



# Zinc-nickel single flow batteries with improved cycling stability by eliminating zinc accumulation on the negative electrode



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## ABSTRACT

Zinc accumulation is recognized as one of the most critical issues that affect the cycle life of zinc-nickel single flow batteries (ZNBs). In this paper, a novel and very specific method has been proposed to solve the above problem. The side reactions, which are always regarded as negative factors, are promoted at negative side to balance the side reactions at positive side. A novel electrode with high reaction area and well mass transport structure has been designed to facilitate parasitic reactions at negative side. The result shows that zinc accumulation has been successfully solved by balancing positive reactions and negative reactions with this novel electrode, and no zinc accumulates on the negative electrode over 400 cycles. This paper provides an effective way to improve the cycling stability of ZNBs, which is the most troublesome for the commercialization of ZNBs.

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## 1. Introduction

Development of promising energy storage technologies is urgent to fulfill the application needs of renewable energy resources (wind, solar and so on).[1] Flow batteries have attracted intense attention due to their high safety and high efficiency. However, the well developed flow battery systems, such as vanadium-vanadium, polysulfide-bromine and zinc-cerium, are of high cost and low energy density inhibiting their widespread use.[2] A novel flow battery, zinc-nickel single flow battery (ZNB) with low cost and high energy density has a wide variety of applications due to the simple structure (without membranes) and earth abundant raw materials. During charging process, a solid-solid transformation of Ni(OH)<sub>2</sub> to NiOOH will occur at positive side, while zincate will be reduced to metallic zinc at negative side through a liquid-solid transformation. Reverse reactions occur during discharging process.

Significant progresses have been achieved since Cheng and coworkers reported the first advanced ZNB prototype.[3] The power density of ZNB has been improved nearly four time (83 W kg<sup>-1</sup>).[4] A 36 kWh battery system has been demonstrated at the campus of The City College of New York.[5] However, zinc dendrite and zinc accumulation are still two major issues

hindering its commercial application, which can span the electrolyte thickness upon extended cycles, causing a short circuit. Great efforts have been focused on precluding zinc dendrite. The flowing solutions mutate the driving force of zincate from diffusion transport to mixed diffusion and convection transport, and prevent the formation of zinc dendrite to some extent.[6,7] And optimal conditions such as moderate current density,[8,9] electrode substrate [10,11] and flow rate [12] can lead to deposit compact zinc. Additionally, electrolyte additives including organic [13–17] and inorganic ions [15,18] also make it easy to prevent the formation of zinc dendrite. Although the cycling stability and coulombic efficiency (CE) of zinc electrode have been improved, the stability of batteries is still depressed by zinc accumulation in long-term rechargeable cycles. The accumulated zinc becomes nuclei of subsequent deposition and thereby protrudes to the positive electrode, causing a short circuit or peeling off to electrolyte by intensity turbulence eventually. Therefore, zinc accumulation is the most troublesome and determining issue for the commercialization of ZNBs.

As the CE of battery can never reach 100%, it indicates that side reactions exist during the cell operation, including hydrogen evolution and corrosion of zinc at negative side, oxygen evolution and corrosion of nickel electrodes at positive side.[19–23] If the electric charge consumed by side reactions is not equal at two sides, charged species cannot discharge completely at the end of discharging process and will accumulate on one electrode along repeated cycles, while the other electrode discharges deeply. The higher intrinsic kinetic rate of zinc deposition/dissolution

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leads to little electric charge consumed by side reactions than that on the positive electrode. As a result, metallic zinc builds up on the negative electrode progressively and eventually causes cell shorting and massive shedding as mentioned in literatures,[3,12] while nickel positive electrode discharges deeply and decreases the cycling stability. It is not surprising that researchers have used various methods to restore the electrodes and electrolytes to their initial condition. One ideal way to solve this problem is depressing side reactions at positive side to match that at negative side. Various additives such as aluminium, cobalt, and manganese have been reported to reduce the quantity of oxygen evolution by improving the activity of nickel hydroxide electrode or enlarging the overpotential of oxygen evolution.[24–27] But the electric charge consumed by oxygen evolution is still much more than that by hydrogen evolution and zinc corrosion on the negative electrode due to their natural difference of kinetic activation, especially at high operating current density. Regardless of the fact that discharging the cell to low cut-off voltage or mechanically removing residual zinc periodically may alleviate zinc accumulation,[6,12] they will make battery control management more complicated and increase the operating and maintenance costs. Additionally, the accumulating mechanism and quantity of metallic zinc have not been clearly clarified, and very few works have focused on the compatibility of positive and negative electrode reactions in ZNBs.

A key advance in this work is the use of a novel and very specific method to solve zinc accumulation. The side reactions, which are usually considered as negative factors, were accelerated at negative side to balance the reactions at positive side. A novel electrode with well mass transfer and high reaction area was designed to adjust side reactions at negative side. The electric

charge consumed by side reactions was clarified by analyzing the quantity of accumulated zinc and the state of charge of positive material after continuous charge-discharge cycles. This paper provided an effective way to improve the cycling stability of ZNBs by adjusting side reactions to balance positive and negative electrode reactions, which is the main obstacle to realizing its commercialization. This method is also presented to guide the electrode design of other zinc-based flow batteries to achieve long-term cycling stability.

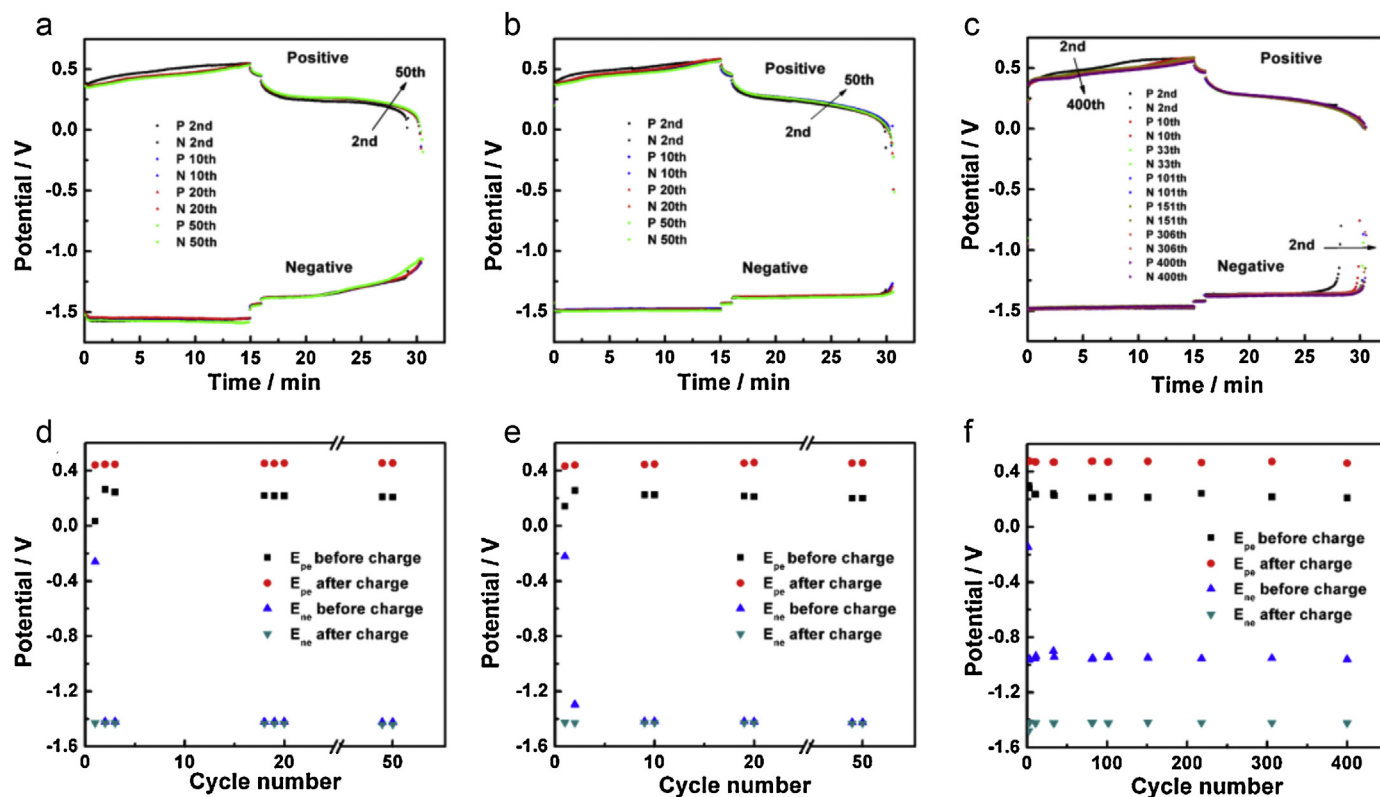
## 2. Experimental Section

### 2.1. Materials and reagents

Electrolytes used in all electrochemical measurements were  $8 \text{ mol dm}^{-3}$  KOH and  $0.4 \text{ mol dm}^{-3}$  ZnO aqueous solutions. All the chemicals were analytical grade and were used without further purification.

### 2.2. Electrochemical measurements

The performance of a single cell was tested by Arbin BT-2000 (Arbin Instruments, America) in a self-designed installation. [28] The positive electrode was a sintered nickel hydroxide ( $30 \times 30 \times 0.7 \text{ mm}$ ,  $25 \text{ mAh cm}^{-2}$ ), while the negative electrode was a piece of nickel sheet (cell A,  $30 \times 30 \times 0.1 \text{ mm}$ ,  $890 \text{ g m}^{-2}$ , Shanghai Jinchang Alloy Co., Ltd., China) or nickel foam (cell B,  $30 \times 30 \times 1 \text{ mm}$  or cell C,  $30 \times 30 \times 2 \text{ mm}$ , 110 PPI,  $420 \text{ g m}^{-2}$ , Changsha Lyrun Material Co., Ltd., China). The electrolyte was circulated through the cell by a pump with the flow rate of  $19 \text{ cm s}^{-1}$ . Cells were charged to  $20 \text{ mAh cm}^{-2}$  and discharged to  $0.8 \text{ V}$  at the current



**Fig. 1.** Electrode potential analysis. a–c, Potentials of positive and negative electrodes during charging and discharging processes in cell A, cell B and cell C (P and N mean positive and negative, respectively). d–f, Equilibrium potentials of positive and negative electrodes before and after charge in the cell A, cell B and cell C ( $E_{pe}$  for equilibrium potential of the positive electrode,  $E_{ne}$  for equilibrium potential of the negative electrode).

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