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Communication

Mesogenic Units Containing Polymer Electrolytes for Light and Safe Batteries

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Abstract: As the core component of solid-state lithium-ion batteries (SSLIBs), the bottleneck of solid-state electrolyte is to achieve fast lithium-ion transport, high electrochemical stability, and mechanical flexibility. Polymer electrolytes offer the possibility of constructing solid-state electrolytes with the above features due to their excellent molecular designability. This preview highlights novel mesogenic (or liquid crystal)-containing polymer electrolytes (MPEs) exhibiting a combination of high ionic conductivity, high electrochemical stability, and mechanical flexibility. Insights into such MPEs enabling light and safe SSLIBs are also discussed.

Keywords: liquid crystal; polymer electrolytes; solid-state batteries; safety; ionic conductivity

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Citation: Zhang, L.; Li, Y.; Wang, S.; Wang, Q. Mesogenic Units Containing Polymer Electrolytes for Light and Safe Batteries. *Coatings* **2023**, *13*, 788. https://doi.org/10.3390/coatings13040788

Academic Editor: Octavian Buiu

Received: 23 March 2023
Revised: 14 April 2023
Accepted: 16 April 2023
Published: 18 April 2023

1. Introduction

The use of solid-state electrolytes instead of liquid electrolytes gives lithium ion batteries higher safety and energy density, and their research has received much attention in recent years [1–4]. Generally, solid-state electrolytes can be divided into inorganic solid-state electrolytes and solid-state polymer electrolytes [5–8]. Although inorganic solid-state electrolytes have high lithium-ion conductivity and high hardness, their brittleness, difficult processing, and high resistance at the interface of corresponding devices have limited their large-scale development [9,10]. Polymer electrolytes are unique in the field of solid-state batteries because of their excellent flexibility and processability. However, polymer electrolytes usually have low ionic conductivity [11–13], and the key issue is how to achieve the regulation of ionic conductivity and mechanical properties while maintaining high electrochemical stability.

Various strategies have been applied to adjust the mechanical properties and ionic conductivity of polymer electrolytes, such as chemical crosslinking, copolymerization, and composition [13]. Despite these methods, the tradeoff between ion conduction and mechanical strength in the polymer electrolytes has continued for more than 40 years, and the ionic conductivity of polymer electrolytes at room temperature is still challenge to reach 10^{-4} S cm^{-1}.

The liquid crystal unit has the ability of orientation, which can enable an ion transport channel for the transmission of lithium ions. Moreover, the liquid crystal unit is usually composed of a rigid structure containing a benzene ring, enabling the regulation of the mechanical properties and ionic conductivity of polymer electrolytes. However, recent advances based on liquid-crystal-containing polymer electrolytes have not been systematically summarized. Based on the advantages of the corresponding electrolytes in mechanical properties and ionic conductivity regulation, it is necessary to discuss the development of this field in order to better promote the development of high-performance polymer electrolytes.

Therefore, in this mini-review, we first briefly introduce the concept of LC materials. Then, we cover the recent developments in LC-based polymer electrolytes based on different structures of polymer matrices. In this part, we also discuss the differences between regular polymer electrolytes and LC-based polymer electrolytes, the composition of LC-based polymer electrolytes, and the transport mechanism of LC-based polymer electrolytes. We hope that this brief review will provide some insight into the development of high-performance polymer electrolytes.

2. Concept of Mesogenic/Liquid Crystal (LC) Materials

Mesogenic/liquid crystal (LC) materials have the liquidity of a liquid and the orderliness of a crystal in the liquid crystal state (also called the intermediate phase) (shown in Figure 1a). The liquid crystal state of liquid crystal materials is sometimes referred to as the "fourth state of matter" [14]. Liquid crystals are capable of forming different nanostructures, such as discoidal, columnar, continuous cubic phases, and one-dimensional nematic phases (Figure 1b gives representative liquid crystal nanostructures). By adjusting the molecular structure and intermolecular forces, liquid crystal substrates can self-assemble into different nanostructures by spontaneously inducing phase separation [15,16]. Self-assembled nano-ordered structured liquid crystals are highly promising materials for ion transport [17–20].

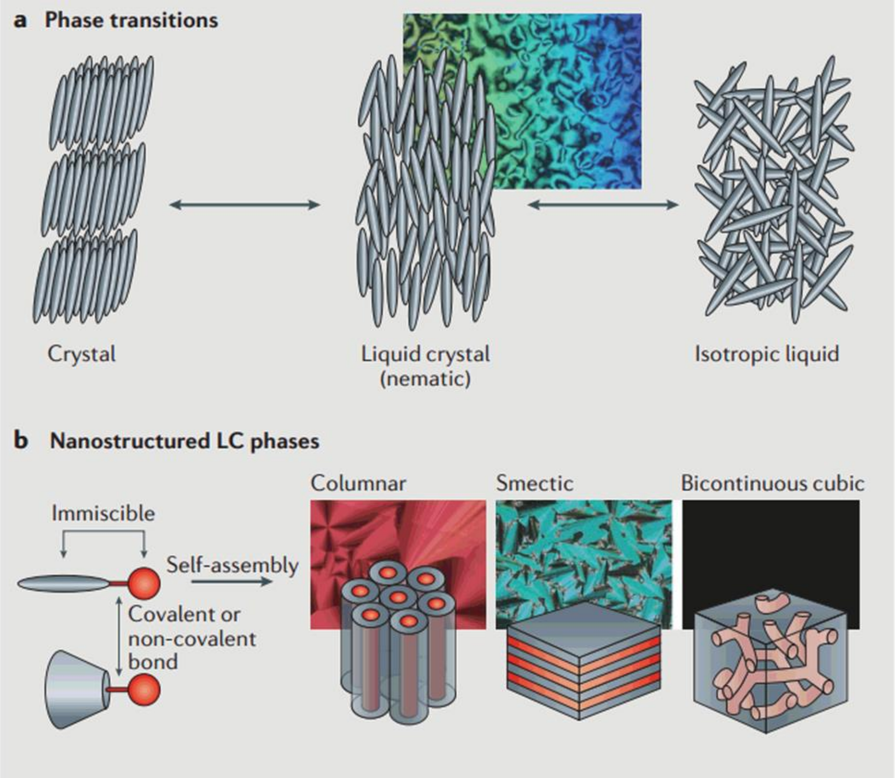

Figure 1. (**a**) Phase transitions and (**b**) nanostructured phases of liquid crystals. Reproduced with permission [21]. Copyright 2017, Nature.

3. Recent Development of LC-Based Polymer Electrolytes

3.1. Differences between Regular Polymer Electrolytes and LC-Based Polymer Electrolytes

Due to the fact that liquid crystal cannot directly conduct ions, the synthesis of electrolytes by liquid crystal and lithium salt is rarely reported at present. It is usually necessary to combine liquid crystal units with other polymers, and plasticizers such as electrolytes and ionic liquids. Generally, LC-based polymer electrolytes can be divided into polymer electrolytes containing a small number of LC units and of polymer electrolytes with LC units as the main element. Based on the orientation ability of LC units under certain conditions, the flexible polymer segments can be coaxed into an ordered arrangement. We prepared LC-based polymer electrolytes only containing polyLC and ionic liquid/lithium salt [22]; the ordered structure of polyLC can also induce ionic liquid/lithium salt to align in a specific direction and promote ion transport. Although the regular polymer electrolytes can form ion channels via microphase separation, the channel is usually not ordered. As shown in Table 1, liquid-crystal-based polymer electrolytes usually show much higher ionic conductivity than conventional polymer electrolytes, and the mechanical properties are also good.

Table 1. Comparison of ionic conductivity and mechanical properties between liquid-crystal-based polymer electrolytes and conventional polymer electrolytes.

Sample	Room Temperature Ionic Conductivity/mS cm^{-1}	Mechanical Strength/MPa	Strain/%	References
PLC-IL	21.4	/	/	[22]
IonoLCE	143.86	0.5	27	[23]
LiMIC	1	200	/	[24]
PEO-LiTFSI	~0.0001	~1	3–5	[25]
G-PPC-CPE	0.164	/	/	
PI-PEO-LiTFSI	0.23	/	/	[26]

3.2. LC-Based Polymer-Electrolyte-Based Linear Polymers

The formation of an ordered structure of the polymer consisting of ion-conducting chain segments and liquid crystal units through the oriented arrangement of the liquid crystal part is very important to improve the ion transport capacity of polymer electrolytes [21,27–29]. That is, liquid crystal materials can provide one- [30,31], two- [32], and three-dimensional ion channels through self-assembly [18], which makes liquid-crystal-based materials a very promising new class of electrolyte materials. More importantly, the rigid feature of liquid crystal units can endow polymer electrolytes with high mechanical strength. Recently, liquid-crystal-based conductive ionic materials have begun to find applications in energy storage, such as in LIBs [33] and dye-sensitized solar cells [34]. In particular, in the field of solid-state electrolytes for lithium ion batteries, Kato et al. have made a very significant contribution to the development of new types of high-performance electrolytes by designing structurally diverse liquid-crystal-based electrolytes that can significantly improve the ionic conductivity of electrolytes after constructing conductive ion channels using the orientation of liquid crystals [21].

By modifying rod-like liquid crystal elements at both ends of PEO, the orientation of liquid crystal can be used to form ordered ion channels. Kato's group designed and synthesized a polymer containing liquid crystal elements, as shown in Figure 2a, which, when compounded with lithium salts, can yield electrolyte membranes with ordered ion channels through controlled orientation, with ion transport paths [35]. However, this ordered structure is very easily disrupted when the temperature is changed, especially in the non-liquid crystal oriented temperature interval. Is it possible to fix the ordered channels to improve the stability of the constructed ordered channels?

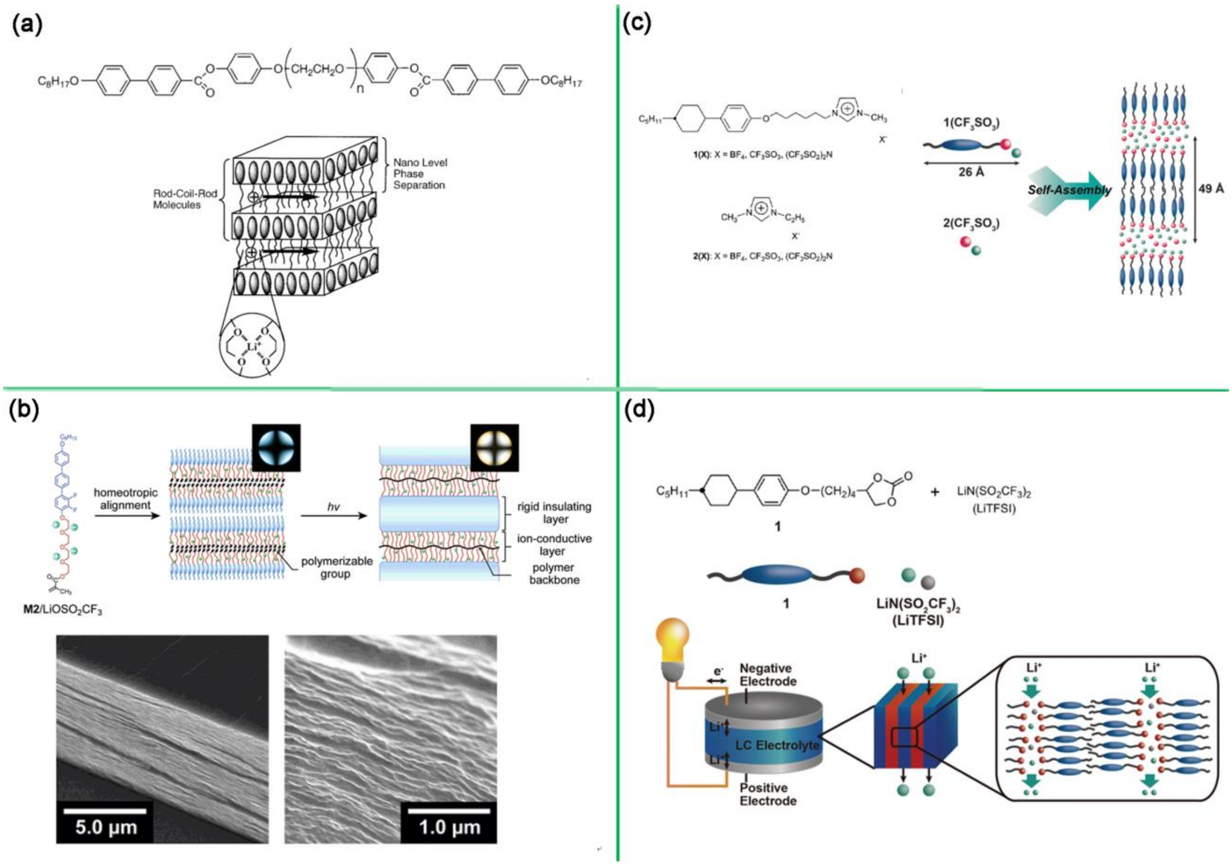

Figure 2. (**a**) Molecular structure of LC-based polymer and ion conduction model. Reproduced with permission [35]. Copyright 2000, American Chemical Society. (**b**) The preparation route of the polymer electrolyte and corresponding SEM images of the electrolyte film. Reproduced with permission [36]. Copyright 2005, American Chemical Society. (**c**) Schematic illustration of the self-assembled structure based on ionic liquid crystals 1(X) and ionic liquids 2(X). Reproduced with permission [37]. Copyright 2015, Royal Society of Chemistry. (**d**) Schematic illustration of the concept and design for LIBs containing the LC electrolyte. Reproduced with permission [33]. Copyright 2015, Wiley-VCH.

Kato's group designed a molecular structure containing liquid crystal elements, as shown in Figure 2a. After adding lithium salts, the ordered arrangement of liquid crystal elements was made by controlling the temperature to obtain a nano-phase separated structure, and the ordered structure was further fixed by photopolymerization [36]. Figure 2b also shows the SEM characterization of the cross section of the obtained liquid-crystal-based electrolyte film, and it can be seen that the prepared film is highly ordered. Due to the construction of ordered ion channels using liquid crystals, which can improve the ion transport capacity, it was found that the room temperature optimal ion conductivity of this electrolyte membrane can reach 10^{-3} S cm^{-1}. However, in the actual prepared devices, we want the lithium ions to be transported efficiently along the direction perpendicular to the membrane, and, obviously, the ion transport of the above-constructed ordered channels is mainly along the direction parallel to the membrane. Inspired by this strategy, we recently used disc liquid crystal to construct ion transport channels, and poly(ethylene glycol) diacrylate (PEGDA) as the cross-linking agent to fix the ion transport channels by photopolymerization [38]. The solid-state LIBs were prepared with good cycling performance by achieving efficient lithium ion transport along the direction perpendicular to the electrolyte membrane.

Kato et al. significantly improved the ionic conductivity of the polymer electrolyte by designing and synthesizing a liquid crystal molecule and compounding it with an ionic liquid and a lithium salt, which could form a two-dimensional ion channel (Figure 2c) through the self-assembly of the liquid crystal [37]. Using a similar method, they modified the end of the rod liquid crystal with a cyclic carbonate (see Figure 2d for the structure) and compounded it with a lithium salt to construct an electrolyte membrane with ordered ion channels using the orientation property of the ionic liquid crystal, and the assembled $LiFePO_4$ (LFP)/electrolyte/Li cell exhibited good cycling performance [33].

Very recently, a raw molecular ionic composite (RMIC) was obtained via interfacial ion-exchange between poly-2,2′-disulfonyl-4,4′-benzidine terephthalamide (Li-form PBDT), a sulfonated aromatic polyamide, and an ionic liquid. PBDT can form a highly ordered lyotropic nematic liquid crystal (LC) phase, which not only can provide fast ion channels but also offer mechanical integrity (Figure 3a) [24]. To further understand the mechanisms of ion transport and ion associations in electrolyte materials, they extracted the diffusion activation energy of ions (E_a) based on the temperature dependence of D_{Li+}, cations, and anions in RMIC and LiMIC electrolytes (obtained from NMR diffusometry). The results show that the density of the PBDT matrix dominates the local energy barrier controlling ion transport and that the PBDT matrix elevates the local energy barrier for cation transport in the lithium ion matrix, mainly because of the interaction of SO^{3-} in the PBDT chain with N-methyl-N-propyl-pyrrolidinium cation ($C3mpyr^+$). Ultimately, they concluded that the unexpectedly high conductivity observed in this solid LiMIC electrolyte results from a fast Li^+ hopping ion transport mechanism in the solid nanocrystal grain boundaries rather than through liquid-like mobile phase transport in the PBDT LC grains. The solid-state electrolytes also display a very high lithium-ion migration number over 0.5 and a high electrochemical window of 5.6 V (Figure 3b). According to the Voltage–time profiles for Li/Li cells incorporating LiMIC, Li dendrite growth is suppressed by increasing the rigid polymer content. However, the cell performance based on a cathode (such as typical $LiFePO_4$, $LiCoO_2$, and $LiNi0.8Co_{0.1}Mn_{0.1}O_2$-based cathodes) and an anode (such as Li anode, graphite-based anode) was not demonstrated in the paper.

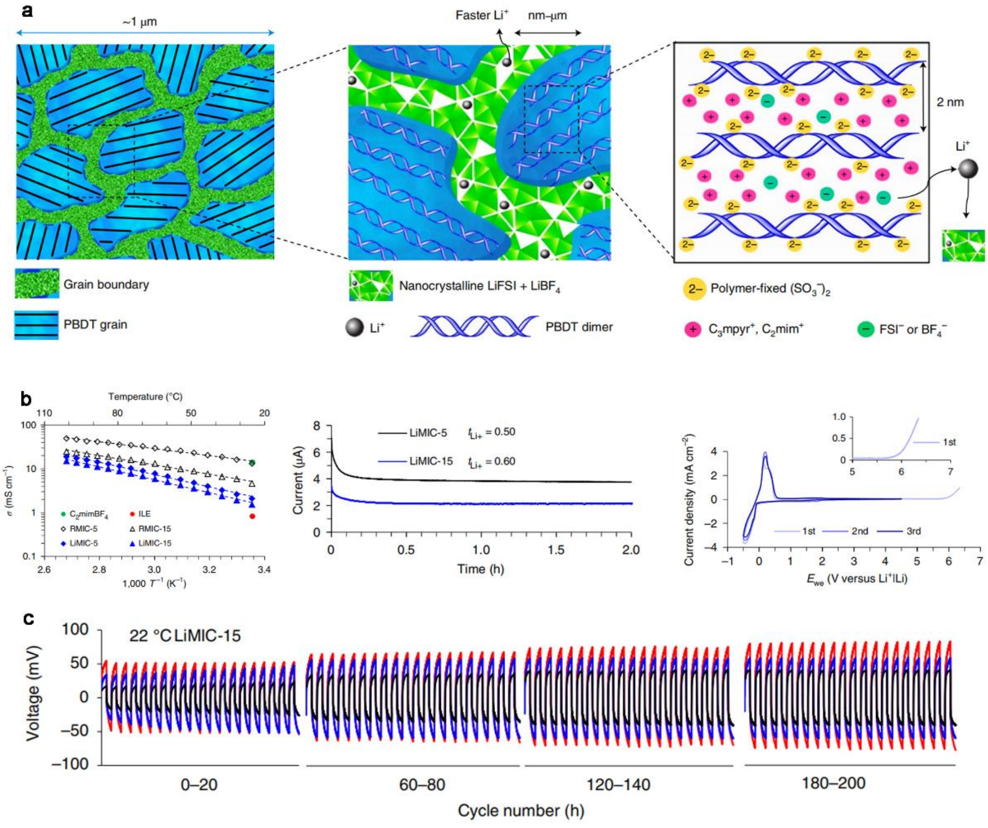

Figure 3. (**a**) Li-loaded molecular ionic composite (LiMIC) can form a conductive network supporting

fast Li$^+$ transport. (**b**) Temperature-dependent conductivity of MICs (RMICs) and LiMICs, related polarization, and CV curves. (**c**) Voltage–time profiles for Li/Li cells incorporating LiMIC. Reproduced with permission [24]. Copyright 2021, Nature.

3.3. LC-Based Polymer-Electrolyte-Based on Crosslinked/Hyperbranched Polymers

The above work provides a feasible method for the preparation of polymer electrolytes with microscopically ordered structures using liquid crystals and points the way to the preparation and application of electrolyte films containing liquid crystal substrates in rich diversity. However, it is very unfortunate that the current reports based on polymer electrolytes containing liquid crystal units are still limited to the optimization of ionic conductivity, and there are almost no reports on other electrochemical properties (e.g., electrochemical stability, lithium ion mobility) or on the cycling and rate performance of assembled half/full cells with liquid crystal units. Very recently, we have continued to develop new methods for polymers containing liquid crystal units, provided several new types of polymer electrolytes containing liquid crystal units such as cross-linked units (Figure 4a–c) [22,39,40], and hyperbranched polymer electrolytes (Figure 4d) containing liquid crystal units [41], and evaluated the practical applicability of the polymer electrolytes in LIBs, favorably advancing the field.

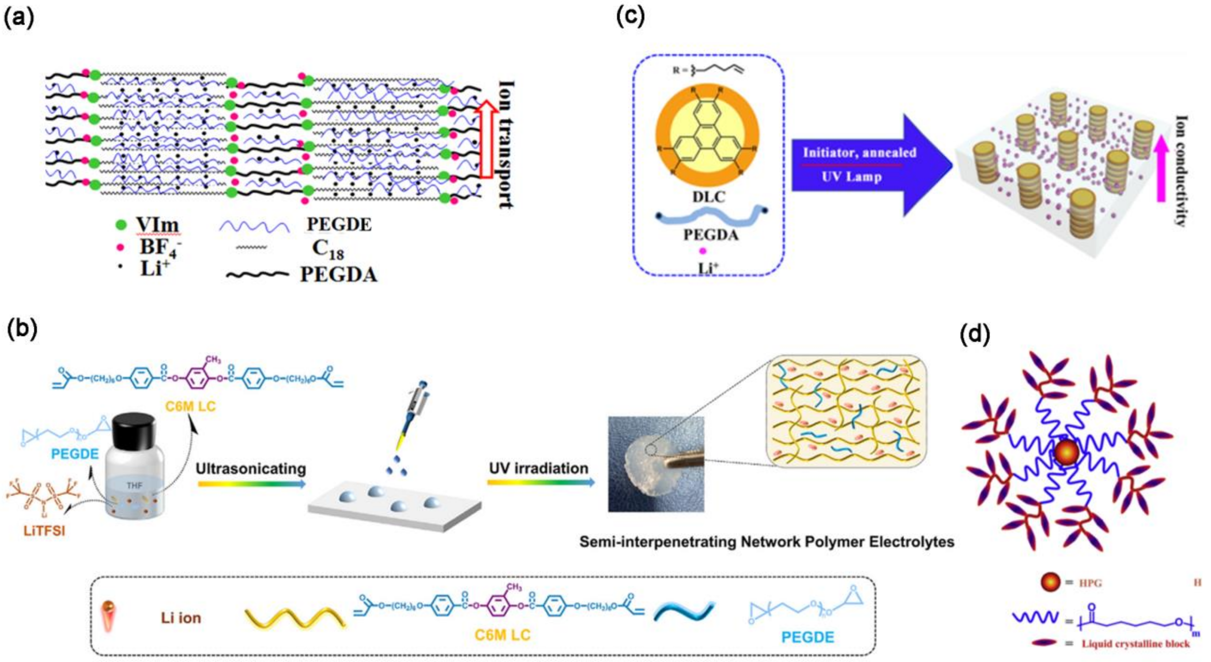

Figure 4. Liquid-crystal-based polymer electrolytes with desirable ionic channels based on different synthetic strategies. (**a**–**c**) Cross-linked (reproduced with permission [22,38,39]. Copyright 2019, 2018, and 2018, Royal Society of Chemistry, Royal Society of Chemistry, and American Chemical Society, respectively.) (**d**) Hyperbranched polymer electrolytes containing liquid crystal units. Reproduced with permission [41]. Copyright 2018, Elesvier.

3.4. Transport Mechanism of LC-Based Polymer Electrolytes

LC units usually are rigid components; they cannot transport Li$^+$ directly. However, the formed ion channels can reduce the ion conduction activation energy, resulting in faster ion transport of LC-based polymer electrolytes than regular polymer electrolytes. The ion transport mechanism of LC-based polymer electrolytes mainly depends on the types of ion conduction segments. The typical ion transport segments come from polyether [42], polyester [41], and polycarbonate [43], which usually transport lithium-ion by the complexation and de-complexation of lithium-ion with ether, ester, and carbonate groups. Recently, a "cation-assisted lithium-ion transport" mechanism was also reported by Atik et al.; they prepared a pyrrolidinium-based ionic liquid containing PEO segment, and it was found that the solvating properties of cation can promote the transport of lithium-ion [44]. So far, liquid-crystal-based polymer electrolytes mainly introduce transport ion components into liquid crystal. Liquid-crystal based elements usually do not participate in the direct transport of ions, but the introduction of some special functional groups such as -CN and -OH in liquid-crystal-based elements may promote the dissociation of lithium salts, which can be considered at a later stage. More importantly, if we can design and synthesize pure liquid crystal polymer, which can transport lithium ions itself, this will be of greater significance and is a direction that could be pursued later.

4. Conclusions

In summary, in order to achieve high-energy-density SSLIBs, the polymer electrolytes should possess high lithium-ion conductivity, high electrochemical stability, and as high flexibility. Through the orientation of liquid crystal units, the lithium-ion transmission channel of polymer electrolytes can be constructed. Meanwhile, the mechanical properties of polymer electrolytes can also be changed by the content of rigid liquid crystal units. Thus, the specific functions obtained by liquid crystal units are promising for the preparation of high-performance polymer electrolytes. Although much progress has been made in recent years in the published works on liquid crystal units containing polymer electrolytes, in the assembly process, attention should be paid to the thickness control, interface, and other issues, and these can be inspired by our recently published paper on the subject [45]. For instance, the energy density of batteries can be increased, and higher area-normalized conductance can be obtained when reducing the thickness of polymer electrolytes. Then, light and safe batteries based on mesogenic units containing polymer electrolytes can be achieved.

Author Contributions: L.Z., Y.L., S.W. and Q.W. proposed the research. S.W., L.Z. and Y.L. wrote the manuscript. S.W. and Q.W. revised it. L.Z., Y.L., S.W. and Q.W. analyzed the data and wrote the manuscript, with suggestions and comments from all of the reviewers. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Natural Science Foundation of Jiangsu Province (BK20210601), Natural Science Foundation of China (52177020), the Fundamental Research Program of Shanxi Province (202103021222006), the Special Fund of "Jiangsu Provincial High-level Innovative and Entrepreneurial Talents Introduction Program" (the first batch) in 2020 (Doctoral Aggregation Program) (CZ030SC20016), the China Postdoctoral Science Foun-dation (2021M691652), and the Jiangsu Province Postdoctoral Science Foundation (2021K323C). The research project was supported by the Shanxi Scholarship Council of China (HGKY2019085), the General Project of Natural Science Research in the Universities of Anhui Province (KJ2021B15), the Research Project of Chuzhou University (2022XJYB08), the Chuzhou University Scientific Research Start Foundation Project (2020qd04).

Conflicts of Interest: There are no conflict to declare.

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