Research Article

Electrochemical Activity of a $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ Catalyst for a Zinc Air Battery Electrode

Seungwook Eom,¹ Seyoung Ahn,² and Sanghwan Jeong¹

¹Battery Research Center, Korea Electrotechnology Research Institute (KERI), 12 Bulmosan-ro 10 Beon-gil, Seongsan-gu, Changwon 642-120, Republic of Korea

²Battery Tech Center, LG Chem, Daejeon 104-1, Republic of Korea

Correspondence should be addressed to Seungwook Eom; sweom@keri.re.kr

Received 29 December 2014; Revised 13 March 2015; Accepted 13 March 2015

Academic Editor: Shijun Liao

Copyright © 2015 Seungwook Eom et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The optimum composition of cathode catalyst has been studied for rechargeable zinc air battery application. $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0-0.4$) perovskite powders were prepared using the citrate method. The substitution ratio of Co^{2+} with Fe^{3+} cations was controlled in the range of 0–0.4. The optimum substitution ratio of Fe^{3+} cations was determined by electrochemical measurement of the air cathode composed of the catalyst, polytetrafluoroethylene (PTFE) binder, and Vulcan XC-72 carbon. The substitution by Fe enhanced the electrochemical performances of the catalysts. Considering oxygen reduction/evolution reactions and cyclability, we achieved optimum substitution level of $x = 0.1$ in $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$.

1. Introduction

The oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) in aqueous solutions occur at a high overpotential ($E(\text{O}_{2,\text{gen.}}) > E(\text{O}_{2,\text{red.}})$). This irreversibility of the reactions is the main problem for developing a cathode of zinc air battery. In addition, bifunctional catalysts for the cathode are an important prerequisite for developing zinc air secondary batteries. Many types of electrocatalysts have been investigated for the ORR and OER: perovskite, spinel, noble metal, and pyrochlore [1–6]. However, most of the catalysts cannot provide suitable performance for both the OER and ORR. A transition metal oxide can be used only for an ORR catalyst, while metal oxide and spinel compounds can be used for OER catalysts.

Compared with noble metal catalysts, metal oxides offer the advantages of avoiding gassing on the zinc electrode when acting as bifunctional electrodes for the ORR and OER [7, 8]. The noble metal catalysts, Pd, Ag, and Pt, exhibit good performance for the ORR; however, these catalysts undergo a sharp degradation in the OER caused by the dissolution of the catalysts [9].

Perovskites, which have the general formula ABO_3 , exhibit excellent catalytic performance in the ORR and OER because of their high oxide ion mobility. Partial substitution of A or B by a cation A' or B' with a different valence leads to ionic defects or changes in the valence state of the catalyst, which affects the catalytic activity and conductivity of the catalyst [1]. The substitution at catalytically active “B” sites in the ABO_3 structure by some transition metal cation can enhance the catalytic activity by leading to valence changes, which causes non-stoichiometry-related microstructural defects in the lattice [10]. Therefore, changing the oxygen content leads to structural rearrangement; increasing the lattice vacancies leads to higher oxide ion mobility, the synergistic role of mixed valence states of cations at “B” sites, and the segregation of active metal components at the surface layer [10, 11].

Fe-doped perovskite-type complex oxides exhibit excellent electron-ion mixed conductivity; therefore, many research groups are interested in these materials for electrode applications [12–16]. In particular, because these materials exhibit electric conductivities over $10^2 \Omega^{-1}\cdot\text{cm}^{-1}$ and ionic conductivities of 10^{-2} – $1.0 \Omega^{-1}\cdot\text{cm}^{-1}$ over 800°C, Fe-doped perovskite-type complex oxides have

FIGURE 1: Manufacturing process of the cathode catalyst.

attracted growing attention [17]. Shimizu et al. synthesized $\text{La}_{1-x}\text{A}'_x\text{Co}_{1-y}\text{B}'_y\text{O}_3$ (A' : Ca, B' : Mn, Fe, Ni, and Cu) using the citrate method and reported that the perovskite catalysts exhibited the best performance for the ORR and cyclability when the Co cation was substituted by a Fe cation [18].

In a previous investigation, $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0-0.4$) oxides were synthesized and applied to the cathode for zinc air secondary batteries. These catalysts exhibited excellent electrochemical properties at room temperature [19].

2. Experimental

$\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0-0.4$) oxide was synthesized using the citrate method for the cathode catalyst of zinc air secondary batteries. As starting materials, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used. Metal nitrates were mixed in a stoichiometric molar ratio of $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0-0.4$) and dissolved in deionized water. Then, citric acid was added as a chelating agent while stirring constantly. After mixing the starting materials, the solution containing a mixture of citric acid and constituent metal nitrates was heated at 90°C for several hours to evaporate the excess solvents and promote polymerization. When the gel precursor was attained, it was heated at 100–120°C until it burned up followed by calcination for 2 hours at 700°C (Figure 1).

The air electrode was prepared as illustrated in Figure 2. First, a polytetrafluoroethylene (PTFE) dispersion (60%, Dupont 30-J) was mixed with deionized water and ultrasonically dispersed for 10 min. Vulcan XC-72 carbon black and prepared $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0-0.4$) perovskite catalyst powder were poured into the PTFE-water mixture.

The mixture was stirred for 2 h and dried at 120°C. The dried electrode powder was mixed again with some drops of isopropyl alcohol and kneaded to make a cathode sheet using a roll press. This cathode sheet was attached to one side of a Ni mesh, and a PTFE sheet for the gas diffusion electrode was placed at the other side of the Ni mesh. Figure 2 shows the process for preparing the air electrode. The compositions of the air cathode were 42.5% $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0-0.4$) perovskite, 42.5% Vulcan XC-72 carbon black, and 15% PTFE dispersion.

The prepared disk-type cathode was used as a working electrode and was placed into an electrochemical cell. On the opposite side, the platinum mesh as a counter electrode was placed with an Hg/HgO electrode as the reference electrode. An 8.5 M potassium hydroxide (KOH) solution was used as the electrolyte.

A potentiostat (VMP3, Princeton Applied Research) was used for electrochemical measurement of the half-cell. The scan rate for the linear sweep voltammograms (LSV) and cyclic voltammograms (CV) was 2 mV s^{-1} and 5 mV s^{-1} , respectively.

The surface morphology of the cathode was examined using a scanning electron microscope (S-2700, Hitachi, Japan). The XRD patterns were obtained using an X-ray diffractometer (1830 X-ray diffractometer, Philips) using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$) in the 2θ range of $20^\circ - 90^\circ$ at a scan rate of 0.1° s^{-1} .

3. Results and Discussion

Based on the XRD analysis presented in Figure 3, we verified that the powder calcined at 700°C contained a single phase of

FIGURE 2: Manufacturing process of the cathode.

FIGURE 3: XRD patterns of $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0-0.4$) catalyst after calcination.

$\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ perovskite structures in all of the Fe-doped levels. Figure 4 shows the representative morphology of the $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0-0.4$) catalysts. The powders exhibit an average particle size of 50 nm (primary particles).

Figures 5 and 6 present the polarization curves for a series of Fe-doped perovskites, $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0-0.4$). The substitutions of cobalt cations by iron cations could improve the catalytic activity; thus, reduced cathodic overpotentials were obtained with the Fe-doped $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ cathode compared with the nondoped materials. Neburchilov et al. reported that the Fe-doped perovskite catalyst has high activity for the decomposition of the HO_2^- in the two-electron pathway in ORR that occurred in alkaline solution

[6, 20]. Similar results were observed for the anodic polarization characteristics, as demonstrated in Figure 6. Considering the cathodic and anodic polarization characteristics, the optimum composition based on the Fe doping level was $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_3$.

As observed in Figures 5 and 6, the doping of $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ with Fe could lead to improvements in the oxygen evolution reaction rather than the oxygen reduction reaction. According to the results obtained by Jörissen, well-crystallized materials improve the oxygen reduction reaction, whereas less crystalline materials are beneficial for the oxygen evolution reaction [9]. The particle size of the synthesized Fe-doped $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ was approximately

FIGURE 4: SEM images of catalyst.

FIGURE 5: Cathodic polarization curves of $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0-0.4$) cathodes. FIGURE 7: Anodic and cathodic polarization curves of $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.0-0.4$) cathodes. FIGURE 6: Anodic polarization curves of $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0-0.4$) cathodes. FIGURE 8: Anodic and cathodic polarization potentials at current density of 50 mA cm^{-2} as a function of Fe doping level.

30 nm, which was smaller than that of the non-Fe-doped $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$, and the XRD intensity of the Fe-doped $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ was smaller. Therefore, it can be concluded that the Fe-doped $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ alloys synthesized in

this study were less crystalline. Therefore, these alloys were beneficial for the oxygen evolution reaction.

When Co in the $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ is substituted with Fe, the lattice contains non-stoichiometry-related microstructural defects due to synergistic valence changes. Therefore, the catalytic activity may be improved. However, high contents of Fe lead to decreased ion mobility because the binding energy of Fe-O is stronger than that of Co-O [12]. Therefore,

FIGURE 9: Cyclic voltammograms of $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ cathode at a sweep rate of 5 mV s^{-1} : (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$, and (d) $x = 0.4$.

as illustrated in Figures 5-6, highly Fe-doped $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ exhibits a larger cathodic or anodic overpotential.

Figures 7 and 8 present the anodic and cathodic polarization curves of $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.1-0.4$) catalysts as a function of the Fe doping level. In these results, the potential differences between charging (oxygen evolution, $i = 50 \text{ mA cm}^{-2}$) and discharging (oxygen reduction, $i = 50 \text{ mA cm}^{-2}$) were 929 mV for $x = 0.0$, 712 mV for $x = 0.1$, 717 mV for $x = 0.2$, 725 mV for $x = 0.3$, and 735 mV for $x = 0.4$.

The fact that the substitutions of cobalt with iron could improve the catalytic activity was demonstrated by several observations. However, as observed in Figure 9, upon increasing the Fe content, the cyclability worsened, which was caused by degradation of the structural properties of the cathode during cycling. Oxygen reduction can take place through two pathways. One leads to water or OH^- through a four-electron reduction; the other one leads to peroxide through a two-electron reduction. It is known that the perovskite catalyst has four-electron pathway reaction; however at high current density region, it follows two-electron pathway as the following two steps:

The peroxide formed during the two-electron reaction diffuses into the bulk solution. During diffusion, the peroxide

oxidizes the Teflon bonding between the catalyst and carbon. Decomposition of Teflon bonding blocks the cathode pore and results in increment of internal resistance. This is the main reason of capacity degradation [6]. It is presumed that the two-electron path ratio is increased along with the doping level of Fe in $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$. Therefore the cathode structure becomes unstable.

4. Conclusions

To improve the catalytic activity, Co in $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ was substituted with Fe. In the anodic and cathodic polarization measurements, the substitution by Fe enhanced the electrochemical performances of the catalysts due to synergistic valence changes and resultant non-stoichiometry-related microstructural defects introduced into the lattice. However highly Fe-doped $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ lost their structural stability.

Overall, by simultaneously considering oxygen reduction/evolution reactions and cyclability, $\text{La}_{0.9}\text{Ca}_{0.1}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_3$ could be applied as a good bifunctional catalyst for cathodes.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

This work was supported by the National Research Foundation of Korea grant funded by the Korean Government (MEST) (NRF-2012-M1A2A2-028739).

References

- [1] O. Haas, F. Holzer, K. Muller, and S. Muller, *Handbook of Fuel Cells: Fundamentals, Technology, Applications*, John Wiley & Sons, 2003.
- [2] N.-L. Wu, W.-R. Liu, and S.-J. Su, "Effect of oxygenation on electrocatalysis of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-x}$ in bifunctional air electrode," *Electrochimica Acta*, vol. 48, no. 11, pp. 1567–1571, 2003.
- [3] S. Royer, F. Bérubé, and S. Kaliaguine, "Effect of the synthesis conditions on the redox and catalytic properties in oxidation reactions of $\text{LaCo}_{1-x}\text{Fe}_x\text{O}_3$," *Applied Catalysis A: General*, vol. 282, no. 1-2, pp. 273–284, 2005.
- [4] W.-D. Yang, Y.-H. Chang, and S.-H. Huang, "Influence of molar ratio of citric acid to metal ions on preparation of $\text{La}_{0.6}\text{Sr}_{0.33}\text{MnO}_3$ materials via polymerizable complex process," *Journal of the European Ceramic Society*, vol. 25, no. 16, pp. 3611–3618, 2005.
- [5] C. Xiulan and L. Yuan, "New methods to prepare ultrafine particles of some perovskite-type oxides," *Chemical Engineering Journal*, vol. 78, no. 2-3, pp. 205–209, 2000.
- [6] V. Neburchilov, H. Wang, J. J. Martin, and W. Qu, "A review on air cathodes for zinc-air fuel cells," *Journal of Power Sources*, vol. 195, no. 5, pp. 1271–1291, 2010.
- [7] O. Haas, F. Holzer, S. Müller et al., "X-ray absorption and diffraction studies of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ perovskite, a catalyst for bifunctional oxygen electrodes," *Electrochimica Acta*, vol. 47, no. 19, pp. 3211–3217, 2002.
- [8] V. Hermann, D. Dutriat, S. Müller, and C. Comninellis, "Mechanistic studies of oxygen reduction at $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ -activated carbon electrodes in a channel flow cell," *Electrochimica Acta*, vol. 46, no. 2-3, pp. 365–372, 2000.
- [9] L. Jörissen, "Bifunctional oxygen/air electrodes," *Journal of Power Sources*, vol. 155, no. 1, pp. 23–32, 2006.
- [10] H. Tanaka and M. Misono, "Advances in designing perovskite catalysts," *Current Opinion in Solid State & Materials Science*, vol. 5, no. 5, pp. 381–387, 2001.
- [11] M. R. Pai, B. N. Wani, B. Sreedhar, S. Singh, and N. M. Gupta, "Catalytic and redox properties of nano-sized $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ mixed oxides synthesized by different routes," *Journal of Molecular Catalysis A: Chemical*, vol. 246, no. 1-2, pp. 128–135, 2006.
- [12] L.-W. Tai, M. M. Nasrallah, H. U. Anderson, D. M. Sparlin, and S. R. Sehlin, "Structure and electrical properties of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$. Part 1. The system $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-y}\text{Fe}_y\text{O}_3$," *Solid State Ionics*, vol. 76, no. 3-4, pp. 259–271, 1995.
- [13] M. Petitjean, G. Caboche, E. Siebert, L. Dessemond, and L. Dufour, " $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Mn}_{1-y}\text{Fe}_y)\text{O}_{3\pm\delta}$ oxides for ITSOFC cathode materials? Electrical and ionic transport properties," *Journal of the European Ceramic Society*, vol. 25, pp. 2651–2654, 2005.
- [14] S. Canulescu, T. Lippert, A. Wokaun et al., "Preparation of epitaxial $\text{La}_{0.6}\text{Ca}_{0.4}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0, 0.2$) thin films: variation of the oxygen content," *Progress in Solid State Chemistry*, vol. 35, no. 2-4, pp. 241–248, 2007.
- [15] V. Dayal and S. Keshri, "Structural and magnetic properties of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{(1-x)}\text{Fe}_x\text{O}_3$ ($x = 0-0.07$)," *Solid State Communications*, vol. 142, no. 1-2, pp. 63–66, 2007.
- [16] F. Tietz, I. Arul Raj, M. Zahid, and D. Stöver, "Electrical conductivity and thermal expansion of $\text{La}_{0.8}\text{Sr}_{0.2}(\text{Mn,Fe,Co})\text{O}_{3-\delta}$ perovskites," *Solid State Ionics*, vol. 177, no. 19–25, pp. 1753–1756, 2006.
- [17] Q. Xu, D.-P. Huang, W. Chen, J.-H. Lee, H. Wang, and R.-Z. Yuan, "Citrate method synthesis, characterization and mixed electronic-ionic conduction properties of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ perovskite-type complex oxides," *Scripta Materialia*, vol. 50, no. 1, pp. 165–170, 2004.
- [18] Y. Shimizu, H. Matsuda, N. Miura, and N. Yamazoe, "Bifunctional oxygen electrode using large surface area perovskite-type oxide catalyst for rechargeable metal-air batteries," *Chemistry Letters*, vol. 21, no. 6, pp. 1033–1036, 1992.
- [19] S.-W. Eom, S.-Y. Ahn, I.-J. Kim, Y.-K. Sun, and H.-S. Kim, "Electrochemical evaluation of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ cathode material for zinc air batteries application," *Journal of Electroceramics*, vol. 23, no. 2-4, pp. 382–386, 2009.
- [20] J. Garche, *Encyclopedia of Electrochemical Power Sources*, vol. 4, Elsevier, 2009.