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Review article

## Rechargeable metal-metal alkaline batteries: Recent advances, current issues and future research strategies



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## HIGHLIGHTS

- Metal-metal alkaline batteries possess long cycle life with a slight capacity decay.
- Additives could effectively protect the electrode materials from deterioration.
- However, the output voltage is limited (>2 V) than other commercial batteries.
- Ni-MH batteries could be a potential candidate for electric vehicles.

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## ABSTRACT

Over the past few decades, remarkable advancement has been attained in the field of rechargeable metal-metal alkaline batteries (RABs). In terms of safety, energy density, charge-discharge capacity, and long-term storage capability, metal-metal RABs (e.g., Ni-Zn, Ni-Fe, Ni-Bi, Ni-MH, Ag-Zn, Co-Zn, Cu-Zn, and Bi-Zn systems) are contemplated as the promising energy storage devices for the applications in electric vehicles (EVs), hybrid EVs, grid-scale energy storage, as well as various implantable and wearable electronic devices. Especially, Ni-MH batteries become competitive with Li-ion batteries for EVs and hybrid EVs applications due to their high tolerance against mechanical abuse, stability under wide temperature ranges, and considerable charge/discharge capacity. Meanwhile, earlier works reviewed only specific topics, so, as a rapidly growing research topic, providing a deep understanding on metal-metal RABs is timely and worthwhile. So, in this work, we discuss the electrochemistry of all metal-metal RABs, then full cell designing with their performance will be discussed thoroughly. Further, issues associated with the existing metal-metal RABs and corresponding improvement approaches will be provided for future advances in high-performance and reliable metal-metal RABs.

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## 1. Introduction

With the ever-rising demands of energy consumption, in parallel, it is a prerequisite to develop highly viable energy storage (e.g., safe, cost-effective, environmentally benign) devices with long-term cycling capability to utilize the electrical energy generated from fossil fuels as well as alternative environmentally friendly energy sources including wind, tidal, and solar [1,2]. Since the commercialization of rechargeable Li-ion batteries (LIBs) in 1991 [3,4], rapid expansion of smart electronic devices has been noticed [5]. To date, with the remarkable improvement of capacity, cell potential, energy density, and cycle life of LIBs, recently, LIBs are most widely used in EVs and HEVs [6,7]. Nevertheless, the flammability of organic electrolytes raises severe safety concerns, and deterioration of electrode active materials triggers serious capacity fading [3]. Furthermore, costly raw materials and complicated manufacturing processes limiting from large-scale applications [8]. Due to the comparable energy density with LIBs, sodium-ion batteries (SIBs) have also emerged during the early 1980s, and have attracted ongoing research attention since 2010 [9]. Despite SIBs being well-thought-out and equally feasible for various stationary applications, however, poor cycle performance and safety concerns still hinder the large-scale applications [10]. On the other hand, redox flow batteries (RFBs) have also been set into several practical applications in different technological areas due to their advantageous merits, nonetheless, low energy efficiency, high self-discharge rates, and complicated cell configuration restrict their widespread applications [11,12].

Large-scale storage systems require high power and energy densities with long term cyclability, cost-effective installation and ease of operation, as well as low toxicity and environmental benignity [13]. Accordingly, aqueous-state batteries have been realized as the most promising candidate that may follow the abovementioned features, and could be utilized for the smart grid as well as large-scale storage systems [8]. Despite lead-acid (Pb-H) aqueous batteries having captured a significant global market share, poor rate capability, short cycle life and toxicity of Pb are the main obstacles that have to be replaced with better systems [14]. So, alkali metals (e.g.,  $\text{Li}^+/\text{Na}^+$ )-based rechargeable aqueous batteries (AMRAs) come into the spotlight, which possess some excellent features including higher ionic conductivity through the environmentally compatible aqueous electrolytes, cost-effect assembly process with ease operation, and higher safety [15]. The overall electrochemistry (insertion/exertion) of AMRAs is similar to the conventional organic electrolyte-based batteries, which have come into the research viewpoint since the emergence of aqueous LIBs in 1994 [16]. However, the electrolysis of water under the battery environment abruptly limits the operating potential window that is stable within  $\sim 1.23$  V leading to the low energy density for the full cell. Further, even though the 'water-in-salt' electrolyte enabled the energy density of about  $200 \text{ W h kg}^{-1}$  electrochemically stable at  $>3.0$  V, nonetheless, the cost for the practical applications could be very high due to the uses of this highly concentrated electrolyte [17,18]. On the other side, the rational employment of aqueous Zn-/Al-ion batteries is restrained by the unwanted  $\text{H}_2$  evolution reaction (HER) and deterioration/dissolution of electrode active materials under an alkaline environment [19,20].

Existing RABs have been developed based on the electrochemistry and fundamentals of primary alkaline batteries, e.g., Ni-Cd, Ni-Zn, Ni-Fe and Cu-Zn systems [21]. These RABs demonstrated a completely different electrochemical mechanism (i.e., insertion/extraction of  $\text{H}^+$  and conversion mechanism) compared to AMRAs (i.e., mainly rocking chair mechanism) [21]. Except for the similar advantageous features including safety, cost-effectiveness, environmental compatibility and low toxicity, RABs possess higher theoretical energy density than that of AMRAs [22]. For practical purposes, for decades, Ni-Fe batteries have been commercialized, though lost a certain market share after the cost minimization of Pb-H batteries [8]. Market share of Ni-Cd batteries still had an up to 50% globally in 2001, thanks to a viable production method and substantial economic benefits in terms of cost per cycle [23].

However, for over two decades, Ni-MH batteries captured a significant amount of market share of Ni-Cd batteries as Cd-free energy storage with no memory effect and low self-discharge rate [24,25]. Furthermore, Ni-MH could be a promising alternative to LIBs in EVs and HEVs due to their excellent withstand ability against high temperature and mechanical abuse, and greater volumetric energy density [26]. Besides, a pouch cell with the specific energy density of  $127 \text{ W h kg}^{-1}$  under the Advanced Research Projects Agency-Energy (ARPA-E) program and projected target to surpass  $148 \text{ W h kg}^{-1}$  [27], along with a current breakthrough demonstrated that Si-based anode could deliver the specific capacity of  $3635 \text{ mA h g}^{-1}$  (about 10 folds of the current  $\text{A}_2\text{B}_7$  alloy) [28], these results could be the landmark for the development of future Ni-MH batteries for various specific technological applications. Moreover, after years of research efforts, Ni-Zn (i.e., cycle life reached over 50,000 cycles) [29], Ni-Co, and Ni-Bi RABs are also successfully implemented, and extensive research works still go on to improve their performances [21,30,31]. Besides, over the years of development, current Co-Zn (no capacity loss after 10,000 cycles with the energy density of  $295.5 \text{ W h kg}^{-1}$  at the peak power density of  $15.4 \text{ kW kg}^{-1}$ ) [32], Bi-Zn and Cu-Zn RABs demonstrated remarkable energy density and cycle life [33,34], which could meet the commercial demands in near future. Therefore, in terms of their growing demands and ongoing research works it is timely needed and worthwhile to provide a comprehensive review on metal-metal RABs.

Prior to this work, reviews related to the RABs are discussed by several researchers. For instance, Jindra et al. [35,36] reviewed the research progress of Ni-Zn RABs during the period of 1991–1998. Shukla et al. [21] discussed the electrochemistry of Ni-Cd, Ni-MH, Ni-Fe, Ni-Zn, and Ni- $\text{H}_2$  batteries in 2001. In 2007, Fetcenko's group reviewed the advancement in electrode components for Ni-MH batteries [37], meanwhile, in 2016, Young et al. [38] deeply analyzed the capacity deterioration mechanism of Ni-MH batteries. In 2017, Aqueous batteries for grid-scale energy storage systems were reviewed by Posada's group. [8], in which Ni-MH and Ni-Fe batteries are also briefly described. Lai et al. [39] analyzed the electrode materials and electrolytes for the Ni-Zn RABs. Recently, Huang et al. [22] systematically summarized the rational designing of electrode materials for the RABs with a brief highlight on cell performances. Recently, Shang et al. [40] summarizes the cell performances of Zn-based rechargeable alkaline batteries. Even though earlier reviews are attentive to topical reviews with specific aspects, no comprehensive review has not yet focused on the overall spectrum of rechargeable alkaline batteries.

In this regard, this work will systematically discuss the electrochemistry of all metal-metal RABs along with the progress in high-performance cell designing. Then, a deep understanding of issues and corresponding improvement strategies associated with current metal-metal RABs are also provided as the future directions. Expectantly, this review will be a direction for future development in the field of high-performance metal-metal rechargeable alkaline batteries.

## 2. Fundamentals and electrochemistry of metal-metal RABs

### 2.1. Electrochemistry of Ni-based RABs

(i) **Ni-Cd RABs:** Early 1899s, the Ni-Cd battery (NCB) was first explored by Waldemar Junger, then Neumann (1946) first assembled its sealed form. A typical NCB is composed of  $\text{NiOOH}$ , or  $\text{NiO}_2$  as the positive electrode materials, KOH as the electrolyte, and metallic Cd used as the negative electrode material. During the discharge process, **reaction 1** and **reaction 2** take place in the positive and negative electrode, respectively [41]. Charge process is the reverse reaction of the discharge reaction, following **reaction 3** described the overall reversible discharge-charge process. However, it is well known that the positive electrode is less readily charged than the negative electrode resulting in  $\text{O}_2$  evolving from the positive electrode via the following **reaction 4**, when the battery reached the