

# Three solid electrolyte interphases of aqueous zinc batteries

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**Abstract.** With the increasing demand for enhanced safety performance of rechargeable batteries, water-based zinc-ion batteries have witnessed rapid development due to their exceptional safety characteristics. And, zinc batteries have been widely used in a diverse of various fields such as electric vehicles and electric bicycles. However, the dendrite issue and limited cycle life of the negative electrode pose significant challenges that hinder further advancements in this technology, which greatly limits the development of zinc batteries. For this reason, extensive research has been conducted on various solid electrolyte interphases related to the battery anode. By comprehensively understanding and comparing three materials of solid electrolyte interphase (SEI) utilizing similar controlled negative ion techniques, it can validate the accuracy of this theoretical approach. The utilization of these three materials results in a substantial improvement in battery performance compared to the original battery, particularly in terms of service life; however, each material also exhibits distinct advantages and drawbacks.

**Keywords:** Aqueous Zinc Ion Battery, Solid Electrolyte Interphase, Dendrites.

## 1. Introduction

In the current world, lithium-ion batteries have played an indispensable role in human lives and are widely used in all kinds of household appliances, smart phones, and even electric vehicles. This is due to the excellent energy density (theoretical: 372 mAh/g) and low self-discharge of lithium-ion batteries [1]. However, there are quite a few safety risks in lithium-ion batteries. Many well-known incidents of spontaneous combustion in electric vehicles following collisions and explosions of energy storage devices utilizing lithium-ion batteries are caused by self-flammability which is the most serious shortage of lithium-ion batteries. Furthermore, the scarcity of lithium element and high reactivity of lithium cause high cost of production and storage of lithium metal.

Zinc-powered batteries have been under development for over a century, and it has been 90 years since the commercialization of zinc-air batteries first took place. Due to the invertibility and unreliable cycle performance of zinc-ion batteries [2], limited investment has been allocated towards the research and development of zinc-ion batteries. The recent years have witnessed significant advancements in both areas, leading to a resurgence of interest in zinc-ion batteries. The energy capacity of zinc metal is also significantly high with theoretical number value of 820 mAh/g [3]. In contrast with lithium-ion batteries, zinc ion batteries are very safe, and it nearly would not burn or explode because of the stability of zinc metal and internal structure. From the aspect of cost, zinc ranks as the 23rd most prevalent constituent in the earth's crust and the price of production, processing and recycling are very cheap [4].

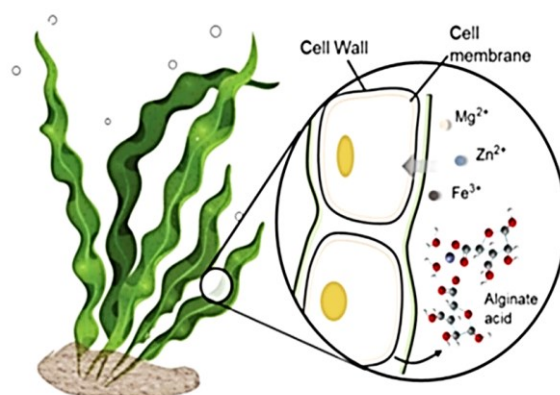
These advantages indicate a growing possibility for the replacement of lithium-ion batteries with zinc-ion batteries in the future.

With the latest research, the aqueous zinc ion batteries in the laboratory are only 240 mAh/g and after 3000 cycles the capacity is about 95% [5]. The performance of current aqueous zinc ion batteries is not as good as that of the commercialized lithium-ion batteries, which means the disparity between the market and the laboratory persists. The primary factor contributing to this is zinc dendrites formed during the charging process. The simultaneous occurrence of corrosion and by-product generation resulting from electrolyte and electrode reactions poses additional challenges that require resolution because they may decrease the lifetime and safety of batteries.

An effective solution to this issue is the implementation of a zinc anode solid electrolyte interphase (SEI). The SEI is the layer which between liquid electrolyte and anode materials [6]. The field of anode coating materials has been extensively researched, and advancements in these materials hold great potential for mitigating the dendrite issue and enhancing battery cycle life. In the forthcoming articles, three specific materials will be highlighted, their respective advantages and any possible drawbacks will also be discussed and compared.

## 2. Application of three solid electrolyte interphases in zinc batteries

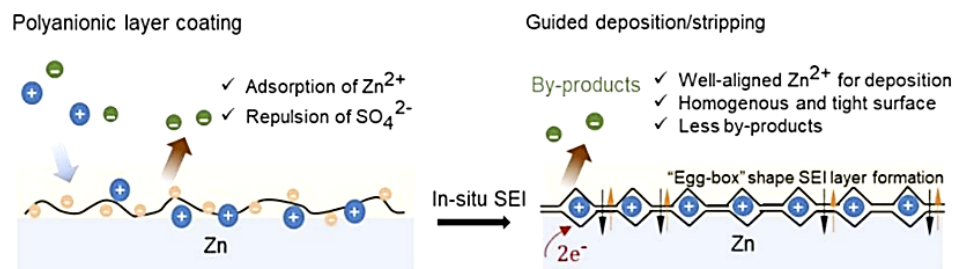
The underlying concept behind these coatings is highly similar. They emphasize the utilization of materials to regulate anions, thereby facilitating the unhindered movement or diffusion of zinc ions within the electrolyte. Through a specific sedimentation process, zinc ions are selectively deposited at the zinc (002) position [7]. Consequently, this enables the formation of a diverse range of compact sedimentary layers composed primarily of zinc ions, effectively minimizing dendrite formation and enhancing battery longevity.



**Figure 1.** Seaweed absorbing metal cations [7].

### 2.1. Sodium Alginate

He et al. was inspired by property of seaweeds and designed a bionic polymer [8]. The seaweed is a kind of plant which can accumulate metals by chemicals in its cell walls, as shown in Figure 1. Algal cell walls provide specific binding sites for heavy metals, including hydroxyl (R-OH), carboxylic (R-COOH), and sulfonic (R-S(=O)<sub>2</sub>-OH) groups, which play a crucial role in determining the selectivity of algal enrichment towards different metal ions [8]. Hence, they used sodium alginate (SA) which has this property to design a solid electrolyte interface which can limit the formation of dendrites. The main reason to achieve this purpose is that SA layer played a role of anionic layer on zinc anode and generated an accelerating channel. The accelerating channel can decrease the energy barrier of forming more tightness and thinner zinc layer. This allows zinc ions to move more freely and induces them to deposit uniformly on the (002) plane, thereby reducing dendrites due to uneven distribution [7], as shown in Figure 2.



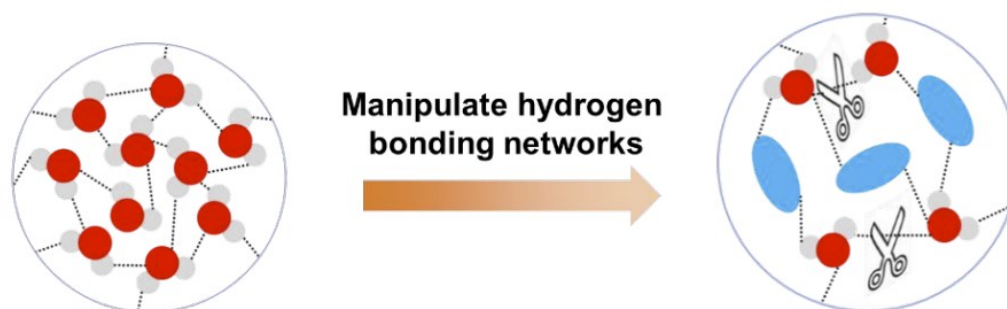
**Figure 2.** The working mechanism of SEI layer [7].

The performance of electrochemical were analysed by using the Zn||Cu cell. There is an outstanding elevation on Coulombic efficiency (CE) and recycle times. The first cycles CE of bare zinc electrode is 88.59% and decline rapidly after 85 cycles, but the one with SA layer can achieve 90.1% and keep 99.8% after 1400 cycles. Furthermore, they also tested the battery with high depth of discharge which is higher than 50% and the zinc anode can keep very well plating behaviour with only 0.114V. To validate the practicability of this technology in industrial production, the team also tested Zn||MnO<sub>2</sub> battery and the stability and reversibility represented well during the experiments which proved the ability of SA coating on confining the random dendrites [7].

## 2.2. Imidazolidiny Urea

Organic compounds have garnered significant attention in the realm of solid electrolytes as well. Ma et al. used imidazolidiny urea (IU) as electrolyte to enhance the performance of reversibility and plating/stripping. The research and development concept of IU bears striking resemblance to the SA mentioned before, as they both govern the kinetic behaviour of zinc ions through anionic control [7, 9]. However, they diverge significantly in terms of their operational details. The strength of the hydrogen bond nearly determines the reactivities of aqueous electrolyte. Therefore, disrupting a portion of the hydrogen bond network or reconfiguring the hydrogen bond structure has emerged as pivotal in resolving this issue. Imidazolidylated urea molecules can simultaneously modulate the electric bilayer adsorption, solvation structure of zinc ions, and hydrogen bond network by utilizing the carbonyl group (-C=O) and amino group (-NH), thereby promoting the reversibility of zinc anode and minimizing side reactions [9], as shown in Figure 3.

They hypothesize that the IU molecule facilitates the formation of a hydrogen bond network between the Zn<sup>2+</sup> ion and water, thereby disrupting the pre-existing water-hydrogen bond network. This interaction consequently leads to a reduction in water molecule activity, resulting in weakened H-O bond strength. Simultaneously, the presence of IU molecules hinders contact between water molecules and the Zn electrode, effectively mitigating corrosion of the zinc electrode. The paper also discussed the calculation of theoretical energy, determining the enhancement of reductivity of IU towards zinc ions and its impact on electrostatic interaction. This further validates assistance of IU in facilitating zinc diffusion and its positive influence on reducing zinc dendrites. The samples were subjected to various environmental conditions throughout the experiments. In Zn||Zn symmetric cell exhibits remarkable reversibility and long-term stability for over 1500 hours. Besides, the Zn||Cu symmetric cell demonstrates excellent operational durability, completing over 2000 cycles with a Coulombic efficiency exceeding 99%. Notably, a high-areal-capacity (~5.7 mAh/cm<sup>2</sup>) Zn||Br<sub>2</sub> full cell achieves sustainable operation for 300 cycles under harsh conditions, maintaining a capacity retention of 94.6% at nearly perfect Coulombic efficiency while utilizing approximately 84.03% of the available zinc [9].

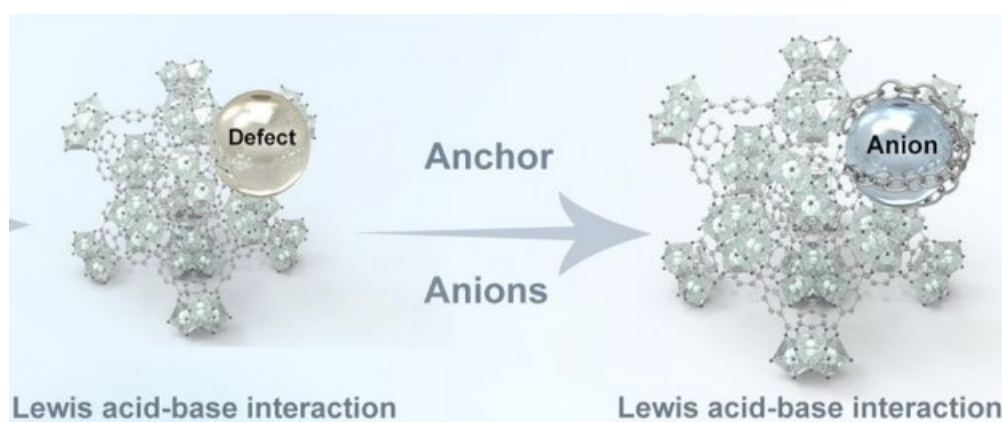


**Figure 3.** IU weaken hydrogen bonds between water molecules [9].

### 2.3. D-UiO-66

The sand capacity formula inspired Gu et al. to use a material called defective UiO-66 (D-UiO-66) nanoparticle. The presence of a small amount of liquid electrolyte notwithstanding, this finding further substantiates the beneficial impact of solid electrolyte on optimizing battery performance. D-UiO-66 nanoparticles possess the capability to immobilize anions and reduce their mobility, while simultaneously promoting the transfer of cations, as shown in Figure 4. Consequently, this inhibits the formation of zinc dendrites. The nano porous structure, in addition to partially desolvating, also mitigates the current density by facilitating the formation of an electrolyte with a high salt concentration within the channel.

From the perspective of experimental data, the design of this electrolyte is highly advanced. It demonstrates a stable operation for 1800 hours under the condition of  $1 \text{ mAh cm}^{-2}$ , the Coulomb efficiency remains consistently high at 99.8%, effectively controlling dendrite formation. Even in challenging conditions such as  $10 \text{ mA cm}^{-2}$ , it maintains a cycle life of 480 hours. The all-battery combinations also demonstrate exceptional stability, and the battery capacity remains remarkably high even after multiple cycles of charging and discharging. The  $\text{Zn}||\text{MnO}_2$  battery retained 92.9% of its capacity after undergoing 2,000 cycles, while the  $\text{Zn}||\text{NH}_4\text{V}_4\text{O}_{10}$  battery maintained 84% of its capacity after completing 800 cycles [10].



**Figure 4.** Interaction between D-UiO-66 and anions [10].

## 3. Discussion and comparison

Regarding the listed experiment data, from an experimental data perspective, all three options demonstrate exceptional capacity maintenance with over 1400 tests showing a capacity maintenance rate of above 99%. Besides, the SA batteries were subjected to testing with discharge depths exceeding 50% and soft bag batteries, the excellent parameter were also displayed in the figure. The above experimental evidence demonstrates that the manipulation of anions to control zinc ion deposition can

effectively enhance dendrite formation and increase the number of battery cycles. This provides a more robust empirical foundation for future research directions [7, 10].

The test environments for these three materials may vary slightly, but even when compared to the extreme conditions of the test environment, IU is still able to maintain a stability of 1500 hours in an environment with a current density of 1 mA/cm and a charge density of 0.5 mAh/cm<sup>2</sup>. This suggests that IU may exhibit superior stability compared to the other two materials. The three materials were simultaneously subjected to testing in an environment with different counterparts. In the battery containing zinc and manganese dioxide, D-UiO-66 exhibited a remarkable 92.5% retention after 2500 cycles at 5c, surpassing the mere 81.65% maintenance observed in IU-based zinc and bromine batteries after only 1000 cycles. Furthermore, D-UiO-66 demonstrated superior performance compared to the other two materials when exposed to various counterparts, indicating its excellent compatibility and suggesting potential for wider applications.

Although the theoretical and experimental properties of these three materials are excellent, there may still be some imperfections. The first one is an anode coating utilizing SA. Although the acidic material exerts a potent inhibitory effect on dendrite formation, it concurrently induces electrode corrosion. Prolonged usage may lead to the erosion of this protective coating [11], thereby diminishing the overall quantity of effective negative electrode material and subsequently reducing battery capacity. Additionally, by-products generated during this process have the potential to contaminate the electrolyte [12], potentially elevating its resistance and compromising battery safety.

In aqueous zinc-ion batteries, temperature plays a crucial role in determining battery performance. However, excessively low or high temperatures do not contribute to improved product performance [13]. Among the three materials under investigation, D-UiO-66 has been subjected to rigorous testing at -20 °C and has demonstrated remarkable stability. Conversely, the other two materials have primarily undergone testing at room temperature only, which limits the ability to make meaningful comparisons in this experiment.

The price of raw materials is also a crucial factor in the eventual commercialization of products. Among them, SA stands out as the most cost-effective option at 2122 Chinese yuan per kilogram, while IU comes with a significantly higher price tag of 14,696 Chinese yuan per kilogram, nearly seven times more expensive than the former. Furthermore, H<sub>2</sub>BDC, the primary material used in D-UiO-66 production, commands a unit price of 5,673 Chinese yuan per gram. This substantial increase in battery production costs undoubtedly poses a negative impact on commercialization development. Therefore, effective cost control measures must be considered when developing anode coating technology.

#### 4. Conclusion

The free movement of zinc ions is enhanced by employing anion control with three distinct battery anode film materials, thereby facilitating their deposition on the Zn (002) surface and forming a compact deposit layer. Consequently, the objective of dendrite growth control and cycle number increase is achieved. By comparing experimental parameters and reference materials, it can be observed that all three exhibit significant improvements in original performance. However, each material possesses its own advantages and disadvantages. Among them, D-UiO-66 demonstrates relatively superior experimental results across different environments at present, while SA offers the most competitive price.

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