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Transformation of Leaf-like Zinc Dendrite in Oxidation and Reduction Cycle

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ABSTRACT

Zinc is a promising negative electrode material for aqueous battery systems whereas it shows insufficient rechargeability for use in secondary batteries. It has been reported that leaf-like dendrite deposits are often the origin of cell-failure, however, their nature and behavior on discharge (oxidation) - charge (reduction) cycling have been only poorly understood. Here we investigate the transformation of the leaf-like zinc dendrites using *ex-situ* scanning electron microscopy, X-ray computational tomography and *in-situ* X-ray diffraction. It is shown that the leaf-like zinc dendrites obtained under diffusion-limited conditions are nearly completely dissolved at a low oxidation current density of 1 mA cm^{-2} and cause re-evolution of the zinc dendrites. Oxidation at a high current density of 10 mA cm^{-2} leads to the formation of leaf-like zinc oxide residual products that result in particulate zinc deposits in the following reduction process, enabling good rechargeability. The reaction behavior of this oxide residue is detailed and discussed for the development of long-life zinc electrodes.

1. Introduction

Zinc is known as a negative electrode material that has been used in various primary batteries because of its low cost and high specific capacity. Zinc is baser than hydrogen but can be used in aqueous electrolytes as it has a high overvoltage against hydrogen evolution, enabling a high cell voltage and thus safe and inexpensive high energy batteries. The merits of the zinc electrode are attractive also for secondary battery systems, especially those for large scale applications [1–3]. Thus, zinc-based secondary batteries such as MnO_2/Zn [4], AgO/Zn [5], NiOOH/Zn [6], and O_2/Zn batteries [7] have been intensively studied and partially commercialized. However, they are not widely used mainly because the short cycle life of the zinc electrode remains as a significant issue that should be overcome. Though the formation of a complex $CaZn(OH)_4$ is beneficial to enhance the cycle life, its low specific capacity is less attractive than zinc itself.

The origin of the short cycle life can be classified into a few categories by the deterioration modes and the zinc morphology under oxidation-reduction cycles [3,8]. On the oxidation in alkaline electrolytes, metallic zinc is first oxidized to zincate anion as a dissolved intermediate (Eq. (1)), and then zincate anion is decomposed to zinc oxide precipitation as a final product by the subsequent chemical reaction (Eq. (2)). It is desirable for secondary battery systems to keep the electrode morphology during cycling, however, the zinc electrode often suffers from electrode dissolution and shape changes, due to the equilibrium shown in Eq. (2). Even with the electrolyte containing a sufficient amount of zincate, ZnO precipitation often takes time, owing to zinc supersaturation [9]. Accordingly, the appearance of the zincate greatly affects the morphology and the performance of the zinc electrode.

$$Zn + 4OH^- = Zn(OH)_4{}^{2-} + 2e^- \qquad (1)$$

$$Zn(OH)_4{}^{2-} = ZnO + 2OH^- + H_2O \qquad (2)$$

Among various kinds of zinc morphology, leaf-like zinc dendrites, which consist of hexagonal zinc metal deposits with its size of several tens of micrometers and appear in the early stage of discharge-charge cycles, are considered as the origin of cell-failure [10–13]. Though there are many studies that focus on the suppression of the leaf-like zinc dendrite using additives [11–16],

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the details of the transformation during charge-discharge cycles including the composition and morphology changes have so far only poorly understood. Such knowledge is crucial to evaluate the impact of leaf-like dendrite on cell-failure.

In this report, we investigate the behavior of the leaf-like zinc dendrite during oxidation-reduction cycling using *ex-situ* scanning electron microscopy (SEM), X-ray computational tomography (XCT) and *in-situ* X-ray diffraction (XRD). The leaf-like zinc dendrite to be examined was obtained under the diffusion-limited condition of zincate dissolved in an alkaline electrolyte [17–21]. The XCT offers the detailed inner structure of the zinc deposits while the *in-situ* XRD gives spatially averaged but temporal changes of the the zinc electrode material during the oxidation-reduction processes. We here show how the leaf-like zinc dendrites are transformed depending on its oxidation conditions and how this influences on the rechargeability of zinc electrodes for secondary batteries.

2. Experimental

2.1. Preparation and electrochemical measurements

We prepared a 4 mol dm^{-3} (4 M) KOH aqueous alkaline electrolyte containing 0.25 M ZnO by dissolving zinc oxide powder in a concentrated aqueous KOH solution. A 3-electrode cell used for electrochemical measurements had its working electrode of a copper plate (0.5 cm^2) set on the bottom of the 3-electrode cell. Counter and reference electrodes were zinc plate (ca. 5 cm^2) and zinc wire respectively, which were suspended in the prepared electrolytes. The electrolyte volume was 4 cm^3. Zinc oxidation and reduction experiments were employed using potentio-galvanostat equipment (Ametek, Celltest). The leaf-like zinc dendrite was formed on the copper working electrode under the diffusion-limited condition [18] (see details in Results and Discussion) and was dissolved up to the cut off potential of 0.2 V versus Zn/Zn^{2+}.

2.2. Analytical methods for electrode

The morphology and the constituent of the zinc was examined *ex-situ* by SEM (FE-SEM, Hitachi, SU6600) and XCT. For protecting the sample from the reaction with oxygen and water of ambient atmosphere, the sample was taken out from the cell and processed under inert or vacuum conditions. The XCT images of the electrode were obtained with a focused X-ray method at beamline BL47XU of SPring-8 (Hyogo, Japan). The X-ray energy was set at either 9.690 keV or 9.650 keV, which results in virtually no difference in the obtained images. For preparing the XCT sample, the zinc deposit was cut into a cylindrical tip with its diameter of ca. 30 μm using a focused ion beam. The *in-situ* XRD was employed at beamline BL28XU of SPring-8. For the *in-situ* measurement, a small cell was used with the working and counter electrode areas of 0.1 cm^2 and 1.0 cm^2, respectively. The X-ray energy and the beam size diameter were 30.0 keV ($\lambda = 0.413$ Å) and 1 mm, respectively.

3. Results and Discussion

3.1. Formation of leaf-like zinc dendrite accompanying with potential oscillation

We first employed a galvanodynamic scanning experiment to determine an optimal condition for obtaining the leaf-like zinc dendrite. The current density was swept from 0 mA cm^{-2} to -36 mA cm^{-2} at a scan rate of 0.1 mA s^{-1}. The potential curve changes monotonously in the beginning of current sweeping and starts to oscillate at around 15 mA cm^{-2}, which is known as the signal of leaf-like zinc dendrite formation under the diffusion-limited condition [18]. Since the diffusion-limited condition is satisfied above the threshold current density, we set the galvanostatic deposition (reduction) condition of 20 mA cm^{-2} for 0.5 h (10 mAh cm^{-2}) to obtain the leaf-like zinc dendrites on copper electrode.

As shown in the potential-specific capacity curve in Fig. 1, frequent potential oscillation appears in the early stage of reduction process. After reducing for ca. 5 mAh cm^{-2}, the electrode potential becomes stable and is finally nearly constant at -0.1 V vs. Zn/Zn^{2+}, as shown in Fig. 1. This potential stabilization is ascribed to that the zinc surface area becomes large enough to have sufficient supply of zincate ions from the electrolyte and the diffusion-limited condition changes to the charge transfer-limited condition along with the reduction process [18]. Fig. 2 shows the FE-SEM images of thus obtained zinc deposits, showing the typical leaf-like dendrite morphology.

3.2. Galvanostatic oxidation-reduction cycle of leaf-like zinc dendrite

To evaluate the reactivity of the leaf-like zinc dendrite, several oxidation-reduction experiments were carried out. The oxidation process was employed at either 1 or 10 mA cm^{-2} until the potential reaches at 0.2 V vs. Zn/Zn^{2+} whereas the reduction process was carried out at 20 mA cm^{-2} for 0.5 h (10 mAh cm^{-2}). The oxidation at 1 mA cm^{-2} proceeds with high coulombic efficiency of 96.0% as shown in Fig. 2(a), indicating that the most of the leaf-like zinc dendrites are oxidized under this condition. In the following (2nd) reduction process, potential fluctuation is also observed, suggesting the leaf-like deposits is formed again under the diffusion-limited condition. The efficiency in the 2nd cycle is nearly unity, indicating that hydrogen evolution including self-discharge can be well disregarded. In the 5th reduction process, typical potential oscillation does not appear, but overpotential increase is observed after ca. 4 mAh cm^{-2}, showing concentration overpotential under diffusion-limited condition to result in the dendrite formation again as is observed by SEM analysis shown later.

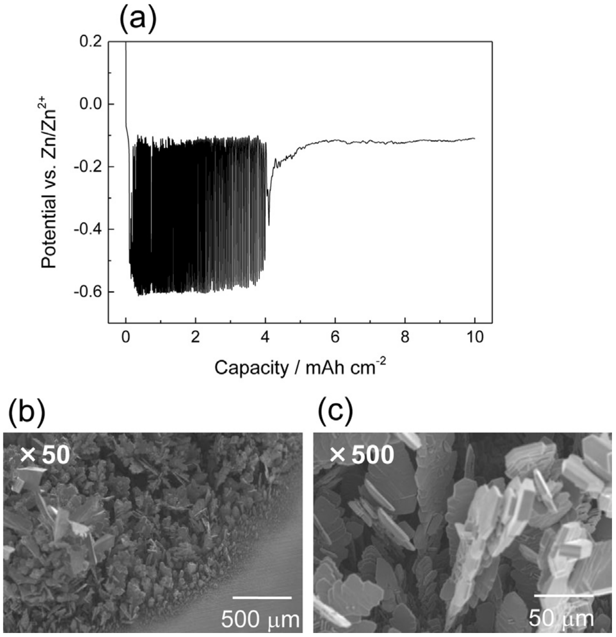

Fig. 1. (a) Galvanostatic profile during zinc reduction in alkaline electrolyte (4 M KOH with 0.25 M ZnO) at 20 mA cm^{-2}, and (b)-(c) thus obtained deposits observed by FE-SEM.