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Computational analysis of the zinc utilization in the primary zinc-air batteries

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ABSTRACT

A one-dimensional mathematical model is implemented in order to explore the design parameters of the zinc-air batteries. The proposed model provides a realistic prediction by considering the effect of the hydroxide ion on formation of the zinc oxide precipitates. The predicted discharge curves are in more reasonable agreement with experimental data at a typical discharging current density of 10 mA cm^{-2}. The proposed model is subsequently used to predict the discharge performance with varying the thicknesses of the zinc anode and the microporous separator. It is demonstrated that the highest zinc utilization of 97% is obtained for the compact anode (0.61 mm thick) assembled with the sufficiently thick microporous separator (0.11 mm thick).

1. Introduction

Increasing concerns on the growing energy demands and the global climate changes are accelerating the research and the development of the electrical energy storage devices, in order to utilize the renewable energy sources, such as solar energy [1]. Until now, the lithium-ion batteries are widely used for the portable electronics as well as the electric vehicles [2]. However, their energy density is limited by the intercalation chemistry in the electrode materials, where the state-of-the-art performance barely reaches a specific energy of 150 Wh kg^{-1} at the cell level [3]. Hence, the zinc (Zn)-air batteries have received much attention due to their high practical specific energies reported up to 400 Wh kg^{-1} [4]. Compared to other battery systems, such as lithium-based [5] and sodium-based batteries [6], the Zn-air batteries may provide relatively safe, cheap and environment-friendly operation with considerably high capacity [7].

During discharge, the Zn anode is oxidized to form the tetrahydroxozincate ions [8]:

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

where the tetrahydroxozincate ions can precipitate as the zinc oxide (ZnO):

$$Zn(OH)_4^{2-} \leftrightarrow ZnO + 2OH^- + H_2O \quad (2)$$

At the air cathode, the hydroxide ions are balanced by the oxygen reduction reaction:

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (3)$$

Based on the proposed mechanism, the Zn consumption and the ZnO formation simultaneously occur in the Zn anode. Therefore, the numerical investigations of the Zn-based batteries have been initiated by the half-cell model of the porous Zn–ZnO anode.

Choi et al. developed the one-dimensional mathematical models for the porous Zn anode based on the concentrated ternary electrolyte theory [9]. By using similar model, Sunu and Bennion conducted the numerical investigation of the Zn–ZnO redistribution during cycling that is found to be the main cause of operational failure [10]. Their model predictions were in accordance with experimental observation of the ZnO distribution. After a decade, Isaacson et al. have performed a numerical investigation on the porous Zn anode, in which the model predicted the redistribution of Zn and ZnO [11]. Mao and White extended Sunu and Bennion's

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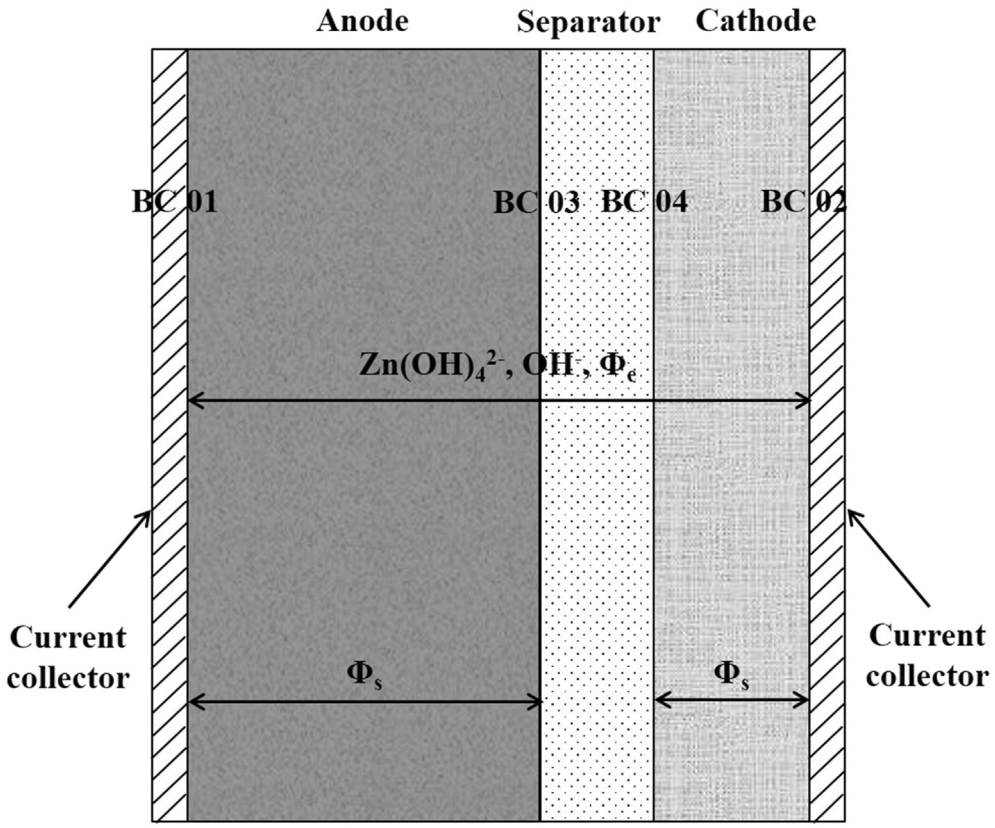

Fig. 1. Schematic illustration of the computational domain used in the proposed model.

model to the Zn-air battery with the microporous separator and the air cathode [12]. In their model, the effect of precipitation of the ZnO and the potassium zinc hydroxide was included. Subsequently, based on the Mao and White's model, Deiss et al. developed a mathematical model for the rechargeable Zn-air battery [13]. Later, Song et al. established a one-dimensional Zn anode model to investigate the influence of the precipitated ZnO distribution on the electrode's failure [14]. Schröder and Krewer extended Deiss' model to explore the effect of the air composition on the battery's cycle performance [15]. Recently, several researchers made contributions on model prediction of local phenomena occurring in the Zn-air battery anode or cathode. In particular, the dendrite formation in the Zn anode [16] and the oxygen bubble generation at the electrode-electrolyte interfaces [17] are explored by an integration of sub-model kinetics into the macroscopic model. However, the majority of previous models describe only part of the Zn-air battery's components. The current literature still lacks on the model-based optimization of a full-cell design [18]. Key design parameters, e.g., the mass loading of Zn in the anode, porosity or thickness of microporous separator, etc., can be mutually influential and are yet to be optimized in a full-cell model.

Here, we report a one-dimensional mathematical model of the Zn-air battery by taking into account the effect of the ZnO precipitates. Unlike previous models, an incorporation of the measured values on the effective surface area and thickness of the cathode enables a full-cell scale simulation and thereby more realistic prediction on the discharge performance. Subsequently, the model validation is performed by comparing the predicted discharge curve with our experimental data. The proposed model provides distributions of the key variables, such as the hydroxide ion and the electrolyte volume fraction, which may be critical to determination of the Zn utilization rate. The effects of the Zn

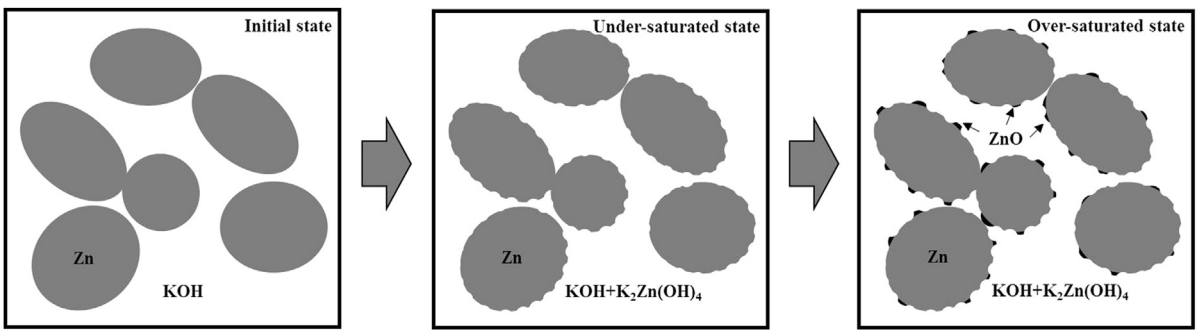

Fig. 2. Illustration of the morphology variation of the zinc/zinc oxide particles during discharge [20].