Mechanism and Optimizations of Aqueous Zinc-ion Battery

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Abstract. Nowadays, more and more problems of environmental deterioration make the development of environmentally friendly energy imminent. For the requirements of low cost, high security, and high efficiency, aqueous Zn-ion batteries are a promising trend for research. In this paper, the mechanism of aqueous Zn-ion batteries will be illustrated in three aspects: cathode materials, zinc anode, and electrolytes. Moreover, possible alternatives for each part of the batteries will be comprehensively illustrated in detail. In addition, the challenges such as short capacity, zinc dendrites, and corrosion and passivation will be analyzed and the possible corresponding solutions will be proposed. Finally, a concise conclusion will be given.

Keywords: Aqueous Zinc-ion Battery, Cathode material, Zinc anode, Electrolyte.

1. Introduction

With the deterioration of the conflict between energy and the environment, people never stop seeking new environmentally friendly energy. Many forms of renewable energy, such as solar, hydro, and wind, are substitutions for petroleum, even though they are far less efficient than petroleum. In the field of batteries, most electric vehicles are currently using Li-ion batteries, which is characterized by resource shortness, high cost, safety concern, etc. Although there are Na-ion and K-ion batteries that are more economical compared to Li-ion batteries, they are all using organic electrolytes which are flammable, and thus the potential safety hazards remain. Opposite to the organic electrolyte, aqueous batteries possess high security, low cost, and easy-to-assemble. Lead battery, NI-MH battery, and vanadium redox battery are epitomes of aqueous battery, applied for large-scale energy storage. But environmental pollution is still potent due to the corrosion of electrolytes and toxins of these aqueous batteries [1].

Among many possible materials for the development of new batteries, zinc is considered an ideal cathode due to its inexpensiveness, innocuousness, low redox potential, and stability in aqueous solutions. In the aqueous Zn-ion battery, Zn produces Zn2+ without by-products such as zinc hydroxide and zinc oxide during discharging. The large amount of Zn2+ rapidly deposits and dissolves in the cathode, and they can be reversibly embedded and removed from the anode α-MnO2. Based on its reaction mechanism, aqueous Zn-ion batteries manifest high specific capacity, high power, high security, low cost, and other advantages. However, there are still many unsolved problems in the aspects of the development of electrodes, electrolytes, and the entire battery system. This paper summarizes the recent research progress on aqueous Zn-ion batteries with neutral or slightly acidic electrolytes, from the materials for cathode and zinc anode to electrolyte, and analyzes the main difficulties and corresponding resolutions. And in the end, this paper provides some ideas for the optimizations of aqueous Zn-ion batteries.

2. Background and development of zinc batteries

The development of zinc batteries has been around for a while. In 1836, Daniel and Besenhard invented Copper-zinc batteries and successfully applied them to the signal lamp of the railroad. In 1869, zinc-air batteries arose and achieved commercial application. Afterward, in about 1970, we had the arrival of rechargeable Zn-MnO2 batteries, using alkaline electrolytes [2]. Usually, in alkaline zinc batteries, energy is stored by conversion reaction, in which the anode and cathode have the proclivity of irreversible side reactions, causing a decrease in coulombic efficiency and cycle

performance. In 1988, a new rechargeable aqueous Zn-MnO2 battery has been invented, which replaces alkaline electrolytes with slightly acidic electrolytes (ZnSO4). In recent years, rechargeable zinc batteries based on neutral or slightly acidic electrolytes, characterized by high security, low cost, high capacity, and environmental affinity, sparked researchers' interest again. In 2012, the introduction of Xu to weakly acidic ZnSO4 and Zn (NO)3 aqueous electrolytes made the rechargeable aqueous Zn-ion battery first plausible. Rechargeable aqueous Zn-ion battery in MgSO4.ZnSO4 hybrid electrolytes was shown in figure 1.

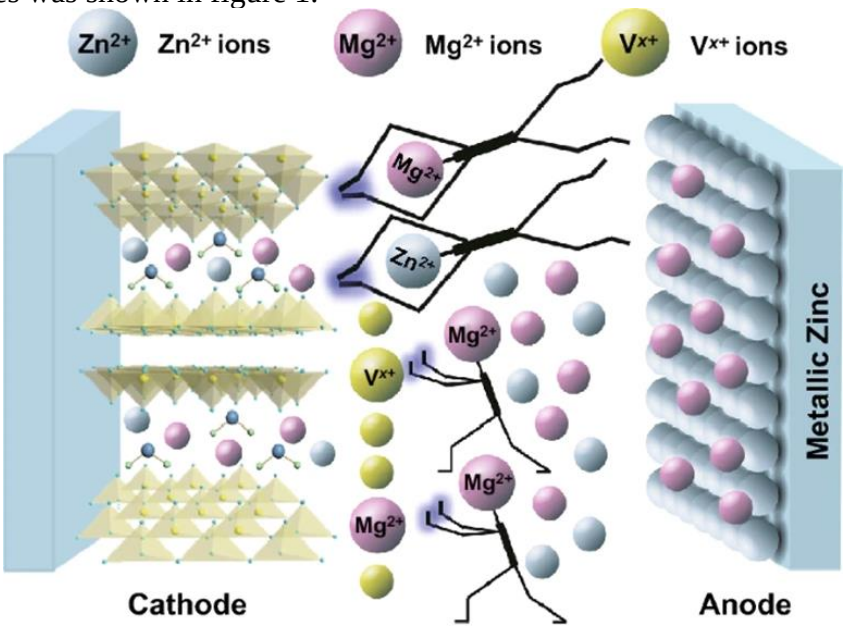


Figure 1. Rechargeable aqueous Zn-ion battery in MgSO4.ZnSO4 hybrid electrolytes

3. The cathode material

Zn ions, which have high charge density, have much stronger electrostatic interaction with the crystal structure of cathode materials than Li ions do, so it is a great challenge to find a suitable Zn host material. Vanadium oxides, Prussian Blue Analogues, and polyanionic compounds are considered possible materials for the cathode.

3.1. Vanadium-based compound

Vanadium has abundant valence states and coordination configurations. And vanadium-based compounds are usually layered or tunneled, which is conducive to the migration of ions. From the crystal structure, V2O5 is an unstable single layer made by the connection of VO5[3]. When it is used for making cathode, the repetitive embedding and unplugging will cause structural collapse. Compared with V2O5, tunneled VO2 and V6O13 can provide channels for ion diffusion and maintain a stable structure during the cycle[4]. V6O13 consists of alternating single and double layers of vanadium oxide, in which there are a mixed valence of V4+ and V5+ promoting ion storage with more active sites.

However, During the process of charging and discharging, the serious structural changes of vanadium oxides hinder its further development. But the introduction of metal ions, water, and organic molecules, and organolithium molecules into vanadium-based materials is conducive to the alleviation of structural collapse, functions as a pillar, stabilizes the main structure, and expands the ion diffusion channel, thus improving its comprehensive electrochemical performance.

Even though vanadium-based materials show high capacity and excellent cycling stability, vanadium dissolution during the cycling process and poor reaction kinetics, casued by strong interaction between Zn2+ and vanadium-based materials, results in poor cycling performance at small current densities, which need to be further optimized.

3.2. Polyanionic compounds

In 2016, the study of making Na2V2(PO4)3 the cathode material for rechargeable aqueous Zn-ion batteries has been initiated. During the first charge, Na+ strips from Na3V2(PO4)3, abling the reversive storage of Zn2+, and there is a structural evolution between NaV2(PO4)3 and ZnNaV2(PO4)3. Fluoride-doped Na3V2(PO4)2F3 can also be exerted on aqueous Zn-ion batteries as cathodes. In Na3V2(PO4)2F3 the fluorine is strongly ionic, giving a high operating voltage, high energy density, and excellent cycling performance to Na3V2(PO4)2F3[5].
However, despite its relatively high operating voltage and remarkable cycling stability, due to the large mass of the anion group of polyanionic compounds, the battery lacks capacity, requiring more optimizations.

3.3. Prussian Blue Analogues

Prussian Blue Analogues (PBAs) are usually present in cubic structures, having a 3D open frame and large ion embedding sites, allowing ions to be quickly embedded and released. Such a special structure determines their fast charging and discharging ability, thus PBAs are seen to be one of the potential cathode materials[6]. There are some crucial characteristics of Zn-ion batteries using PBAs as cathode: (1) the large and stable 3D ion channels enable Zn2+ quickly embed and release, and the structure stability remains good. (2) High charging and discharging platform. (3) Some PBAs can provide two types of electrochemically active sites with high specific capacity. (4) low cost, environmentally friendly, and easy to prepare.

Despite their high output voltage, PBAs have many defects when used as cathodes, such as low capacity (lower than 100 mAh/g), short lifetime (lower than 1000 cycles), and poor magnification capability.

4. Zinc anode

Within so many possible anode materials for batteries, zinc draws lots of attention from researchers due to its abundance, low cost, environmentally friendly, low redox potential, large theoretical capacity, and great corrosion resistance in aqueous electrolytes. However, there are also several fatal problems of zinc anode preventing the practical applications of Zn-ion batteries [7]. This part will illustrate all the problems of zinc anodes and provide extant solutions and optimizations.

4.1. Challenges of zinc anode

4.1.1. Zinc dendrite

The formation of zinc dendrite is caused by the unevenly distributed electric field on the surface of the anode resulting in the uneven deposition of zinc ions on the surface of the anode. In detail, zinc ions have the proclivity to deposit on energetically favorable charge transfer sites on the anode, presenting in small humps at the beginning. In order to lower the interface energy, other zinc ions are also apt to deposit on these humps, gradually growing and forming the preliminary dendrites. And this will incur an exaggeration of the unevenly distributed electric field, increasing the formation of dendrites which can cause a lower capacity and short circuits [8].

4.1.2. Corrosion and passivation

The corrosion and passivation of zinc anodes will decrease the utilization rate of the anode, affecting the electrochemical performance of the battery. The corrosion of zinc in aqueous electrolytes is mainly two types: self-corrosion and electrochemical corrosion. In alkaline electrolytes, for the lower redox potential of ZnO and Zn than the hydrogen evolution potential, self-corrosion is prevalent. But in neutral and slightly acid electrolytes, self-corrosion is relatively uncommon. Thus electrochemical corrosion is the overriding challenge [9].

In the process of discharge, the zinc anode is experiencing a transformation from Zn0 to Zn2+. A small range of electrolytes near the anode has a large density of zinc ions and net positive charges

somewhere, facilitating complexation reaction of OH- and other anions in the electrolytes and forming electrochemical corrosion products, such as ZnSO4, Zn(OH)2, and ZnO. Due to their low solubility and conductivity, when these corrosion by-products achieve supersaturation they will precipitate on the surface of the anode, inevitably slowing the transmission of electrons and ions. Besides, these corrosion and passivation are irreversible and cause depletion of electrolytes.

4.1.3. Hydrogen evolution

Hydrogen evolution and zinc deposition are a pair of competitive reactions. It has a huge influence on the anode, reducing the coulombic efficiency of precipitations and stripping and resulting in a constant loss of zinc on the anode. In order to ensure the cycle of the battery, it requires far more zinc than theoretically needed, which is one of the most important reasons why current aqueous Zn-ion batteries are using excessive zinc [10]. Furthermore, the generation of gas has a terrible influence on the button battery who has a closed battery system, causing an increase in the pressure in the battery and finally leading to the crack and destruction of the battery.

Also, hydrogen evolution will increase the pH in some parts of the electrolytes, which is an important provenance for OH-. With the increase of the pH, there is a decrease in the critical potential of hydrogen evolution. And thus, hydrogen evolution is easier to present in acid environments than in alkaline environments [11].

4.2. Optimization of zinc anode

The surface modification of zinc can reduce the formation of zinc dendrites, increasing the hydrogen evolution potential and restraining the generation of by-products. A layer of TiO2, deposited on the zinc sheet by the atomic layer deposition method, can remarkably reduce the corrosion, resulting in less generation of gas and Zn(OH)2. The decrease in the gas increases the effective contact area between electrolytes and zinc anode, so the coulombic efficiency increases [12].

On the other side, increasing the specific surface area of the zinc anode can reduce the overpotential of zinc deposition, minimizing the formation of zinc dendrites and passivation. Zinc anode designed in a 3D porous spongy structure has a high specific surface area, which is conducive to the interfacial contact between electrolytes and zinc anode and abridging the distance for ion diffusion, increasing the utilization of zinc anode. With such a porous structure, there is no obvious zinc dendrites formation after 54000 cycles under the condition of 40% discharge depth [13].

5. Electrolytes optimization

Aqueous electrolytes are favored by their low cost, high-level security, and high ionic conductivity, but due to the existence of a large amount of active water, such problems as dissolution of the cathode, zinc dendrites, corrosion, and passivation are easy to occur. Moreover, in aqueous electrolytes, the voltage window is too narrow, only 1.23 V, to reach a high operating voltage. Therefore, in order to restrain the side reaction, alleviate the change of cathode, and guarantee electrochemical performance, the optimization of electrolytes of an aqueous Zn-ion battery is crucial.

5.1. Electrolyte composition optimization

In the electrolytes, except zinc ions, the characteristics of different anions and their compatibility with the anode and cathode can affect the performance of the battery. In ZnSO4 electrolytes, batteries have better electrochemical performance because SO4^2- ions have higher stability and compatibility to the anode and cathode than CL-, CH3COO-, and NO3-, giving it better reversibility and faster deposition and dissolution of zinc ions [14].

To the aspect of zinc anode, it can optimize the location of deposition of zinc ions by some additives, inhibiting dendrite. For example, the influx of Na+ into ZnSO4 electrolytes can generate a positively charged electrostatic shielding, reducing the generation of zinc dendrites through the electrostatic shielding effect.

Moreover, zinc exhibits more stability in the organic solvent than in water electrolytes, thus the addition of organic solvent into aqueous electrolytes can stabilize the zinc anode reducing side reactions. When adding triethyl phosphate (TEP) into aqueous electrolytes, the surface of the zinc anode is prone to the deposition of Zn3(PO4)2 rather than ZnO, and the former can be seen as a molecular polymer for the nucleation of zinc to form a porous structure, restraining zinc dendrites[15].

5.2. Solvent optimization

Not only can improve the performance of the battery by modifying the composition of electrolytes, but also by changing the concentration of electrolytes. With the increase in the concentration of Zn(CF3SO3)2 electrolytes from 1 mol/L to 3 mol/L, the coulombic efficiency increases by 100%. Meanwhile, a high concentration can reduce the amount of active water, reducing side reactions with water. However, while increasing in concentration and viscosity, the conductivity will decrease, then affecting the rate performance [16].

Recently, ultra-high concentration electrolytes (water-in-salt) have grabbed lots attention of from researchers. In the electrolyte mixed by 1 mol/L Zn(TFSL)2 and 2 mol/L LiTFSI, due to the huge amount of anions of TFSI and the lack of water molecules, Zn2+ has more tendency to act with TFSI^-, forming a new solvated structure (Zn-TFSI)+ instead of (Zn-(H2O)6)2+. Such a structure can eliminate the formation of zinc dendrites and inhibit side reactions, making the battery have nearly 100% coulombic efficiency. But the drawback of Zn(TFSI)2 and LiTFSI is their high price, which makes it not possible for a large-scale application [17].

5.3. All-solid-state electrolyte

Since there are not any free-water molecules in all-solid-state electrolytes, side reactions with water in the battery are not possible to happen. But all-solid-state electrolytes usually have a very low ionic conductivity, which is hard to meet the usage of batteries. However, in recent years. The PVDF-HFP-PMMA all-solid-state polymer electrolyte has been invented, which has high ionic conductivity (1.69*10^-2. S/cm), making it possible for all-solid-state electrolytes to have high reversibility, no dendrite, and no side reaction during the processes of zinc deposition [18].

6. Conclusion

For vanadium-based compounds, they have the advantage of allowing more efficient ion migrations, but their unstable structure is the main problem circumventing further development. However, the introduction of metal ions, water molecules, organic molecules, and organolithium molecules can alleviate structure corruption. Polyanionic compounds are marked by their high operating voltage and good cycling performance. But such batteries lack capacity due to the large mass of the anion group of polyanionic compounds. In order to meet quick embedding and releasing of ions and high charging and discharging platform, PBAs are one of the best choices. However, the key problem to solve is low capacity and short lifetime when used as cathodes.

Zinc dendrites are one of the most challenging problems. The modification of the zinc surface can improve the evolution potential, reducing the generation of by-products. Except for the surface modification, the deposition of a layer of TiO2 on a zinc sheet can reduce corrosion, improving coulombic efficiency.

The modification of electrolytes should pay attention to the compatibility with the cathode and anode materials, since ions in electrolytes can influence the redox potential and electrochemical reaction rate. Adding electrolyte additives can not only stabilize the cathode and anode but also restrict the cathode dissolution, anode corrosion, and the generation of zinc dendrites.

Compared with Li batteries, even though the energy density of water-based Zn-ion batteries is quite inadequate, their characteristics of low cost and long lifetime make them valuable for further development. Furthermore, water-based Zn-ion batteries can also be the substitution for lead-acid batteries which often exert detrimental effects on the environment.

References

[1] Li, L., Kim, S., Wang, W., Vijayakumar, M., Nie, Z., Chen, B., Zhang, J., Xia, G., Hu, J., Graff, G., Liu, J., & Yang, Z. (2011, March 11). A Stable Vanadium Redox-Flow Battery with High Energy Density for Large-Scale Energy Storage. Advanced Energy Materials, 1(3), 394–400.

[2] Cheng, F. Y., Chen, J., Gou, X. L., & Shen, P. W. (2005, November 18). High-Power Alkaline Zn-MnO2 Batteries Using γ-MnO2 Nanowires/Nanotubes and Electrolytic Zinc Powder. Advanced Materials, 17(22), 2753–2756.

[3] Zhou, J., Shan, L., Wu, Z., Guo, X., Fang, G., & Liang, S. (2018). Investigation of V2O5 as a low-cost rechargeable aqueous zinc ion battery cathode. Chemical Communications, 54(35), 4457–4460.

[4] Liu, Y., Zhang, D., Jing, L. I., Tingting, L. I., Xie, J., & Hongfang, S. U., et al. (2015). Preparation and electrochemical performances of the v6o13/vo2 for mg rechargeable battery as cathode material. Journal of Functional Materials.

[5] Hu, P., Zou, Z., Sun, X., Wang, D., Ma, J., Kong, Q., Xiao, D., Gu, L., Zhou, X., Zhao, J., Dong, S., He, B., Avdeev, M., Shi, S., Cui, G., & Chen, L. (2020, April). Uncovering the Potential of M1‐Site‐Activated NASICON Cathodes for Zn‐Ion Batteries. Advanced Materials, 32(14), 1907526.

[6] Nie, P., Shen, L., Luo, H., Ding, B., Xu, G., Wang, J., & Zhang, X. (2014). Prussian blue analogues: a new class of anode materials for lithium-ion batteries. J. Mater. Chem. A, 2(16), 5852–5857.

[7] Yang, H. (2004, March 29). Improved discharge capacity and suppressed surface passivation of zinc anode in dilute alkaline solution using surfactant additives. Journal of Power Sources, 128(1), 97–101.

[8] Kan, J., Xue, H., & Mu, S. (1998, July). Effect of inhibitors on Zn-dendrite formation for zinc-polyaniline secondary battery. Journal of Power Sources, 74(1), 113–116.

[9] Sziráki, L., Cziráki, Geröcs, I., Vértesy, Z., & Kiss, L. (1998, January). A kinetic model of the spontaneous passivation and corrosion of zinc in near neutral Na2SO4 solutions. Electrochimica Acta, 43(1–2), 175–186.

[10] Toele, P., Zhang, H., Trieflinger, C., Daub, J., & Glasbeek, M. (2003, January). Femtosecond fluorescence upconversion study of a boron dipyrromethene dye in solution. Chemical Physics Letters, 368(1–2), 66–75.

[11] Kralik, D., & Jorne, J. (1980, November 1). Hydrogen Evolution and Zinc Nodular Growth in the Zinc Chloride Battery. Journal of the Electrochemical Society, 127(11), 2335–2340.

[12] Siahrostami, S., Tripković, V., Lundgaard, K. T., Jensen, K. E., Hansen, H. A., Hummelshøj, J. S., Mýrdal, J. S. G., Vegge, T., Nørskov, J. K., & Rossmeisl, J. (2013). First principles investigation of zinc-anode dissolution in zinc–air batteries. Physical Chemistry Chemical Physics, 15(17), 6416.

[13] Saeri, M. R., & Keyvani, A. (2011, September). Optimization of Manganese and Magnesium Contents in As-cast Aluminum-Zinc-Indium Alloy as Sacrificial Anode. Journal of Materials Science &Amp; Technology, 27(9), 785–792.

[14] EDMAN, K. A. P. (1958, August). The Effect of Zinc and Certain Other Bivalent Metal Ions on the Isometric Tension Development of Glycerol-extracted Muscle Fibre Bundles. Acta Physiologica Scandinavica, 43(3–4), 275–291.

[15] Cao, L., Li, D., Deng, T., Li, Q., & Wang, C. (2020, August 20). Hydrophobic Organic‐Electrolyte‐Protected Zinc Anodes for Aqueous Zinc Batteries. Angewandte Chemie International Edition, 59(43), 19292–19296.

[16] Takei, T. (1987, August). Properties of non-aqueous solutions of Zn(CF3SO3)2. Surface and Coatings Technology, 31(2), 173–182.

[17] Mhin, B. J., Lee, S., Cho, S. J., Lee, K., & Kim, K. S. (1992, September). Zn(H2O)2+6 is very stable among aqua-Zn(II) ions. Chemical Physics Letters, 197(1–2), 77–80.

[18] Chen, Z., Wang, Q., Zhang, X., Lei, Y., Hu, W., Luo, Y., & Wang, Y. (2018, May). N-doped defective carbon with trace Co for efficient rechargeable liquid electrolyte-/all-solid-state Zn-air batteries. Science Bulletin, 63(9), 548–555.