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Research on PVDF-based electrolytes for dual-ion batteries

Hanbin Mao[*]

College of Energy, Soochow University, Suzhou, 215021, China
[*]Corresponding author: m18862760002@163.com

Abstract: *The production of new batteries and their application are becoming more and more important as the world's energy demands and environmental stress increase. Due to their long lifespan, high energy density, and affordability, dual-ion batteries have garnered a lot of attention as a novel battery type in recent years. When compared to other conventional electrolytes, PVDF-based polymer electrolytes with high conductivity and superior mechanical qualities greatly enhance battery performance. Therefore, a comprehensive analysis of the techniques for enhancing the characteristics of electrolytes based on PVDF is presented in this study. The statement demonstrates how a smooth surface can improve the stability of electrochemical processes and raise ion conductivity. Moreover, ion transport rate, capacity, energy density, and duration of cycle of dual-ion batteries can all be markedly increased by strengthening structural stability and adding inorganic fillers. These measures can provide useful references for the optimization and improvement of dual-ion batteries and promote their application in electric vehicles and energy storage area.*

Keywords: *Dual-ion Battery, Polymer, PVDF-based Electrolyte*

1. Introduction

It is now essential to research and create new types of batteries due to the intensifying global demand for energy resources. These days, a lot of different applications use lithium-ion batteries, including energy storage, electric cars, and mobile electronics. Li^+ is released from the lithium cobaltate anode during charging and moves through the electrolyte and diaphragm before becoming imbedded in graphite. Electrons from the positive electrode can pass through an external circuit, which causes the Co^{3+} in the substance of the positive electrode to oxidize. The discharge process is the opposite, with the concentration of lithium ions decreasing in the anode material and increasing in the cathode material [1]. Lithium resources are becoming scarce due to the world economy's rapid expansion, and extracting these from the earth's crust is now more challenging. Lithium-ion battery prices have gone up as a result of this [2]. Dual-ion batteries, on the other hand, are becoming more popular because of their extended lifespan, great energy density, and affordable price. Not only can graphite be used as both the positive and negative component in dual-ion batteries, but they also do away with the need for transition metal oxides containing lithium in the electrode material. By implementing this approach, the production cost of the batteries is effectively reduced. Consequently, dual-ion batteries have the potential to both alleviate and enhance the current state of energy scarcity.

The battery's primary component is the electrolyte. In addition to having great electrochemical stability and full contact with the anode and cathode materials, traditional organic electrolyte is also more soluble and conducts better. It does, however, also provide a number of serious safety risks, including as insufficient thermal stability. Because of its vulnerability to moisture influence, the battery's life and safety may be considerably shortened. Water seeps into the electrolyte, resulting in aberrant expansion and redox reactions that shorten battery life and compromise safety. Therefore, improving electrolyte stability is essential.

Liquid, inorganic ceramic, and organic polymer electrolytes are the three types of conventional electrolytes used with lithium batteries. Furthermore, gel polymer electrolytes (GPEs) and all-solid polymer electrolytes are the two main categories of organic polymer electrolytes. Polymer electrolytes are simpler to synthesize and process, have lower production costs, and are more flexible than inorganic electrolytes [3]. Gel polymer electrolytes exhibit both outstanding mechanical qualities of solid polymer electrolytes and great conductivity of liquid electrolytes. The creation of ion pairs by ions within the polymer is the conductive mechanism of polymer electrolytes, and cations migrate via cavities in the solid electrolyte or polymer chain wounds to produce conductivity [4]. Specifically, the polymer electrolyte's cations and anions are pulled toward one another, forming ion pairs and promoting charge conduction via a leapfrogging mechanism. Thus, increasing the efficiency of polymer electrolytes is crucial for raising the energy density and durability of dual-ion batteries. Moreover, it can minimize energy waste and lower internal impedance of batteries.

Therefore, this paper systematically summarizes the measures to improve the properties of PVDF-based electrolytes from the surface morphology, structural optimization, polymer modification and inorganic filler doping, etc. Finally, the polymer electrolyte with smooth surface, stable structure, reduced crystallinity and inorganic fillers improves the performance of dual-ion batteries. It builds a steady conduit for lithium-ion transfer, and the increased ionic conductivity also improves the capacity and properties of dual batteries. So, this paper could enhance the properties of the dual-ion batteries and to alleviate energy constraint in the world.

2. Surface morphology

Surface morphology normally possesses a comparatively large electrochemical window, and it can accommodate all cathode materials under current high-voltage [5]. In general, smooth and dense surface can serve as a bridge for transportaton and expedite the conduction of lithium ions.

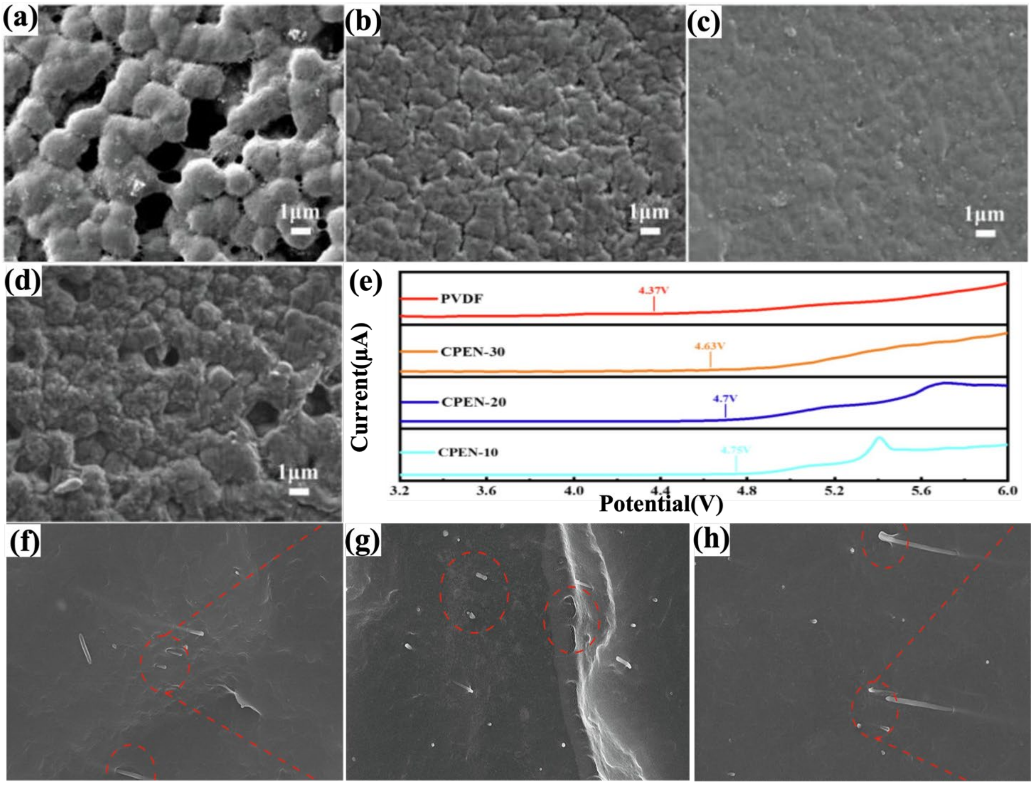

Figure 1: SEM images. (a) PVDF; (b) CPEN-10; (c) CPEN-20; (d) CPEN-30. (e) The electrochemical window pure PVDF and CPEN; (f) and (g) SEM image of cross-sections of AgNW/PVDF-HFP; (h) SEM image of AgNW@PIL/PVDF-HFP

Nickel oxalate was added to the exterior of the PVDF-based solid electrolyte to change it by Jiang et al, and the result was perfect impedance and superior lithium-ion transfer performance. As seen in Fig. 1(a), the surface was riddled with holes. To cover these holes and increase the closedness of the PVDF solid electrolyte, the PVDF chains were connected using a nickel compound as a bridge. CPEN-10, CPEN-20 and CPEN-30 mean the mass ratio of NiC_2O_4: PVDF: $TFSI^-$= x:10:2 (x = 1, 2, 3). The surface of the CPEN solid electrolyte smoothed out as the concerntration of nickel oxalate rose, according to the SEM images in Fig. 1(b,c,d). When the nickel oxalate content was raised to 30%, the electrochemical window expanded from 4.37 V to 4.75 V using linear scanning voltammetry (LSV), as indicated in 1(e). It enhanced the cross-face interaction between the electrolyte and the electrode, resulting in an improved configuration of the PVDF-based solid electrolyte that was more stable and secure. It in turn enhanced the transport of lithium ions [5]. Qin et al. discovered that by covering the surface of silver nanowires (AgNWs) with an extra coating of polyionic liquid (PIL), a novel functional hybrid (AgNW@PIL) could be produced. Subsequently, it was incorporated into PVDF-HFP, enabling the development of conductive films with high dielectric constants and high strength (AgNW@PIL/PVDF-HFP). Voids were discovered at the AgNW/PVDF-HFP interface (Fig. 1f) for the original AgNW/PVDF-HFP. The observation suggested there was no interaction between AgNWs and PVDF-HFP. AgNW/PVDF-HFP's cross-section did not show a homogeneous distribution of AgNW polymerization (Fig. 1g). Nevertheless, in the AgNW@PIL/PVDF-HFP cross-section, there are no cavities apparent at the interface between AgNW@PIL and PVDF-HFP and (Fig. 1h). This electrolyte's mechanical and flexible qualities might be improved, and it would eventually improve its overall performance [6]. Kawai was the first to report on the remarkable piezoelectric activity of PVDF. PVDF has five crystalline forms called α-, β-, γ-, δ-, and ε-phases. The β-phase with high polarization exhibits exceptional ferroelectric and piezoelectric properties. Furthermore, if the concentration of the β-phase is relatively increased, PVDF will display outstanding piezoelectric qualities [7].

Therefore, smooth, dense, non-porous and homogeneously dispersed PVDF surface of the mixture could show higher ionic conductivity values [6] by improving the surface morphology of PVDF. It improved the strong piezoelectric properties of the PVDF, induced better cycling stability, and improved the performance of the PVDF-based polymer electrolytes.

3. Structural optimization

In order to maximize PVDF-based composite polymer electrolytes, unsaturated organic small molecules can be added, and matrix membranes can be built. This will increase the number of carriers available to transport lithium ions and enhance the stability and electrochemical performance of GPEs. Additionally, the polymer electrolyte system's enhanced electrical conductivity helps with ionic conduction and stabilizes the electrolyte's structure.

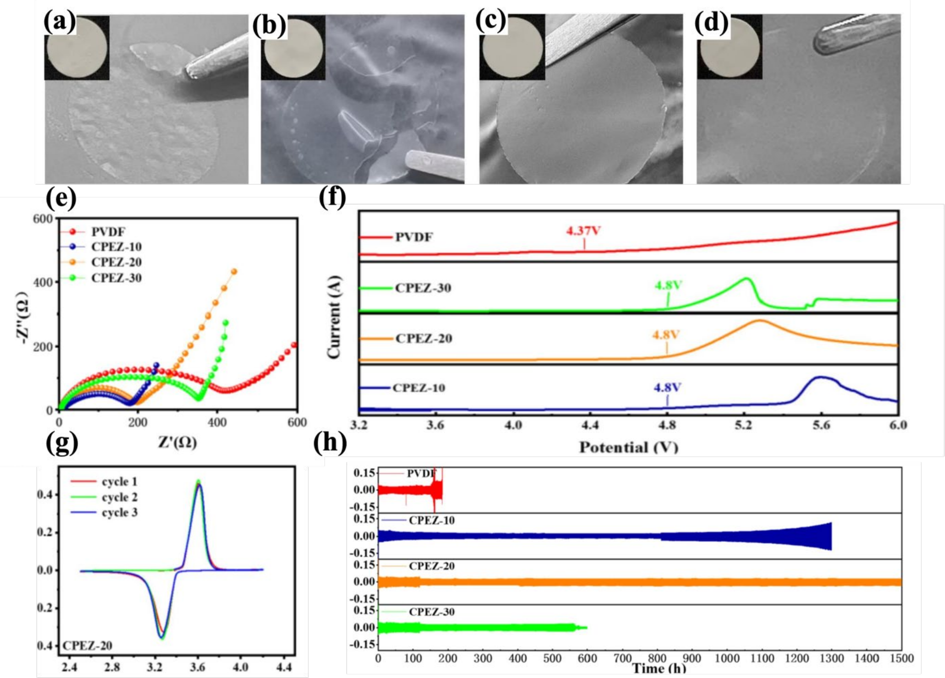

Figure 2: (a) Pure PLA; (b) PVDF-HFP: PLA is 1:9; (c) PVDF-HFP: PLA is 2:8; (d) PVDF-HFP: PLA is 3:7. (e) EIS patterns of LiFePO4|CPEN|Lithium cells. (f) The electrochemical window pure PVDF and CPEN. (g) The CV curve. (h) Electrochemical stability test

Zhao et al. introduced maleic acid (MA), and it has two carboxylate groups and C=C. More carriers for the transportation of lithium ions can be supplied by the carboxylate group, and C=C aids in the self-polymerization of MA to create a continuous conductive network. By self-polymerizing MA, the interfacial contact between PVDF, LLZTO, and $LiClO_4$ is maximized [8]. By incorporating a small quantity of PVDF-HFP into the composite polymer and employing a non-solvent-induced reverse transference technique, Chen et al. created innovative porous PLA-based bio composite membranes [9]. The two polymer solutions combined to create a stable porous structure. As seen in Fig. 2(a,b,c,d), the membranes progressively stabilized and maintained their integrity when the ratio of PVDF-HFP to PLA was changed from 1:9 to 3:7. PMMA is a non-crystalline polymer that has outstanding wettability, mechanical stability, and chemical stability [10]. Blends of PVDF-HFP and PMMA for lithium-ion conducting polymer electrolytes were studied by Gebreyesus et al. It was discovered that using these blends improved the ionic conductivity and thermal stability of polymer electrolytes. To enhance the structural integrity of PVDF-based solid electrolyte, Jiang et al. created and manufactured a solid polymer electrolyte comprising ZIF-8 and polystyrene fluorine. In addition, it offered a dependable path for lithium-ion battery transfer [11]. The solid electrolyte that was manufactured as shown in Fig. 2 (f) was subjected to an electrochemical window evaluation using linear scanning voltammetry (LSV). The electrochemical window increased from 4.37 V to 4.8 V when ZIF-8 was added to PVDF, indicating that there is considerable electrochemical stability in the CPEZ electrolyte. As shown in Fig. 2g, the $LiFePO_4$|CPEN-20|Lithium battery presented the reation peak of lithium iron phosphate. The CPEN-20 sample showed a minimal and steady polarization voltage during a cycle of greater than 1500 hours. It could potentially be linked to the smooth interface it offers (Fig. 2h) [5].

As a result, MA molecules improve the electrolyte's strong adherence to the electrode and its great compatibility with the electrode. The PLA, serving as the primary support system, has excellent degradability and renewability. It increases the stability of the cell's function and guarantees the membrane's structural stability. Amorphous PMMA added to the PVDF-HFP/PMMA blend may increase ion mobility in the amorphous phase, supporting structural stability of the membrane and improving dual-ion batteries' performance [8]. Similarly, including ZIF-8 into the PVDF electrolyte offers a reliable channel for the transit of lithium ions.

Overall, the stability and ionic conductivity of PVDF are augmented by the addition of small organic molecules and the creation of a porous base film. This increases the electrical conductivity and promotes the movement of lithium ions within the polymer electrolyte system. For PVDF, structural optimization is a successful way to enhance electrochemical performance.

4. Polymer modification

Polymer modification methods use copolymerization, blending, or adding initiators to combine various polymer materials for cross-linking, grafting, and so on. The crystallinity of PVDF-based electrolytes can be diminished by these measures. The suppression of the polymer's crystalline behavior enhances the liquid absorption and movement of segments, consequently boosting the ionic conductivity of the electrolyte [8].

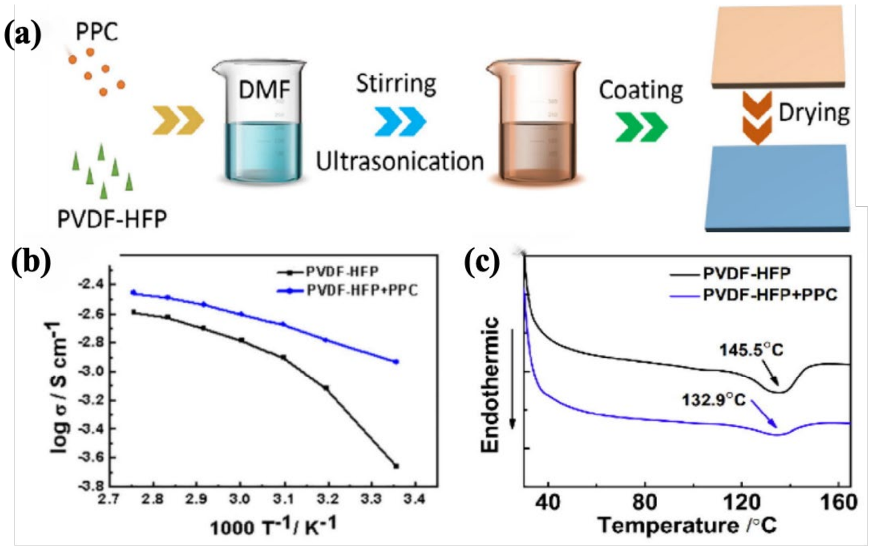

Figure 3: (a) The blending polymer electrolyte preparation process; (b) Ionic conductivity comparison between two electrolytes; (c) DSC results of blending PVDF-HFP-PPC and pure PVDF-HFP gel electrolytes

Zhong et al. created a newly mono-ionic polymer electrolyte [12] by using an in-situ polymerization process. This electrolyte was then cross-linked using electrospinning and radiation to create a three-dimensional network structure. Through cross-linking, the ethylenic bonds in this lithium salt can be joined with the thiol groups in the polymer chain. This might significantly raise the lithium ion transfer number to 0.91, producing a battery with exceptional cycle life. PVDF-HFP electrolyte was exposed to electron beam radiation by Yesappa et al. in order to create crosslinks and split chains. It also bound certain functional groups to the backbone [13], resulting in a reduction in the crystallinity and an rise in the ionic conductivity of the electrolyte [7]. In order to generate hybrid electrolytes, Idris et al. combined poly(methyl methacrylate) (PMMA) with PVDF, and it effectively reduced the crystallinity of the polymer. Highly porous electrolyte films were formed by manipulating the ratio between the two polymers. As the material was submerged in the liquid electrolyte, the figure shows that the ionic conductivity increased to 1.21 mS·cm^{-1} [14]. Liang et al. reported on a hybrid technique of producing a GPE battery, as illustrated in Fig. 3(a). By adding poly (propylene carbonate) to the PVDF-HFP matrix and maximizing the benefits, the electrolyte performs better [15]. There is a powerful polar carbonyl group in the PPC chain. It lowers the extent of crystalline structure, improves the participation with the molecular chain, and encourages the diffusion of lithium ions. As illustrated in Figure 3(b), the hybrid membrane exhibited a greater ionic conductivity of 1.18 mS·cm^{-1} at ambient temperature and more uniform pores when compared to pure PVDF-HFP. The hybrid gel electrolyte adding PPC absorbed more heat at the same temperature, as shown in Fig. 3(c) [16].

Therefore, when additional raw materials are added to the PVDF polymer electrolyte, it increases the possibility of forming an amorphous structure, improves porosity, and enhances the ability to hold liquid electrolyte. As a result, the reversible capacity of dual-ion batteries is significantly increased.

5. Inorganic filler doping

The introduction of fillers disrupts the crystalline structure of the polymer matrix, leading to an expansion of the amorphous region. This enhances the transportation of lithium ions to both the cathode and anode [15]. Inorganic fillers are classified into inert materials (e.g., SiO_2) and active materials (e.g., $Li_{10}GeP_2S_{12}$ (LGPS)). Active fillers conduct lithium ions, whereas inert fillers do not partake in lithium-ion transport [17].

Through the synergy of polymers and inorganic materials, electrolyte performance can be improved by balancing mechanical strength, interfacial stability, and ionic conductivity. These inorganic materials are hard and have a high modulus. In addition to offering ion migration binding sites, it also creates a composite system that can enhance the mechanical qualities of polymers. This makes it easier to stop the formation of lithium dendrites and prevent damage to the electrolyte during fabrication and assembly.

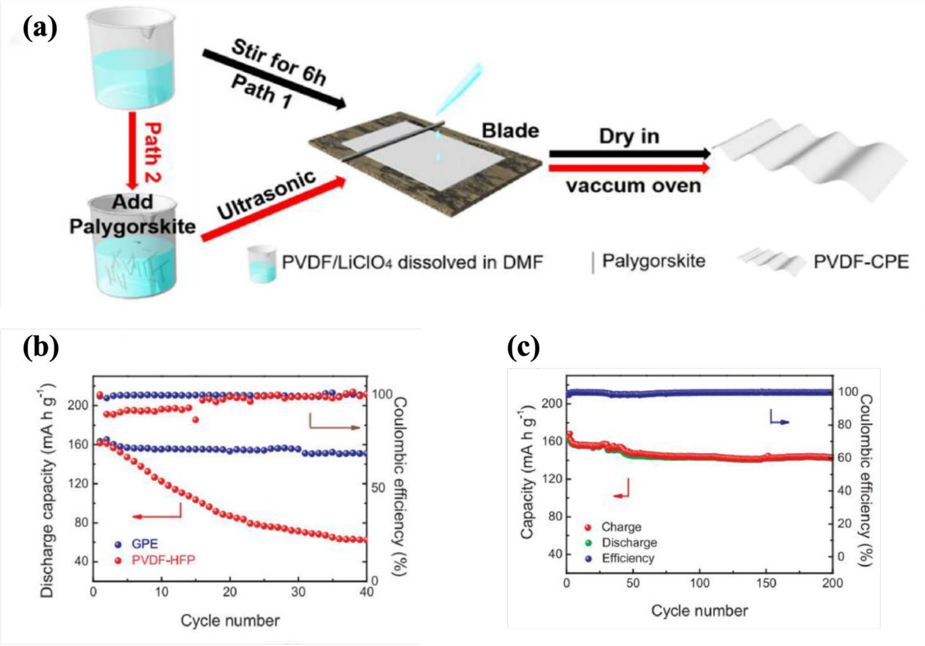

Figure 4: (a) A schematic diagram of the synthesis of PVDF-based and PVDF/palygorskite nanowires GPEs; (b) Cycling performance of Li/GPE/LFP and Li/PVDF-HFP/LFP cells; (c) Cycling performance of Li/GPE/LFP cell

Palygorskite, a fiber mineral, was doped into PVDF by Yao et al. to create a gel-type polymer electrolyte (GPE) (Fig. 4a). The main components of Palygorskite are MgO and SiO_2, and it contributed to its high specific surface area and ability for adsorption. The addition significantly raised PVDF's modulus and yield stress. It was helpful in preventing dendritic development. It was beneficial for preventing dendritic formation. The lithium-ion transfer number increased from 0.21 to 0.54, implying an enhancement in cycling property. Liang et al. reported a GPE based on $Li_7La_3Zr_2O_{12}$ (LLZO) ceramic powder incorporated into PVDF-HFP via a simple combinatorial approach. Because an inorganic electrolyte was involved in this process, the ion transfer number and ionic conductivity increased. The dual-ion battery containing LLZO-GPE exhibits higher intriguing capacity and retention when compared to the pure PVDF-HFP electrolyte (Fig. 4b). This suggests that there is a way to prolong the battery's life. The batteries made with this electrolyte, $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ cathode, and lithium anode were able to cycle over 200 times at 0.3C while remaining 97% capacity (Fig. 4c) [3]. The GPEs showed an amazing 0.58 lithium-ion transfer number and an 8.8 mS·cm-1 ionic conductivity at ambient temperature. Additionally, this filler raised the membrane's oxidation potential to 7.3 V. The preparation procedure gets more intricate, but the electrical qualities are improved [18]. Due to its strong electrochemical stability, excellent thermal resistance, favorable lithium salt breakdown, and high dielectric constant, etc. PVDF-HFP has garnered a lot of interest. PVDF-HFP hybrid solid electrolyte membrane based on garnet ($Li_7La_3Zr_2O_{12}$) was initially reported by Sun et al. It was demonstrated that by utilizing PVDF-HFP as a matrix and a composite with inorganic fillers, solid electrolytes with improved electrical conductivity could be produced [16]. $Li_7La_3Zr_2O_{12}$ (LLZO) solid-state electrolytes co-doped with Al and Ta were created by Zou et al. using a solid-state reaction. The dimensions of the Li^+ transport channel is typically affected by Ta doping at the Zr site and Al doping at the Li site. The distribution of Li^+ throughout the structure is impacted by this [19]. Co-doping the two elements will further enhance their synergistic effects and improve the solid-state electrolyte's performance. Therefore, tincorporating inorganic fillers enhances the polymer electrolyte's mechanical flexibility and potential, while also reducing interfacial resistance via direct contact between the electrolyte and the electrodes. On the flip side, though, the inorganic fillers can act as solid plasticizers to increase the dielectric constant and greatly improve the transportation properties of PVDF-based polymer electrolytes.

6. Conclusions

The scarcity of energy resources and increase of environmental pressure have prompted the development of new types of batteries. Therefore, dual-ion batteries have been widely noticed and studied for their longer service life, cheaper manufacturing cost, and less environmental pollution. The electrolyte plays a vital role in dual-ion batteries as it generally demonstrates excellent ionic conductivity and favorable mechanical properties. Therefore, this paper compiles the strategies for enhancing the performance of PVDF-based electrolytes and concludes that polymer electrolytes possessing smooth surfaces, stable structures, and high conductivity exhibit positive effects on the cycling stability of batteries. Most importantly, it could improve the efficiency of dual-ion batteries and alleviate the energy shortage in the world.

References

[1] Goodenough J B, Park K S. The Li-ion rechargeable battery: a perspective[J]. Journal of the American Chemical Society, 2013, 135(4): 1167.

[2] Wang C, Teng Liu, Yang X, etal. Fast charging of energy-dense lithium-ion batteries[J]. Nature, 2022(611): 485-490.

[3] Wu Y, Li Y, Wang Y, etal. Advances and prospects of PVDF based polymer electrolytes[J]. Journal of Energy Chemistry, 2022(64): 62-84.

[4] Chen J, Zhou Y, Huang X, etal. Ladderphane copolymers for high-temperature capacitive energy storage [J]. Nature, 2023(615): 62-66.

[5] Jiang Y, Xu C, Xu K, etal. Surface modification and structure constructing for improving the lithium-ion transport properties of PVDF based solid electrolytes[J]. Chemical Engineering Journal, 2022(442).

[6] Tan Q, Yuan L, Liang G, etal. Flexible, transparent, strong and high dielectric constant composite film based on poly ionic liquid coated silver nanowire hybrid[J]. Applied Surface Science, 2022(576).

[7] Li J, Zhao C, Xia K, etal. Enhanced piezoelectric output of the PVDF-TrFE/ZnO flexible piezoelectric nanogenerator by surface modification[J]. Applied Surface Science, 2019(463): 626-634.

[8] Peng L, Lu Z, Zhong L, etal. Enhanced ionic conductivity and interface compatibility of PVDF-LLZTO composite solid electrolytes by interfacial maleic acid modification[J]. Journal of Colloid and Interface Science, 2022(613): 368-375.

[9] Yang C, Bai Y, Xu H. Porosity Tunable Poly (Lactic Acid)-Based Composite Gel Polymer Electrolyte with High Electrolyte Uptake for Quasi-Solid-State Supercapacitors[J]. Recent Advances in Polymers for Rechargeable Batteries, 2022 (14).

[10] Mishra K, Arif T, Ram Kumar & Deepak Kumar. Effect of Al_2O_3 *nanoparticles on ionic conductivity of PVDF-HFP/PMMA blend-based* Na^+*-ion conducting nanocomposite gel polymer electrolyte [J]. Journal of Solid-State Electrochemistry, 2019(23): 2401-2409.*

[11] WANG G X, HE P G, FAN L Z. Asymmetric polymer electrolyte constructed by metal-organic framework for solid-state, dendrite-free lithium metal battery[J]. Advanced Functional Materials, 2021, 31(3): 2007198.

[12] Y. Zhong, L. Zhong, S. Wang, J. Qin, D. Han, S. Ren, M. Xiao, L. Sun, Y. Meng. Ultrahigh Li-ion conductive single-ion polymer electrolyte containing fluorinated polysulfonamide for quasi-solid-state Li-ion batteries. Journal of Materials Chemistry A, 2019(7): 24251-24261.

[13] Wang X, Sun J, Feng C, etal. Lithium bis(oxalate)borate crosslinked polymer electrolytes for high-performance lithium batteries[J]. Journal of Energy Chemistry, 2021(55): 228-235.

[14] Y.F. Liang, Y. Xia, S.Z. Zhang, X.L. Wang, X.H. Xia, C.D. Gu, J.B. Wu, J.P. Tu. A preeminent gel blending polymer electrolyte for poly (vinylidene fluoride-hexafluoropropylene)-poly (propylene carbonate) for solid-state lithium-ion batteries. Electrochimica Acta, 2019(296): 1064–1069.

[15] Wu Y, Li Y, Wang Y, etal. Advances and prospects of PVDF based polymer electrolytes[J]. Journal of Energy Chemistry, 2022(64): 62-84.

[16] Yang Q, Deng N, Zhao Y, Gao L, Cheng B and Kang W. A Review on 1D Materials for all-solid-state lithium-ion batteries and all-solid-state lithium-sulfur batteries. Chemical Engineering Journal, 2022(451): 138532.

[17] Liu X, Xiao Z, Peng H, Jiang D, Xie H, Sun Y and Wang R. Rational design of LLZO/polymer composite electrolyte for solid state battery. Chem-An Asian Journal, 2022, 17(24).

[18] Huang Y, Zhang Z, Gao H, et al. $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$ *enhanced polyethylene oxide polymer electrolyte for all-solid-state lithium batteries[J]. Solid State Ionics, 2020(356): 115437.*

[19] Zou J, Gao X, Zhou X, etal. Al and Ta co-doped LLZO as active filler with enhanced Li^+ *conductivity for PVDF-HFP composite solid-state electrolyte[J]. Nanotechnology, 2023(34).*