

The Stable Rechargeability of Secondary Zn-Air Batteries: *Is It Possible to Recharge a Zn-Air Battery?*

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Abstract : The rechargeable Zn-air battery is considered as one of the potential candidates for the next generation secondary batteries due to its many advantages. However, its further applications and commercialization have been limited by the complexity of the reactions on air electrode which are oxygen reduction and evolution reactions (ORR/OER) upon discharging and charging processes, respectively. In the present study, lanthanum was impregnated into a commercial Pt/C gas diffusion electrode, and it clearly verified significantly enhanced cycling stability and reversibility. The results presented in this study show the possibility of repeated charge/discharge processes for Zn-air batteries with a La-loaded air electrode, and they demonstrate the potential as a promising next generation secondary battery.

Keywords : Secondary battery, Zn-air battery, Rechargeable, Oxygen evolution reaction, Oxygen reduction reaction

1. Introduction

Recent developments in consumer electronics bring products which use more energy, and the potentiality for high performance power sources as well as electric vehicles demand a system which efficiently stores and/or generates more energy. Currently, the lithium-ion battery is the most widely used secondary battery for portable consumer electronics. However, current knowledge cannot satisfy the need to give sufficient power and run-time for the rapid development of technology. Even though lithium-ion batteries have been extensively studied, there are still some challenges. Moreover, it is faced with some limitations, such as stability, relatively low theoretical energy density, natural abundance of lithium, etc. Hence, it is absolutely necessary to study the development of new strategies to replace the lithium ion battery technology, so-called a next-generation secondary battery or a post lithium-ion secondary battery, which has a higher performance and reduces production costs.

One of the most feasible candidates is a zinc-air bat-

tery. It is an electro-chemical system powered by the reaction of zinc with oxygen from the air in a basic electrolyte. Since Zn-air batteries have many advantages including high specific energy, competitive cost, abundant resources, and environmentally benign property,¹⁻⁷⁾ it is expected to be a promising power source and energy storage device in the near future. Specifically, Goldstein *et al.*⁸⁾ reported that zinc-air battery has four times higher specific energy density with respect to lithium-ion battery while the cost of zinc-air battery is five times cheaper. Currently, there are two kinds of Zn-air batteries, primary and secondary (rechargeable) systems. Primary Zn-air batteries have been widely commercialized in the market for low-power consumer electronics, such as hearing aid, and emergency power sources because of its high specific energy density. However, the utilization of rechargeable Zn-air batteries has been limited by some barriers related to the electrodes. Although Zn-air batteries are currently applied to electrical vehicles, it is basically a primary battery system because it needs mechanical charging which replaces the Zn electrode physically. Up to now, the problems^{7,9)} originating from the zinc electrode, such as its low cycling stability, high degradation rate, passivation, and self-

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discharge have been gradually overcome through the recent studies of electrochemical cells using Zn electrode.^{7,9-12)} However, a key to improve this system is the development of an air electrode with high performance. The drawbacks to air electrode have not been overcome due to the complexity of the electrochemical reactions on the electrode. Oxygen reduction and evolution reactions (ORR/OER) are basic processes in a rechargeable Zn-air battery upon discharging and charging, respectively. In addition, the choice of electro-catalysts for these reactions is limited because the air electrode is employed in a highly irreversible system with a high activation overvoltage in aqueous solutions.¹³⁾

Recent studies¹³⁻¹⁵⁾ have demonstrated that La-containing species, such as lanthanum-containing perovskite type oxides and lanthanum hydroxide, play a role as a catalyst for air electrode of a secondary Zn-air battery. Lanthanum oxides have been used as a catalyst which allows the reversible addition and removal of oxygen due to the non-stoichiometric property,¹⁶⁾ and lanthanum hydroxide can be used as a catalyst for the air electrode because of a change in the valence of the hydroxide by interaction with oxygen.¹⁴⁾ Moreover, Wahlen *et al.*¹⁷⁾ recently reported that La(III) salts and La(III) ions on zeolite supports have higher catalytic activities for the disproportionation reaction of H₂O₂ into molecular oxygen, and La(NO₃)₃ among them shows a superior initial rate for the disproportionation reaction.¹⁷⁾

The main purpose of this publication is to demonstrate the possibility of repeated charge/discharge processes for Zn-air batteries with a La-loaded air electrode as one of the promising next generation secondary batteries because most of previous studies have been focused on not the cycling stability for the integrated system but the property of each component. The detailed discussion and description of this system will provide in forthcoming publications.

2. Experimental

2.1. Preparation of Electrodes

2.1.1. Zn Electrode (Anode)

Zn electrode was prepared by pasting a mixture consisting of 82 wt.% commercial ZnO powder (Umico, 99.8%), 10 wt.% Ketjen Black (KB), 3 wt.% Bi₂O₃ (Daejung), 1 wt.% Ca(OH)₂ (Junsei), and 4 wt.% of polytetrafluoroethylene (PTFE) on a porous Ni foam support. It was reported that the positive effect of the addition of KB on the mechanical and electrochemical

properties. Ca(OH)₂ suppresses the shape change and lengthens cycle life of Zn electrode because it causes to form the passivating film of calcium zincate (CaZn(OH)₄) on the electrode/electrolyte interface. Therefore, it greatly reduces the dissolution of Zn.¹⁸⁾ While the formation of calcium zincate gives several advantages, its poor conductivity limits to cell performance. To alleviate this problem, Bi₂O₃ was added as a conductive additive. The prepared Zn electrode was dried at 70°C and pressed to a thickness of 0.3 mm.

2.1.2. Air Electrode (Cathode)

Lanthanum-loaded air electrodes were prepared by a wet impregnation method using a La(NO₃)₃·6H₂O (Aldrich, 99.99%) precursor and a commercial Pt/C gas diffusion electrode (GDE, E-Tek HT-140E-W, Pt loading = 0.5 mg/cm²). The La-impregnated GDE was dried and subsequently heated at 200-250°C for 3 hours under atmospheric conditions. The compositions of La of prepared air electrodes were 3.43, 14.0, and 28.6 wt.%.

2.2. Characterization

The structure of the samples was characterized by X-ray diffraction (XRD) using Bruker D8 Focus diffractometer equipped with a Cu target. The morphology of the samples and the distribution of constituents were investigated by field emission-scanning electron microscopy energy (FE-SEM, Jeol JSM-7500F) coupled with an energy dispersive spectroscopy (EDS). For measurements of the electrochemical performance, a Zn-air cell was assembled with several main components which are Zn and air electrodes, electrolyte, and separators. The electrolyte is an aqueous solution consisting of 3.8 M KOH, 2.5 M NaOH, and 1.2 M LiOH, and it has a maximum ionic conductivity and reduces the shape change of Zn electrode.^{11-12,19)} The charge/discharge tests were performed using WBCS 3000 instrument (WonA Tech, Korea).

3. Results and Discussion

The charge/discharge cycles of the cell consisting of ZnO and commercial Pt-loaded gas diffusion electrodes were monitored to examine the charging ability and the rate and degree of oxygen evolution reaction. Fig. 1 shows the results of the charge/discharge cycle performance of the cell (charge: 1.25 mA/cm² and discharge: 0.25 mA/cm²). The charge/discharge characteristics were very unstable and cycling performance rapidly decayed

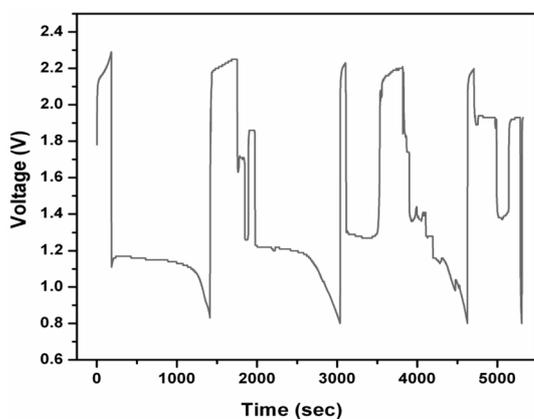
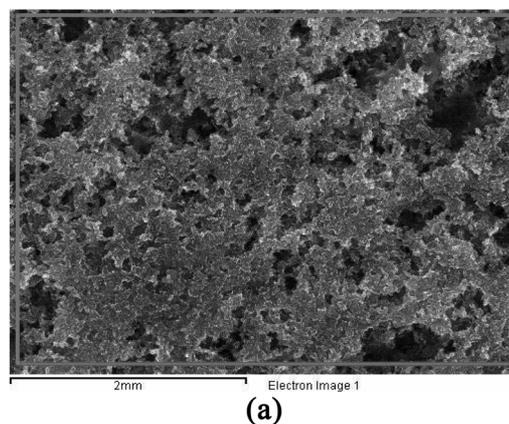


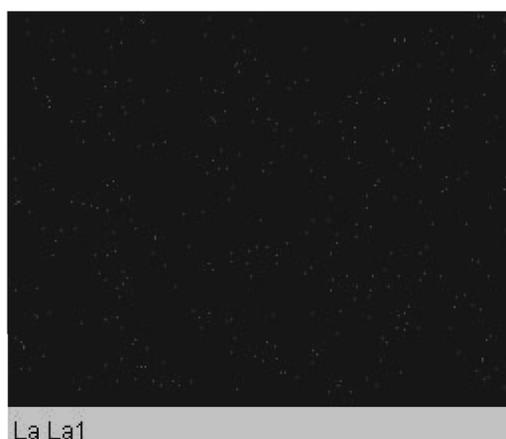
Fig. 1. Cyclic sweeps of a Zn-air battery with the Pt/C air electrode.

as the number of cycle increases. After few cycles, this cell cannot play a role as a secondary battery. Since Pt is the catalyst applied to the oxygen reduction reaction, oxygen reduction is possibly happened during discharging; however, oxygen evolution reactions would not take place on air electrode during charging process. In accordance with previous publications,^{6,13,20} it is necessary to add oxygen evolution catalysts into the air electrode. As mentioned above, lanthanum-containing catalysts were used as oxygen evolution and/or bifunctional (for oxygen reduction and evolution reactions) catalysts.^{16,21-22} For instance, some lanthanum containing transition metal oxide catalysts have been used as a catalyst which allows the reversible addition and removal of oxygen due to their non-stoichiometry (deviations from ideal stoichiometry).¹⁶ The catalytic activity of La-containing catalysts is closely related to the defect sites or its non-stoichiometric properties, and the oxygen migration on the catalysts causes to increase the activity.^{16,21} The relationship between the catalytic activity and the defect structure is not fully understood, but it has been generally accepted. In addition, lanthanum nitrate shows a high catalytic activity for the disproportionation reaction of H_2O_2 into molecular oxygen.¹⁷ Hence, in this study, lanthanum species was impregnated into the air electrode to enhance the reversibility of charge/discharge process.

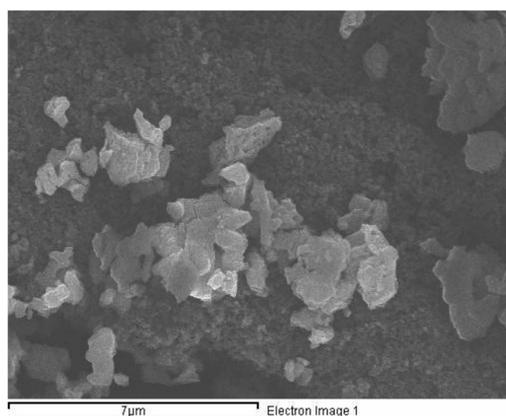
Fig. 2 displays the morphology and La distribution of prepared air electrode in which the composition of La is 14.0 wt.%. The morphology of the air electrode shown in Fig. 2 (a) was not changed in comparison with that of bare Pt/C GDE. Fig. 2 (b) shows La distribution of air electrode obtained from EDS, and it shows homo-



(a)



(b)



(c)

Fig. 2. Morphology of a La-loaded air electrode. (a) a low resolution SEM image, (b) EDS for lanthanum distribution, and (c) high resolution SEM image.

geneously dispersed La in a whole air electrode. The

detailed morphology of the lanthanum-loaded air electrode was shown in Fig. 2 (c). XRD data (not shown for brevity) of the lanthanum-loaded air electrode show the mixed phases consisting of the main phases, lanthanum nitrate and partially decomposed or oxidized lanthanum species (including lanthanum oxynitrate), and the minor phases, lanthanum carbonate and lanthanum hydroxide species. For a bulk-type lanthanum nitrate, the decomposition temperature is higher than our calcination temperature.²³⁻²⁴⁾ However, after the impregnation process, the behaviors of lanthanum species are not exactly the same as the bulk-type one, and the decomposition process of lanthanum nitrate strongly depends on the experimental conditions, such as residual H₂O pressure, atmospheric condition, and the interaction with a substrate. In addition, it is well known that fully or partially oxidized or decomposed lanthanum species usually react with H₂O and CO₂ in the atmosphere, and it readily forms carbonate and/or hydroxide species. Hence, small amounts of carbonate and/or hydroxide species are probably originating from the reaction of the final product with atmospheric gas molecules. However, the formation of carbonate and hydroxide species cannot be ruled out in main products in the preparation of air electrodes.

At a constant charging condition (30 mAh), cycling behaviors (charge: 7.5 mA/cm² and discharge: 1.25 mA/cm²) of the cell with ZnO and 28.6 wt.% La-loaded Pt/C gas diffusion electrodes were investigated to examine the reversibility and stability with repeated charge/discharge cycles, and the stability and the discharge capacity are shown in Figs. 3 (a) and (b), respectively. It is clearly showed the enhanced reversibility and stability. However, for 3.43 wt.% La-loaded air electrode, it showed unstable charge/discharge profiles which are similar to the Pt/C electrode case, and performance of the cell gradually improved as the amount of La loading increases. It should be noted that the formation of white powder was observed on outside of air electrode after several tenth cycles, and it was verified carbonate species by Fourier transform infrared spectroscopy. It is probably formed from the reaction between hydroxide ions in the electrolyte and CO₂ in the atmosphere. The formation of carbonate species affects the diffusion rate and path for oxygen into air electrode to occur the reaction of chemical species with catalyst, and therefore it is one of the reasons that discharge capacity reduces as the number of cycle increases since the formed carbonate species block diffusion path (or channel) of oxygen. After charge/discharge tests (72 cycles), the morphology of Zn

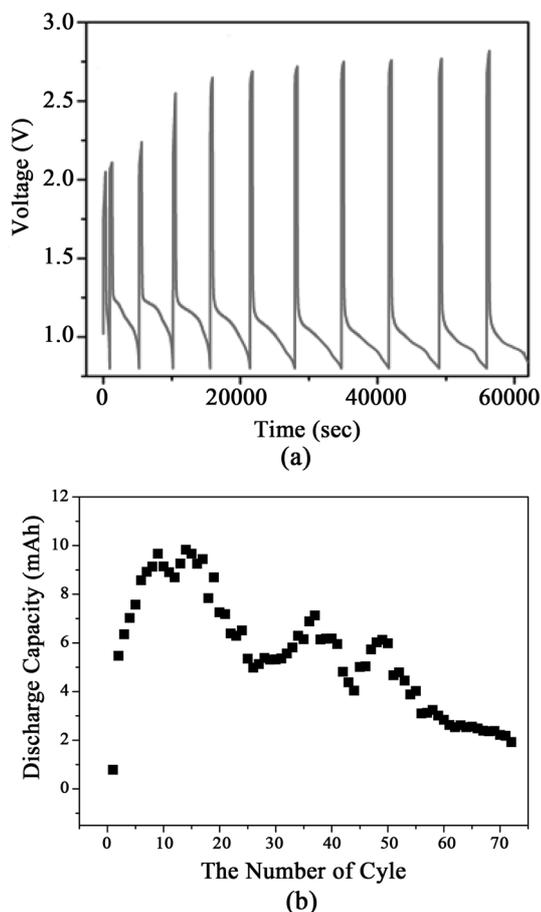


Fig. 3. (a) Cyclic sweeps of a Zn-air battery with the La-loaded air electrode and (b) Discharge capacity as a function of the number of charge/discharge cycle.

electrode was investigated by SEM, and the small amount of dendrite and the shape change were observed. The additives including bismuth oxide and calcium hydroxide in the Zn electrode effectively suppress the formation of Zn dendrite and shape change.

4. Conclusion

In this study, the reversibility of rechargeable Zn-air battery was demonstrated with a La-loaded air electrode. La-loaded air electrodes were prepared wet impregnation method using a La(NO₃)₃·6H₂O precursor and commercial Pt/C GDE. It is clearly showed the enhanced reversibility and stability of rechargeable Zn-air battery. Even though small amounts of La-loading show unstable reversibility, performance of the cell is gradually im-

proved as the amount of La loading increases. This study impacts upon verifying the feasibility of rechargeable Zn-air batteries as one of the candidates for the next-generation secondary battery.

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References

1. J. W. Evans and G. Savaskan, 'A zinc-air cell employing a packed bed anode' *J. Appl. Electrochem.*, **105**, 21 (1991).
2. T. Huh, G. Savaskan, and J. W. Evans, 'Further studies of a zinc-air cell employing a packed bed anode part II: Regeneration of zinc particles and electrolyte by fluidized bed electrodeposition' *J. Appl. Electrochem.*, **916**, 22 (1992).
3. C. W. Lee, K. Sathiyarayanan, S. W. Eom, H. S. Kim, and M. S. Yun, 'Novel electrochemical behavior of zinc anodes in zinc/air batteries in the presence of additives' *J. Power Sources*, **159**, 1474 (2006).
4. J. C. Salas-Morales and J. W. Evans, 'Further studies of a zinc-air cell employing a packed bed anode Part III: Improvements in cell design' *J. Appl. Electrochem.*, **858**, 24 (1994).
5. G. Savaskan, T. Huh, and J. W. Evans, 'Further studies of a zinc-air cell employing a packed bed anode part I: Discharge' *J. Appl. Electrochem.*, **909**, 22 (1992).
6. K. A. Striebel, F. R. McLarnon, and E. J. Cairns, 'Laboratory-scale evaluation of secondary alkaline zinc batteries for electric vehicles' *J. Power Sources*, **47**(1), (1994).
7. C. -C. Yang, J. M. Yang, and C.-Y. Wu, 'Poly(vinyl alcohol)/poly(vinyl chloride) composite polymer membranes for secondary zinc electrodes' *J. Power Sources*, **669**, 191 (2009).
8. J. Goldstein, I. Brown and B. Koretz, 'New developments in the Electric Fuel Ltd. zinc/air system' *J. Power Sources*, **171**, 80 (1999).
9. C. -C. Yang, W. -C. Chien, C. L. Wang, and C.-Y. Wu, 'Study the effect of conductive fillers on a secondary Zn electrode based on ball-milled ZnO and Ca(OH)₂ mixture powders' *J. Power Sources*, **435**, 172 (2007).
10. C. -C. Yang, W. -C. Chien, P. -W. Chen, and C. -Y. Wu, 'Synthesis and characterization of nano-sized calcium zincate powder and its application to Ni-Zn batteries' *J. Appl. Electrochem.*, **39**, 39 (2009).
11. R. Jain, T. C. Adler, F. R. McLarnon, and E. J. Cairns, 'Development of long-lived high-performance zinc-calcium/nickel oxide cells' *J. Appl. Electrochem.*, **1039**, 22 (1992).
12. E. G. Gagnon, 'Effect of Ten Weight Percent KOH Electrolyte on the Durability of Zinc/Nickel Oxide Cells Containing Zinc Electrodes with Calcium Hydroxide' *J. Electrochem. Soc.*, **3173**, 138 (1991).
13. V. Nikolova, P. Iliev, K. Petrov, T. Vitanov, E. Zhecheva, R. Stoyanova, I. Valov, and D. Stoychev, 'Electrocatalysts for bifunctional oxygen/air electrodes' *J. Power Sources*, **727**, 185 (2008).
14. Y. -K. Shun and C. -L. Lou. Catalytic air cathode for air-metal batteries In *US Patent*; High-Density Energy, Inc. (Azusa, CA) 2000.
15. X. Wang, P. J. Sebastian, M. A. Smit, H. Yang, and S. A. Gamboa, 'Studies on the oxygen reduction catalyst for zinc-air battery electrode' *J. Power Sources*, **278**, 124 (2003).
16. M. S. Islam and D. J. Ilett, 'Defect structure and oxygen migration in the La₂O₃ catalyst' *Solid State Ionics.*, **54**, 72 (1994).
17. J. Wahlen, S. De Hertogh, D. E. De Vos, V. o. Nardello, S. h. Bogaert, J. -M. Aubry, P. L. Alsters, and P. A. Jacobs, 'Disproportionation of hydrogen peroxide into singlet oxygen catalyzed by lanthanum-exchanged zeolites' *J. Catal.*, **422**, 233 (2005).
18. D. Coates and A. Charkey *Handbook of Batteries*; McGraw-Hill: New York, (2002).
19. A. Renuka, A. Veluchamy, and N. Venkatakrisnan, 'Effect of carbonate ions on the behaviour of zinc in 30% KOH' *J. Power Sources*, **381**, 34 (1991).
20. C. Chakkaravarthy, A. K. A. Waheed, and H. V. K. Udupa, 'Zinc-air alkaline batteries-A review' *J. Power Sources*, **6**, 203 (1981).
21. M. Alifanti, J. Kirchnerova, B. Delmon, and D. Klvana, 'Methane and propane combustion over lanthanum transition-metal perovskites: role of oxygen mobility' *Aool. Catal. A-Gen.*, **167**, 262 (2004).
22. R. N. Singh and B. Lal, 'High surface area lanthanum cobaltate and its A and B sites substituted derivatives for electrocatalysis of O₂ evolution in alkaline solution' *Int. J. Hydrogen Energ.*, **45**, 27 (2002).
23. B. Klingenberg and M. A. Vannice, 'Influence of Pretreatment on Lanthanum Nitrate, Carbonate, and Oxide Powders' *Chem. Mater.*, **2755**, 8 (1996).
24. A. -E. Gobichon, J. -P. Auffr  c, and D. Lou, 'Thermal decomposition of neutral and basic lanthanum nitrates studied with temperature-dependent powder diffraction and thermogravimetric analysis' *Solid State Ionics*, **51**, 93 (1996).