

Controlled Construction and Properties Study of PDMS Coatings for Stabilizing Zinc Metal Anode

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Abstract: Polydimethylsilane (PDMS) is a promising coating material. The subject proposes a SiO₂-doped PDMS coating material (defined as SO-PDMS), which is hydrophobic and can help desolvate ions in solution, regulate the electric field distribution on the electrode surface, inhibit the formation of dendrites, and reduce the side reactions such as the evolution of oxygen and hydrogen. SiO₂ is rich in silanol groups, which can coordinate with zinc ions to promote the rapid transport of zinc ions and facilitate the uniform deposition of zinc ions on the anode surface. The SO-PDMS@Zn symmetric battery has a lower overpotential (25 mV) and a cycle life (240 h) much higher than that of the bare Zn-Zn battery during charge-discharge cycles, showing the excellent ability of SO-PDMS to activate rapidly and then remain stable. The SO-PDMS-coated half-cell maintains a good Coulombic efficiency during operation, with an average Coulombic efficiency of 97.21%, and no obvious loss is seen after 130 cycles, showing the high reversibility of the battery reaction. The CA curve shows that SO-PDMS can significantly regulate the ion diffusion on the surface of the Zn anode, which can restrict the Zn ions to nucleate in situ. The full cell using V₂O₅ as the cathode performed well with a considerable capacity increase in the early cycles (240 mAh g⁻¹ at 2 A g⁻¹).

Keywords: Zinc metal anode, PDMS, SiO₂-doping.

1. Introduction

With the rapid development of industrialization of human society, the demand for energy in various industries is increasing day by day. Traditional fossil energy has inevitably caused many problems, posing a threat to the environment on which human beings live. To develop a greener and cleaner way of energy utilization became the focus of attention. Among them, metal batteries (MBs) are widely used. Such batteries directly provide ions involved in battery charge-discharge reactions through metal anode (including aluminum, lithium, zinc, magnesium, etc.), and are efficiently exchanged at the electrode-electrolyte interface. Energy Density. After a long period of development and improvement of MBs, various battery designs with various functions and structures have been derived.

Lithium metal battery (LMB) is a type of battery that directly uses lithium metal as an electrode, which was proposed by M.S. Whittingham of Exxon in 1970 [1]. As an active metal, lithium is prone to side reactions with oxygen when it is used as an electrode, causing severe deformation in the battery and destroying the battery structure. The existing technology cannot solve the commercial safety problem for the time being. Better intercalation lithium-ion battery (LIBs) technology. LIBs is a relatively mature energy storage technology. It retains the advantages of high self-discharge rate, high discharge voltage, and excellent cycle performance of lithium metal batteries to a certain extent [2-4]. It is widely used in mobile communications, power storage, and in the field of electric vehicles. However, the price of lithium as a metal raw material is high while the supply is limited, and the ternary cathode material matched with lithium batteries also has a high price, which limits the development of the entire lithium battery field. At the same time, most of the organic electrolytes in lithium-ion batteries are flammable and volatile, and there is a safety hazard that cannot be ignored during its long-term cycles.



Figure 1-1 Schematic diagram of potassium-sodium liquid alloy anode concept battery [6]

Sodium and potassium, elements which belong to the same family as lithium, have also received attention. Due to their similar characteristics, sodium-ion batteries (SIBs) and potassium-ion batteries (KIBs) have the potential to become substitutes for lithium-ion batteries. Their metal raw material reserves are relatively abundant and cheaper [5]. The two can even form a liquid battery electrode in the form of a liquid alloy at room temperature [6]. There are many unexplored possibilities, but both also have safety issues that cannot be ignored [7-9].

Aluminum-ion batteries (AIBs) are the concept batteries proposed in recent years. Aluminum metal has low cost, is non-flammable, and has high safety. At the same time, aluminum battery has excellent charge storage capacity, high energy density and high charging efficiency, which is a potential new battery material [10]. However, the existing anode materials for aluminum ion batteries still have many defects, and stable voltage supply is a major difficulty in current AIBs research. The reported electrode materials cannot maintain sufficient voltage output after long-term charge-discharge cycles.

Relatively speaking, Aqueous Zinc Ion Batteries (AZIBs) are widely used in practical applications due to their mild electrolyte environment, high theoretical capacity (820 mAh g^{-1}) and relatively low redox potential (-0.76 V). application has greater potential [11]. AZIBs use aqueous electrolytes, which are safer and more environmentally friendly than most other organic electrolytes of MBs. The mild electrolyte environment also greatly reduces the risk of battery production and charge-discharge working process. At the same time, compared with organic electrolytes, aqueous electrolytes have higher ionic conductivity, enabling AZIBs to charge and discharge rapidly and with high efficiency. power output [12].

On the other hand, the metal electrode of MBs generally have the problem of uneven diffusion and deposition at the interface between the electrolyte and the electrode. In the research of various MBs, it is an important research direction to summarize the kinetics of dendrite growth and to find ways to inhibit dendrite growth for overall cell stability. Stable methods are important research directions. A large number of existing studies have shown that the nucleation kinetics of dendrite growth on the electrodes of different MBs are different, and the corresponding dendrite growth phenomena also have certain differences. The difference is evident from Figure 1-3.

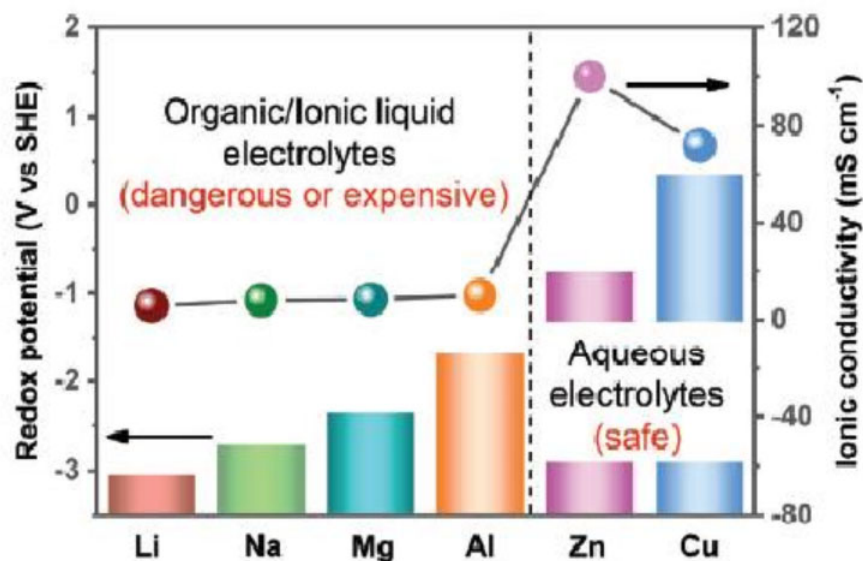


Figure 1-2 Comparison of redox potential and ionic conductivity between zinc and other metal anodes[13]

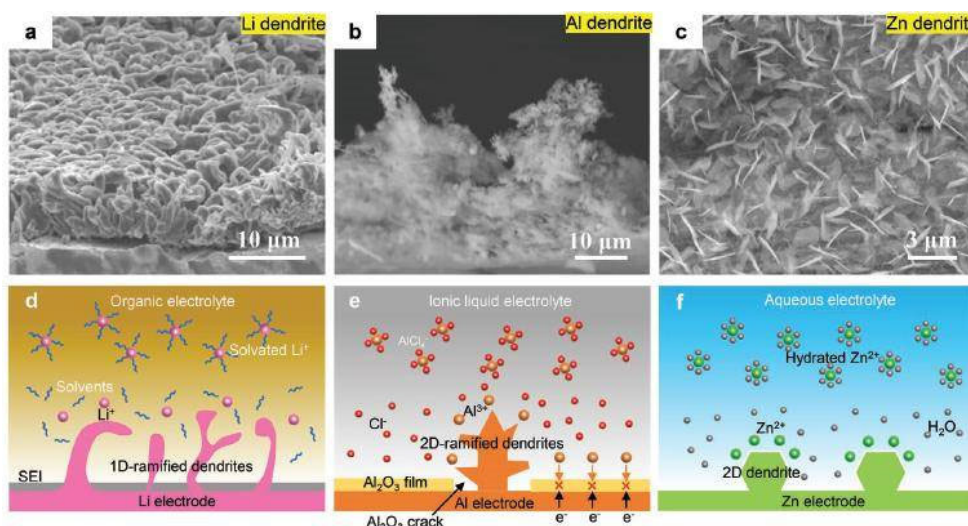


Figure 1-3 Comparison of topological and ionic environments between Zn dendrites, Li dendrites, and Al dendrites [14]. (a-c) SEM images of Li, Al, and Zn dendrites; (d-f) schematic diagrams of Li, Al, and Zn dendrite topologies and associated ionic environments [13]

In terms of dendrite growth, although the Young's modulus of lithium electrode is the lowest [15], the dendrite problem exhibited by lithium batteries is the most serious in practical applications. Li dendrites are essentially inhomogeneous solid-electrolyte interfaces (SEI) formed on the electrode surface [16,17], which are related to the uneven electric field distribution and electrolyte decomposition on the electrode surface. Ideally, the initially grown SEI passivation layer can continuously cover the electrode surface during cycling to form a new flat ion-exchange interface, which separates the lithium electrode from the electrolyte, protects the electrode from corrosion, and maintains the stability of the battery. However, the inevitable deformation of the lithium electrode causes the SEI layer to crack and produce protrusions, and the new SEI film cannot be restored to flatness in time. During this reciprocation, lithium dendrites grow rapidly in multiple directions in a one-dimensional topological form of body-centered cubic accumulation on the surface of the electrode. (As shown in Figure 1-3a, d), the SEI layer is eventually destroyed and the separator is pierced, short-circuiting the battery.

The dendrite problem also exists in aluminum-ion batteries. Previous studies have shown that the formation of Al dendrites is mainly due to the rupture of the Al₂O₃ passivation film on the electrode

surface, which increases the nucleation sites and induces uneven Al deposition [18]. Since the SEI film on the anode of AIBs is a completely inorganic phase, the SEI film is less stable than the organic phase of LIBs and is more easily damaged at low redox potentials [19]. As shown in Figures 1-3b, e, Al dendrites are topologically arranged, extending continuously from nucleation sites and branching into 2D structures. Metal batteries often use ultra-concentrated ionic liquid electrolytes (IL) to suppress dendrites, but in the IL electrolytes of aluminum ion batteries, the carriers are AlCl_4^- anions with large radius and low transfer efficiency, meaning that the suppression of dendrites is at the expense of reducing the ion transfer efficiency between the electrolyte and the cathode [20, 21]. The lower ion transfer efficiency also promotes the formation of dendrites.

Compared with most metal batteries using organic electrolytes, AZIBs use a mild aqueous solution as the electrolyte, which has great advantages in terms of safety. However, since the ion exchange of aqueous zinc batteries occurs at the interface of solid-liquid two-phase, there is also a very serious problem of dendrite growth. The mechanisms of Zn dendrite growth are not consistent under different electrolyte environments. In the alkaline electrolyte, $\text{Zn}(\text{OH})_4^{2-}$ acts as an intermediate product to bear the load, which is similar to the dendrite growth mechanism of the aluminum battery mentioned above, and also easily promotes the growth of zinc dendrites; in weakly acidic or neutral electrolytes, it is not easy to form $\text{Zn}(\text{OH})_4^{2-}$, but due to the solvation effect, there are also corresponding intermediate products. During the cycle of the aqueous zinc battery, the irregular ion movement at the microscopic scale such as turbulence and convection on the surface of the anode causes rapid 2D non-uniform diffusion of ions on the interface, making the surface of the electrode gradually rough, and the roughness of the surface further makes the electric field distribution. The inhomogenization promotes the formation of zinc dendrites (Fig. 1-3c, f) [22].

Therefore, the dendrite growth phenomenon of aqueous zinc batteries is studied, and a feasible optimization scheme is proposed, which will enable the development of AZIBs with excellent performance, high safety and full potential, and lay the foundation for subsequent research and application. Tightening the status quo and increasing the use of green energy has a positive impact.

2. Experiment-related reagents, equipment and characterization methods

2.1 Experimental equipment

The name, signal and manufacturer of the instruments used in the experiment are listed in Table 2-1:

Table 2-1 Experimental equipment

equipment name	model	Manufacturer
Precision Electronic Balance	BSA224S	Sartorius Scientific Instruments Ltd.
Ultrasonic cleaner	KQ-4000E	Kunshan Ultrasound Instrument Co., Ltd.
Magnetic heating stirrer	HJ-6	Hunan Lichen Instrument Technology Co., Ltd.
Electric blast constant temperature drying oven	DHG-9055A	Gongyi Yuhua Instrument Co., Ltd.
Vacuum drying oven	DZF-6030A	Gongyi Yuhua Instrument Co., Ltd.
Muffle furnace	—	Tianjin Zhonghuan Electric Furnace Co., Ltd.
X-ray diffractometer	Rigaku Miniflex 600I	Rigaku Corporation
Punching machine	JK-CPJ-20	Shenzhen Jingnuoer Automation Technology Co., Ltd.
LANHE Battery Test System	CT2001A	Wuhan Landian Electronics Co. , Ltd.

2.2 Representation means

2.2.1 X-Ray Powder Diffractometer (XRD)

X-Ray powder diffractometer (XRD) is one of the important instruments that use X-ray to irradiate the material, analyze the X-ray diffraction effect in the material for elemental qualitative analysis, and then obtain surface structure information. Combined with the 2θ value and peak intensity of the diffraction peaks in the XRD pattern, and compared with the standard JCPDS card data, the material structure and crystalline strength of the analyzed samples can be judged.

Test method: The powder sample is placed in the ground glass groove, and the sample is pressed flat with a glass plate for analysis. If the analytical counterpart is an electrode sheet, it can be directly pasted on the back of the ground glass sheet and then tested.

2.2.2 Fourier Transform Infrared Spectrometer (FTIR)

An infrared spectrometer (FTIR) is an instrument for qualitative analysis of substances. It scans the measured sample with infrared radiation in different wavelength bands, and determines the chemical composition and bonding state of the sample according to the specific absorption of the infrared light by the sample, thereby inferring the molecular structure of the sample.

Test method: use potassium bromide tableting method, grind and mix the sample powder and dried KBr at a mass ratio of 1:100, take an appropriate amount of mixed powder and add it to the abrasive tool and press it with a tablet machine, and put the tablet into the infrared test. instrument to measure.

2.3 Experimental reagents

The names, chemical formulas, specifications and manufacturers of the reagents used in the experiment are listed in Table 2-2:

Table 2-2 Experimental reagents

Reagent name	Specification/Purity	Manufacturer
Hydroxy silicone oil (2000 molecular weight)	—	Shenzhen Jipeng
isopropyl alcohol	AR	Aladdin Reagent Ltd.
Toluene	AR	Guangzhou Chemical Reagent Factory
anhydrous ethanol	AR	Guangzhou Chemical Reagent Factory
Dibutyltin dilaurate	95%	Aladdin Reagent Ltd.
Boric acid	99%	Aladdin Reagent Ltd.
vanadium pentoxide	AR	Aladdin Reagent Ltd.
Zinc sulfate heptahydrate	AR	Aladdin Reagent Ltd.
superconducting carbon black	battery level	—
polyvinylidene fluoride	battery level	—
cetyltrimethylammonium bromide	AR	Aladdin Reagent Ltd.
Tetraethylorthosilicate	AR	Maclean's Reagent Co., Ltd.

3. Controlled construction and properties study of PDMS coatings for stabilizing zinc metal anode

3.1 Experimental part

3.1.1 Pre-preparation of SiO₂ and PDMS

Unless otherwise mentioned in this experiment, the external conditions are normal temperature and pressure (25 °C, 1 atm), and the water used in the experiment is deionized water.

In the atmospheric environment, use an oil bath to directly heat the PDMS materials required for the experiment: measure 8 mL of isopropanol and 10 mL of hydroxysilicone oil (2000 molecular weight) into the beaker, stir evenly, weigh 0.8 g of boric acid, and stir for 10 minutes. Add 600 μL of dibutyltin dilaurate as a catalyst for PDMS cross-linking through a pipette, adjust the speed to 1000 rpm, and ramp the temperature to 80 °C under high-speed stirring. In this process, the temperature rise rate should be controlled to avoid rapid gasification of isopropanol into bubbles, resulting in explosion. As the reaction progressed, it was observed that the rotor agitation slowed down, implying an increase in the degree of PDMS crosslinking. After the system was stabilized at 80 °C, the speed was reduced to 200 rpm and the reaction was carried out for 2 h. Then, the temperature was gradually increased to 120 °C for 1 h, and the system as a whole appeared as a viscous and transparent liquid. The temperature was continued to rise to 180 °C for 3 h to solidify, and the product was the PDMS material required for the experiment.

The preparation process of SiO_2 is as follows: Weigh an appropriate amount of CTAB into a beaker, mix ethanol, ammonia water and distilled water in a ratio of 1:1:1 and add to the beaker until cetyltrimethylammonium bromide (CTAB) dissolves, vigorously at room temperature. Under stirring, tetraethyl orthosilicate (TEOS) was added dropwise to the mixed solution, stirring was continued for 6 h, and then centrifuged. The solid phase was washed three times with deionized water, and dried under vacuum at 100 °C for 12 h. The dried samples were calcined at 560 °C for 6 h in a muffle furnace to obtain SiO_2 required for the experiment.

3.1.2 Preparation of SiO_2 -doped PDMS-coated anode

Mix 0.2 g of SiO_2 with 5 mL of toluene evenly, then take 1 g of the prepared PDMS material and add it into the solution, stir for 10 h to dissolve the material, and the obtained viscous liquid is the solution used for film coating. About 20 cm^2 of zinc foil was cut and attached to a clean glass plate, and the solution was evenly coated on the zinc foil with a 100 μm scraper, and left to air dry under a fume hood for 24 h to obtain SO-PDMS@Zn pole pieces.

3.1.3 Cathode preparation and assembly of button symmetrical battery and full battery

The experiments directly used commercialized V_2O_5 as the cathode active material. The positive electrode slurry was prepared by mixing V_2O_5 with super P and PVDF in a ratio of 7:2:1, adding 10 mL of NMP, and stirring for 10 h. An appropriate amount of cathode slurry was poured onto the current collector titanium foil, and the slurry was uniformly coated on the titanium foil with a 100 μm scraper, and vacuum-dried for 24 h to obtain a V_2O_5 cathode.

Assembly of the button full cell: V_2O_5 sheet was used as the cathode, SO-PDMS@Zn was used as the anode, 2 M ZnSO_4 solution was used as the electrolyte, and the battery case model was CR2032.

The symmetric cell assembly process is similar to the full cell assembly process, both the anode and cathode of the experimental group/control group are SO-PDMS@Zn or uncoated bare Zn. At the same time, uncoated Zn was used as the anode to assemble the control full cell, and copper foil was used as the cathode to prepare the Zn//Cu half-cell by the same method to measure the Coulombic efficiency.

3.1.4 Electrochemical test methods for symmetrical cells and full cells

The plating/stripping performance of symmetrical cells was tested using the Blue Battery Test System. The set parameters are as follows: the current density is 1.0 mA cm^{-2} , the areal capacity is 1.0 mAh cm^{-2} , and the cycles are 250 times.

The CA curve of the symmetrical cell was tested with an electrochemical workstation, and the applied overpotential was set to -150 mV; the Coulombic efficiency of the Zn//Cu half-cell was tested; and the capacity characteristic of the coin-cell full cell was tested.

3.1.5 Characterization method

The phase of experimentally synthesized SiO_2 was characterized by X-ray diffractometer. The element distribution and bonding situation in the samples were characterized by Fourier transform infrared spectrometer.

3.2 Results and Discussion

3.2.1 Structural Characterization

XRD patterns of the experimentally prepared SiO_2 were analyzed. As shown in Figure 3-1, the XRD of SiO_2 prepared in the experiment has an obvious peak at $2\theta = 21.2^\circ$, which corresponds to the absorption peak of SiO_2 standard card at this place, which shows that SiO_2 was successfully synthesized.

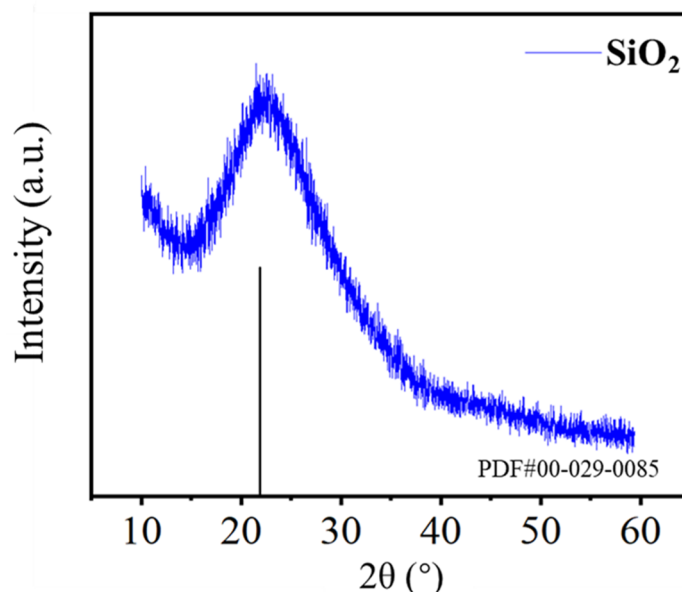


Figure 3-1 Comparison of XRD patterns of experimentally synthesized SiO_2 and standard cards

Figure 3-2 shows the appearance changes of SiO_2 doped PDMS materials during the preparation process. Hydroxy silicone oil is a transparent and viscous liquid. The cross-linking of PDMS makes it solidify into a light white gel. The outer surface of the material is smooth, elastic and has a certain transparency. Compared with PDMS, the appearance of SO-PDMS is off-white, and the transparency is obviously reduced.

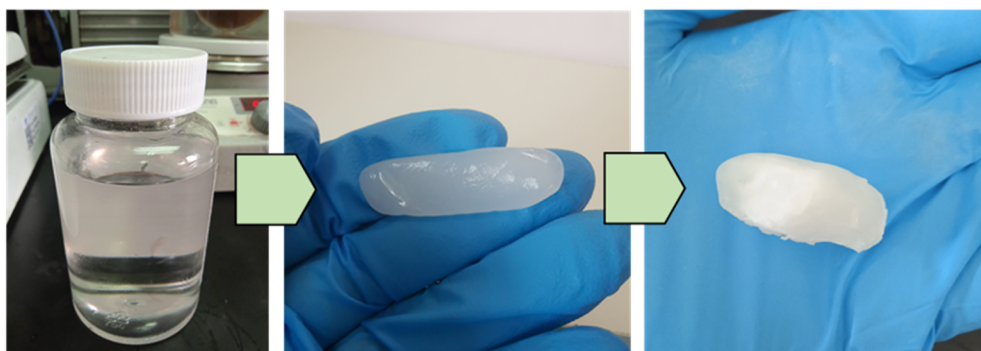


Figure 3-2 Appearance changes during the preparation of SiO_2 -doped PDMS materials. From left to right are hydroxyl silicone oil, PDMS, SO-PDMS.

In order to further understand the composition of the pre-prepared PDMS and the effect of SiO_2 addition on it, the IR spectra of the pre-synthesized PDMS and the PDMS after SiO_2 addition were analyzed, and the results are shown in Figure 3-3.

The absorption peaks of PDMS at 3000-3100 nm are derived from the CH bonds of two methyl groups on the PDMS monomer; the absorption peaks at 800 nm are derived from the C-Si bonds at

the terminal positions of PDMS and the main chain, and the absorption peaks produce tiny inconsistencies. The regular splitting may be caused by the connection of three carbon atoms to the terminal Si; there is an absorption peak of Si-O-Si and Sn-O peak at 1000~1300 nm, which is derived from dibutyltin dilaurate and silicone oil. The combination of; the absorption peak at 1300 corresponds to the BO bond, which is derived from the coupling agent boronic acid. It can be seen from the spectrum that the preparation reaction of PDMS is complete, and the IR spectrum of PDMS doped with SiO₂ is basically consistent with the former. The addition of SiO₂ does not affect the structure of PDMS itself.

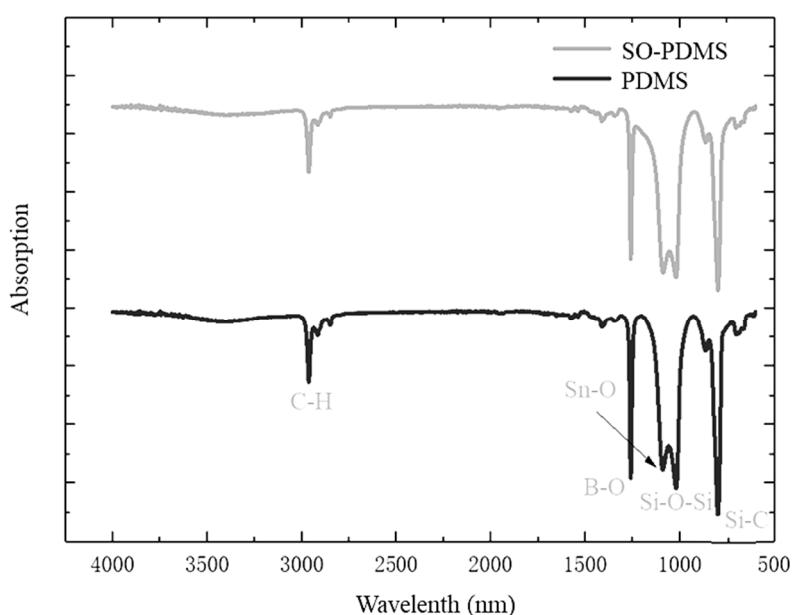


Figure 3-3 Comparison of IR spectra of SO-PDMS and PDMS

3.2.2 Electrochemical tests of symmetrical cells and full cells

The assembled Zn-Zn symmetric cells were analyzed using the LANHE battery test system to test the Zn deposition/dissolution behavior of metallic zinc in aqueous electrolytes, with cycling capacity parameters set to 1 mA cm⁻² and 1 mAh cm⁻². The reason for using a Zn-Zn symmetrical cell for testing is to avoid the influence of the auxiliary electrode on the measurement, and to avoid the production of side reactions on the counter electrode. As shown in Figure 3-4a, the battery with the SO-PDMS protective film covering the anode stably maintained a lower potential (about 25 mV) than the bare zinc battery during cycling. The initial overpotential of SO-PDMS-coated cells is low and rapidly becomes stable potential, which is due to the ion channel being assisted by SiO₂ intercalated in PDMS while promoting the desolvation of hydrated zinc ions, showing SO-PDMS Excellent ability to activate quickly and then maintain stability. With the increase of the number of cycles, the potential of the SO-PDMS-coated battery is basically unchanged, further reflecting the highly reversible reaction of the coated battery. It can be seen that the charge-discharge of bare zinc begins to become unstable after 76 h of operation, manifesting as the fluctuation of the charge potential and the sharp drop of the discharge potential. The occurrence of this phenomenon may be due to the rapid growth of dendrites on one side of the electrode of the symmetrical battery, and a large number of deactivation of the electrode surface, so that the side electrode loses the ability to carry charges. The deactivation of the single-sided electrode will lead to the continuous deposition of zinc on the side electrode, the continuous growth of dendrites, and eventually pierce the separator to destroy the overall structure. This speculation is also confirmed by the phenomenon that the potential of the other phase also disappears quickly after a period of fluctuation. The zinc electroplating/stripping kinetics of the bare-zinc symmetric battery is only stable for about 80 h, while the SO-PDMS-coated symmetric battery has three times the stable working time (240 h), reflecting the SO-PDMS Great contribution to the surface stability of zinc electrode.

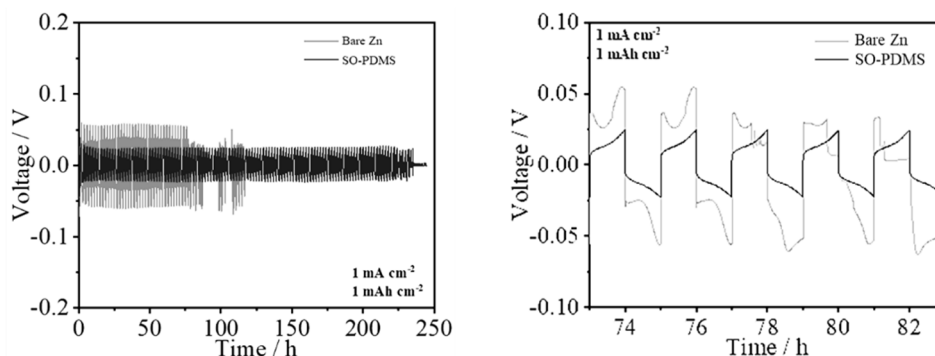


Figure 3-4 Charge-discharge curve of Zn-Zn symmetrical battery. (a) is the overall cycle curve, it can be seen that the overall operating condition of the coated battery is better than that of the bare Zn battery; (b) is the curve of the bare Zn symmetrical battery that begins to fluctuate around 76 h.

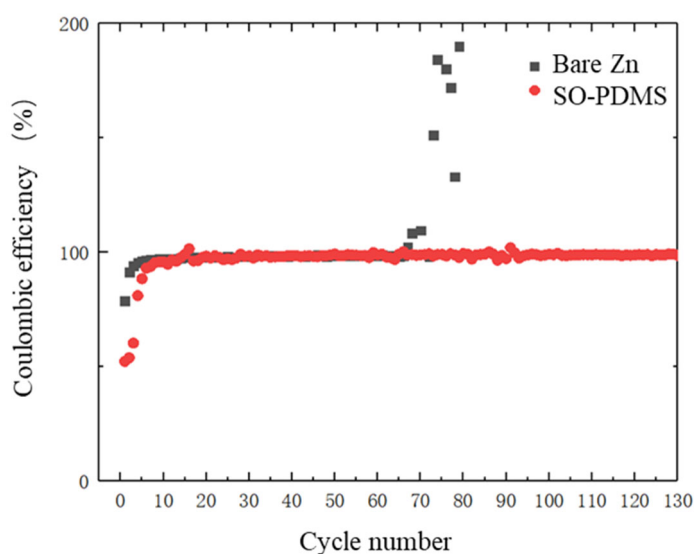


Figure 3-5 Coulomb efficiency analysis of electrode materials

Then, the coulombic efficiency analysis of bare Zn//Cu cells and SO-PDMS@Zn //Cu cells was performed using an electrochemical workstation. It can be seen from Figures 3-5 that the initial coulombic efficiency of the SO-PDMS coated half-cell has a gradual increase process, which is due to the fact that the electrode needs a certain time to activate. This phenomenon can also be seen in the bare zinc half-cell. Relatively speaking, the coulombic efficiency of bare zinc is stable earlier. It can be seen that the SO-PDMS coating has a strong control effect on Zn²⁺, and has a certain influence on the increase rate of the coulombic efficiency at the beginning. The coulombic efficiency of the SO-PDMS coated half-cell and the bare-zinc half-cell remained stable at about 98%, but the coulombic efficiency of the bare-zinc battery began to lose stability around 65 cycles, while the SO-PDMS-coated battery remained stable at 130 cycles. Stable Coulomb efficiency was maintained, and no significant loss was seen. The average coulombic efficiency of the experimentally assembled SO-PDMS-coated half-cell running for 130 cycles is calculated to be 97.21%, showing an excellent cycle reversibility.

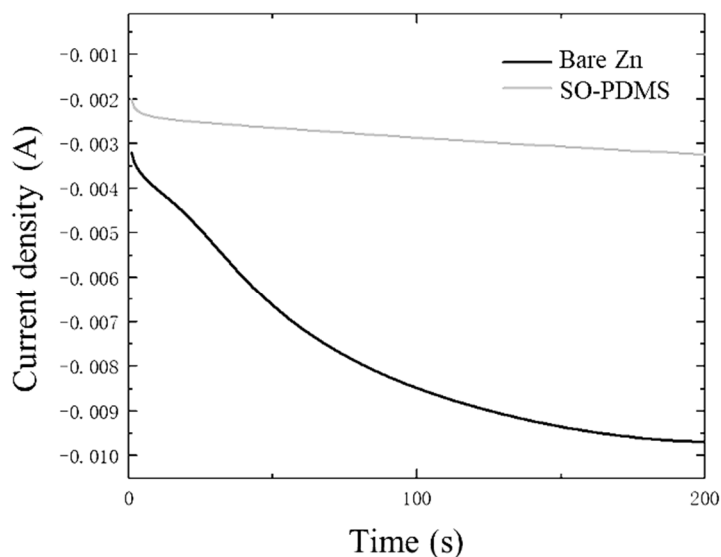


Figure 3-6 CA characteristic curves of bare zinc half cell and SO-PDMS coated half cell

In order to further explore the mechanism of zinc deposition on the electrode surface, CA curves were measured for the bare Zn//Cu half-cell and the SO-PDMS@Zn //Cu half-cell. It can be seen from Figure 3-6 that the current of the bare zinc battery decreases rapidly with time, which corresponds to the rapid and continuous 2D diffusion on the surface of the bare zinc electrode. Ion exchange and deposition occur where the distribution is most dense and where the surface energy is lowest. Due to the existence of the tip effect, the location of the initial deposition of Zn^{2+} ions is often the most suitable location for zinc deposition during the whole process, so zinc dendrites continue to grow throughout the process. From the CA curve of the SO-PDMS coated half-cell, it can be seen that the curve initially decreases for a short period and then becomes flat, which indicates that the initial Zn nucleation and 2D diffusion process are completed in a very short time, and then a relatively stable process is carried out. 3D Diffusion. This is because the SO-PDMS coating imposes an additional energy barrier for the planar diffusion of Zn^{2+} on the surface of the Zn anode, so that Zn^{2+} cannot easily reach the optimal deposition site in the 2D diffusion, but is generated at the Zn^{2+} surface. The vicinity of the site is re-deposited, thereby increasing the number of nucleation sites.

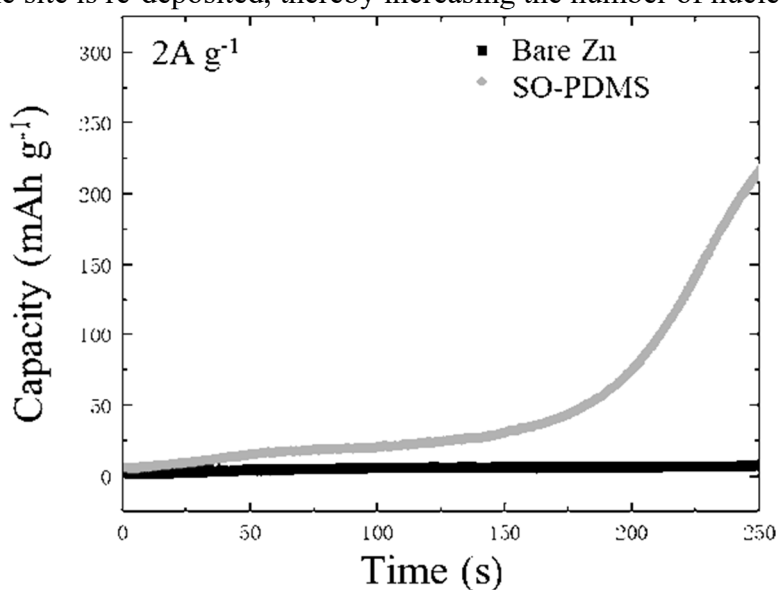


Figure 3-7 Battery capacity curves of bare zinc full cell and SO-PDMS coated full cell

Finally, the capacity curves of the assembled full cells were measured. It can be seen from Figure 3-7 that at a current density of 2 A g^{-1} , the capacity of the zinc-vanadium full battery assembled with

bare zinc as the anode increases slowly with time, while the capacity of the coated zinc-vanadium full battery has a continuous increase. There is an upward trend, and the capacity increases to 240 mAh g⁻¹ after 250 s. It can be seen that the full battery operates normally, and the SO-PDMS coated electrode has far better performance than bare zinc.

4. Conclusions

This paper introduces the advantages and disadvantages of aqueous zinc-ion batteries, and expounds the status quo of its development and various problems currently faced. The dendrite problem is the most important problem in the current development of AZIBs. In this paper, through the analysis of the mechanism of dendrite growth, starting from the initial formation mechanism of dendrites, a SiO₂ doped PDMS film coating is designed to prevent zinc dendrites. It lays the foundation for subsequent research and application, and has a positive impact on alleviating the current situation of energy shortage and enhancing the application of green energy.

References

- [1] WHITTINGHAM M S, CLARK L D. Nuclear magnetic resonance linewidth of thallium tungsten bronze [J]. *The Journal of Chemical Physics*, 1970, 53(10): 4114-5.
- [2] DUNN B, KAMATH H, TARASCON J-M. Electrical energy storage for the grid: a battery of choices [J]. *Science*, 2011, 334(6058): 928-35.
- [3] RUAN Y L, WANG J. Research on the development path of lithium-ion power battery industrialization [J]. *Automotive Industry Research*, 2018, (12): 28-35..
- [4] KIM H, CHOI W, YOON J, et al. Exploring anomalous charge storage in anode materials for next-generation Li rechargeable batteries [J]. *Chemical Reviews*, 2020, 120(14): 6934-76.
- [5] FANG G, WANG Q, ZHOU J, et al. Metal organic framework-templated synthesis of bimetallic selenides with rich phase boundaries for sodium-ion storage and oxygen evolution reaction [J]. *Acs Nano*, 2019, 13(5): 5635-45.
- [6] XUE L, GAO H, ZHOU W, et al. Liquid K–Na alloy anode enables dendrite-free potassium batteries [J]. *Advanced Materials*, 2016, 28(43): 9608-12.
- [7] CHEN S, WANG J, FAN L, et al. An ultrafast rechargeable hybrid sodium-based dual-ion capacitor based on hard carbon cathodes [J]. *Advanced Energy Materials*, 2018, 8(18): 1800140.
- [8] HWANG J Y, MYUNG S T, SUN Y K. Recent progress in rechargeable potassium batteries [J]. *Advanced Functional Materials*, 2018, 28(43): 1802938.
- [9] NAYAK P K, YANG L, BREHM W, et al. From lithium-ion to sodium-ion batteries: a materials perspective [J]. *Angew Chem, Int Ed*, 2017, 56: 2-27.
- [10] LIN M-C, GONG M, LU B, et al. An ultrafast rechargeable aluminium-ion battery [J]. *Nature*, 2015, 520(7547): 324-8.
- [11] YU Y, XIE J, ZHANG H, et al. High-voltage rechargeable aqueous zinc-based batteries: latest progress and future perspectives [J]. *Small Science*, 2021, 1(4): 2000066.
- [12] WANG F, BORODIN O, GAO T, et al. Highly reversible zinc metal anode for aqueous batteries [J]. *Nature Materials*, 2018, 17(6): 543-9.
- [13] YANG Q, LI Q, LIU Z, et al. Dendrites in Zn-based batteries [J]. *Advanced Materials*, 2020, 32(48): 2001854.
- [14] ZHENG G, WANG C, PEI A, et al. High-performance lithium metal negative electrode with a soft and flowable polymer coating [J]. *ACS Energy Letters*, 2016, 1(6): 1247-55.
- [15] SWENSON C. Lithium metal: an experimental equation of state [J]. *Journal of Physics and Chemistry of Solids*, 1966, 27(1): 33-8.
- [16] CAO X, REN X, ZOU L, et al. Monolithic solid–electrolyte interphases formed in fluorinated orthoformate-based electrolytes minimize Li depletion and pulverization [J]. *Nature Energy*, 2019, 4(9): 796-805.

- [17] YANG C-S, KIM J-J, KIM T S, et al. Small heterodimer partner interacts with NLRP3 and negatively regulates activation of the NLRP3 inflammasome [J]. *Nature Communications*, 2015, 6(1): 1-11.
- [18] CHEN H, XU H, ZHENG B, et al. Oxide film efficiently suppresses dendrite growth in aluminum-ion battery [J]. *ACS Applied Materials & Interfaces*, 2017, 9(27): 22628-34.
- [19] WANG H, GU S, BAI Y, et al. High-voltage and noncorrosive ionic liquid electrolyte used in rechargeable aluminum battery [J]. *ACS Applied Materials & Interfaces*, 2016, 8(41): 27444-8.
- [20] KIM D J, YOO D-J, OTLEY M T, et al. Rechargeable aluminium organic batteries [J]. *Nature Energy*, 2019, 4(1): 51-9.
- [21] DING F, XU W, GRAFF G L, et al. Dendrite-free lithium deposition via self-healing electrostatic shield mechanism [J]. *Journal of the American Chemical Society*, 2013, 135(11): 4450-6.
- [22] CHENG X B, HOU T Z, ZHANG R, et al. Dendrite-free lithium deposition induced by uniformly distributed lithium ions for efficient lithium metal batteries [J]. *Advanced Materials*, 2016, 28(15): 2888-95.