

# Feasibility analysis of replacing lithium-ion battery with aqueous zinc-ion battery

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**Abstract.** lithium-ion battery is a battery with intercalated lithium compound as negative electrode material and non-aqueous solution as electrolyte. It is often used as energy supply system for mobile phones, electric vehicles and other equipment. However, due to the instability of lithium and the flammable organic electrolyte, lithium-ion batteries are prone to fire in high temperature or after damage. The paper introduced the technology of aqueous zinc-ion battery and analyzes the merits and drawbacks of it. Aqueous zinc-ion battery is a battery with metallic zinc as negative electrode material. The ingredient of electrolyte is a solution with water as the main component. Compared with lithium-ion battery, it has many excellent characteristics, such as non-toxic, non-flammable, etc. When electronic devices such as smart wearable devices are in close contact with human skin, aqueous zinc-ion batteries can prevent the risk of human skin being burned when the battery damaged or toxic substances penetrating when the battery accidentally leaks. In addition, the high density, high specific energy, much fewer expend and other characteristics of aqueous zinc-ion batteries also increase the possibility that they will replace lithium-ion batteries as energy supply systems for electronic equipment in the future. This paper cites examples to show that the aqueous zinc-ion battery has a good prospect in the field of intelligent wearable devices and has a certain guiding significance for the choice of the energy supply system of intelligent wearable devices in the future.

**Keywords:** Li-ion Battery, non-aqueous solution, organic electrolyte.

## 1. Introduction

At present, lithium-ion battery, as a popular energy supply system, is widely used in various electronic devices. Lithium-ion batteries are secondary batteries. The positive electrode material often uses intercalated lithium compound. The graphite is the material of the negative electrode. In the discharging process, the lithium ions separate from the negative electrode. They transfer in the electrolyte. Positive electrode is the destination of them. When the charging time comes, the lithium ions depart from the anode. After crossing the electrolyte, cathode is going to be the place for them to reduce to atoms. Although the application of lithium-ion batteries are extensive, they have high potential safety hazards. Lithium-ion battery has an electrolyte which is a flammable fluid. When the charging rate is excessive, the appearance of short circuit phenomenon is easily to find in the battery, overheat and catch fire are two manifestations. Overcharging has closed association with battery rupture. Overheating is easy to cause heating out of control. Both of these conditions will lead to the explosion of the cell. Lithium-ion battery has a electrolyte which is a toxic liquid. It may penetrate the skin after accidental leakage. The electrolyte will turn into toxic smoke when exposed to high temperature, which will be harmful to human body after inhalation. Nowadays, the explosion and fire of mobile phones and electric vehicles are often seen. The use of lithium-ion batteries as the energy supply system of electronic devices that directly contact the skin, such as intelligent wearable devices, also poses a great threat to human safety. And non-flammable and non-toxic aqueous zinc-ion battery can be used as an alternative energy supply system for lithium-ion batteries.

In the past decade, abundant articles from the research in the area of aqueous zinc-ion batteries have emerged one after another, which has made a great contribution to the burgeon of the aqueous zinc-ion batteries. The research of aqueous zinc-ion battery is still in its infancy, abundant problems need to be solved, such as short battery life, less charge/discharge cycles and easy to form dendrites. Therefore, many articles are about the improvement of internal materials of aqueous zinc-ion batteries.

Positive electrode material is a research emphasis. Scientists have proposed to use vanadium-based oxides, manganese-based materials, copper sulfides or oxides and prussian blue analogues (PBAs). Some articles have also proposed the protection scheme of positive and negative electrode of aqueous zinc-ion battery. Non-flammable, non-toxic, large capacity and high energy density are the advantages of the cell. It is a new type of battery that can replace lithium-ion battery afterwards. Lithium-ion batteries' characteristics and fire outbreak are expounded in this paper. Aqueous zinc-ion batteries' structure, function and merit characteristics are introduced, the paper also puts forward prospects of the application of it in the future intelligent wearable devices.

By comparing aqueous zinc-ion battery's configuration and property to lithium-ion battery, and comparing their safety in practical application. This paper evaluates the feasibility of aqueous zinc-ion battery replacing lithium-ion battery as an energy supply system for intelligent wearable devices.

## 2. Lithium-ion battery

### 2.1. Lithium-ion battery

Lithium-ion battery belongs to the secondary. Negative electrode uses metal oxide. Polyanion, layered oxides and spinelle are usually used. Positive electrode often uses carbon. The electrolyte is usually organic carbonates containing lithium-ion complexes (such as mixed salts of vinyl carbonate or diethyl carbonate). In Table 1 there is data about the cell.

**Table 1.** Lithium-ion battery's performance [1-3].

| No. | Type of performance       | Numerical value                           |
|-----|---------------------------|---|
| 1   | Volumetric energy density | $2.5 \cdot 10^2 \sim 6.8 \cdot 10^2$ Wh/L |
| 2   | Specific energy density   | $10^2 \sim 2.5 \cdot 10^2$ Wh/kg          |
| 3   | Specific power density    | $3 \cdot 10^2 \sim 1.5 \cdot 10^3$ W/kg   |

### 2.2. Advantages

Lithium-ion battery has several advantages. First, lithium-ion batteries are light. They mainly contain carbon and metal lithium, which have low relative atomic mass. The capacity of lithium-ion batteries is twice that of lead-acid batteries of the same quality. Second, lithium-ion batteries have high fluence. Energy conserved in the lithium is high. Ordinary lithium-ion battery has 3.6 volts voltage. Its 1.2 volts for nickel metal hydride batteries. There are three gaps. Third, extensive charge cycles can be achieved in the cell. Lithium-ion batteries have a long service life and can be used continuously for about 1000 charging cycles. These 1000 charging cycles refer to the situation that the battery is recharged to full after discharged to flat. Last, the lithium-ion battery has small discharge velocity at static. After being fully charged, first day it will release five percent of electricity. Then each month one or two percent will be released. It releases ten to fifteen percent for Nickel battery first day after being fully charged, and then releases same value each month [4].

### 2.3. Disadvantages

Easy to catch fire is the main problem of lithium-ion batteries. Mobile phone explosion, electric vehicle spontaneous combustion and other phenomena are often seen in daily lives. Table 2 shows the recent major fire accidents.

**Table 2.** Accidents of lithium-ion battery fire [5-9].

| No. | Date           | Place  | Accident  | Battery type                                    |
|-----|----------------|--|---|---|
| 1   | 19 April, 2019 | McMicken Battery Energy Storage System, Arizona, USA   | Fire and explosion, 4 injured                                     | Nickel manganese cobalt ternary lithium battery |
| 2   | 6 April, 2021  | Hongseong-gun Energy Storage System, Chungcheongnam-do, South Korea.                                   | Fire and explosion, solar power generation facilities burned down | Nickel manganese cobalt ternary lithium battery |
| 3   | 22 July, 2022  | Tesla Model X, Taoyuan, Taiwan   | Fire, 2 injured   | Nickel manganese cobalt ternary lithium battery |
| 4   | 16 April, 2021 | Beijing Jimei dahongmen 25MWh DC integrated optical storage and charging power station, Beijing, China | Fire and explosion, 3 death and 1 injured                         | Lithium iron phosphate battery                  |
| 5   | 30 July, 2021  | Tesla Megapack energy storage system, Victoria, Australia  | Fire, two container systems slow spontaneous combustion           | Square lithium iron phosphate battery           |

### 2.3.1. Internal causes of lithium-ion battery fire.

Negative electrode material contains lithium element, which has poor chemical stability and thermal stability, and is flammable during deformation and overheating. The positive electrode material of lithium-ion battery contains carbon element. Two electrodes have similar potential. So the carbon positive electrode is easy to precipitate lithium to form lithium crystal branches, causing short circuit that can easily catch fire. LiPF<sub>6</sub> mixed carbonate solution is a familiar electrolyte, which is very flammable. When the lithium-ion battery is damaged, short circuit can easily happen, which causes the temperature to rise. Electrolyte is easy to burn when in contact with air at high temperature.

### 2.3.2. External causes of lithium-ion battery fire.

When the cell is overcharged, it will cause the battery to bulge, damage the internal structure of the battery, cause a short circuit, and overheat the battery and catch fire. High ambient temperature can lift the lithium-ion battery's temperature. As temperature rises, a series of decomposition reactions will occur, and the heat equilibrium will disappear. Butterfly effect will be triggered when the heat is not released. Uncontrolled heat increase will eventually cause the battery fire. Short circuit can happen inside or outside of the battery that can also cause fire. As the cycle charge and discharge times increase, dendrites will grow inside the lithium-ion battery, which will damage the diaphragm inside the battery, resulting in a short circuit and a sharp rise in temperature that causes fire. When the equipment powered by the lithium-ion battery is short circuited, it will lead to high-power discharge of the lithium-ion battery (similar as connecting two poles of a battery with a wire), which will rapidly raise the temperature of the battery and cause a fire. Figure 1 shows the fire accident mechanism of lithium-ion battery.

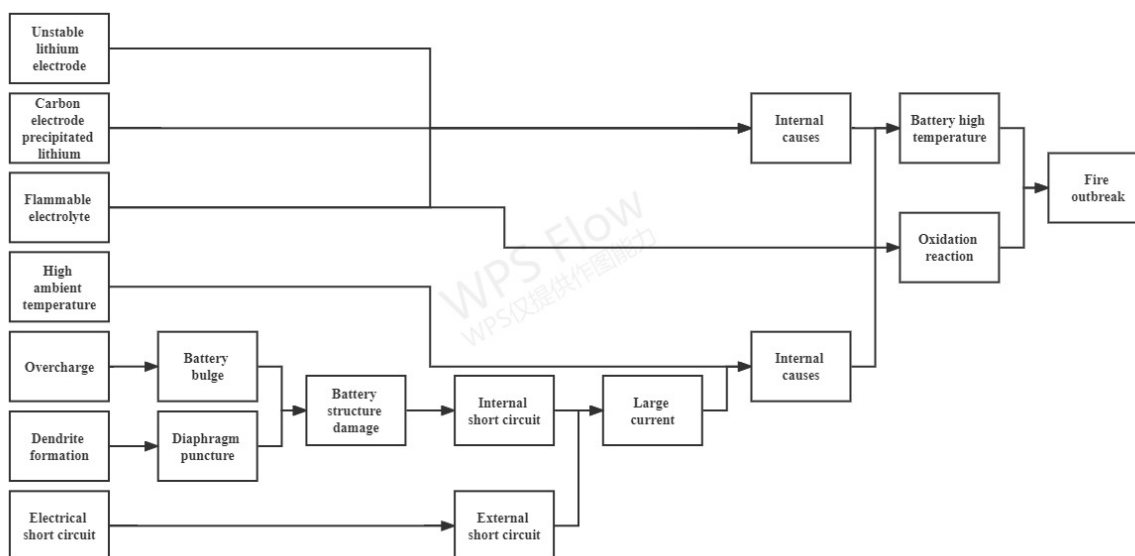


Figure 1. Lithium-ion battery's fire accident mechanism.

### 3. Aqueous zinc-ion battery

#### 3.1. Structure

##### 3.1.1 Positive electrode material.

So far, several positive electrode materials have been explored for zinc-ion batteries, including  $\gamma$ - $\text{MnO}_2$ ,  $\delta$ - $\text{MnO}_2$ , Bismuth Oxide, Layered Sulfide and Prussian blue analogues.  $\gamma$ - $\text{MnO}_2$  has several tunnels,  $\text{Zn}^{2+}$  can entry and exit from them. The combination of  $\gamma$ - $\text{MnO}_2$  with excellent conductive materials will increase the conductivity and adapt better to the structural changes during the cycle. The interlayer distance of  $\delta$ - $\text{MnO}_2$  material is relatively large. And nano flake  $\delta$ - $\text{MnO}_2$  material possesses large superficial space, so that it can reduce the migration distance of electric transport to enhance the diffusion kinetics.  $\delta$ - $\text{MnO}_2$  material makes electrode integrate more with electrolyte meanwhile, accelerates  $\text{Zn}^{2+}$ 's entry and exit, which helps to enhance zinc storage performance. Bismuth materials are easy to synthesize, superior in performance and low in cost. The Bi-O bond formed by high charge density  $\text{Bi}^{3+}$  enhances the stability of the material structure, reduces the band gap and enhances the conductivity. By distorting the electron cloud of O, the attraction between  $\text{Zn}^{2+}$  and O is weakened, and the electrochemical active surface area is increased while increasing the diffusion of solid ions.  $\text{MnS}$  is a-Co and belongs to the Fm-3m space group. It is composed of micron sized particles with high capacity and electromotive force. Graphene and  $\text{MnS}$  can be combined by hydrothermal method to increase the conductivity and mechanical strength of the material. Prussian blue analogs include  $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ ,  $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ ,  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ , etc. The structure of the iron hexacyanoferrate electrode is stable and has a relatively high cycle life. Zinc hexacyanoferrate has a rhombic structure, the structure is easy to change when used as an electrode. When copper hexacyanoferrate is used as an electrode,  $\text{Zn}^{2+}$  may enter the interior of copper hexacyanoferrate material to replace Cu atoms during long-term cycling. Therefore, iron hexacyanoferrate is the most widely used material.

##### 3.1.2 Negative electrode material.

Negative electrode material of the cell is often metallic zinc. There are several methods to optimize the electrode. The porous coating at the zinc surface can screen the ions that pass through and prevent the deformation of the electrode and the formation of zinc dendrites. Making zinc into a sponge state improves its availability. It also improves the capacity of battery. Physical performance of the

electrode can be improved by coating zinc on carbon surface. The procedure improves the charge distribution on its surface and abate zinc dendrites' growing rate [10].

### 3.1.3 Electrolyte.

The electrolyte of aqueous zinc-ion battery is always zinc salt solution. Generally, the performance of the electrolyte is improved by adding additives to the electrolyte and increasing the concentration of the electrolyte. Adding liquid containing  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{ClO}_4^-$  can improve ion abundance and ion solubility, and increase the conductivity of electrolyte. A filter layer on the electrode boundary if adding SDS additive to the equal-proportional mixed solution of sodium sulfate and zinc sulfate. High torsional energy will be created as the electrolyte cross over the filter layer. So gaseous fluid is less likely to be produced by water, thus increasing cell's steadiness. It also contributes to break away from zinc ions' dissolution, so as to prevent dendrite growth and by-product formation, which improves coulomb efficiency. After adding  $\text{Mn}^{2+}$ , its sedimentation can inhibit the precipitate of  $\text{O}_2$  and increase the reaction rate [11]. In aqueous electrolyte,  $\text{Zn}^{2+}$  does not exist as a free single ion, but is surrounded by water molecules to form hydrated zinc ions. When the concentration of electrolyte goes up, number of other particles will decrease, which will increase the movement rate of zinc ions. Therefore, for the same kind of salt solution electrolyte, the increase of concentration can improve the chemical performance of the electrolyte [10].

## 3.2. Characteristics

Compared with lithium-ion batteries, lots of excellent characteristics can be found in aqueous zinc-ion batteries, advanced security and non-toxic are two of them, which are unmatched by ordinary lithium-ion batteries.

### 3.2.1 Safety.

Zinc metal is used as the stuff of aqueous zinc-ion battery's negative electrode. The chemical stability of zinc element is higher than that of lithium element. When the battery ruptures and exposes to air, it is not easy to generate intense oxidation reaction to release heat and cause the battery to fire. Aqueous zinc-ion battery is a kind of aqueous battery, whose electrolyte is mainly inorganic solution. The solvent of these solutions is mostly water, which is a flame retardant. When the battery ruptures and exposes to air or the battery temperature rises sharply, the solution will not burn. Moreover, compared with the toxic organic solution of ordinary lithium-ion batteries, the accidental leakage of electrolyte from aqueous zinc-ion batteries will not cause harm to vital status or pollution to surroundings. As smart wearable devices get prevalent, replacing lithium-ion batteries with aqueous zinc-ion batteries can greatly avoid toxic substances penetrating into the skin due to battery leakage.

### 3.2.2 Raw material reserves.

Metallic zinc is the essential component of this kind of battery. Zinc mine has a high annual output, about 13 million tons. China, Peru and Australia are the main producers of zinc ore. According to the statistics of the US Geological Survey, the global lithium reserves in 2021 are only 21 million tons [12], less than the two-year output of zinc. The huge zinc reserves can ensure the continuous supply of need.

### 3.2.3 Cost.

First of all, metallic zinc is aqueous zinc-ion battery's raw material. Reserve of zinc is 3.7 times that of lithium, and the annual mining volume of zinc is large and it is convenient to mine. Therefore, the cost of batteries using zinc as raw material is generally lower than that of batteries using lithium as raw material. Secondly, the stability of lithium element is low, so lithium-ion batteries often need complex structures and protective measures to avoid the risk of excessive fire caused by overheating or damage of lithium-ion batteries, which will also increase the cost of lithium-ion batteries. The stability of zinc element is high, which can reduce the cost of this part. Finally, most of the lithium-ion batteries use organic oil-based electrolytes, and the production and transportation costs of these

electrolytes are relatively high. The aqueous zinc-ion battery uses zinc salt solution as electrolyte, which is easy to obtain and can reduce the cost of the battery.

### 3.2.4 Performance parameter.

Aqueous zinc-ion batteries have big fluence. At present, specific energy of lithium-ion batteries on the market is  $10^2 \sim 2.65 \cdot 10^2$  Wh/kg [2-3]. Energy density is  $2.5 \cdot 10^2 \sim 6.93 \cdot 10^2$  Wh/L [13]. The specific energy of the aqueous zinc-ion battery with  $K_{0.41}MnO_2 \cdot 0.5H_2O$  as the positive electrode material at 175 mA/g power is 503 W·h/kg [14]. The specific energy of the aqueous zinc-ion battery with  $Co_{0.247}V_2O_5 \cdot 0.944H_2O$  as the positive electrode material at 0.1 mA/g power is 458.7 W·h/kg [15]. Aqueous zinc-ion batteries applied in electronic equipment can improve the product life.

## 4. Future development and challenges

Aqueous zinc-ion batteries do have many advantages, but at present, it is still in the research and development stage and are not widely used in the electronic equipment. There are still many problems in the aqueous zinc-ion battery: the zinc electrode is easy to dissolve or passivate, the electrostatic effect affects the battery efficiency, the zinc dendrite is easy to form, and the by-products are easy to form, which will affect cell's development and commercialization. As the development of science and technology, scientists gradually advance the cell by trying different positive electrode materials and changing the composition of electrolyte. In the future, intelligent wearable devices will become more and more popular. The aqueous zinc-ion battery can become the energy supply system of these devices with its high safety and excellent performance. The research and development of aqueous zinc-ion battery will also provide a strong impetus for the progress of future electronic equipment technology.

## 5. Conclusion

Fire is prone in lithium-ion batteries while it is not common in aqueous zinc-ion batteries. This paper introduces several advantages of lithium-ion battery, and introduces the reasons why lithium-ion batteries are prone to fire from both their own causes (positive electrode materials, negative electrode materials, electrolyte) and external reasons (overheat, overcharge, inside and outside short circuit). This paper also introduces the structure and characteristics of aqueous zinc-ion batteries. Comparisons are made. However, several drawbacks have led to the inadequacy of aqueous zinc-ion batteries developed in the laboratory at present, and the performance has not reached the optimal level, which makes the aqueous zinc-ion batteries still have a great development space in the future. In the future, researchers should strive to solve the above problems and develop batteries with better performance. This will accelerate aqueous zinc-ion batteries' commercialization. This paper compares the lithium-ion battery with the aqueous zinc-ion battery. It proposes that the former can replace the latter to become the energy supply system of intelligent wearable devices in the future.

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