

Advancements and Challenges in Aqueous Zinc-Ion Batteries: Mechanisms, Materials, Electrolytes, and Interface Engineering

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Abstract. Rechargeable aqueous zinc-ion batteries hold significant promise as a safer and more environmentally friendly alternative to conventional lithium-ion batteries for energy storage applications. This paper provides a comprehensive overview of the charge storage mechanism, electrode materials, electrolyte considerations, and electrode interface challenges in aqueous zinc-ion batteries. The complex charge storage mechanism involving zinc ion movement between the cathode and zinc metal anode is discussed in detail. Anode and cathode material selections and design strategies are explored, highlighting their pivotal roles in determining battery performance, energy density, cycle lifespan, and stability. The critical influence of electrolyte choice and design on battery performance is also elucidated, emphasizing the interplay between high ionic conductivity, stability, temperature range, and cost. The paper further delves into the challenges and advancements related to optimizing the electrode interface, addressing issues such as dendrite growth, electrode passivation, and side reactions. Finally, future research directions and strategies to overcome current limitations are outlined, underscoring the potential of aqueous zinc-ion batteries as a viable and sustainable energy storage solution.

Keywords: Zinc-ion batteries, electrolyte engineering, electrode engineering, electrode-electrolyte engineering.

1. Introduction

The global pursuit of sustainable and high-performance energy storage technologies has driven intense research into more advanced battery systems. Aqueous zinc-ion batteries have gained attention as a viable substitute for conventional lithium-ion batteries due to their intrinsic safety, cost efficiency, and environmentally friendly nature [1]. These batteries utilize zinc as the anode material and water-based electrolytes, addressing concerns associated with the flammability and environmental impact of organic electrolytes commonly used in lithium-ion batteries. In order to enhance the efficiency of these batteries and address current obstacles, it is imperative to have a thorough comprehension of their charge storage mechanisms, electrode materials, electrolyte selections, and electrode interfaces [2].

The objective of this work is to present a thorough examination of the key factors that impact the efficiency and effectiveness of aqueous zinc-ion batteries. It delves into the intricate charge storage mechanism involving the movement of zinc ions between the cathode and zinc metal anode, providing insights into the processes of insertion, extraction, co-insertion, and displacement. The selection and design of electrode materials are explored, emphasizing strategies to enhance energy density, cycle lifespan, and stability. Additionally, the importance of electrolyte choice and design is highlighted, considering factors such as ionic conductivity, stability, temperature range, and cost efficiency.

One of the key challenges in aqueous zinc-ion batteries lies in optimizing the electrode interfaces to mitigate issues like dendrite growth, electrode passivation, and undesirable side reactions. This paper discusses the ongoing research efforts in electrode interface engineering, including the development of 3D current collectors and protective layers. Moreover, it presents recent advancements in electrolyte formulations to address issues related to zinc anode corrosion and hydrogen evolution reactions.

By consolidating current knowledge and identifying research gaps, this paper aims to facilitate a deeper understanding of aqueous zinc-ion batteries and inspire further innovation in materials, electrolytes, and interface engineering. The increasing need for energy storage systems that are both safe and sustainable, while also being efficient, has led to a notable interest in aqueous zinc-ion batteries. These batteries show great potential in fulfilling these criteria and playing a crucial role in the development of the energy sector.

2. Principles of zinc-ion aqueous batteries

The charge storage mechanism of a normal battery is simpler than that of a zinc-ion battery, and it offers a possible solution to some issues or worries. Worries are high cost of manufacturing and safety risk (problems associated with inflammability). The flow of zinc ions between the cathode and the zinc metal anode is what drives this mechanism; the cathode can release and adopt zinc ions, and the zinc anode undergoes reversible reaction, stripping, and plating. The procedure may be broken down into six sections for additional clarity.: (1) Zn^{2+} insertion/extraction, during the discharging process, zinc at the anode dissolves into the electrolyte and forms Zn^{2+} , and then Zn^{2+} gradually permeates the concentration gradient before inserting into the cathode; during charging, to keep the process' charge balance, Zn^{2+} exits the cathode and releases electrons. (2) H^+/Zn^{2+} co-insertion/extraction, H^+ and Zn^{2+} inserted into the cathode. (3) H^+ insertion/extraction, the water dissociates to release H^+ and OH^- . H^+ inserts to the cathode first due to its quicker kinetics. As H^+ is used, more OH^- is produced, which interacts with the electrolyte to form zinc salt such as $Zn_4(OH)_6SO_4 \cdot nH_2O$. (4) displacement/intercalation mechanism, which involves Zn^{2+} replacement of cathode sites to form a new phase. (5) dissolution/deposition mechanism, which takes place concurrently with H^+ / Zn^{2+} co-insertion for the MnO_2 cathode and MnO_2 deposit on the cathode's surface. (6) conversion, which excludes the insertion or extraction of H^+ or Zn^{2+} [3].

An aqueous battery comprises several components: electrode (anode and cathode) and electrolyte. The anode possesses high stability due to the fact that zinc metal exhibits balanced kinetics and greater stability in aqueous conditions than other metals. Most of the group 1 metals are unstable in water, and Al has a lower redox potential than other electrolytes, making it challenging to be plated. But zinc anode continues to face difficulties, including dendrite growth and hydrogen evolution, which result in low reversibility and battery failure. Interfacial design, which includes the zinc-host interface, allows for the anode to enable a homogeneous electric field and Zn^{2+} ion distribution and thus realizes zinc plating/stripping. For the cathode, materials mainly include MnO_2 and V_2O_5 . To optimize the cathode and facilitate zinc ions/ Zn^{2+} , conductive layer coating and guest species pre-intercalation have been improved and done [3]. For zinc ion batteries, an aqueous electrolyte with neutral pH water is used because compared to combustible organic electrolytes, it is harmless and much safer., such as acetonitrile and propylene carbonate [4]. Occasionally, the addition is used to address problems caused by dendrite development in zinc metal, which leads to a lower efficiency and unstable cycling performance.

3. Electrode materials's impact on zinc-air batteries

The selection and design of anode and cathode materials have a paramount effect on the performance of water batteries. When selecting and designing the anode and cathode materials for aqueous batteries, various factors interplay and exert a direct influence on battery performance. Firstly, the energy density and voltage platform of the materials directly determines the battery's energy storage capacity and level of electrical output. Simultaneously, the cycle lifespan and stability of the materials impact the battery's operational longevity and stability, which are crucial for long-term use and applications. The efficiency of charge and discharge, stemming from the materials, directly affects the battery's energy utilization efficiency, thereby influencing its performance and economic viability. Furthermore, the cost and availability of the materials, along with compatibility with the

electrolyte, are critical factors that must be considered, as they determine the feasibility of battery manufacturing and commercial prospects. Ultimately, the safety of the materials to make cathode and anode and interface engineering directly affects the battery's operational safety and electrochemical performance.

The selection of positive and negative electrode materials plays a critical role in the design and development of aqueous batteries. The positive electrode material is responsible for energy release, while the negative electrode material stores and facilitates the charge-discharge cycle. From common lithium-ion batteries to sodium-ion batteries, the selection and design of positive and negative electrode materials directly impact battery performance, lifespan, and sustainability. Therefore, gaining an in-depth understanding of the characteristics of different materials and their applications in aqueous batteries is of paramount importance in the development of efficient and reliable battery technologies. In the following paragraphs, we will focus on exploring the positive and negative electrode materials of aqueous batteries and their pivotal roles in battery performance.

The cathode material in aqueous batteries plays a pivotal role in energy storage and release. Among commonly used materials, vanadium oxide (V_2O_5) stands out due to its high capacity and reversible electrochemical reactions, enabling efficient energy conversion. However, vanadium oxide has certain drawbacks, including higher material cost and rapid capacity degradation. Another prevalent positive electrode material is manganese dioxide (MnO_2), known for its excellent electrochemical activity and relatively lower cost. Nonetheless, its capacity is relatively lower, which may necessitate more frequent charge-discharge cycles.

The choice of cathode significantly influences energy storage and battery stability in aqueous batteries. Sodium metal has garnered attention as a negative electrode material, despite its lower energy storage density. The potential suitability of sodium for large-scale energy storage is attributed to its abundance and cost-effectiveness. However, issues like polarization and electrolyte corrosion might arise during cycling, posing safety concerns. On the other hand, sodium titanate is widely employed as a negative electrode material due to its benefits in terms of cycle life and stability. However, its relatively lower energy density might limit its application scope. Metal hydrides as negative electrode materials enable hydrogen adsorption and release, though challenges lie in material design and engineering complexities.

4. Electrolyte engineering of aqueous batteries

Positively charged ions are transported between the cathode and anode by the electrolyte, which is an essential part of the battery. During the reaction, the electrolyte puts the chemicals needed in contact with the anode and cathode; therefore, stored energy is converted into usable electrical energy. In the market, there are already many different electrolytes, and different electrolytes consist of different soluble salts, acids, or other bases; electrolytes can also be polymers, solid ceramics, molten salts, or water. To find an appropriate electrolyte, lots of aspects should be considered. Electrolytes used in batteries are often intended to have the following properties: (1) higher level of ionic conductivity; (2) good stability while interacting with electrodes; (3) broad temperature application; and (4) low cost[5]. Lead acid batteries use highly corrosive diluted sulfuric acid as their electrolyte. While charging a lead-acid battery, lead oxide would form on the positive plate, causing the electrolyte to become denser. The process reverses during the recharging process, causing the battery to reinstate. The issue is that some oxidation would remain, gradually weakening the battery. The most common one-- the lithium-ion battery, the battery uses liquid, gel, or polymer electrolytes. The discharge and charge efficiency is relatively high, and the battery is long-lasting and requires no active maintenance. Still, the liquid version is moderately flammable, and the battery might easily overheat during discharging and recharging. Compared to other forms of electrolytes, water is relatively safer, less flammable, and more environmentally friendly. The use of this electrolyte also offers competitiveness in many aspects: (1) lower cost; (2) high tolerance against electrical and mechanical mishandling, including bending, washing, and cutting. But water as electrolyte is cursed

with low energy density and less efficiency. Nowadays, to improve that, scientists have done research, and many efforts have been made to reformulate the electrolyte. While there isn't a single ideal electrolyte composition, increasing the electrolyte concentration will undoubtedly increase the solid electrolyte stability of interphase and widen the electrochemical stability window[6]. It also produces ion pairs, however, which raises viscosity. For aqueous zinc-ion batteries, because zinc in aqueous electrolytes is thermodynamically unstable, prolonged operation results in Zn metal corrosion at the anode and substantial hydrogen buildup, which poses a major risk to battery safety. To counter that, researchers developed internal mechanisms for electrolyte regeneration that regulate the synthesis of H₂ and successfully stifle the cell's tendency toward electrolyte depletion and pressure buildup[7]. A large number of scientists and researchers attach importance to the aqueous battery, instead of some ordinary one, because the aqueous battery is the future and it is long-lasting and safer.

5. Electrolyte-electrode engineering

Rechargeable aqueous batteries based on zinc have attracted significant attention due to their high theoretical capacity, environmentally favorable characteristics, and remarkable cost-effectiveness. Notably, the remarkable potential of these batteries is further accentuated by the utilization of alkaline electrolytes, which allows for a high operating voltage. Nevertheless, transitioning rechargeable alkaline zinc-based batteries to commercial platforms encounters considerable hurdles, predominantly stemming from the restricted reversibility associated with zinc electrodes.

Central concerns encompass dendritic growth, electrode passivation, morphological alterations, and undesirable side reactions, all of which exert a significant influence on the battery's discharge capacity, Coulombic efficiency, and cyclic stability. These challenges are intrinsically linked to the characteristics at the electrode interface, particularly revolving around the electron and ion transfer dynamics present at this juncture.

In aqueous batteries, the electrode interface is a crucial component responsible for the transport of current and the conduction of electrochemical reactions [8]. The performance and optimization of the battery have a direct impact on its overall performance and stability. The improvement of the electrode interface, including the selection of materials with good electrical conductivity and chemical stability, and the fine design of the micro- and nanostructure of the electrode to optimize the reaction kinetics and conductivity of the interface, are key steps that cannot be ignored. However, there are also some common problems at the electrode interface, such as interfacial impedance and side reactions, which may increase the inner resistance of the battery and make it less efficient. To address these issues, researchers may need to improve the stability of the electrolyte or introduce a stable interfacial layer.

Extensive efforts are being made to enhance the battery performance by optimizing the chemistry at the zinc electrode interface. This includes strategies like constructing 3D hosts with high surface areas, designing zinc sponge configurations, introducing electrode additives, establishing protective layers, optimizing electrolyte compositions, and developing solid-state electrolytes to limit side reactions and Zn (OH)₄²⁻ diffusion. Despite significant advancements, further research is urgently required to address persistent challenges and meet the demands of next-generation power sources [9]. Further studies are crucial in understanding the interface chemistry of batteries, particularly focusing on dendrite growth and passivation during operation. It's vital to delve deeper into the ongoing zinc dissolution and deposition cycles, including investigating the nuances of 3D zinc powder electrodes, which have longer ion diffusion pathways and inconsistent electronic transitions. Enhanced attention towards the mechanisms of electrokinetic mass transportation and comprehensive analysis of electrolyte degradation processes, employing sophisticated in-situ and ex-situ characterisation methodologies alongside theoretical computations, will be essential in fostering the development of more efficient and reliable zinc batteries. Further, to enhance the performance and rechargeability of zinc-based batteries, it is imperative to develop high-performance electrodes and electrolytes with a focus on cycling stability and coulombic efficiency. While advancements have been made in

designing 3D current collectors to mitigate dendrite growth, it's vital to further optimize zinc loading and discharge capacity. Exploring new avenues such as water-in-salt electrolytes and incorporating functional groups in semi-solid electrolytes could potentially curb existing challenges and foster better ion transport performance. Additionally, establishing standardized assessment methods is urgently needed to accurately evaluate various modification strategies and fabricated batteries, considering factors such as specific energy, power densities, and testing depth of discharge (DOD) [10]. This will facilitate a more precise evaluation of the batteries' durability and promote their practical applications.

6. Conclusion

Although aqueous zinc-ion battery is safe and efficient, several issues still need to be addressed: (1) Severe electrostatic interaction, the interaction between the cathode (made of MnO₂) and Zn²⁺ causes problems. Compared with lithium-ion, Zn²⁺ has lower diffusion kinetics. (2) Desolvation penalty: Instead of being present in the electrolyte as bare Zn²⁺, Zn²⁺ is present in the hydrated form with solvation sheath. Hydrated Zn²⁺ must desolvate at the cathode-electrolyte interface after being intercalated into the cathode. There will ultimately be a desolvation penalty due to the increased difficulty of desolvation brought on by the contact between solvated Zn²⁺ and the solvation sheath. The design of the whole aqueous zinc-ion battery is intended to address those problems in different aspects that have a significant impact on this kind of battery and its efficiency. For the cathode, the material directly determines the storage capacity of the battery. Thus, it is pivotal. To enhance a material's qualities, defect engineering and some strategies are done, and the unstable crystal structure is improved; eventually, cycling performance is improved. Regarding zinc anode, dendrite formation is a big problem of previous zinc-ion batteries. In order to solve this issue, the design for uniform Zn²⁺ nucleation is predicated on a number of factors, including lowering the local current density at the contact between the host and zinc, homogenizing the electric field during zinc deposition, and reducing the gradient of ion concentration. For electrolytes, the layout provides a clear route between the cathode and zinc anode for the zinc ion diffusion, the regulation of water decomposition widens the voltage window, and the stability of electrodes is improved. Some problems: cathode material dissolution and zinc anode corrosion are improved by adjusting concentration, applying electrolyte gel, and adding additive. To conclude, aqueous zinc-ion battery is a promising project that can replace the most common lithium-ion battery, and it's cheaper, environmentally friendly, and highly safe. But still, the zinc-ion battery is facing issues like cathode dissolution. Thus, much work and research should be done on those aspects and problems.

Author contributions

The authors have equal contributions and the names are listed in alphabetical order.

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