

Towards a uniform distribution of zinc in the negative electrode for zinc bromine flow batteries

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HIGHLIGHTS

- Achieving a uniformly distributed zinc electrode is crucial to ZBFBs.
- A bottom-to-up strategy is adopted to promote the uniform distribution of zinc.
- The zinc distribution can be controlled by adjusting the carbon surface properties.
- A negative electrode with abundant defects is prepared and tested experimentally.
- The prepared electrode has a more uniform zinc distribution than the original one.

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ABSTRACT

Achieving a uniform distribution of zinc in the negative electrode is crucial to increase the electrode utilization, maximize the discharge capacity, suppress the dendrite formation and enhance the cycling stability for zinc bromine flow batteries (ZBFBs). To promote the uniform distribution of zinc and thus propel the commercial applications for ZBFBs, in this work, a first-principles study is carried out to investigate the zinc adsorption and diffusion on representative carbon surfaces, including a pristine graphite (0001) surface, two surfaces with vacancies, and three surfaces with oxygen-functional groups, aiming to unravel the effect of carbon defects on the ion transport inside the porous electrode, clarify the underlying zinc anchoring mechanism and seek effective ways to promote the uniform distribution of zinc. It is found that the zinc distribution and morphology can be varied by adjusting carbon surface properties, especially by increasing the number of single vacancy. A graphite felt negative electrode with a high content of carbon defects is then prepared and tested in ZBFBs. Experimental results reveal that a much more uniform distribution of zinc is achieved in the prepared electrode than the original electrode does after charging, demonstrating the validity of our proposed mechanism and method. The results reported here provide new insights and novel methods to fabricate uniformly distributed zinc negative electrode, which can guide the rational design of electrode and promote the future applications of ZBFBs and other hybrid flow batteries (e.g. Zn-I₂, Zn-Ce and all-iron).

1. Introduction

With the widespread utilization of clean, renewable but intermittent energy sources such as solar and wind powers, an imperative need has been taken to develop efficient, reliable and cost-effective large-scale energy storage systems [1,2]. Unfortunately, the most investigated energy storage technology, lithium-ion battery, is not suitable for large-scale application because of their high cost and safety concerns [3–8]. On the contrary, redox flow batteries have attracted burgeoning attention to be used for large-scale energy storage because of their high efficiency, high reliability, flexible design, fast response and long cycle

life [8–13]. Among the state-of-art redox flow batteries, zinc bromine flow batteries (ZBFBs) arouse great interests from the fields of both research and industry, attributed to their advantages including low cost, high cell voltage (1.84 V) and high energy density (440 Wh kg⁻¹) [14,15]. The typical schematic of ZBFBs is presented in Fig. 1, consisting of two separated tanks and a stack. The tanks are used to store electrolytes containing active materials and the stack with two electrodes that are separated by an ion-exchange membrane or a separator is the place for redox reactions. The basic electrochemical reactions of ZBFBs can be expressed as:

Negative electrode:

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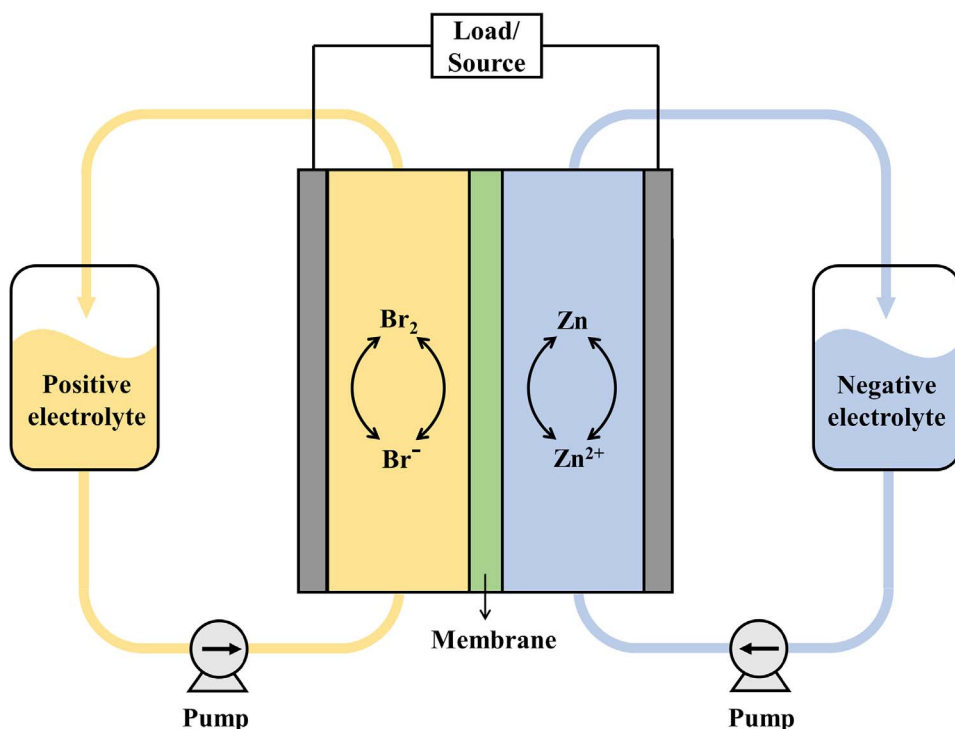
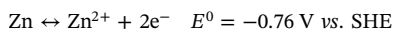


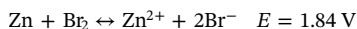
Fig. 1. The typical schematic of ZBFb.



Positive electrode:



Overall:



During the charge process, the metallic zinc is electrodeposited onto the surface of negative electrode and the Br^- is oxidized to Br_2 at the positive electrode, which would then complex with bromide ions and exist in the form of Br_3^- or Br_5^- [16].

Although great progress has been made in the development of ZBFb, their widespread commercial applications are still hindered by many critical issues. For example, in the positive electrode, the poor kinetics of Br_2/Br^- redox reaction results in a high cell polarization, and the toxic charge product Br_2 leads to the safety concerns. In the electrolyte, to avoid the severe self-discharge caused by the side reactions between zinc and electrolyte, weak acidic ZnBr_2 solution is generally employed as the electrolyte, inducing the low ionic conductivity and high ohmic resistance. To address these issues, a great number of nanomaterials have been used to modify the positive electrode to enhance the electrochemical performance, such as SWCNT [17], MWCNT [18] and bimodal highly ordered mesostructure carbons [19], while other works focus on electrolyte additive to increase the ionic conductivity and decrease the volatility of Br_2 , such as KCl, NH_4Cl and quaternary ammonium bromide (QBr) [20,21].

Unfortunately, up to now, little attention has been taken to the negative side. It is known that the rational design of negative electrode plays an important role in advancing the development of ZBFb, because it not only provides reaction sites for Zn/Zn^{2+} redox couple, but also is the substrate for zinc deposition, and thus greatly influences the ZBFb's performance. Unlike the full-flow systems (e.g. vanadium redox flow batteries, iron chromium redox flow batteries), the active materials of which dissolve in the electrolyte at all times and the energy can be decoupled with power, ZBFb are indeed the hybrid-flow systems with metallic zinc deposited onto the negative electrode in the charge process. Thus, the energy is depended on the size of stack and cannot be completely decoupled with power [22]. In other words, at a given stack

size, the capacities of ZBFb are decided by the amount of deposited zinc on the electrode instead of the amount of electrolytes in the tanks. In this regard, achieving the uniform distribution of zinc is of vital significance, as it tightly relates to the space utilization of the negative electrode and the charge capacities of ZBFb. Moreover, the uniform distribution avoids the localized nucleation of zinc, suppresses the zinc dendrite formation and leads to an enhanced cycling stability for ZBFb, which are all crucial to the commercial application of ZBFb and other zinc-based flow batteries, such as Zn-Cl_2 , Zn-I_2 and Zn-Ce . However, different from the zinc deposition process in the field of electroplating industry which adopts metallic plate electrodes as the substrates [23], the commonly used electrodes in flow batteries are three-dimensional carbon-based materials, such as graphite felt and carbon felt [24], attributed to their merits including large specific surface area, high porosity, good chemical/electrochemical stability and low cost. Therefore, not only the zinc deposition on the electrode surface, but also that inside the porous electrode, become essential. Previously, Leung et al. [25] systematically investigated the zinc deposition in methanesulfonic acid on a carbon poly-ester composite substrate under the influence of ion/acid concentration, operating conditions and electrolytic additives; Pan et al. [26] then compared the zinc electrodeposition onto a graphite-resin composite electrode in sulfuric acid with additives. However, previous works mainly focus on the influence of electrolytes, but how the carbon electrode itself affects the zinc deposition process is still not clear. In addition, only the distribution and morphology of coated zinc layer on the surface of carbon-based electrode are investigated, while the zinc distribution inside the porous electrode is unknown. More importantly, the zinc electrodeposition process is still poorly mechanistically understood, which greatly hinders the footsteps to rationally design the zinc negative electrode. Therefore, in order to achieve the uniform distribution of zinc in the negative electrode and promote the commercial applications for ZBFb, seeking an effective method by adopting the bottom-to-up strategy to enhance the ion/mass transport inside the porous electrode and vary the zinc distribution on the carbon fibers is in great need.

In this work, a bottom-to-up strategy is adopted to seek methods to promote the uniform distribution of zinc for ZBFb. Similar as previous works which adopt theoretical and fundamental studies to solve

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