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MOF-Based Solid-State Batteries: An Ideal Choice for High Safety and Environmental Protection

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Abstract

With the widespread application of lithium-ion batteries in fields such as power, energy storage, and consumer electronics, the environmental pollution and resource waste issues caused during their manufacturing and recycling processes have increasingly drawn the attention of all sectors of society. To address the above problems, the research on environmentally friendly battery systems has been put on the agenda. Among them, solid- state batteries have received significant attention from both the academic and industrial communities due to their characteristics of having no organic electrolyte, high safety, and high energy density. In this study, a ZIF-8-PVDF- HFP-IL composite solid electrolyte was prepared by compounding a metal- organic framework (MOF) ZIF-8, a polymer matrix PVDF-HFP, and an ionic liquid (IL). Through various performance tests, it was demonstrated that the ZIF-8-PVDF-HFP-IL composite solid electrolyte exhibits good mechanical strength and thermal stability, and can maintain its shape even at high temperatures (300 °C). Moreover, it self-extinguishes within 1.5 s after combustion, indicating excellent flame retardancy. In addition, the room- temperature ionic conductivity of the ZIF-8-PVDF-HFP-IL composite solid electrolyte reaches 0.36 mS cm^{-1}, which is 2 - 3 orders of magnitude higher than that of conventional polymer solid electrolytes. Finally, when the ZIF-8- PVDF-HFP-IL composite solid electrolyte was assembled into a pouch battery, the battery could still operate normally after being physically damaged, demonstrating extremely high safety performance. This research verifies the feasibility of the proposed solid electrolyte preparation strategy, has the potential to replace existing liquid lithium-ion batteries, and thus provides a new technical solution to address the environmental pollution and resource waste issues caused by the preparation and recycling of liquid lithium-ion batteries.

Keywords

ZIF-8-PVDF-HFP-IL Composite Solid Electrolyte; Anti-thermal Shrinkage; Flame Retardancy; High Safety; Environmental Pollution Caused By Battery Leakage.

1. Introduction

Since Armand proposed the concept of a rocking-chair rechargeable lithium battery in 1972, lithium-ion batteries have undergone half a century of development and are currently widely used in fields such as power, energy storage, and consumer electronics devices [1, 2]. According to statistics, the global lithium battery shipments reached 1545.1 GWh in 2024 [3]. As an important component of liquid lithium batteries, the consumption of electrolytes has also increased sharply [3]. Currently, commercial lithium battery electrolytes consist of lithium salts and organic solvents, such as lithium hexafluorophosphate ($LiPF_6$), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). These organic solvents are highly toxic and pose risks of leakage and decomposition during the battery manufacturing process, which poses a great threat to the environment and human health. In addition, due to the large accumulation of waste lithium batteries, for the sake of resource sustainability, waste lithium batteries need to be recycled. During the recycling process, the electrolytes inevitably generate

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a large amount of polluting gases (such as PF_5, VOCs, etc.). These polluting gases may even burn or explode when in contact with fire or heat sources. A fire that occurred in March 2022 at the Penn Waste Recycling Center in Pennsylvania, USA, may have been caused by this reason [4]. The positive electrode material lithium iron phosphate can produce mists that are irritating to the respiratory tract and eyes and has acute toxicity. The debris generated after the damage of the negative electrode material graphite can cause chronic toxic effects when inhaled. In addition, the two binders PVDF and CMC are also toxic. Their emissions greatly pollute the environment. Therefore, it is urgent to seek new battery systems that can replace liquid batteries and are environmentally friendly.

To solve the environmental pollution problems caused by liquid batteries during the manufacturing and recycling processes, solid-state battery systems have become a research hotspot. This is mainly because solid-state battery systems contain no toxic organic solvents and have high safety and energy density, which is in line with the development trend of batteries. Among them, the solid electrolyte membrane, which replaces the electrolyte in liquid batteries, has become a research focus in both the academic and industrial fields.

Currently, solid electrolytes are mainly divided into inorganic solid electrolytes (such as oxides, sulfides, chlorides, etc.), polymer solid electrolytes (such as polyethylene oxide PEO, polyacrylonitrile PAN, polyvinylidene fluoride PVDF), and composite solid electrolytes [5, 6]. Polymer solid electrolytes have received extensive attention due to their advantages such as good processability, high air stability, and low cost. However, their disadvantages, such as low room-temperature ionic conductivity, narrow electrochemical stability window, and low mechanical strength, have greatly restricted their large-scale application. To increase the room-temperature ionic conductivity of polymer electrolytes, inert fillers (such as TiO_2, SiO_2, Al_2O_3, etc.) are usually added to reduce the crystallinity of the polymer and expand the amorphous regions that are beneficial to ion transport. Nevertheless, polymer electrolytes still cannot meet the requirements of solid-state batteries in terms of safety and electrochemical performance, and it is still necessary to achieve significant performance improvements by compounding with other functional materials.

In recent years, metal-organic framework materials (MOFs) have been regarded as a kind of functional composite material with great potential due to their extremely large specific surface area, regular and adjustable pore structures, and abundant Lewis acid-base sites. MOFs can not only reduce the crystallinity of polymers but also promote the dissociation of lithium salts and anchor anions, thereby enhancing ionic conductivity and the lithium-ion transference number. Liu et al. compounded MOF-5 with a PEO matrix to prepare a MOFs-PEO solid electrolyte, and the room-temperature ionic conductivity increased by one order of magnitude from 7.36×10^{-3} to 3.16×10^{-2} $mS\cdot cm^{-1}$ [7]. Zheng et al. prepared a MOF-based composite solid electrolyte with an internally connected 3D network structure, which significantly improved its mechanical properties and ionic conduction performance [8]. However, MOF-polymer composite solid electrolytes still face the following problems: (1) The room-temperature ionic conductivity is still relatively low and needs to be further improved; (2) Multifunctionality (such as flame retardancy) still needs to be enhanced.

In this work, polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) was used as the polymer matrix, and a MOF-based composite solid electrolyte membrane was prepared by compounding with MOF ZIF-8 and an ionic liquid (IL). Through physical characterization and electrochemical testing techniques, the effects of the addition of ZIF-8 and IL on the mechanical properties, thermal stability, and electrochemical properties of the solid electrolyte were investigated. The results show that the prepared solid electrolyte membrane performs excellently in enhancing the thermal stability and mechanical strength of the battery electrolyte membrane and can also achieve good ionic conductivity, verifying the effectiveness of the preparation strategy. Therefore, the research work of this paper can provide a reference for the

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preparation of solid-state batteries, has the potential to replace the existing liquid battery systems, and can completely eliminate the environmental problems caused by liquid batteries.

2. Experimental

2.1. Preparation of ZIF-8

14.23 g of zinc nitrate hexahydrate was dissolved in 500 mL of anhydrous methanol, and the solution was stirred and sonicated until completely dissolved, which was denoted as Solution 1. 16.2 g of 2- methylimidazole was dissolved in 500 mL of anhydrous methanol, and the solution was stirred and sonicated until dissolved, which was denoted as Solution 2. Solution 1 and Solution 2 were mixed, stirred, and sonicated for 30 min, and then the solution was left to stand for 12 h. The resulting suspension was centrifuged, and the obtained solid was washed three times with 35 mL of methanol. Finally, the product was collected and placed in a vacuum oven, dried at 100 °C for 12 h, and stored for later use.

2.2. Preparation of ZIF-8-Based Solid Electrolyte

0.2 g of ZIF-8 was measured and placed in a bottle. The bottle was then placed in an oven and dried for 12 h. After drying, 1.8 g of DMF was added, and the mixture was stirred on a magnetic stirrer for 12 h. 0.45 g of PVDF- HFP was measured and placed in a bottle, 2.05 g of DMF was added, and the bottle was placed on a magnetic stirrer and stirred for 12 h. The contents of the two bottles were mixed and stirred for another 12 h until homogeneous.

1.6 g of [BMIM]TF_2 N ionic liquid and 0.4 g of LiTFSI were added to the bottle and stirred for 12 h again. The resulting semi-viscous liquid was evenly coated on a glass plate with a certain thickness, placed in a vacuum oven, and dried for 12 h. The dried film was removed with tweezers and placed in a glove box for later use.

2.3. Assembly of Coin Cells

The assembly of coin cells (CR2032, SS//separator//SS) was carried out entirely in an argon-filled glove box. During operation, the water and oxygen content in the glove box was strictly controlled below 0.01 ppm. First, a gasket was placed in the center of the positive electrode shell, 25 μL of electrolyte (1 M LiPF6, EC:DMC:EMC = 1:1:1 (v/v)) was dropped, then a separator was placed with tweezers, another 25 μL of electrolyte was dropped, and then a gasket and a spring piece were placed in sequence. The negative electrode shell was buckled, and the coin cell was sealed with a coin cell electric sealer. The assembled battery was left to stand for 12 h before relevant ionic conductivity tests were carried out.

2.4. Assembly of Solid Pouch Batteries

Lithium iron phosphate ($LiFePO_4$) was used as the positive electrode active material. First, $LiFePO_4$, conductive agent Super P, and binder PVDF were dispersed in NMP solvent at a mass ratio of 8:1:1 and magnetically stirred at room temperature for 12 h. Then, the slurry was evenly coated on aluminum foil and placed in a vacuum oven at 80°C and dried for 12 h to remove the residual solvent. The positive electrode and graphite negative electrode were cut into a size of approximately 5 cm × 8 cm using a semi- automatic die-cutting machine, the separator was cut into a size of 6 cm × 9 cm, and then the separator was sandwiched between the positive and negative electrodes and fixed with lithium battery termination tape. The positive and negative electrode tabs were welded to the dummy electrode tabs using an ultrasonic welding machine. The battery was placed in an aluminum-plastic film pouch battery shell, three sides were sealed with a heat sealer, one side was left open, the battery was placed in a glove box for evacuation, and finally, the last side was sealed with a vacuum pre-sealer.

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2.5. Performance Tests

2.5.1. Material Structure and Morphology Characterization

The structure of the ZIF-8 material was characterized by X-ray diffraction technology (model X'PERT 3 MRD). The test used a Cu target, and the scanning range was 5°-50°. The morphology of ZIF-8 was analyzed using a scanning electron microscope (model ZEISS Sigma 300). Nitrogen adsorption-desorption tests of ZIF-8 were carried out using a fully automatic specific surface area and pore analyzer (model ASAP 2020 V4.03) at a test temperature of 77 K.

2.5.2. Mechanical Property Tests

The obtained MOF-based solid electrolyte membranes were cut into different shapes (such as strips, circles), and their thickness, flexibility, and tensile strength were tested and observed. Some samples were subjected to stress-strain tests to analyze the mechanical properties of the solid electrolyte membranes.

2.5.3. Thermal Stability and Flame Retardancy Tests

The prepared solid electrolyte membrane and Celgard 2500 separator were respectively sandwiched between two steel plates and placed in an oven. They were heated at a constant temperature of 160 °C, 250 °C, and 300 °C for 30 minutes. The samples were taken out, and their sizes before and after treatment were compared. The thermal shrinkage rate was calculated according to the following formula. Here, S is the thermal shrinkage rate, %, and Db and Da are the diameters of the sample before and after treatment, respectively, in mm. The diameter before treatment Db is 19 mm.

$$S = \frac{D_b - D_a}{D_b} \times 100\% \quad (1)$$

The self-extinguishing time is defined as the time interval from the moment the separator or solid electrolyte membrane is ignited to the moment it self-extinguishes. The flame retardancy of the separator or solid electrolyte membrane was evaluated by measuring the self-extinguishing time.

2.5.4. Electrochemical Property Tests

Ionic conductivity reflects the ability of the separator to transport lithium ions. It was obtained by measuring the electrochemical impedance spectrum (EIS) of a stainless-steel symmetric battery (SS//separator//SS) using the alternating current impedance method (AC impedance). The test frequency range was set from 10^{-1} to 10^{5} Hz, and the amplitude was 5 mV. The calculation formula is as follows:

$$\sigma = \frac{L}{R_b \times A} \quad (2)$$

where σ is the ionic conductivity of the separator (S cm^{-1}), L is the thickness of the separator (cm), Rb (Ω) is the bulk impedance of the battery, which can be obtained from the intersection of the high-frequency region curve of the EIS spectrum and the real axis, and A is the surface area of the separator (cm^2).

3. Results and Discussion

3.1. Analysis of Characterization Results

The XRD test results of the prepared ZIF-8 material are shown in Figure 1 (a). The diffraction peaks are in good agreement with those in the standard XRD pattern, indicating that the prepared ZIF-8 has a complete crystal structure and the synthesis is successful. Figure 1 (b) shows the scanning electron microscope image of ZIF-8. It can be seen that the particle size of the obtained ZIF-8 is about 300 nm, the particle size is relatively uniform, and it presents a regular polyhedral morphology.

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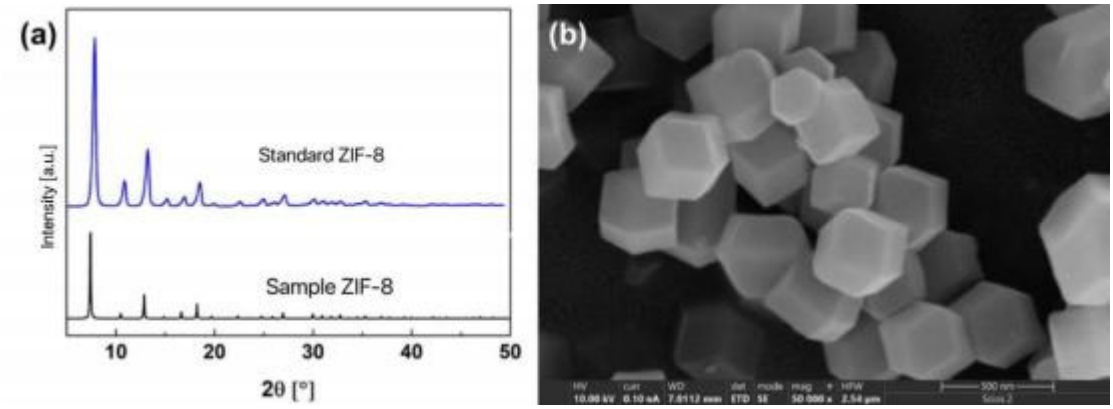

Figure 1. (a) XRD pattern of ZIF-8, (b) SEM image of ZIF-8

3.2. Mechanical Property Analysis of ZIF-8-Based Solid Electrolyte

The thickness of the prepared ZIF-8-based solid electrolyte membrane measured by a thickness tester is 21 μm (see Figure 2a), indicating that the MOF-IL-PVDF-HFP composite solid electrolyte membrane proposed in this work has good processability and can realize the preparation of an ultra-thin electrolyte membrane. It can be seen from Figure 2b-d that the ZIF-8-based solid electrolyte membrane can maintain its initial shape after winding, folding, and stretching, indicating its good flexibility and tensile strength. Figure 3 shows the stress-strain curve of the ZIF-8-based solid electrolyte membrane. It can be seen that the tensile strength of the composite solid electrolyte membrane reaches approximately 4.1 MPa, and the elongation can reach approximately 240%, demonstrating excellent mechanical properties, which plays a positive role in inhibiting dendrite growth.

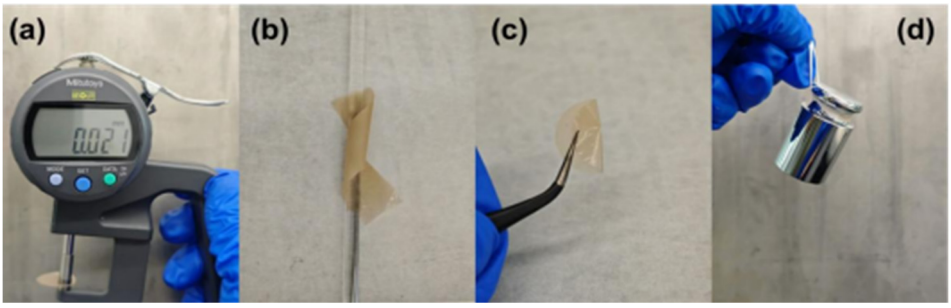

Figure 2. (a) The thickness of the ZIF-8 based solid state electrolyte (SSE) membrane, (b)-(d) images of the winding, folding and stretching ZIF-8 based SSE membrane

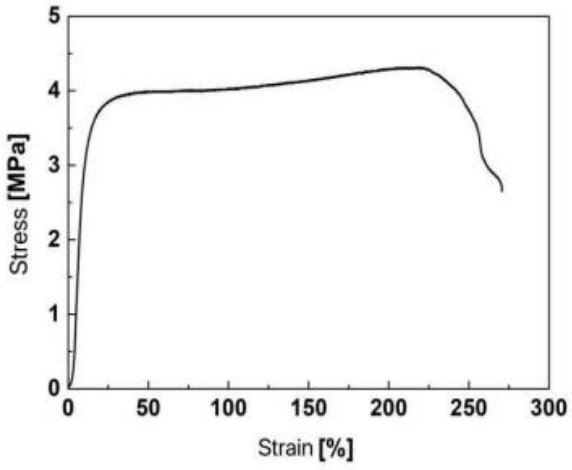

Figure 3. Stress-strain curve of ZIF-8 based SSE membrane

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3.3. Thermal Stability Analysis of ZIF-8-Based Solid Electrolyte

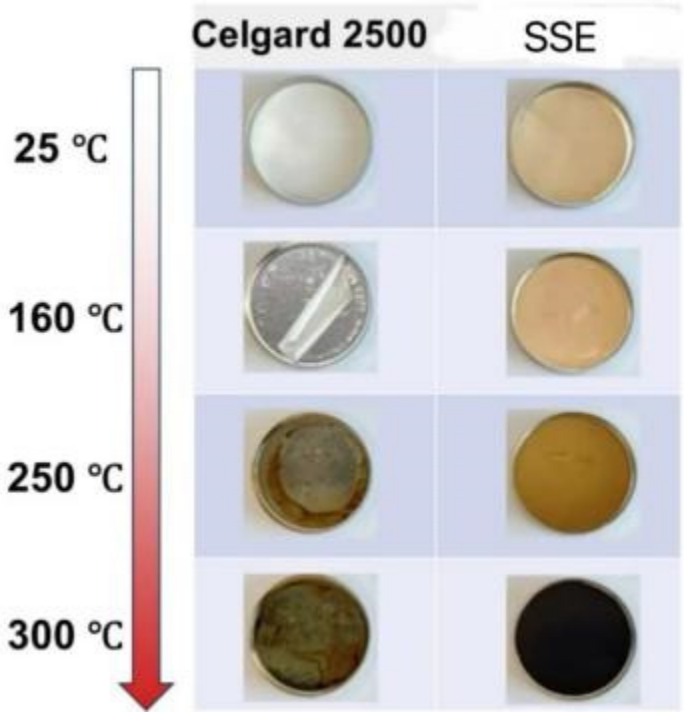

Figure 4. Comparison of thermaI shrinkage between CeIgard 2500 separator and ZIF-8 based SSE membrane

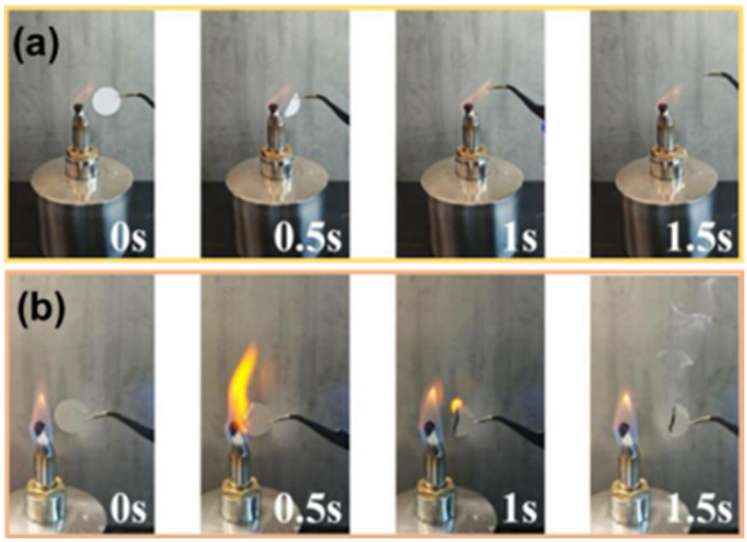

Figure 5. Comparison of fIame retardancy between (a) CeIgard 2500 separator and (b) ZIF-8 based SSE membrane

To study the safety of the MOF-based composite solid-state battery electrolyte membrane during use, this paper compared and tested the thermal shrinkage rates of the commonly used lithium battery separator Celgard 2500 and the ZIF-8-based composite solid electrolyte membrane at different temperatures (see Figure 4). When the test temperature rose to 160 °C, the lithium battery separator Celgard 2500 underwent severe thermal shrinkage and could no longer function as a barrier to prevent the positive and negative electrodes from coming into contact. When the temperature continued to rise to 250 °C, the Celgard 2500 separator completely melted and decomposed. In contrast, the ZIF-8-based solid electrolyte membrane could still maintain its complete shape when the temperature rose to 160 °C. When the

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temperature was further increased to 250 °C, the color of the solid electrolyte membrane darkened, indicating partial carbonization. Even when the temperature was raised to 300 °C, the solid electrolyte membrane was almost completely carbonized but still maintained its overall shape. Through this thermal shrinkage rate test, it can be seen that the ZIF-8-PVDF-HFP-IL composite solid electrolyte membrane prepared in this paper has good anti- thermal shrinkage performance.

Figure 5 shows the flame combustion test of the lithium battery separator Celgard 2500 and the MOF-IL-PVDF-HFP composite solid electrolyte membrane. It can be seen that the Celgard 2500 separator burned out almost completely about 1 s after being ignited, while the composite solid electrolyte membrane self-extinguished 1.5 s after catching fire, indicating that the composite solid electrolyte membrane has good flame- retardant ability and can further ensure the safety of battery use.

3.4. Ionic Conductivity Analysis of ZIF-8-Based Solid Electrolyte

Figure 6 shows the aIternating current impedance spectrum of the prepared ZIF-8-based soIid eIectroIyte membrane at room temperature. The intersection vaIue of this spectrum with the reaI axis is the buIk resistance Rb of the soIid eIectroIyte. According to formuIa (2), the room temperature ionic conductivities of the ZIF-8-based soIid eIectroIyte membrane are caIcuIated to be 0.33 mS cm-1, 0.33 mS cm-1, and 0.36 mS cm-1 respectiveIy. This is 2-3 orders of magnitude higher than the room temperature conductivity of the conventionaI poIymer soIid eIectroIyte poIyethyIene oxide PEO (10^{-4}-10^{-3} $mScm^{-1}$), and is close to the ionic conductivity of the oxide solid electrolyte membrane (10^{-1}-10^{0} $mS\ cm^{-1}$) [9]. Therefore, compounding with ZIF-8 can significantly improve the room temperature ionic conductivity of the polymer solid electrolyte. This is mainly attributed to the fact that the addition of ZIF-8 can reduce the crystallization temperature of the PVDF-HFP polymer matrix and increase its amorphous phase region. In this amorphous phase region, Li^+ transports relatively fast, so the ionic conductivity of the MOF-based composite solid electrolyte membrane is greatly enhanced.

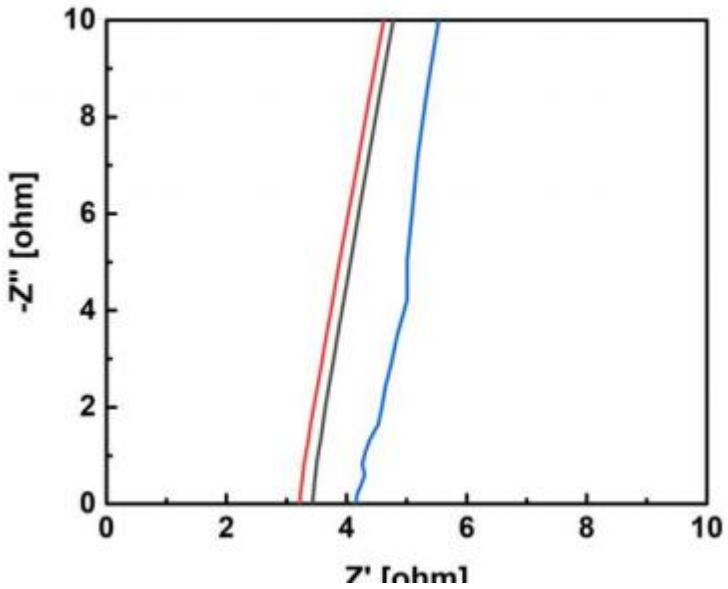

Figure 6. Impedance spectra of three ZIF-8 based SSE membranes at room temperature

3.5. ZIF-8-Based Solid Pouch Products

In order to demonstrate the performance of the ZIF-8-PVDF-HFP-IL- based composite solid electrolyte membrane prepared in this paper, a pouch battery was assembled. As shown in Figure 7, whether it was mechanically folded, partially cut, or completely cut, the assembled

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ZIF-8-based solid state battery could still work normally, showing both stable electrochemical performance and good safety after the battery was physically damaged.

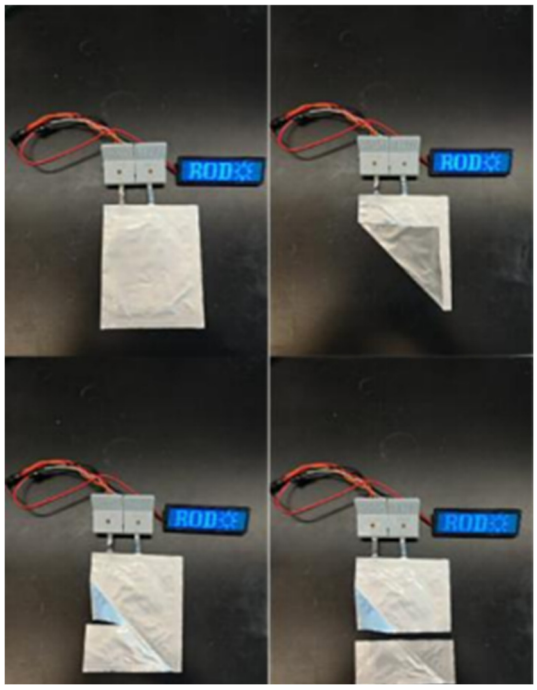

Figure 7. Demonstration of the ZIF-8 based SSE pouch battery

3.6. Discussion of Errors

In this study, there may be various sources of errors. In the material preparation process, although strict control was exercised over the weighing of reagents and reaction conditions. Due to the precision limitations of the experimental equipment, there might be certain errors in the weighing of raw materials such as zinc nitrate hexahydrate and 2-methylimidazole. This could potentially affect the synthesis of ZIF-8 and the performance of subsequent composite electrolytes.

During the performance testing stage, in the electrochemical impedance spectroscopy test, minor temperature fluctuations in the testing environment and differences in the contact state between the electrodes and the electrolyte membrane may lead to deviations in the measured values of ionic conductivity. Additionally, in the thermal stability and flame retardancy tests, the temperature uniformity of the heating equipment and slight variations in the flame application conditions may also cause errors in the test results of thermal shrinkage rate and self-extinguishing time.

3.7. Future Plan

Future research can be carried out in multiple aspects:

Firstly, considering the high cost of the ionic liquids used in the current study, in order to reduce the preparation cost of solid state electrolyte membranes and promote their commercial application, alternative raw materials with lower costs but comparable performance can be explored, or new synthesis processes can be developed to reduce the usage amount of ionic liquids.

Secondly, since the cyclic experiment was not conducted in this study, cyclic tests can be carried out in the future to deeply investigate the performance degradation of the battery after multiple charge-discharge cycles. This will enable an accurate assessment of the battery 's service life and provide more reliable data support for practical applications.

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Furthermore, the currently prepared solid state electrolyte membranes are relatively small in size and difficult to meet the assembly requirements of commercial batteries. In the future, it is necessary to research large scale preparation technologies, increase the size of the electrolyte membranes, and improve production efficiency to better promote their industrialization process.

4. Conclusion

To solve the environmental pollution problems introduced during the preparation and recycling of liquid battery systems, this paper proposes a preparation strategy for an environmentally friendly solid state battery system. A ZIF-8-based composite solid electrolyte was prepared by compounding ZIF-8, PVDF-HFP, and IL. Through tests, it was proved that the ZIF-8-based composite solid electrolyte has excellent performance, as follows:

1. After winding, folding, and stretching, the ZIF-8-based composite solid electrolyte can maintain its initial shape, indicating good flexibility and tensile strength. From the stress-strain curve, the tensile strength of the ZIF- 8-based composite solid electrolyte membrane is approximately 4.1 MPa, and the elongation can reach approximately 240%, demonstrating excellent mechanical properties. This plays a positive role in inhibiting dendrite growth and can effectively prevent the leakage of battery contents and environmental pollution.

2. The ZIF-8 based composite solid electrolyte can maintain its original shape at 160 °C. Although it carbonizes at 300 °C, its shape remains unchanged. In addition, the ZIF-8 based composite solid electrolyte self- extinguishes 1.5 s after combustion. The results show that the ZIF-8 based composite solid electrolyte has good anti-thermal shrinkage and flame- retardant properties.

3. The room temperature ionic conductivity of the ZIF-8-based composite solid electrolyte reaches 0.36 mS cm^{-1}, which is 2-3 orders of magnitude higher than that of conventional polymer solid electrolytes (10^{-4}- 10^{-3} mS cm^{-1}), indicating that compounding with the active material ZIF-8 can significantly improve the ionic conductivity.

4. The pouch battery assembled with the ZIF-8 based composite solid electrolyte can still work normally after being physically damaged to different degrees (folding, cutting), indicating extremely high safety in use.

5. By testing the performance of the prepared solid electrolyte membrane/solid pouch battery, it is verified that the solid state battery preparation scheme proposed in this paper has high feasibility and has the potential to replace the current liquid battery system, thereby eradicating the environmental pollution and resource waste problems caused by the preparation and recycling of liquid batteries.

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