Electrochemical Behaviors of Zn Anode in Carbonate-based Aqueous Solutions

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ABSTRACT

Electrochemical behaviors of Zn in various concentrations of K₂CO₃ and KOH containing 5 M K₂CO₃ (M = mol dm⁻³) aqueous solutions (carbonate-based electrolytes) have been investigated. The electrochemical reactions of Zn in diluted K₂CO₃ and KOH containing 5 M K₂CO₃ were suppressed while they were activated in concentrated K₂CO₃. In the point of view of the ratio of the cathodic charge q_c to the anodic q_a and Zn oxidation current, 0.5 M KOH containing 5 M K₂CO₃ showed the best performance among all examined electrolytes. The dendritic growth of Zn was not observed during redox cycles in the carbonate-based electrolytes.

Keywords: Zinc Electrodes, Conc. Carbonate Aqueous Solution, Metal Secondary Batteries, Dendrite Formation

1. Introduction

Zinc is the most widely used non-ferrous metals after aluminum and copper. Every year, 13 million tons of zinc is produced and consumed all over the world.¹ Zinc is known as one of the most promising anode material candidates for rechargeable aqueous batteries² due to following reasons. Zn anode is reversible, compatible with the aqueous electrolyte even though its redox potential is below hydrogen potential, abundance metal, low in its cost, low toxicity, and small in its equivalent weight. However, Zn has not become an active material of anode in commercial secondary batteries due to its short and unpredictable lifetime. This problem is originated from the shape change and unwanted electrode morphologies (dendrites, filamentary growth, nodules) of Zn anode during charge-discharge cycles.² Prevention of dendrite formation and shape change of Zn during charge-discharge cycles has not been completely solved even though Diggle and Bockris reported the mechanism of the dendritic growth of Zn in 1969.³ To prevent dendrite growth of Zn, following three strategies have been reported.³⁻⁵ First of all, it can be pointed that a modification of the electrode morphology or the electrolyte composition to hold the oxidized Zn in the vicinity of the Zn electrode surface.⁵⁻⁶ Other two strategies are a modification of Zn anode with noble metals to control the kinetics of Zn reduction⁶⁻⁷ and the addition of surfactants into the electrolyte²⁻⁸ to hold oxidized Zn near a Zn electrode. Miyazaki et al. demonstrated the dendrite growth was suppressed by modification of a Zn electrode surface with anion exchange ionomer.³ Since ZnO easily dissolves into alkaline solution as Zn(OH)₃⁴ or Zn(OH)₂,⁵ lowering a Zn solubility is also one of the most fundamental strategies to prevent not only dendrite growth but also shape changes of a Zn electrode. Lowering in Zn solubility was achieved by addition of carbonate into alkaline electrolyte.³⁰ There are few papers found that deals with the electrochemistry of Zn in carbonate aqueous electrolyte solutions.³⁻ⁱ¹ Among them, redox behavior of Zn in concentrated carbonate system have not been reported. In this paper, Zn electrode behaviors in carbonate-based aqueous solutions (the aqueous solutions of K₂CO₃ and concentrated K₂CO₃ containing KOH) were examined.

2. Experimental

Cyclic voltammetry was applied to investigate the electrochemical oxidation and reduction behaviors of Zn in the carbonate-based aqueous solutions. Potassium carbonate (K₂CO₃) aqueous solutions of 0.5–6 M (M = mol dm⁻³) and 5 M K₂CO₃ aqueous solutions containing 0.05–1.0 M potassium hydroxide (KOH) were prepared by dissolving reagent grade K₂CO₃ and KOH into deionized reverse osmosis water of 18.2 MΩ cm. From now on 5 M K₂CO₃ aqueous solutions that contain x M of KOH are denoted by x M KOH and 5 M K₂CO₃. A 10 mm square polycrystalline 99.5% Zn sheet 0.8 mm in thickness purchased from Nilaco Co. Ltd. was used as a working electrode (WE). The WE was polished with aluminum suspension (3.0, 1.0, 0.1, 0.05 µm) to obtain a mirror-like surface, and another side was sealed with insulating wax (Maruto Instrument Co., Ltd. Arco wax 542M). A WE and a 20 mm square Zn sheet counter electrode (CE) placed parallel to each other were set in a cylindrical electrochemical glass cell of 20 mm in diameter and 50 mm height. The cell was filled with 40 cm³ electrolyte solution, and all potentials were referred to a 1 M Hg/HgO reference electrode mounted in a separate vial through a salt bridge.

The solubility of Zn in the carbonate-based aqueous solutions were measured as follows. An excess quantity of ZnO was rigorously mixed with the electrolyte solutions and was kept stationary for a week at room temperature in an airtight glass vial. Excess of nitric acid was added to the skimmed clear supernatant for ICP (Shimadzu ICPS-8100) measurements. Solution pH were measured using a pH meter (HORIBA F-52). SEM (HITACHI SU3500) and XRD (RIGAKU Smart Lab 3K) measurements were used to characterize the oxidized Zn electrodes. All experiments were carried out at room temperature.

3. Results and Discussion

3.1 The electrochemical redox behaviors of Zn in K₂CO₃ aqueous solutions

The typical cyclic voltammogram for Zn electrode in 1.0 M K₂CO₃ is shown in Fig. 1(a) is in good agreement with that reported by Conway et al.⁷ The anodic current peak A₁ at around −1.2 V vs. Hg/HgO corresponds to dissolution of Zn and a flatter peak A₂ observed at around −1.0 to −0.8 V vs. Hg/HgO is the formation of...
ZnO or Zn(OH)₂ passive layers on the Zn electrode.\(^9\-\^11\) As shown in Fig. 1(b), two strong anodic current peaks were observed when the concentration of K₂CO₃ was higher than 4.0 M, while the extent of anodic oxidation of Zn in 0.5–3.0 M K₂CO₃ aqueous solutions were quite small. In the concentrated K₂CO₃ aqueous solutions, increasing in the peak cathodic currents which is corresponding to the reduction of oxidized Zn was observed. The anodic charge \(q_a\) and the cathodic charge \(q_c\) were calculated by integrating the anodic currents at the potential ranging from -1.4 to -0.5 V and the cathodic currents ranging from -1.2 to -1.6 V, respectively. Figure 1(c) shows the K₂CO₃ concentration dependence of \(q_a\), \(q_c\), and the ratio \(q_a/q_c\). The ratio can be used to characterize the extent of dissolution of the oxide product of zinc. The anodic charge \(q_a\) in 5 M K₂CO₃ (pH 13.9) was 2 C cm\(^{-2}\) which was 30 times higher than that in 3 M K₂CO₃ (pH 13.1), while the charge ratio \(q_a/q_c\) of 0.4 in 5 M K₂CO₃ was lower than that in 3 M K₂CO₃. When the concentration of K₂CO₃ is higher than 4 M, steep rise in both \(q_a\) and \(q_c\) was observed while the ratio \(q_a/q_c\) decreased with increasing the K₂CO₃ concentration.

Figure 2(a) shows the pH-potential diagrams of Zn both in KOH and K₂CO₃ systems. As expressed by Eqs. (1a) to (2b), ZnO is in the pH region of 12 to 14.5. After an anodic sweep of the Zn WE in Fig. 1(b), two strong anodic current peaks were observed when the pH of the electrolyte was higher than 4 M, steep rise in both \(q_a\) and \(q_c\) was observed while the ratio \(q_a/q_c\) decreased with increasing the K₂CO₃ concentration.

The results indicated that Zn is dissolved in K₂CO₃ as Zn(OH)\(_3\)\(^{-}\) in the pH region of 12 to 14.5. After an anodic sweep of the Zn WE in 0.5 M and 5 M K₂CO₃, XRD data indicated that the oxidized Zn at peaks A₁ and A₂ were identified as ZnO and no Zn(OH)\(_2\), no zinc carbonate nor its derivatives were detected. Zn solubility in 5 M K₂CO₃ was too low to support the complete dissolution of ZnO produced at the Zn electrode during the anodic scan because the amount of ZnO was precipitated under the WE after an anodic scan of CV. These results indicated that there are no specific differences in oxidation product of Zn in 3 M K₂CO₃ and 5 M K₂CO₃, and Zn(OH)\(_3\)\(^{-}\) was assumed to be saturated near the WE surface and the surface was covered with ZnO layer. The ZnO deposition mechanisms that might be affected by the difference in solubility of Zn in concentrated K₂CO₃ is one of the possible reasons for anodic charge \(q_a\) increase in the concentrated K₂CO₃.

To clarify the reason steep rise in \(q_a\) and \(q_c\) occurs in concentrated carbonate electrolyte, characteristics or formation mechanisms of the ZnO film on a Zn electrode are needed to be clarified.

### 3.2 The electrochemical redox behavior of Zn in x M KOH + 5 M K₂CO₃

In alkaline zinc-air batteries, the oxygen reduction reaction taking place at the cathode results in the pH increase of the electrolyte. The effect of KOH addition into 5 M K₂CO₃ on redox reaction of Zn was investigated. As shown in Fig. 3, the solubility of Zn in the solution decreased when a small amount of KOH was added to 5 M K₂CO₃. In the solutions of KOH + 5 M K₂CO₃, whose pH was higher than 15.5, the logarithm of Zn solubility was proportional to the solution pH with the slope of the line of 2. It is assumed that the dissolved Zn species in this pH region was Zn(OH)\(_2\)\(^{-}\), though the solubility of ZnO was hundred-thousand of that in carbonate free alkaline solutions which are estimated by Eq. (1b). When the solution pH was from 14 to 15.5, on the other hand, ZnO solubility was ca. 20 mg dm\(^{-3}\) and was almost constant in this pH region.

Figure 4(a) and (b) showed cyclic voltammograms of Zn in KOH + 5 M K₂CO₃ aqueous solutions and Fig. 4(c) showed the KOH concentration dependence of \(q_a\), \(q_c\), and \(q_a/q_c\) at the second cycle of CVs. As shown in Fig. 4(b) and (c), an immediate drop of redox currents, \(q_a\) and \(q_c\), was observed when a small amount of KOH was added to 5 M K₂CO₃.
KOH less than 0.15 M was added to 5 M \( \text{K}_2\text{CO}_3 \). The solution pH in this region was from 14 to 15.5, where the solubility of ZnO was not influenced by the solution pH (Fig. 3). When the concentration exceeded 1.0 M, the currents, \( q_a \) and \( q_c \), increased with increasing the KOH concentration. In the point of view of the ratio of \( q_c/q_a \), almost 80% of zinc was recovered in the x M KOH + 5 M \( \text{K}_2\text{CO}_3 \) aqueous solutions of 0.15 < x < 0.75. When KOH concentration was 0.5 M, the ratio \( q_c/q_a \) showed its maximum values of 0.93 and \( q_c \) was 10 times larger than that in 3 M \( \text{K}_2\text{CO}_3 \) at which the ratio \( q_c/q_a \) was only 0.6. In this study, no Zn species was added to the electrolyte prior to CV measurements. The higher in the ratio \( q_c/q_a \) means that Zn is easy to accumulate beneath the electrode surface during discharge and charge cycles.

Figure 5 shows the SEM images of Zn surface in (a) 5 M \( \text{K}_2\text{CO}_3 \), and (b) 0.5 M KOH + 5 M \( \text{K}_2\text{CO}_3 \) after 50 cycles of charge-discharge cycles with charge and discharge current density of 3.2 mA cm\(^{-2}\) for 10 mins.

4. Conclusion

The electrochemical redox behaviors of Zn in concentrated \( \text{K}_2\text{CO}_3 \) aqueous solutions are different from those observed in diluted \( \text{K}_2\text{CO}_3 \). The possible reason for the difference in the redox behavior is the difference in the equilibrium of ZnO/\( \text{Zn(OH)}_3 \) and ZnO/\( \text{Zn(OH)}_2 \) which affects the formation of passivation film on a Zn electrode.

Though Zn oxidation was significantly inhibited by the addition of small amount of KOH in 5 M \( \text{K}_2\text{CO}_3 \), \( q_a \) is higher than that in diluted \( \text{K}_2\text{CO}_3 \) aq. In the point of view of \( q_c/q_a \) and suppression of dendrite formation of Zn, Zn showed the best performance as an anode for a secondary battery in 0.5 M KOH + 5 M \( \text{K}_2\text{CO}_3 \) aqueous solution. The differences in the solubility of ZnO and dissolution equilibrium in the concentrated carbonate-based alkaline solutions were observed. The differences are assumed to affect the formation of oxidation product on the electrode. When the oxidation product was kept in the vicinity of the electrode surface, the dendritic growth of zinc did not occur. Further study is required to clarify the redox reaction in concentrated carbonate alkaline solution.

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