoO<sub>3</sub> powders. (a) Untreated, (b) 1 hour, (c) 2 hour and (d) 4 hour

of  $\text{LaCoO}_3$  continuously decreased. It's also confirmed by the particle size analysis.

Particle size distributions of the ball-milled  $\text{LaCoO}_3$  powders were shown in Fig. 3(a). Before the ball-milling, the powder has single modal distribution with average particle size of  $\sim 8\mu\text{m}$ . During the ball milling for 1~2h, the distribution changed to bimodal. Fig. 3(b)



**Fig. 3** Particle size distribution (a), and mean particle size & BET surface area (b) of ball-milled  $\text{LaCoO}_3$  powders

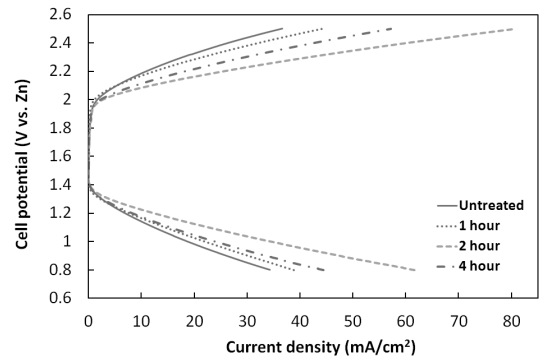
**Table 1** Mean particle size, BET surface area, and electric conductivity of untreated and ball-milled  $\text{LaCoO}_3$  powders

Ball mill time (h)	Mean particle size ( $\mu\text{m}$ )	BET surface area ( $\text{m}^2/\text{g}$ )	Electric conductivity ( $10^{-5}$ S/cm)
0	8.11	1.92	5.68
1	1.51	8.85	0.93
2	0.85	10.9	1.09
4	0.66	12.6	0.95
6	0.64	13.6	-

shows the change of the mean particle size and the surface area of  $\text{LaCoO}_3$  by the ball milling. By only 1 hour of the ball-milling, the particle size sharply decreased to  $\sim 18\%$  of that of the untreated powder, and then size decreased to  $\sim 0.6\mu\text{m}$  after 4 hours. As generally well known, when the particle size decreased continuously, the surface area increased in contrast<sup>17,18</sup>. Also, Table 1 shows values of the mean particle size and the surface area for the untreated and the ball-milled  $\text{LaCoO}_3$  powders.

It has been reported in several literatures that electric conductivity of  $\text{LaCoO}_3$  is in the range from  $0.1^{19-21}$  to  $10^{-5}\text{S/cm}^{22}$  with different synthetic processes and sample preparations. The electric conductivities of the pellets prepared with the  $\text{LaCoO}_3$  powder are listed in Table 1. The electric conductivity of the  $\text{LaCoO}_3$  powder ball-milled for 1 hour was lower than that of untreated one. But the ball-milled samples show similar values regardless of the ball milling times. The surface area of the powder increased by the ball milling due to smaller particle size, comparing untreated one, and it also may be caused by increasing the roughness on the surface. It may lead to increase contact resistance between the particles.

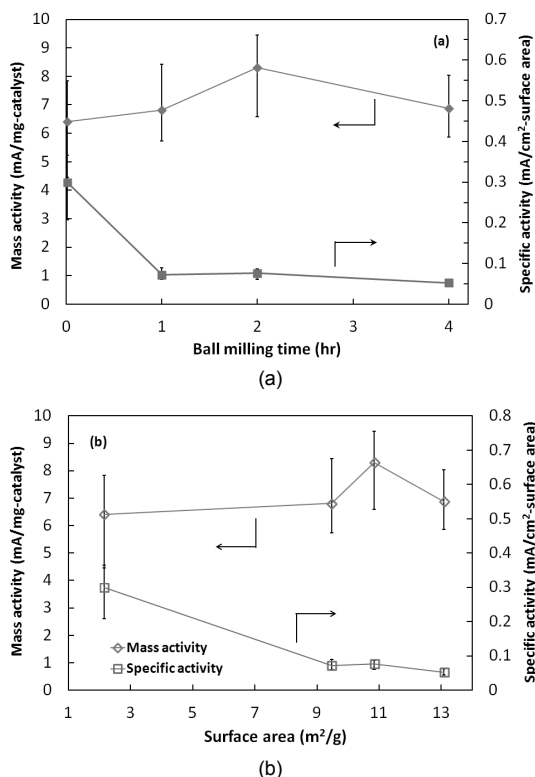
Fig. 4 shows the current-potential curves of the untreated and ball-milled  $\text{LaCoO}_3$  for ORR and OER by the linear



**Fig. 4** Current-potential curves of ball-milled  $\text{LaCoO}_3$  as a function of ball milling time

sweep potentiometry. ORR occurs with decreasing the potential and OER are reverse. The current density shown in the figure is apparent one based on the electrode area. The  $\text{LaCoO}_3$  ball-milled for 2 hours shows the highest performance among all samples, and the untreated one shows the lowest performance. The ball-milling gives a positive effect to the cell performance of  $\text{LaCoO}_3$  because all ball-milled samples showed higher performance than untreated sample. However, the ball-milling for 4 hours decreased current for both ORR and OER.

Fig. 5 shows mass activity based on the catalyst loading amount in the electrode, and specific activity based on the surface area of the catalyst at 1.0V (vs. Zn) for ORR, respectively, which are converted from apparent current density in Fig. 4. As shown in Fig. 5(a), the mass

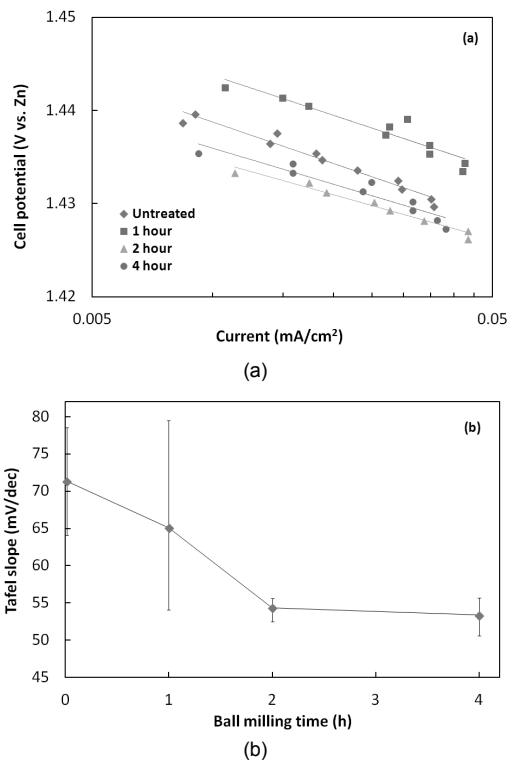


**Fig. 5** Specific activity and mass activity of  $\text{LaCoO}_3$  at 1.0V (vs. Zn) as a function of ball mill time (a) and surface area (b)

activity increased with increasing the ball-milling time up to 2 hours, and then decreased. However, the specific activity significantly decreased by the ball-milling. But the ball-milled samples show similar specific activity regardless of the ball-milling times. Fig. 5(b), which is shown as a function of the surface area of the powders, also shows same behavior. Ball-milling for 2 hours shows maximum mass activity, and the specific activity continuously decreases with increasing the surface area. This decrease of specific activity by the ball-milling may mean deterioration for the catalytic activity on the surface of the powders. However, the cell performance was enhanced by the ball-milling except for 4 hours. The reason is because the catalytic active area in electrode was increased around ~460% by the increase of the surface area of the powder, even though the specific activity for the sample ball-milled for 1 hour decreased to 24%.

Fig. 6 shows Tafel plot and slope, which are assigned to an activation polarization region, of the untreated and ball-milled  $\text{LaCoO}_3$  electrodes as a function of ball-mill time. Tafel slope decreased with the increasing ball-mill time, which is similar to the specific activity. This means that ball-milling diminished the activation polarization for ORR. This result is strongly related to the enlargement of the surface area of the ball-milled powder. The activation polarization could be decreased by the increase of the surface area, even though the catalytic activity of the unit surface area is reduced.

The characterization of the ball-milled  $\text{LaCoO}_3$  powders for OER was investigated in same way shown above. Detail results are not shown here because the electrochemical parameters for OER were also similar to those for ORR. Conclusively, the ball-milled  $\text{LaCoO}_3$  powders showed better cell performance than untreated sample,



**Fig. 6** Tafel plot (a) and slope (b) of  $\text{LaCoO}_3$  as a function of ball mill time

even though they had lower catalytic activity. It may need further studies for chemical and electrochemical stability and durability of the ball-milled  $\text{LaCoO}_3$  powders in alkaline solution.

#### 4. Conclusions

$\text{LaCoO}_3$  powders synthesized by Pechini process were pulverized by the planetary ball-milling to decrease the particle size and characterized as the catalyst in the alkaline solution for oxygen reduction and evolution reaction (ORR & OER). The particle size continuously decreased, which was observed by SEM and PSA, and the surface area significantly increased with increasing ball-milling time. The diminution of the crystallinity with the ball-milling was confirmed by XRD. The

electrochemical performances of the electrodes with the ball-milled  $\text{LaCoO}_3$  powders were improved in comparison to the untreated sample and maximum at 2 hours ball-milling. However, their specific activity based on the surface area of the powder decreased with the increasing ball-milling time. It means that the cell performance could be improved by the increase of the surface area of the powder, even though intrinsically catalytic activity was declined by the ball-milling.

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