

β -Cyclodextrin is Used as a Solid-state Electrolyte Additive to Improve the Electrochemical Properties of Zinc-Ion Batteries

Bofan SU[†], Rong LI[†], Ying LIU, Haizhu SUN^{*}

National & Local United Engineering Laboratory for Power Batteries, Faculty of Chemistry, Northeast Normal University, Changchun Jilin 130024, China

^{*}Corresponding Author: Haizhu SUN, E-mail: sunhz335@nenu.edu.cn

[†]Co-first Authors: Bofan SU, Rong LI

Abstract

Solid-state zinc-ion batteries (SSZIBs) have become a promising alternative energy storage system in the field of large-scale energy storage and flexible electronics due to their high safety, low cost, environmental friendliness and excellent theoretical specific capacity. However, there are still bottlenecks such as low ionic conductivity at room temperature, high solid-solid interface impedance, and poor zinc dendrite growth and interface stability. In order to solve these problems, polyethylene oxide (PEO) based solid-state electrolyte was used, and its polymer skeleton structure can inhibit the formation of zinc dendrites. However, PEO-based solid electrolytes still have defects such as insufficient ionic conductivity at room temperature and insufficient interface contact, which need to be further improved by functional additives. With its unique caged supramolecular structure, β -cyclodextrin can form host-guest complexes with zinc ions, significantly improving the ionic conductivity of PEO-based solid electrolytes. In this study, β -CD was introduced into the system as a modified additive, and the optimized β -CD solid-state electrolyte Zn||Zn was used Zn symmetric batteries exhibit an ultra-long cycle life of 675 h at a current density of 10 mA cm⁻² and a capacity density of 1 mAh cm⁻², and an ultra-long cycle life of 813 h at a current density of 4 mA cm⁻² and a capacity density of 1 mAh cm⁻². For Zn||I₂ cell, with an initial discharge specific capacity of about 144.51 mAh g⁻¹ at a current density of 0.5 A g⁻¹, still maintains 91% capacity after 1800 cycles. This study not only provides a feasible scheme for zinc anode stabilization, but also confirms that β -CD provides a practical technical path for the practical application of PEO solid-state electrolyte batteries.

Keywords: β -cyclodextrin; PEO solid electrolyte; zinc anode dendrite inhibition; interface control

1 Introduction

In recent years, solid-state zinc-ion batteries (SSZIBs) have attracted widespread attention in the field of large-scale sustainable energy storage due to their high safety, low cost, environmental friendliness, and high theoretical capacity^[1]. However, the practical application of SSZIBs is still plagued by many bottlenecks, such as zinc dendrite growth caused by uneven zinc ion deposition^[2], as well as problems of high solid-solid interface impedance and interfacial side reactions (such as metal corrosion), which significantly reduce the coulombic efficiency (CE) and cycle life of the battery, severely restricting its commercialization process^[3].

To overcome the key challenges of SSZIBs, researchers have developed a series of effective strategies, including zinc anode substrate modification, artificial interface protection layer construction, electrolyte system optimization, and research and development of new solid-state electrolytes^[4]. Among the many technical routes, solid-state electrolyte

modification and the introduction of functional additives have shown irreplaceable practical value in regulating interface behavior, optimizing ion transport, and improving battery performance due to their outstanding advantages such as no need for complex equipment, low modification cost, and good compatibility with existing industrial processes, and have become the most promising solutions for large-scale promotion^[5]. Organic additives have attracted widespread attention due to their good dispersion in solid electrolytes and their unique regulatory mechanisms^[6]. Most organic molecules have a strong affinity for zinc matrix and Zn²⁺, which can preferentially adsorb on the surface of zinc anode, effectively hinder the disordered growth of zinc dendrites and alleviate interfacial side reactions, and improve the interfacial contact between solid electrolyte and electrode, thereby significantly improving the overall performance of SSZIBs^[7]. For example, Wang et al. reported a strategy to regulate zinc ion deposition orientation while inhibiting side reactions by β -cyclodextrin (β -CD). The macrocyclic supramolecular

cyclodextrin with hydrophobic cavity and hydrophilic surface can be horizontally adsorbed to the surface of the zinc anode, effectively shielding the charge on the electrode surface, standardizing the diffusion path of zinc ions, and allowing them to be horizontally epitaxial deposited at the lowest non-energy position.

Among various organic molecules, β -CD is a typical cyclic oligosaccharide, with a unique hydrophobic cavity structure and a large number of hydrophilic hydroxyl groups distributed on the outer surface, showing excellent dispersion and chemical stability^[8]. Its rich hydroxyl group can be used as a zincophilic site, which strongly interacts with Zn^{2+} and electrolyte components, reconstructs the Zn^{2+} transport pathway, optimizes ion transport kinetics, and guides the uniform deposition of Zn^{2+} ^[9]. Its unique cavity structure can encapsulate active small molecules, further inhibit the electrode/electrolyte interface side reaction, improve interface stability, and provide a good material basis for the optimization of SSZIBs performance^[10].

However, the systematic research on the application of β -CD as a multifunctional additive to SSZIBs solid electrolyte systems is still insufficient, and its regulatory mechanism on the stability of zinc anode, solid electrolyte ionic conductivity and overall electrochemical performance of batteries still needs to be further revealed. In this work, β -CD is introduced into polyethylene oxide (PEO) based solid-state electrolytes as green and efficient functional additives to solve the problems of instability, high interface impedance and insufficient ionic conductivity of SSZIBs zinc anode. The effects of β -CD on Zn^{2+} solvation structure, ion transport kinetics, zinc deposition behavior and interfacial stability were systematically studied. This study is expected to provide a simple and effective strategy for constructing highly stable and long-life SSZIBs, and broaden the application of cyclodextrin-based materials in the field of electrochemical energy storage. Zn||Zn assembled with PEO electrolyte with β -CD The Zn symmetric battery achieves an ultra-long cycle life of 675 h under the condition of 10 mA cm⁻² current density and 1 mAh cm⁻² capacity density, and a cycle life of 813 h under the condition of 4 mA cm⁻² current density and 1 mAh cm⁻². For Zn||I₂, with an initial discharge specific capacity of about 144.51 mAh g⁻¹ at a current density of 0.5 A g⁻¹, still maintains 91% capacity after 1800 cycles

2 Experimental Section

2.1 Materials

The experimental reagents selected in this experiment were polyethylene oxide (PEO), β -cyclodextrin (β -CD) (96%), zinc trifluoromethanesulfonate $Zn(CF_3SO_3)_2$, purity 98%, acetonitrile (CH₃CN, AR), all reagents were used directly without further purification. Ultrapure water is used in the experimental process.

2.2 Solid electrolyte preparation

Blank PEO solid electrolyte: weigh 1 g of PEO, 0.5 g of $Zn(CF_3SO_3)_2$, add to 30 mL of acetonitrile, and stir magnetically at room temperature for 6 h until completely dissolved, to obtain a homogeneous precursor; Pour into the Teflon mold and let it stand at room temperature for 48 h, and wait for the acetonitrile to fully volatilize and solidify to obtain a pure PEO solid electrolyte.

β -CD modified PEO solid electrolyte (PEO/ β -CD): 1 g of PEO, 0.5 g of $Zn(CF_3SO_3)_2$, and 5 mg of β -CD were weighed, added to 30 mL of acetonitrile, and magnetically stirred at room temperature for 6 h until completely dissolved, and a homogeneous transparent precursor was obtained. The Teflon mold was poured into a PTFE mold and cured at room temperature for 48 hours to obtain a β -CD-modified PEO solid electrolyte.

2.3 Cell assembly

Solid-state electrolyte battery is assembled in an air environment, and is assembled in sequence according to the anode shell, zinc anode, solid electrolyte, cathode sheet, gasket, shrapnel, and cathode shell, and is pressed with a button battery sealer to ensure that the battery is well sealed. All batteries are coin cell type CR2032 cells.

2.4 Material characterization

Fourier transform infrared spectroscopy (FTIR) was used to characterize β -CD and solid-state electrolyte functional groups. Scanning electron microscopy (SEM) was used to observe the surface morphology of the zinc anode after cycling. Electrochemical tests are performed at CHI660E electrochemical workstations.

2.5 Electrochemical measurements

Electrochemical impedance spectroscopy (EIS): amplitude 5 mV, frequency 0.01 Hz-1.0 MHz. Linear scanning voltammetry (LSV): scanning rate 1 mV s⁻¹, hydrogen evolution 0-0.5 V, oxygen evolution 0-3 V. Tafel curve: Sweep rate 1 mV s⁻¹, voltage -0.3-0.3 V. The chronometric current method (CA) records the current-time curve. Ionic conductivity by stainless steel gasket-solid electrolyte-stainless steel gasket battery combined with EIS test, formula:

$$\sigma = \frac{L}{RS}$$

Ionic conductivity (S cm⁻¹), L is the electrolyte thickness (cm), R is the impedance (Ω), and S is the contact area (cm²).

The number of Zn^{2+} migrations is via Zn||Zn symmetrical battery combined with i-t curve with EIS test, formula:

$$t_{Zn^{2+}} = \frac{I_s (\Delta V - I_0 R_0)}{I_0 (\Delta V - I_s R_s)}$$

where $t_{Zn^{2+}}$ is the Zn^{2+} migration number, ΔV is the

polarization voltage, I_0 is the initial current, I_s steady-state current, and R_0 and R_s are impedance before and after polarization.

Half-cell cyclic voltammetry (CV): Scan rate 2 mV s^{-1} , voltage range -0.2-0.4 V.

3. Results and Discussion

3.1 Characterization of solid-state electrolytes and analysis of the mechanism of action of β -CD

As shown in Figure 1a, the characteristic peak of stretching vibration appears at $3200\text{-}3500\text{ cm}^{-1}$, $2850\text{-}2950\text{ cm}^{-1}$ is the carbon-hydrogen bond telescopic vibration absorption peak, and $1000\text{-}1200\text{ cm}^{-1}$ belongs to the molecular backbone C-O-C, indicating that the molecular structure of β -CD is intact. XRD was used to investigate the β -CD. As shown in Figure 1b, a distinct broad peak is observed in the range of $1\text{-}30^\circ$. The PEO and PEO/ β -CD composite electrolytes were characterized. As shown in Figure 1c, the incorporation of β -CD leads to a blue shift. This is because the introduction of β -CD provides more contact sites for Zn^{2+} . As shown in Figure 1d, after the addition of β -CD, the intensity of the two characteristic diffraction peaks of PEO was significantly weakened and the peak shape was widened, and there was no obvious crystal diffraction peak of β -CD. The results showed that β -CD could effectively disrupt the regular arrangement of PEO molecular chains, inhibit crystal growth, and reduce the

crystallinity of the system. The increase of the amorphous zone ratio can improve the motion ability of polymer chain segments and construct a continuous ion transport channel, which is conducive to accelerating the migration rate of zinc ions.

Figure 2. shows a SEM comparison image of PEO/ β -CD composite electrolyte and pure PEO electrolyte, which is used to visually reflect the microscopic morphological differences of the materials. PEO/ β -CD composite electrolyte (Figures 2a-b): At $50\text{ }\mu\text{m}$ and $20\text{ }\mu\text{m}$, the sample surface showed a uniform, dense, and continuous morphology, with no obvious holes, cracks, or phase separation. This indicates that β -CD has good dispersion in the PEO matrix, and the two form a homogeneous composite system through intermolecular interaction, constructing a continuous ion transport path. Pure PEO electrolyte (Figure 2c-d): The surface of pure PEO is rough, with obvious wrinkles, agglomeration and even microcracks, which is caused by its high crystallinity leading to regular stacking of chain segments and stress concentration. This inhomogeneous structure can easily cause ion transport path interruptions and affect electrolyte performance. In contrast, the introduction of β -CD significantly improved the microscopic morphology of PEO-based electrolytes, inhibited the crystal agglomeration of PEO, and formed a more uniform and dense film structure, which was mutually confirmed by the results of XRD and FTIR, and provided favorable conditions for improving the ionic conductivity and interface stability of the electrolyte.

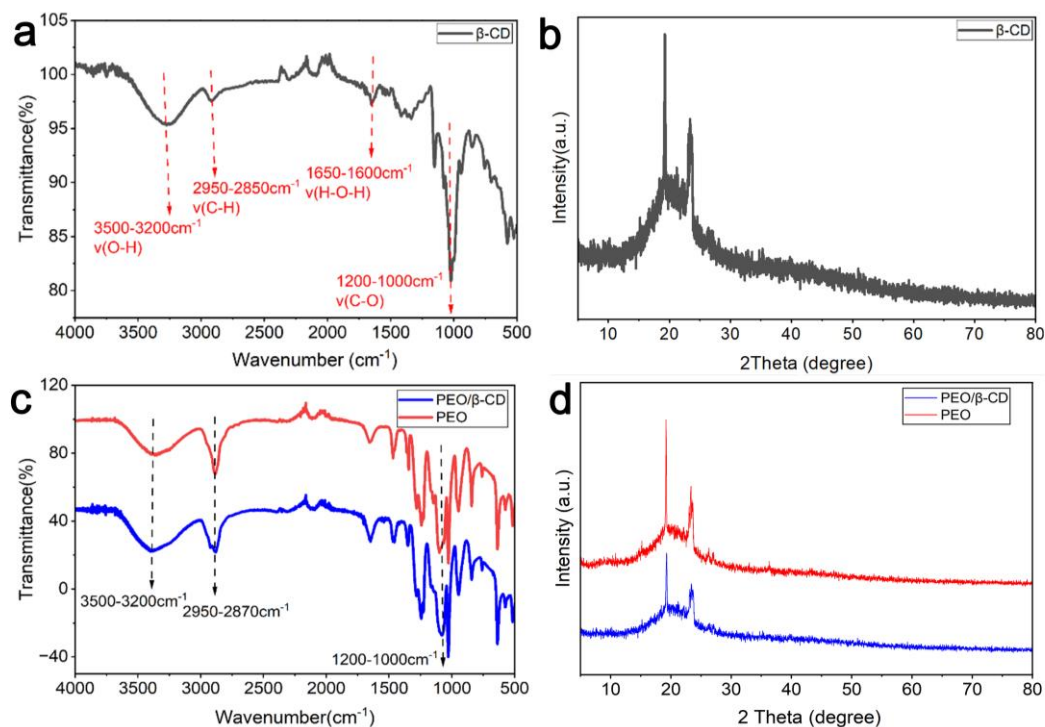


Figure 1 (a) FTIR spectra of pure β -CD. (b) XRD pattern of pure β -CD. (c) FTIR spectra of pure PEO and PEO/ β -CD composite electrolyte. (d) XRD patterns of pure PEO and PEO/ β -CD composite electrolyte

3.2 Effect of β -CD on the electrochemical properties of PEO solid electrolytes

Firstly, the electrochemical stability windows of PEO and PEO/ β -CD composite electrolytes were evaluated via LSV. As shown in Figure 3a-3b, the introduction of β -CD greatly broadens the electrochemical stability window of the PEO/ β -CD composite electrolyte. The negative voltage range shifts from -0.5 V to -1.0 V, while the positive voltage range expands from 1.80 V to 2.25 V, exhibiting a wider electrochemical stability window. This indicates that the incorporation of β -CD effectively improves the oxidation resistance of the PEO matrix, allowing the electrolyte to

maintain chemical stability within a broader voltage range and thereby providing a safer and more stable operating environment for batteries. Figure 3c shows the AC impedance spectra of pure PEO and PEO/ β -CD composite electrolytes for calculating ionic conductivity. The ionic conductivity of the pure PEO electrolyte was only $0.0198 \text{ mS cm}^{-1}$, while the PEO/ β -CD composite electrolyte was significantly increased to $0.0482 \text{ mS cm}^{-1}$. It can be seen that the addition of β -CD reduces the impedance of the electrolyte body, destroys the highly crystalline structure of PEO, constructs a smoother zinc ion transport channel, and significantly improves the ion conduction ability.

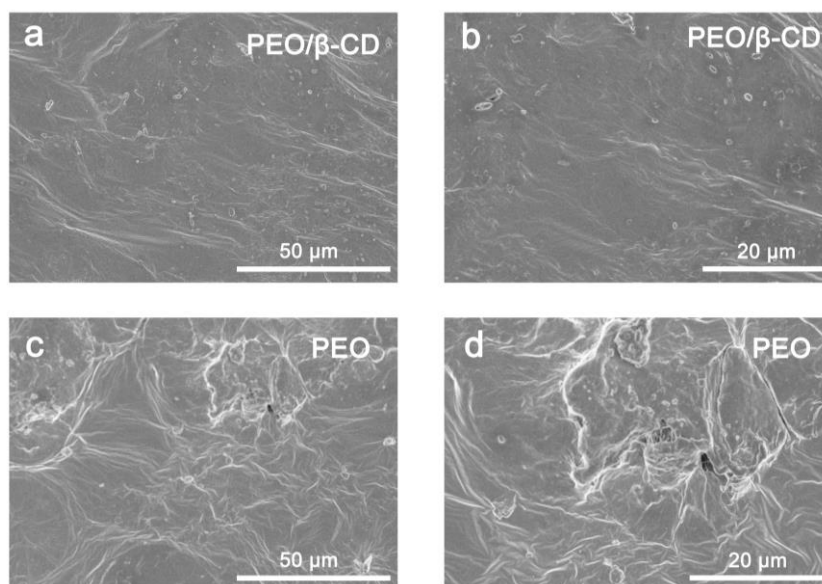


Figure 2 SEM image of PEO/ β -CD electrolyte. (a) 50 μm . (b) 20 μm . SEM image of pure PEO electrolyte. (c) 50 μm . (d) 20 μm .

Interfacial kinetics was analyzed based on electrochemical impedance spectroscopy (EIS). Figure 3d shows the interface impedance comparison of the two electrolytes. The interface impedance of pure PEO electrolyte is 420000Ω , and the load transfer resistance is high. The interfacial impedance of the modified PEO/ β -CD composite electrolyte is 175000Ω , which is small. The results show that β -CD optimizes the interface adhesion between the electrolyte and the electrode, reduces the charge transfer barrier, and facilitates the rapid migration of ions between interfaces. The zinc ion migration number ($t_{\text{Zn}^{2+}}$) determined by potentiostatic polarization combined with impedance method. Figure 3e shows the zinc ion migration number of pure PEO electrolyte is only 0.20, indicating that most of the current is contributed by anion migration, and the proportion of zinc ion directional transport is low, which can easily lead to serious concentration polarization and local current unevenness, and induce zinc dendrite growth. The $t_{\text{Zn}^{2+}}$ of PEO/ β -CD composite electrolyte increased to 0.55 (Figure 3f), which was significantly higher than that of the pure PEO system. This

improvement is due to the complexation and binding effect of the cage structure of β -CD on anions, which effectively inhibits the migration of anions and promotes the directional transport of zinc ions, which is conducive to achieving uniform zinc deposition and inhibiting dendrite growth, thereby improving the cycle stability of the battery.

In conclusion, the electrochemical characterization results show that the β -CD modified PEO electrolyte shows significant advantages in electrochemical stability window, interface and body ion transport performance and zinc ion migration number, which corroborates the conclusions of the previous structural characterization, and fully proves the positive role of β -CD in optimizing the structure and performance of PEO-based solid electrolytes.

3.3 Effects of β -CD on zinc deposition behavior

Figure 4a shows the tafel polarization curves of pure PEO and PEO/ β -CD composite electrolytes to characterize the corrosion current density of the zinc anode. The corrosion current density of the pure PEO

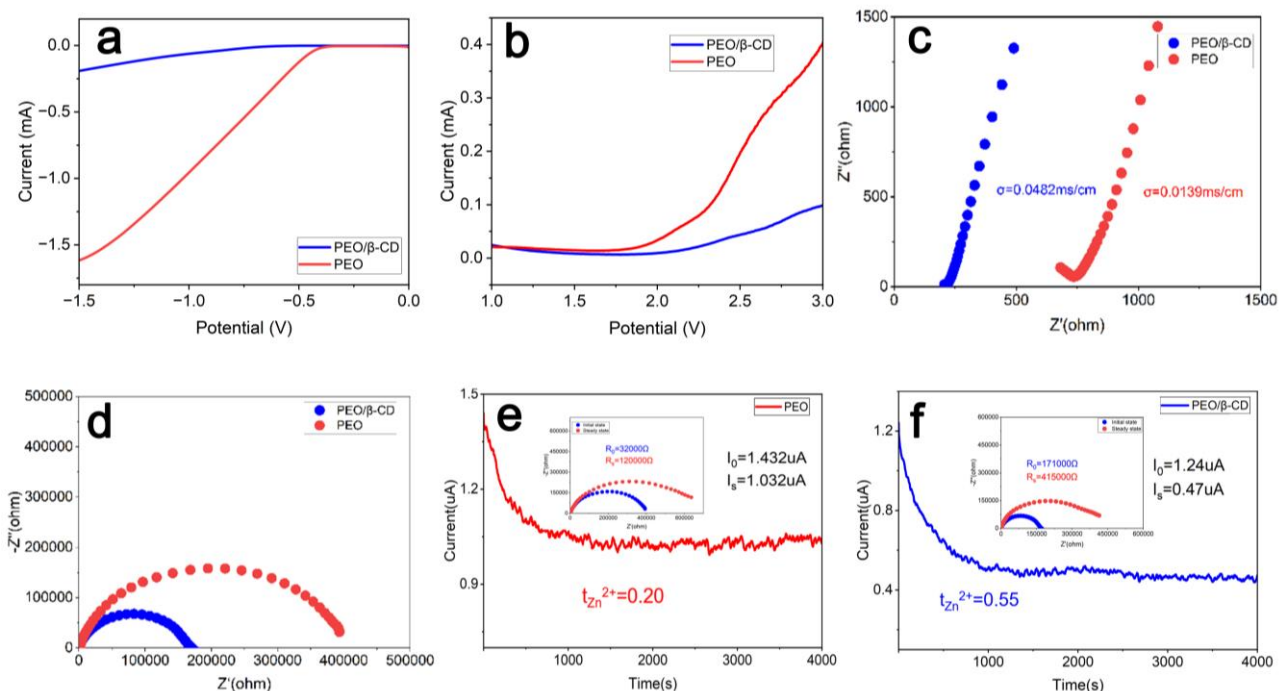


Figure 3 (a) LSV curves of PEO and PEO/ β -CD electrolytes. (b) High-potential LSV curves of PEO and PEO/ β -CD electrolytes. (c) EIS curves for ionic conductivity of PEO and PEO/ β -CD electrolytes. (d) EIS of PEO and PEO/ β -CD composite electrolyte. Fitting data of ion transference number. (e) PEO. (f) PEO/ β -CD composite electrolyte.

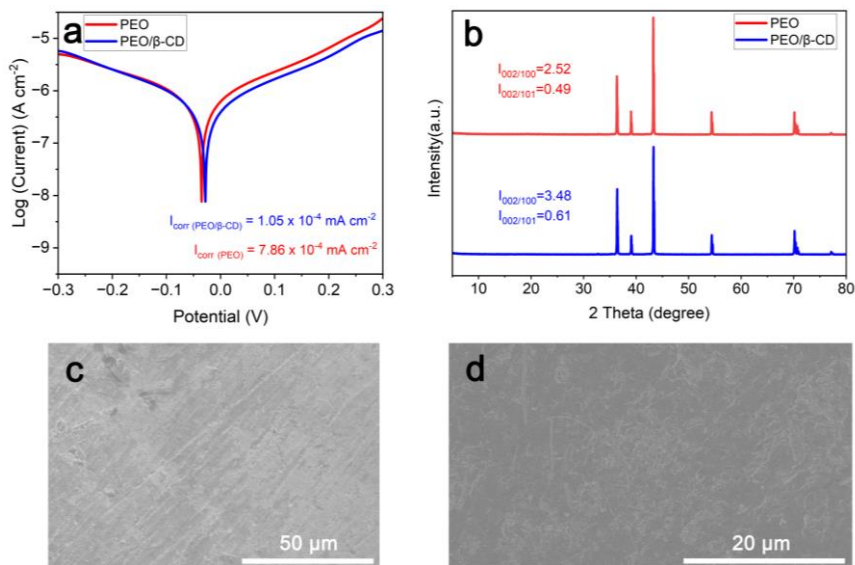


Figure 4 (a) Tafel polarization curves of Zn anodes in PEO and PEO/ β -CD electrolytes. (b) XRD patterns of Zn anodes after cycling in PEO and PEO/ β -CD electrolytes. (c) SEM image of Zn anode cycled in PEO electrolyte. (d) SEM image of Zn anode cycled in PEO/ β -CD electrolyte.

system was 7.86×10^{-4} mA cm $^{-2}$, and after the introduction of β -CD, the corrosion current density of the PEO/ β -CD system was reduced to 1.05×10^{-4} mA cm $^{-2}$, and the corrosion current was significantly reduced, indicating that β -CD effectively inhibited the side reaction and self-corrosion of the zinc anode, improved the interface stability of the zinc anode, and was conducive to the long-cycle cycle of the battery. Figure 4b shows the XRD patterns of the zinc anode after

cycling in pure PEO and PEO/ β -CD composite electrolytes, and the crystal plane orientation of zinc is analyzed by using the crystal surface strength ratio. In the pure PEO system, $I_{(002)}/I_{(100)} = 2.52$ and $I_{(002)}/I_{(101)} = 0.49$. After the introduction of β -CD, the intensity ratios of $I_{(002)}/I_{(100)}$ and $I_{(002)}/I_{(101)}$ are 3.48 and 0.61, respectively. The proportion of the (002) crystal plane increases significantly. The 002 crystal surface has a low zinc deposition energy barrier, which can induce uniform zinc

deposition along the horizontal direction parallel to the electrode surface, and effectively inhibit vertically growing zinc dendrites. β -CD regulates the crystal plane orientation of zinc, preferentially induces the optimal growth of 002 crystal plane, optimizes zinc deposition behavior, constructs a flat and stable zinc anode interface, and greatly improves the cycle stability of the battery.

The SEM diagram of PEO/ β -CD composite electrolyte (Figure 4c), with a flat and dense surface, uniform structure, significantly reduced defects, and a continuous ion transport channel, reduced body impedance, and increased ion conductivity, while constructing a stable electrode-electrolyte interface, inhibiting zinc dendrites, and improving cycle stability. Figure 4d shows the SEM diagram of pure PEO electrolyte, with uneven surface and messy texture, a

large number of defects and grooves, discontinuous ion transport pathways, high body impedance, and low ion conductivity, which is easy to cause local zinc dendrite growth.

3.4 Effect of β -Cyclodextrin on the stability of zinc anode

Figure 5a shows the long-cycle comparison curves of symmetrical batteries between pure PEO and PEO/ β -CD composite electrolytes under the conditions of current density 10 mA cm^{-2} and capacity of 1 mAh cm^{-2} . Severe voltage fluctuations and polarization distortions occur in the pure PEO system at the beginning of the cycle, indicating that the interfacial side reactions and zinc dendrite growth have led to the rapid failure of the battery. The PEO/ β -CD composite

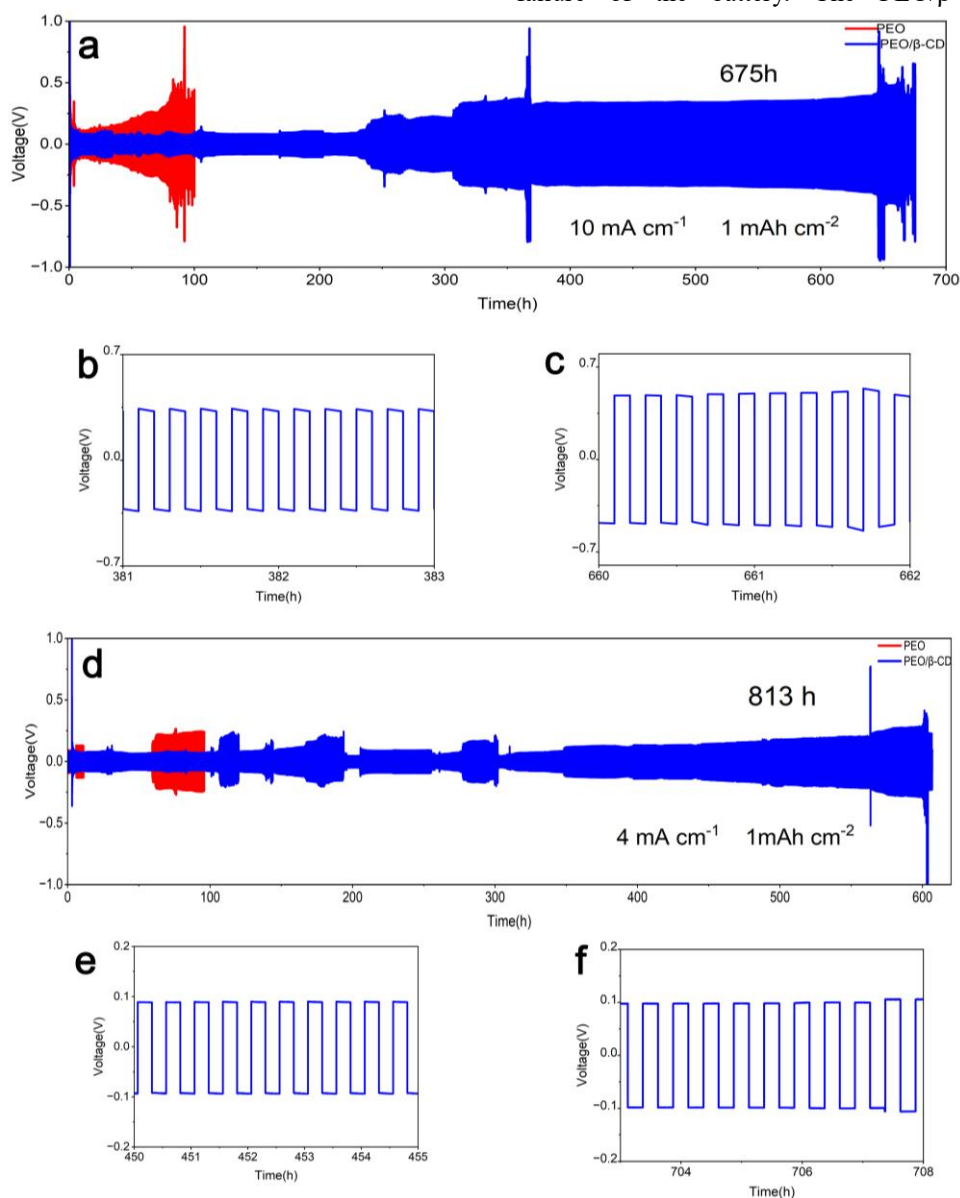


Figure 5 (a) Long-cycle performance of Zn||Zn cells at 10 mA cm^{-2} , 1 mAh cm^{-2} . Magnified voltage profiles at 10 mA cm^{-2} , 1 mAh cm^{-2} . (b) Middle cycle. (c) Late cycle. (d) Long-cycle performance of Zn||Zn cells at 4 mA cm^{-2} , 1 mAh cm^{-2} . Magnified voltage profiles at 4 mA cm^{-2} , 1 mAh cm^{-2} . (e) Middle cycle. (f) Late cycle.

electrolyte can be stably cycled for 675 h, the voltage curve is stable throughout the whole process, and the polarization voltage does not rise significantly, showing excellent interface stability and long cycle life. Figure 5b shows the voltage plateau amplification curve of the PEO/ β -CD composite electrolyte at a current density of 10 mA cm^{-2} in the middle of the cycle. Figure 5c shows the amplification curve of the voltage platform at the end of the cycle under a current density of 10 mA cm^{-2} of the same system. The curve presents a clear, symmetrical rectangular platform, and the polarization voltage is stable at about $\pm 0.5 \text{ V}$ with no significant fluctuations or distortions. It shows that the zinc deposition/dissolution process is highly reversible, the interface polarization is stable, there is no voltage abnormality caused by dendrite growth or side reactions, and the interface state remains good. It was proved that after long-term cycling, the composite electrolyte could still maintain a stable interface environment, effectively inhibit dendrite puncture and interface deterioration, and showed excellent long-period interface stability. Figure 5d shows the long-cycle comparison curves of symmetrical PEO and PEO/ β -CD composite electrolyte under the conditions of current density of 4 mA cm^{-2} and capacity of 1 mAh cm^{-2} . The pure PEO system has violent voltage fluctuations at the beginning of the cycle and fails quickly, indicating that the interfacial side reactions and dendrite growth lead to rapid deterioration of the battery.

The PEO/ β -CD composite electrolyte can be stably cycled for 813 h, and the voltage curve is stable throughout the process, and the polarization does not increase significantly, indicating that the composite electrolyte can also regulate zinc deposition behavior for a long time, inhibit dendrite and side reactions, and significantly extend the battery life under low and medium current density. Figure 5e shows the voltage plateau amplification curve of the PEO/ β -CD composite electrolyte at a current density of 4 mA cm^{-2} in the middle of the cycle. Figure 5f shows the amplification curve of the voltage platform at the end of the cycle under the current density of 4 mA cm^{-2} of the same system. The voltage platform is symmetrical and regular, and the polarization voltage is stable at about $\pm 0.1 \text{ V}$, which is much lower than the polarization value at high current density, indicating that the interfacial reaction is better at low and medium currents, and the zinc deposition/dissolution process is more uniform and stable.

3.5 Effect of β -CD on full cell performance

Figure 6a presents the cyclic voltammetry curves of $\text{Zn}||\text{I}_2$ full cell in PEO and PEO/ β -CD composite electrolyte. Both sets of curves show a clear pair of oxidation/reduction peaks, corresponding to the embedding/de-intercalation of zinc ions. The peak current of the PEO/ β -CD system is higher, the peak shape is sharper, and the potential difference of the redox

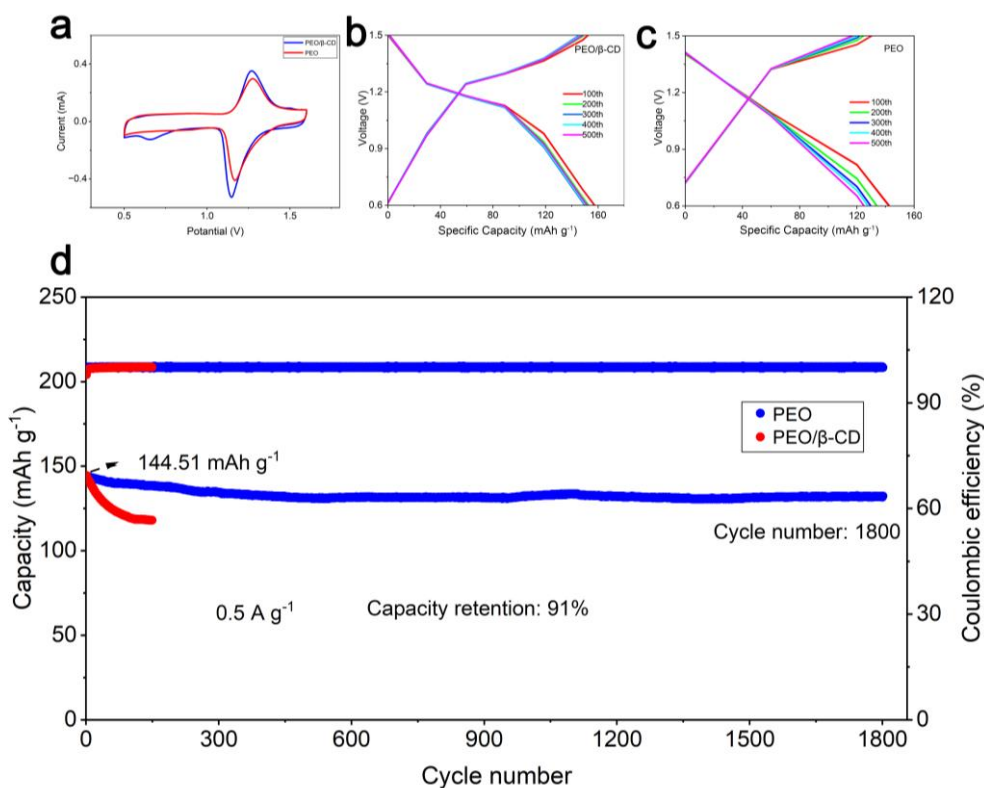


Figure 6 (a) CV curves of $\text{Zn}||\text{I}_2$ full cells with PEO and PEO/ β -CD electrolytes. (b) GCD curves of PEO-based full cell at different cycles. (c) GCD curves of PEO/ β -CD-based full cell at different cycles. (d) Long-cycle performance of full cells with PEO and PEO/ β -CD electrolytes at 0.5 A g^{-1}

peak is smaller, indicating that the reversibility of the system is better, the polarization is lower, and the zinc ion transport kinetics are better.

The current constant charge-discharge (GCD) curve exhibits excellent stability. The current constant charge-discharge curve of PEO/ β -CD battery showed excellent stability (Figure 6b): the charging and discharging platform was still clear after multiple cycles, the capacity decay was slow, and the voltage polarization did not increase significantly, indicating that the β -CD modification effectively stabilized the electrode-electrolyte interface, inhibited the zinc dendrite and side reaction, and improved the reversibility and structural stability. In contrast, pure PEO Zn||I₂ cells (Figure 6c) have rapid deterioration of battery performance due to rapid capacity decay, continuous intensification of polarization, gradual deformation of the platform, and serious interfacial side reactions and dendrite growth with the increase of cycle times. Figure 6d shows the long-cycle performance comparison curve of Zn||I₂ cell at 0.5 A g⁻¹ current density. The specific capacity of the pure PEO system decays rapidly at the beginning of the cycle, and the battery fails quickly after 170 cycles. The initial specific capacity of the β -CD composite electrolyte system is 144.51 mAh g⁻¹, and after 1800 long cycles, the capacity retention rate is still as high as 91%, and the coulomb efficiency is always close to 100%, showing excellent long-cycle stability and reversibility.

It was shown that the β -CD composite electrolyte significantly improved the reaction kinetics and interface stability of Zn||I₂ cell, effectively inhibited the growth and side reactions of zinc dendrites, greatly improved the reversible charge-discharge performance and long cycle life of the battery, and provided a feasible solution for the construction of high-stability zinc-based whole batteries.

4 Conclusion

In this work, PEO-based solid electrolytes were taken as the research object, and the regulatory mechanism of β -cyclodextrin modification on the interface stability and electrochemical properties of zinc-ion batteries was systematically explored. Through structural characterization and electrochemical testing, it was confirmed that the introduction of β -CD effectively destroyed the high crystallinity of PEO, increased the amorphous region, and constructed a continuous and smooth transport channel for zinc ions, which significantly improved the conductivity of electrolyte ions. Tafel plot and XRD analysis showed that β -CD could reduce the corrosion current of the zinc anode, induce the optimal deposition of zinc along the (002) crystal plane, inhibit the growth of vertical dendrites, and construct a flat and stable electrode interface. The test results of zinc symmetric batteries show that the PEO/ β -CD composite electrolyte can achieve ultra-long stable cycles of 813 h and 675 h at the current density of 4 mA cm⁻² and 10 mA cm⁻², respectively, with an areal capacity of 1 mAh cm⁻². And the voltage polarization is always

maintained at a low level, showing excellent interface stability and cycle reversibility. On this basis, the Zn||I₂ cell test further verifies the effectiveness of the modification strategy. After 1800 cycles at a current density of 0.5 A g⁻¹, the PEO/ β -CD-based Zn||I₂ cell retains a high capacity retention of 91% with an initial capacity of 144.51 mAh g⁻¹. This performance is significantly superior to that of the pure PEO system, fully demonstrating the critical role of β -CD modification in enhancing the long-cycle stability of the battery. In this study, the synergistic improvement of the ionic conductivity of PEO solid-state electrolyte and the interface stability of zinc anode was realized by β -CD modification, which provided an effective interface regulation strategy for the development of high-performance and long-life zinc-based solid-state batteries.

Acknowledgements: This work was supported by Jilin Province Science and Technology Development Plan Project (International cooperation 20240402073GH), the National Natural Science Foundation of China (22275030).

References

- [1] ZHU Y, HAN T, LIN X, ZHANG H, HU C, LIU J. [J]. Chem Commun, 2023(59):2640–2643.
- [2] MA L, CHEN S, LI N, et al. Hydrogen-Free and Dendrite-Free All-Solid-State Zn-Ion Batteries [J]. Advanced Materials, 2020(32): 1908121.
- [3] ZHANG Y, ZHANG T, GAO S, et al. 3D porous polymer framework induced by molecular bridging reaction enables quasi-solid zinc-ion batteries [J]. Science China Chemistry, 2026(25): 11426.
- [4] ZHANG H, WU H, WANG L, et al. Benzophenone as indicator detecting lithium metal inside solid state electrolyte [J]. Journal of Power Sources, 2021(492): 229661.
- [5] SU J, PASTA M, NING Z, et al. Correction: Interfacial modification between argyrodite-type solid-state electrolytes and Li metal anodes using LiPON interlayers [J]. Energy & Environmental Science, 2023(16): 698.
- [6] YANG S, MENG T, WANG Z, et al. Polymeric ionic conductor networks enable stable cycling of high-voltage lithium metal batteries using solid-state poly-ether electrolytes [J]. Journal of Materials Chemistry A, 2024(12): 29630.
- [7] ZHOU T, LEI Y, XUE Y, et al. Application, improvement and prospective advancements of solid electrolytes in zinc-ion batteries [J]. Journal of Energy Storage, 2025(139): 118765.
- [8] CHEN S, FENG F, YIN Y, et al. A solid polymer electrolyte based on star-like hyperbranched β -cyclodextrin for all-solid-state sodium batteries [J]. Journal of Power Sources, 2018(399): 363–371.
- [9] ABDELHAY A H, BANI-YASEEN A D. Exploring cyclodextrin-driven advancements in aqueous Zn-ion battery: A review [J]. Carbohydrate Polymers, 2025(349): 123041.
- [10] GUO H, SU Y, ZHAO J, et al. Ultra-stable and long-life zinc anodes enabled by porous cyclodextrin-based polymer coatings [J]. Journal of Energy Storage, 2025(123): 116856.