Article

A Study on the Self-Discharge Behavior of Zinc-Air Batteries with CuO Additives

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Abstract: Zn-air batteries have promise as the next generation of batteries. However, their self-discharge behavior due to the hydrogen evolution reaction (HER) and corrosion of the Zn anode reduce their electrochemical performance. Copper (II) oxide (CuO) effectively suppresses the corrosion and HER. In addition, different electrochemical behavior can be obtained with different shape of nano CuO. To improve the performance of Zn-air batteries, in this study we synthesized nano CuO by the hydrothermal synthesis method with different volumes of NaOH solutions. Materials were characterized by XRD, FE-SEM, and EDX analysis. The sphere-like nano CuO (S-CuO) showed a specific discharge capacity of 428.8 mAh/g and 359.42 mAh/g after 1 h and 12 h storage, respectively. It also showed a capacity retention rate of 83.8%. In contrast, the other nano CuO additives showed a lower performance than pure Zn. The corrosion behavior of nano CuO additives was analyzed through Tafel extrapolation. S-CuO showed an I_{corr} of 0.053 A/cm², the lowest value among the compared nano CuO materials. The results of our comparative study suggest that the sphere-like nano CuO additive is the most effective for suppressing the self-discharge of Zn-air batteries.

Keywords: Zn-air; additives; self-discharge; nano CuO; hydrothermal synthesis; hydrogen evolution reaction

Citation: Jeong, B.J.; Jo, Y.N. A Study on the Self-Discharge Behavior of Zinc-Air Batteries with CuO Additives. *Appl. Sci.* **2021**, *11*, 11675. <https://doi.org/10.3390/app112411675>

Academic Editors: Angeles Sanroman Braga and Aliaksandr Shaula

Received: 11 October 2021

Accepted: 7 December 2021

Published: 9 December 2021

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1. Introduction

As the battery market has developed, both existing lithium-ion batteries and their alternatives have attracted attention. Lithium-ion batteries (LIBs) are used in various fields, such as electric vehicles (EV) [1], energy storage systems (ESSs) [2] and mobile devices due to their high specific energy density and charging efficiency [3–9]. However, they have demerits such as high cost and safety issues [10,11]. Therefore, many researchers have focused on advanced battery systems to replace LIBs. Metal-air batteries are promising for the next generation of batteries [12]. Because they use the oxygen in the air to produce energy by the air cathode, they can be smaller and store more metal. Many metal-air batteries have been studied, such as Li-air, Mg-air, Al-air, and Zn-air batteries [13,14]. Li-air batteries have the potential to deliver the highest energy density and a large cell voltage. However, they have a safety issue due to an unstable anode in the presence of atmospheric moisture [15]. Mg-air and Al-air batteries provide energy densities comparable to Li-air batteries, but their low reduction potentials cause rapid self-discharge through the hydrogen evolution reaction (HER) [16,17].

Zn-air batteries have many effective properties, including a higher theoretical capacity (1085 Whkg^{−1}), which is based on the molecular weight of ZnO (658 Whkg^{−1}) and the theoretical cell voltage of 1.65 V [18,19]. In addition, Zn-air batteries use zinc for an anode and an aqueous electrolyte like potassium hydroxide [20], therefore, the risk of explosion is reduced and they are environmentally safe. The overall redox reaction of the Zn-air battery is shown in the following equations [21].

Anode:

Cathode:

Overall:

As above, oxygen from the air is reduced to provide OH^- and Zn is oxidized in response to the OH^- provided. However, the corrosion of the zinc anode progresses more quickly when using an aqueous electrolyte, resulting in a hydrogen evolution reaction (HER). The following equation describes the HER that occurs during a discharge reaction.

HER:

Therefore, the amount of zinc that participates in the reaction is reduced. In addition, dendrite formation occurs because of corrosion, and external environmental factors due to the open-cell structure can greatly affect the performance of the batteries. Many methods using electrolyte additives are available to solve this problem. Several additives have been studied, including organic and inorganic materials, as well as conductive polymers [22–24]. Among them, inorganic materials including metal species have been used due to their a higher reduction potential than Zn. Hg is one of the effective additives which can effectively suppress the HER. However, its use is limited due to its impact on the environment. Several researchers have reported that some transition metals, such as Ni, Mg, Sn, Fe, Bi, and Al, are effective in reducing dendrite formation and the HER [25–27]. In and Cu also have similar effects [28,29]. Inorganic additives such as In_2O_3 , Al_2O_3 , SnO , and Bi_2O_3 have been reported to have similar effects [30–32].

CuO has good electrical properties; it has a band gap of about 1.2 eV and high carrier concentration. Using this advantage, CuO is used in p-type semiconductors and supercapacitors [33]. It is a low-cost material and has the advantage of being producible via a variety of synthesis methods. Additionally, depending on the synthesis method used, a variety of nanostructures (e.g., sphere-like, cross-like, hexagonal, and flower-like) can be synthesized [33–35]. In addition, the large surface area of nano CuO gives this material much better chemical properties than bulk materials. Lee et al. reported that copper compounds have been shown to affect the corrosion behavior in Zn-air batteries [36].

In this work, various shapes of nano CuO were synthesized by the hydrothermal synthesis method and used as an additive. The discharge performances of the nano CuO additives were compared. In addition, to identify the self-discharge behavior, the discharge capacities after 1 h and 12 h storage were compared. Additionally, the corrosion factors were measured using the Tafel extrapolation method.

2. Experimental

2.1. Materials

We used the following materials for the Zn-air cell: zinc powder (99%, Daejung, Siheung-si, Korea) for the anode, potassium hydroxide (85%, Daejung, Siheung-si, Korea), polyacrylic acid (Mv ~1,250,000, Sigma Aldrich, St. Louis, MO, USA) for the gel electrolyte, and Ni mesh (99.95%, GFM, Suwon-si, Korea) for the current conductor. In addition, copper (II) sulfate pentahydrate (99.5%, Daejung, Siheung-si, Korea), sodium phosphate (96%, Sigma Aldrich, St. Louis, MO, USA), and sodium hydroxide (97%, Daejung, Siheung-si, Korea) were used to synthesize the nano CuO.

2.2. Synthesis and Characterization of Nano CuO

The nano CuO was synthesized by the hydrothermal method, as follows. Firstly, 0.250 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.3 g of Na_3PO_4 were separately dissolved in 20 mL of deionized distilled water until they became homogeneous solutions at room temperature. The Na_3PO_4 solution was rapidly added to the CuSO_4 solution, which led to the synthesis of a CuNaPO_4 suspension. Different volumes of 2.0 M NaOH solution were added into the CuNaPO_4 suspension and stirred for 5 min. After stirring, the solution was transferred to a 100 mL PTFE liner

in a hydrothermal reactor and kept in the oven at 120 °C for 6 h. The as-formed brown precipitates were collected, washed in deionized distilled water and ethanol several times, and dried at 30 °C. Sphere-like and leaf-like types of nano CuO were synthesized. Sphere-like and leaf-like nano CuO as well as commercial CuO were characterized and named S-CuO, L-CuO, and C-CuO, respectively. C-CuO (99%, Sigma Aldrich, St. Louis, MO, USA) was purchased for the purpose of comparison with the synthesized CuO. Information on the synthesis process of nano CuO is shown in Table 1.

Table 1. Information about the nano CuO synthesized by the hydrothermal synthesis method.

Nanostructure	CuSO ₄ ·5H ₂ O	Na ₃ PO ₄	2.0 M NaOH	Hydrothermal Condition	
				Temperature	Time
Sphere-like	0.250 g	0.3 g	0.1 mL	120 °C	6 h
Leaf-like	0.250 g	0.3 g	0.2 mL		

Each nano CuO was investigated by x-ray diffraction (XRD, D8 advance, Bruker, Billerica, MA, USA) patterns with an angle range of 3° to 90°. In addition, the morphology was determined by field-emission scanning electron microscope (FE-SEM, LEO SUPRA 55, Carl Zeiss, Jena, Germany) and energy-dispersive X-ray analysis (EDX, Spectra 300, Thermo Scientific, Waltham, MA, USA).

2.3. Preparation of the Zn-Air Cell

Battery performance can be influenced by the concentration of electrolytes, which is increased due to the evaporation of water species during the discharging process. We used 6M KOH is used, and the electrical conductivity is suitable for gel-type electrolytes. [37]. Gel electrolytes were produced by quantifying a solution of 25.5 g of 6 M KOH and 0.5 g of PAA, stirring at 50 °C, 300 rpm for 1 h, and stirring at room temperature for 23 h at 100 rpm.

The test cell was composed of a bottom part, Ni mesh as an anode current collector, a slurry, an electrode container, a separator (Celgard 3401, Charlotte, NC, USA), an air cathode (MEET ADE-72B, Hwaseong-si, Korea), and a top part. The applied slurry was mixed with 0.6 g of Zn powder, 0.6 mL gel electrolyte, and nano CuO as an additive, which was located in an electrode container having length, width, and height dimensions of 2.5, 2, and 0.1 cm, respectively. In addition, the top part had holes to allow air to flow through. The composition of the Zn-air cell used in this study is shown in Figure 1.

Figure 1. Components of the Zn-air battery.

2.4. Electrochemical Behavior Test

To compare the self-discharge behavior of the different types of nano CuO in a Zn-air cell, 1.0 wt% of S-CuO, L-CuO, and C-CuO were added to the electrolytes. After 1 h and 12 h of storage, the discharge capacity and capacity retention rate were compared. The specific discharge capacity was measured using an electrochemical analyzer (WonAtech, WBC3000L, Seoul, Korea) and discharging to 0.2 V at a constant current of 100 mA. To identify the corrosion behavior of the Zn anode with different nano CuO additives, we constructed a Tafel extrapolation. The cell was prepared for the half cell that excluded the top part and air cathode on the working electrode, Hg/HgO on the reference electrode, and Pt on the counter electrode. Measurement was conducted in a 6 M KOH solution using an electrochemical analyzer (HSTech, IVIUM Vertex, Plano, TX, USA).

3. Results and Discussion

3.1. Characterization Synthesized CuO

Figure 2 shows the XRD patterns of the synthesized and commercial CuO. In the figure, all synthesized materials exhibit the same peaks as commercial CuO (JCPDS # 48-1548), confirming that they had a monoclinic crystal structure of CuO. For the two strongest peaks, those of L-CuO are sharper than those observed in S-CuO, which is seen as an increase in the volumes of NaOH. The results of the FE-SEM and EDX analyses for each material are shown in Figures 3 and 4, respectively. The hydrothermal synthesis method can adjust the shape and size of particles through the control of several variables, including pH, NaOH concentration, solvent, temperature, and time. The volume of NaOH was adjusted to control the shape of CuO. As shown in Figure 3a,c, S-CuO was synthesized in sizes of about 500–700 nm. In addition, the agglomeration of small rod-like primary particles led to the formation of a sphere-like secondary phase. Figure 3b,d shows the L-CuO, which had a leaf-like shape because of increases in the volume of NaOH, and its particle size was about 800 nm. The C-CuO, shown in Figure 3c,f, had a layered structure with a particle size of 800 nm–1 μ m. The surface of the particle was also smooth. Figure 4 is the result of the EDX analysis of each material. As shown, all characterized materials were composed of Cu and O. Moreover, the spectra of Cu and O are shown in Figure 4d–f. There were no significant differences between synthesized materials (S-CuO and L-CuO) and the commercial material (C-CuO), meaning that the S-CuO and L-CuO materials were well synthesized.

Figure 2. XRD patterns of nano CuO.

Figure 3. FE-SEM images of (a) S-CuO, (b) L-CuO, and (c) C-CuO; the corresponding magnified images of (d) S-CuO, (e) L-CuO, and (f) C-CuO.

Figure 4. EDX mapping images of (a) S-CuO, (b) L-CuO, and (c) C-CuO; EDX spectra of (d) S-CuO, (e) L-CuO, and (f) C-CuO.

3.2. Electrochemical Discharge Behaviors

To compare electrochemical discharge capacity and self-discharge behavior, we applied 1.0 wt% of S-CuO, L-CuO, and C-CuO as additives for the Zn anodes. Discharging was performed using a constant current mode up to 0.2 V. We made and compared two cells for each material to characterize the self-discharge behavior. One was characterized after being stored for 1 h and the other after being stored for 12 h, both at room temperature. Figure 5 shows the discharge profiles after (a) 1 h storage and (b) 12 h storage. Discharge capacity and capacity retention rate are summarized in Table 2. The S-CuO showed the highest discharge capacity compared to other nano CuO additives after 1 h storage. L-CuO showed the lowest performance, with 399.91 mAh/g. Furthermore, after 12 h storage,

S-CuO showed excellent performance with 359.42 mAh/g of discharge capacity, and 83.8% retention rate. However, the other forms of CuO showed lower performance than pure Zn, with a retention rate below 80%. The electrochemical discharge performance of the Zn-air cell was improved by the S-CuO additive. Each type of nano CuO has different morphology, therefore, the electrochemical behaviors are different in the electrolyte during discharge [38]. There is a difference in reactivity within the electrolyte because the surface area also depends on the morphology. The structure also affects the diffusion rate of ions. As the rate changes, the distance at which ions spread also varies, which directly affects the performance of the batteries [39]. One study reported that the benefits of the sphere-like form increased battery capacity and preservation [40]. Among the CuO forms in this study, S-CuO has a sphere-like form, and its surface area is also wide due to primary particles. This morphological advantage leads to an increase in the spread rate of OH^- within the electrolyte, which is considered to be relatively capacity-preserving compared to other forms of CuO.

Figure 5. Specific discharge profiles of nano CuO additives after (a) 1 h storage and (b) 12 h storage.

Table 2. Specific discharge capacity and capacity retention rate of nano CuO additives after 1 h and 12 h storage.

Material	Specific Discharge Capacity (mAh/g)		Capacity Retention Rate (%)
	1 h Storage	12 h Storage	
Pure Zn	476.48	390.14	81.8%
S-CuO 1.0 wt%	428.8	359.42	83.8%
L-CuO 1.0 wt%	399.91	302.92	75.7%
C-CuO 1.0 wt%	420.15	328.78	78%

3.3. Tafel Polarization

The corrosion of the Zn anode is a critical issue in Zn-air batteries. Specifically, the HER is due to the reaction caused by the contact of Zn with water which leads to water evaporation. This process decreases discharge performance. One solution to this problem is to add a gelling agent in the electrolyte for gelation. The polarization curve indicates the degree of HER and corrosion in the anode. The anodic Tafel line is higher and the HER is increased [41]. Figure 6 shows the polarization curves of Zn-air cells with nano CuO additives. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) analyzed through Tafel extrapolation are summarized in Table 3. L-CuO showed poor values for E_{corr} (-1.3124 V) and I_{corr} (0.0585 A/cm²) among the additives. In contrast, S-CuO exhibited an E_{corr} of -1.2795 V and an I_{corr} of 0.053 A/cm². These results verified the corrosion behavior of each nano CuO and were consistent with the results of the electrochemical discharge test correspond as well. S-CuO showed the best performance compared to the characterized material. In other words, our results indicate that a sphere-like morphology is more effective for a nano CuO additive. This advantage provided a positive effect for the suppression of the self-discharge in the electrolyte.

Figure 6. Tafel polarization curves of nano CuO additives after 1 h storage.

Table 3. Corrosion parameters of the nano CuO additives.

Material	E_{corr} (V)	I_{corr} (A/cm ²)
Pure Zn	-1.3419	0.04326
S-CuO 1.0 wt%	-1.2795	0.053
L-CuO 1.0 wt%	-1.3124	0.0585
C-CuO 1.0 wt%	-1.2418	0.05482

4. Conclusions

To suppress the self-discharge behavior of Zn-air batteries, we compared the electrochemical discharge and corrosion behavior using different forms of nano CuO as additives. The materials were synthesized by the hydrothermal synthesis method with different volumes of NaOH solution with S-CuO and L-CuO. S-CuO showed a discharge capacity of 428.8 mAh/g after 12 h with a capacity retention rate of 83.8% , indicating that it effectively inhibited self-discharge. L-CuO and C-CuO showed relatively low performance compared to pure Zn, which is explained by differences in electrochemical performance due to different morphology. Furthermore, S-CuO showed the best value with an I_{corr} of 0.053 A/cm², compared to other additives. Consequently, the sphere-like nano CuO additive was found to be the most effective in suppressing self-discharge for Zn-air batteries.

Author Contributions: Conceptualization, B.J.J. and Y.N.J.; methodology, B.J.J. and Y.N.J.; validation, B.J.J. and Y.N.J.; formal analysis, B.J.J.; investigation, B.J.J. and Y.N.J.; resources, Y.N.J.; data curation, B.J.J.; writing—original draft preparation, B.J.J.; writing—review and editing, Y.N.J.; visualization, B.J.J. and Y.N.J.; supervision, Y.N.J.; project administration, Y.N.J.; funding acquisition, Y.N.J. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2019R1G1A1007782).

Institutional Review Board Statement: This study did not involve humans or animals.

Informed Consent Statement: This study did not involve humans.

Data Availability Statement: Not applicable.

Acknowledgments: This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2019R1G1A1007782).

Conflicts of Interest: The authors declare no conflict of interest.

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