



# Morphology control of zinc regeneration for zinc–air fuel cell and battery



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## HIGHLIGHTS

- Solutions to morphology control of zinc regeneration.
- Effect of variables on morphological evolution analyzed by COMSOL.
- Discussing mechanism of morphological change by Monte Carlo method.
- Microstructures of deposited zinc were examined by way of SEM.

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## ABSTRACT

Morphology control is crucial both for zinc–air batteries and for zinc–air fuel cells during zinc regeneration. Zinc dendrite should be avoided in zinc–air batteries and zinc pellets are yearned to be formed for zinc–air fuel cells. This paper is mainly to analyze the mechanism of shape change and to control the zinc morphology during charge. A numerical three-dimensional model for zinc regeneration is established with COMSOL software on the basis of ionic transport theory and electrode reaction electrochemistry, and some experiments of zinc regeneration are carried out. The deposition process is qualitatively analyzed by the kinetics Monte Carlo method to study the morphological change from the electrocrystallization point of view. Morphological evolution of deposited zinc under different conditions of direct currents and pulse currents is also investigated by simulation. The simulation shows that parametric variables of the flowing electrolyte, the surface roughness and the structure of the electrode, the charging current and mode affect morphological evolution. The uniform morphology of deposited zinc is attained at low current, pulsating current or hydrodynamic electrolyte, and granular morphology is obtained by means of an electrode of discrete columnar structure in combination with high current and flowing electrolyte.

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## 1. Introduction

Appropriate energy storage plays a more important role in a wide range of applications, including frequency regulation of renewable energy sources, peak-shaving of electrical grid, emergency power and portable power [1,2]. Metal–air batteries have received much attention due to their high energy densities [3], where oxygen from the air employed as their cathode material. Compared with other metals, zinc possesses a variety of advantages: low equilibrium potential, high specific energy, good environmental compatibility, good reversibility, it is found in

abundance and it is easy to handle [4]; therefore, zinc material is widely applied to the electrochemistry field in either the galvanization or in cathode active material [5,6]. However, several major problems in zinc regeneration need to be addressed including zinc pellets of appropriate size, shape change of zinc electrode and dendritic growth [7]. These are particularly important for zinc–air battery due to seriously affecting the battery's durability and performance, limiting the applications of the zinc–air secondary battery. Moreover, zinc–air fuel cells' performance is subject to zinc pellets size, because it can determine active surface area, and influence electrolyte flowing and contact resistance.

Although such morphological changes arise from ionic transport through diffusion, migration and convection, the mechanism for causing morphological changes remains unknown. Some researchers have made significant progress in exploring the

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mechanism for the morphological changes of zinc electrodes [8–10]. McBreen [11] developed a concentration-cell model that accounted for the shape change of zinc electrodes during charge/discharge, but for slow or fast diffusion further explanation are needed. Choi et al. [12,13] proposed a hydrodynamic model for shape change based on electrolyte flows in a battery as a consequence of osmotic and electro-osmotic forces which explains the ionic movement from the zinc electrode's top toward its bottom, but this method cannot provide reasonable explanations for the zinc accumulation at the center of the electrode. Bockris et al. held that dendritic growth might be closely related to the overpotential at the tip of the dendrites [8]. They also investigated the relationship between the dendritic formation and the physical properties of an electrolyte such as composition, temperature, viscosity, and hydrodynamics [14]. In addition, some researchers have done some work in solutions to zinc dendrites. Parker et al. [15] designed a porous electrode to suppress growth of zinc dendrites. Smedley et al. [16] provided a solution of zinc regeneration with optimizing the structure of zinc electrode to control zinc morphology. Shaigan et al. [17] employed pulsating current as morphological control of electrodeposited zinc. Other researchers have also made some attempt to model the zinc electrode. Deiss et al. [18] developed a one-dimensional numerical model of an electrically rechargeable alkaline zinc–air battery that can predict decrease of the zinc redistribution with increasing cycle number. Song et al. [19] established a one-dimensional mathematical model of the discharge process and of the failure mechanisms of zinc electrode, predicting variable distributions within the electrode itself. Bauer et al. [20] put forward a model of the numerical simulation of copper electrodeposition. Braff et al. [21,22] established a two-dimensional model for simulating a hydrogen bromine laminar flow fuel cell based on COMSOL software. To control the morphological change, the mechanism for shape change must be further studied, and then put forward reasonable solutions.

In this work, we investigated the morphological change of zinc electrode related to parametric conditions with COMSOL software, and experiments on zinc electrodeposition under the conditions of different current and flowing electrode were also conducted. Furthermore, we implemented zinc depositing process simulation relying on the three-dimensional kinetics Monte Carlo method, analyzing morphological evolution.

## 2. Experiment methods and numerical model

### 2.1. Experiment methods

An experimental apparatus for zinc electrodeposition was fabricated, where the cathode employed stainless steel, the anode used nickel network with the same dimension as the cathode, and the electrolyte was made of weight 40% potassium hydroxyl mixed with zinc oxide. The distance between the anode and the cathode is 5 mm, and the effective dimension of the cathode is about 30 mm × 30 mm. Zinc electrodeposition experiments were carried out at the room temperature, where the power supply with pulsating and galvanostatic mode was EA-PS 8065-10, and data acquisition instrument used for recording current signals was NI-PXI-1033. In addition, auxiliary components were not described here including a pump used for the flowing electrolyte. The morphology of deposited zinc was examined by scanning electron microscopy (JSM-6460). For some reason, hydrodynamic conditions, charging mode, and electrode structure can influence morphological change of electrodeposited zinc. Table 1 lists the different testing parameters including flowing electrolyte, charging mode and structure.

**Table 1**  
Testing parameters for zinc electrodeposition.

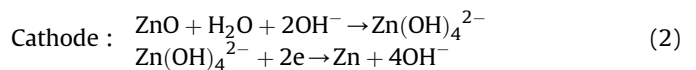
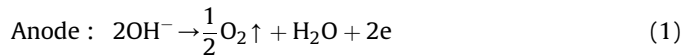
Parameters	Feature I	Feature II
Electrode structure	Planar electrode	Porous electrode
Electrolyte state	Quiescent	Hydrodynamic
Charging mode	Direct current	Pulsating current

### 2.2. Numerical model

#### 2.2.1. Electrode kinetics

Zinc electrodeposition involves energy conversion transforming electrical energy into chemical storage energy, accompanied by phase changes. Fig. 1 shows that chemistry and electrochemistry reactions occur near or on the electrodes of a zinc–air rechargeable battery during charge, where the morphological change of zinc regeneration is a concern because it reduces the capacity of the battery. Pulsating currents from new clean energy is more beneficial to suppress dendritic growth.

Zinc oxide or zincate is reduced at the cathode, and hydroxyl is oxidized at the anode during charge. The electrochemical reactions can be expressed as:



The required charge voltage can be determined by the thermodynamic equilibrium voltages and the activation overpotentials at the anode and cathode, and ohmic loss of the electrolyte. Thus,

$$\Delta\varphi = E_{\text{eq}}^a - E_{\text{eq}}^c + \eta_a + \eta_c + iR_{\text{el}} \quad (3)$$

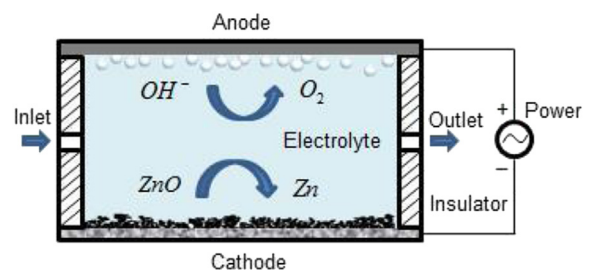
Butler–Volmer equations are used to describe the electrode reaction kinetics.

$$i_{\text{loc}} = i_0 \left[ \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right] \quad (4)$$

where  $i_{\text{loc}}$  denotes the local current density at the solid–liquid interface,  $i_0$  exchange current density,  $\alpha_a$  anodic transfer coefficient,  $\alpha_c$  cathodic transfer coefficient,  $F/RT$  the Nernst factor, and  $\eta$  activation overpotential for the electrode reactions, which can be defined as the below equation:

$$\eta = \phi_s - \phi_l - E_{\text{eq}} \quad (5)$$

where  $\phi_s$  is electrode potential, and  $\phi_l$  is electrolyte potential. According to the Nernst equation, equilibrium potentials  $E_{\text{eq}}$  are calculated by:



**Fig. 1.** Schematic view of zinc electrodeposition.

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