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# Growth of oxygen bubbles during recharge process in zinc-air battery

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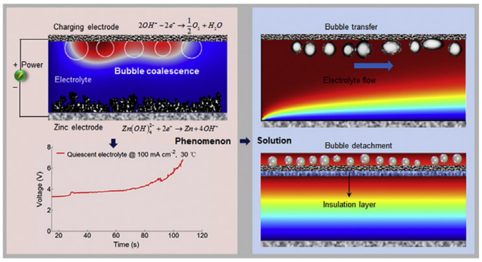
## HIGHLIGHTS

- The law of oxygen bubble growth achieved by the phase-field model.
- Bubble detachment by way of partial insulation structure.
- Inhibition of bubble coalescence by means of electrolyte flow.
- Rechargeable zinc-air battery with two tri-electrode configurations.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Rechargeable zinc-air battery used for energy storage has a serious problem of charging capacity limited by oxygen bubble coalescence. Fast removal of oxygen bubbles adhered to the charging electrode surface is of great importance for improving the charging performance of the battery. Here we show that the law of oxygen bubble growth can be achieved by means of phase-field simulation, revealing two phenomena of bubble detachment and bubble coalescence located in the charging electrode on both sides. Hydrodynamic electrolyte and partial insulation structure of the charging electrode are investigated to solve the problem of oxygen bubble coalescence during charging. Two types of rechargeable zinc-air battery are developed on the basis of different tri-electrode configurations, demonstrating that the charging performance of the battery with electrolyte flow (I) is better than that of the battery with the partially insulated electrode (II), while the battery II is superior to the battery I in the discharging performance, cost and portability. The proposed solutions and results would be available for promoting commercial application of rechargeable zinc-air batteries or other metal-air batteries.

## 1. Introduction

Energy storage technologies are widely used in many fields including load and frequency regulation, intermittency balance, supply power and emergent contingency [1,2]. A variety of solutions have been put forward, such as lithium ion batteries, flow redox cell and sodium–sulphur batteries so forth [3]. Metal-air batteries receive more attention due to high specific energy [4], where zinc-air batteries have safety, technology, and cost advantages over other metal-air batteries [5,6]. However, lifetime problem of rechargeable zinc-air battery is still unresolved [7], where air electrode is exposed to severely charge–discharge environment, especially oxygen bubble coalescence accompanied in the charging process, leading to the battery failure.

Sluggish kinetics of oxygen evolution reaction (OER) primarily depends on activity of the catalyst [8–13], the electrode structure [14,15], and removal of oxygen bubble. Oxygen evolution reaction occurs at the charging electrode of zinc-air battery during charging

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$2OH^- \rightarrow 1/2O_2 + H_2O + 2e^-$, resulting in a lot of bubbles involved in the electrolyte near the charging electrode and reduction of conductivity of the electrolyte. The bubbles easily adhere to the charging electrode surface in the case of synergistic effects among surface tension of the electrolyte, properties of electrode material and bubbles interaction [16–19]. When the bubble grows up to a critical value, it will move along the electrode surface and coalesce with other bubbles. Bubble coalescence easily gives rise to a layer of gas membrane in the vicinity of the charging electrode, which can increase ohmic resistance, reduce the charging efficiency, and even damage the battery [20]. If bifunctional air electrode is employed in rechargeable zinc-air battery [21], oxygen bubble coalescence will bring about catalyst failure and even devastate the air electrode due to high potential. Moreover, increase of the charging voltage caused by oxygen bubble coalescence can also influence shape change of electrodeposited zinc and even trigger the short circuit of the battery [22]. To address the problem of bubble coalescence, one is to increase the salt concentration in the electrolyte [23–27], which can inhibit bubble coalescence but decrease conductivity of the electrolyte. The other is to make the electrolyte flow [28,29], which would take away the evolving bubbles but increase the electrolyte management costs and additional energy consumption, moreover, the electrolyte flow may cause loss of catalyst and decrease the activity of air electrode. In addition, several researchers focused on the low-adhesion electrode where the catalysts may be distributed with appropriate morphologies with the electrode microstructure [13,30,31]. Therefore, oxygen bubble growth must be effectively controlled, which will facilitate commercial application of rechargeable zinc-air battery.

In this work, we investigated oxygen bubble growth in the electric field by way of COMSOL software, proposed two viable solutions to inhibiting bubble coalescence, and developed two types of rechargeable zinc-air battery with different tri-electrode configurations based on experimental analysis.

## 2. Methods

### 2.1. Bubble growth model

Bubble evolution is due to pressure difference between gas phase and liquid phase, leading to the interface movement [32]. To study oxygen bubble growth in the electric field, we employed a phase-field method coupled to the electric force in COMSOL Multiphysics 4.3. Gas bubble is assumed to be compressible, while the electrolyte is incompressible. To model oxygen bubble evolution and bubble coalescence in the electrolyte, the Navier–Stokes equations for the laminar two-phase flow can be set up as follows [33]:

$$\rho\frac{\partial u}{\partial t} + \rho(u\cdot\nabla)u = \nabla\cdot\left[-pI + \mu\left(\nabla u + (\nabla u)^T\right)\right] + F_{st} + \rho g + F \tag{1}$$

where $u$ is the electrolyte velocity, $\rho$ is the electrolyte density, $\mu$ is the dynamic viscosity of the electrolyte, $p$ is the pressure inside the bubbles, $g$ is the gravity, $I$ is the identity tensor, $F_{st}$ is the surface tension force, and $F$ is the electric force.

To track the gas–liquid interface, a phase field method may be used for the interface [33]:

$$\frac{\partial\phi}{\partial t} + u\cdot\nabla\phi = \nabla\cdot\frac{3\chi\sigma\varepsilon}{2\sqrt{2}}\nabla\left(-\nabla\cdot\varepsilon^2\nabla\phi + \left(\phi^2 - 1\right)\phi\right) \tag{2}$$

where $\phi$ is the phase field variable distinguishing between the oxygen bubble ($\phi = 0$) and the electrolyte ($\phi = 1$), $\sigma$ is the surface tension coefficient, $\varepsilon$ is the gas–liquid interface, and $\chi$ is the mobility of the interface.

### 2.2. Experimental setup

To solve the problem of bubble coalescence, we proposed two solutions by way of experimental study. The first is the electrolyte flow taking oxygen bubbles away in time; the second is a partial insulation structure of charging electrode to change the location of oxygen evolution reaction which makes oxygen bubbles actively detach from the electrode surface. Meanwhile in situ voltage signal between the charging electrode and zinc electrode was used for detecting bubble coalescence under different experimental conditions of the quiescent/hydrodynamic electrolyte, and low/high temperature electrolyte.

The charge–discharge polarization characteristics of rechargeable zinc-air battery with two different tri-electrode configurations were tested, where a nickel mesh is employed as the third electrode, stainless steel serves as zinc electrode, and the air electrode is made up of a diffusion layer of porous Teflon film, a current collection layer of nickel mesh, and a catalytic layer of manganese dioxide. The experiment on the internal resistance of the battery was carried out by means of a CHI660D electrochemical workstation. The impedance spectra were recorded by sweeping frequencies over the range of 3000 Hz–1 Hz with the amplitude of 0.005 V.

## 3. Discussion

### 3.1. Oxygen bubble evolution

Highly active catalysts are required to improve the sluggish kinetics of oxygen evolution reaction. The OER activity can be facilitated by precious metal containing catalysts, whereas the scarcities of these materials and their poor stability in alkaline solution limit the commercial applications. Therefore, nickel mesh is employed as the OER electrode from the point of inexpensive cost and corrosion resistance. Nickel is a transition metal which plays a crucial role in absorbing hydroxide ion, where the proposed mechanism for electrolytic evolution of oxygen is followed by the electrochemical adsorption of $OH^-$, the rate-determining electrochemical desorption of OH, the formation of $H_2O_2$, and catalytic decomposition to $HO_2^-$ and $O_2$ [34]. To enhance oxygen evolution reaction activity, an $e_g$ orbital may occupy in between surface transition metal ions and surface-anion adsorbate to reduce the binding force of intermediate species [35]. It can be found that oxygen evolution reaction is relatively slow due to four electrons transfer involved in the process of one oxygen molecule. Although the above mentioned OER catalysts can improve the overpotential of activation, oxygen bubble growth and bubbles coalescence cannot be controlled by means of the catalysts.

Once the oxygen concentration in the electrolyte near the electrode gets saturated, the phenomenon of bubbles will arise. Oxygen bubble evolution generally undergoes three stages including gas nucleation, growth, and detachment or coalescence. Bubble growth depends on electrolyte viscosity, current density, electrode surface structure and electrode material, and the state of the bubble is related to buoyancy, gravitational force, and surface adhesive force. With increase of oxygen molecules inside a bubble, bubble movement would happen. When internal energy of oxygen in the bubble is enough to destroy the internal and external equilibrium of the bubble, the bubble will detach. If gas bubble evolution occurs at the upper surface of the electrode, as shown in Fig. 1, gas-side contact angle becomes gradually bigger and bubble pressure increases with time, resulting in bubble detachment. The