



# Morphological evolution of mossy structures during the electrodeposition of zinc from an alkaline zincate solution



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## ABSTRACT

The morphological evolution of zinc during electrodeposition from an alkaline zincate solution, i.e., corresponding to charging operation in secondary zinc batteries, was investigated. The initiation and propagation of mossy structures were particularly focused; mossy structures represent one of the undesired, irregular morphologies at low cathodic overpotential. Scanning electron microscopy observations showed that mossy structures formed transiently from layer-like morphology followed by the formation of protrusions with a size of submicrometers. These protrusions still exhibited layer-like features in the initial stage. In addition to this transition behavior, the propagation of mossy structures was monitored *in situ* by optical microscopy. At  $-5.0 \text{ mA cm}^{-2}$ , mossy structures formed successively and propagated, while there was no clear change in layer-like morphology during deposition outside these characteristic structures. At  $-20 \text{ mA cm}^{-2}$ , the layer-like growth proceeded for longer duration and the population of the mossy structures apparently decreased. However, they continuously increased in size followed by successive formation of mossy structures once initiated. From these results, growth mode of zinc at low cathodic overpotential transiently changed from layer-like growth to mossy structure evolution accompanied with dynamic variations in local current density.

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## 1. Introduction

Zinc is currently considered to be one of the promising candidates for use as negative electrode materials in secondary batteries, featuring its higher energy density and lower cost as compared with those of conventional Li-ion batteries [1–3]. Moreover, it can be electrochemically cycled (reduced and oxidized) in an aqueous environment, which results in safe operation conditions. In particular, these characteristics are advantageous for grid-scale energy storage linked with conventional electrical network, for which safety and low cost aspects are indispensably required for applications.

Despite these attractive characteristics, the practical utilization of zinc as a negative electrode in energy storage systems is still limited. One of the main obstacles for its applications lies in the morphological change of zinc during charging and discharging cycles, resulting in fatal operation conditions [1–4].

For this reason, the profound understanding of the correlation between charge-discharge conditions and morphological variations has become an important research topic [5–10]. Among many papers on morphological variations of zinc, the fact is emphasized that mossy structure is dominant at low overpotential [11–13]. The mossy structure comprises nanosized filamentous zinc with three-dimensional structures having a large surface area [13]. This morphology must be avoided for battery operation as it exhibits low corrosion resistance, which results in poor coulombic efficiency during charge-discharge cycles [14]. It is also noteworthy that concentration dependence of mossy structure is considerably different from dendrite formation mechanism conventionally accepted; mossy structure is preferred at higher concentration of zincate [7]. This makes it complicated to establish optimum charge-discharge conditions because coulombic efficiency is worsened at both high and low current densities. Electrolyte flow which is generally effective to suppress dendritic growth has minor effects on mossy structure evolution [14].

As an origin of the anomalous behavior of zinc electrodeposition at low overpotential, Wiart et al. pointed out a possibility that a surface protective layer comprising zinc oxidative species existed at low overpotential, which localized deposition sites [15].

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Electrochemical impedance spectroscopy (EIS) indicated that the properties of protective layer surely depended on the applied potential [16,17]. Measurements of *in situ* Raman scattering showed ZnO layer on the zinc surface at the initial stage of reduction [18].

Although qualitative trend of mossy structure formation at low overpotential and its origin are partially recognized, there are few studies focusing on the growth behavior (initiation and propagation) of the structures. For example, compact film tends to be maintained at higher current density, but longer deposition duration results in mossy structures formation. In the case of dendritic growth, the time dependence of dendrite initiation and evolution can be explained by concentration change of ions near electrode surface [19]. However, such a simplified mass transfer limitation model cannot be applied to the mossy structure evolution phenomena. It is because the observed dependences on concentration or current density are apparently opposite to a conventional diffusion limited model. Therefore, we are engaged in careful observing the morphological evolution of mossy structures in order to understand nucleation and growth behavior of zinc at low overpotential.

In this study, at the initiation of mossy structures, morphological transition from compact to mossy morphology is evaluated by laser scanning confocal microscopy (LSCM) and scanning electron microscopy (SEM). The propagation of mossy structures is also observed by *in situ* optical microscopy. Based on the comparison of morphological evolution at different applied potentials or current densities, characteristic nucleation and growth behavior of zinc at low overpotential are discussed.

## 2. Experimental

### 2.1. Experimental setup for electrochemical measurement

Zinc was electrodeposited from an alkaline zincate solution, which has been widely studied as a common electrolyte for zinc-based batteries. For the preparation of the electrolyte, 0.50 mol dm<sup>-3</sup> of ZnO (Kanto Chemicals, reagent grade) was dissolved in 6.0 mol dm<sup>-3</sup> KOH (Kanto Chemicals, UGR grade). Before electrochemical measurements, the electrolyte was deaerated by bubbling with nitrogen gas. The working and counter electrodes were zinc plates (Nilaco, >99.5%). During deposition, the working electrode vertically faced to the counter electrode. The Hg/HgO electrode (Inter Chemie. Inc.) was specifically chosen as the reference electrode as it could tolerate highly alkaline conditions. All potentials shown below were measured vs. Hg/HgO. For attaining reproducibility particularly for morphological analysis, the zinc working electrodes were mirror-finished using an automatic lapping polishing machine (MA-400D, Musashino Denshi Co., Ltd.) with a colloidal silica slurry (Semi-Sperse 25, Cabot Microelectronics Corp.). Before electrodeposition, the zinc surface was slightly etched using 1.0 mL 35% hydrochloric acid + 100 mL pure water for 10 s.

### 2.2. Electrochemical measurements and analysis on deposition behavior

Electrochemical measurements were performed using an electrochemical measurement system (HZ-7000, Hokuto Denko) at 30 °C. The cathodic polarization behavior of zinc in 6.0 M KOH + 0.50 M ZnO was characterized by linear sweep voltammetry (LSV) by sweeping the potential from open circuit potential (OCP) to -2.0 V with a scan rate of 20 mV s<sup>-1</sup>.

The potentiostatic deposition was performed in order to discuss the morphological evolution process of zinc. From the previous papers on electrochemical measurements of zinc in alkaline

electrolytes, it is known that a special care must be taken with respect to the initial state of the zinc surface [20,21]. In this study, after immersing the zinc working electrode in electrolytes, zinc was deposited at -1460 mV for 60 s (cathodic charge, 1.5 C cm<sup>-2</sup> was passed) in order to avoid the additional effect referred to the native state of zinc. Then, the electrodeposition was further performed on the initially deposited zinc surface at various potentials. By performing this procedure, layer-like morphology was deposited after the initial passage of current (See results section). This electrochemical operation certainly ensured the better reproducibility of morphological variations and surface chemical state before objective electrochemical measurements. (When passed charge for deposition is mentioned in following results and discussion section, this initial condition is considered as 0 C cm<sup>-2</sup>.)

LSCM (Keyence, VK-9510) was then engaged in characterizing the morphology of electrodeposits. It is capable of obtaining three-dimensional images by acquiring optical images at different depth, making it effective to distinguish morphological variations. Morphological features on the scale of submicrometers were characterized by SEM (Hitachi, S-5500).

### 2.3. *In situ* observation of propagation of mossy structure

For discussing the dynamic growth mode change of zinc electrodeposits, *in situ* optical microscopy was adopted. Microscope (Union Optical Co., Ltd., DZ2 Zoom Microscope) equipped with a CCD camera (ARTRAY Co., Ltd., ARTCAM-130) was utilized. In this measurement, the zinc working electrode was placed on the bottom of a polystyrene cell using a polytetrafluoroethylene tape. The same preparation procedure was adopted for the working electrode as mentioned above. As the counter electrode, zinc wire (Nilaco, >99.99%) was placed around the working electrode. Galvanostatic electrodeposition experiment was conducted in two-electrode configuration at -5.0 mA cm<sup>-2</sup> and -20 mA cm<sup>-2</sup> by HZ-7000. For regulating the initial state of the zinc surface before microscopic observation, zinc was deposited at -20 mA cm<sup>-2</sup> for 500 s (10 C cm<sup>-2</sup>). A relatively large amount of zinc was deposited as compared to above described potentiostatic deposition (1.5 C cm<sup>-2</sup>) because layer-like structures (micro-steps) could be roughly imaged even using an optical microscope for this amount of deposits. After the initial passage of current, galvanostatic deposition was further performed at -5.0 mA cm<sup>-2</sup> or -20 mA cm<sup>-2</sup>, and the propagation of mossy structures was monitored *in situ* by optical microscopy.

## 3. Results

### 3.1. Potentiostatic deposition of zinc and analysis on morphological evolution

Before investigating the evolution of mossy structures at low overpotential, morphological variations of zinc in the electrolyte containing 6.0 M KOH + 0.50 M ZnO were investigated at several applied potentials.

Fig. 1 shows the LSV measured from OCP to -2.0 V. Initially, the current increases, a peak corresponding to deposited zinc is observed after -1.4 V, followed by current increase around -1.7 V due to hydrogen evolution.

Fig. 2 shows SEM images of potentiostatically electrodeposited zinc at (a) -1420 mV, (b) -1460 mV, (c) -1540 mV, and (d) -1720 mV. The amount of electricity utilized for deposition is set at 5.0 C cm<sup>-2</sup>. The morphology of zinc changes depending on the applied potential. From positive potential toward negative potential, mossy, layer-like, boulder-like, and dendritic features are observed. These morphological variations well agreed with

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