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**FABRICATION OF FLEXIBLE POLYMER-
BASED HIGH-VOLTAGE SOLID-STATE
LITHIUM METAL BATTERIES**

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**Fabrication of flexible polymer-based high-voltage solid-
state lithium metal batteries**

Wei Zhenyao

**A thesis submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy**

August 2023

CERTIFICATE OF ORIGINALITY

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ABSTRACT

Commercial lithium-ion batteries have been widely applied in electric vehicles, portable electronics, and large-scale energy systems. The emergency of solid-state electrolytes could increase energy density and improve the safety concerns of batteries. However, many challenges must be addressed to meet the requirements of industrial applications. Firstly, the interfacial contact between solid-state electrolytes needs to be improved due to the solid-solid contact. Secondly, the electrochemical stability of polymer electrolytes restricts the further enhancement of energy density because of the poor compatibility with high-voltage cathodes. Impressively, the solid-state feature of solid-state electrolytes enables the realization of internal bipolar configuration once the compatibility of the current collector for lithium metal anode and cathodes are optimized.

Firstly, UV-cured polymer electrolyte is synthesized via photo-polymerization of poly (ethylene glycol) methyl ether methacrylate and poly (ethylene glycol) diacrylate. The obtained polymer electrolyte exhibits a high ionic conductivity of $2.95 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C, a wide electrochemical stable window of up to 4.69 V (vs. Li/Li⁺), and excellent compatibility against lithium metal electrodes over 800 h. Besides, an integrated cathode/electrolyte interface is constructed by pouring the polymer electrolyte precursor onto the cathode layer. This integrated cell exhibits faster Li-ion diffusion in cathodic electrochemical reactions than conventional cells. Moreover, LiMn_{0.8}Fe_{0.2}PO₄||Li cells with integrated cathode/electrolyte interface deliver a reversible capacity of 164.7 mAh g⁻¹ at 0.1 C and retain a capacity of 134.4 mAh g⁻¹ after 240 cycles at 0.2 C. Furthermore, the integrated cells perform satisfactorily under disastrous conditions, presenting high safety. The UV cross-linked polymer electrolyte is a promising candidate for high energy density all-solid-state lithium metal batteries.

Secondly, we designed and synthesized a fluorine-based polymer electrolyte with

poly(ethylene glycol) diglycidyl ether copolymerizing with glycidyl 2,2,3,3-tetrafluoropropyl ether for safe and stable all-solid-state lithium batteries. Introducing TFE enhances the ionic conductivity, widens the electrochemical stable window, and improves the stability with the lithium metal anode. Moreover, the constructed LiF-rich solid electrolyte interface ensures the symmetric lithium metal cell cycling for 2000 h under 0.2 mA cm^{-2} . The assembled all-solid-state lithium batteries paired with $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ demonstrate outstanding capacity retention after 300 cycles with coulombic efficiency of 99.95% and long-term charge/discharge stability with LiFePO_4 for 700 cycles. Notably, the assembled pouch cell exhibits excellent flexibility with a capacity retention of 93.8% after 3000 bending cycles under a radius of 4 mm. Therefore, introducing fluorine-based components into the polymer structure effectively stabilizes high-voltage cathode during long-term operation.

Thirdly, nickel--coated PET (Ni-PET) fabric was fabricated through a polymer-assisted metal deposition method to support cathodic and anode materials. Ni-PET fabric shows excellent flexibility after bending 10000 cycles under a bending radius of 5.0 mm. The electrochemical performance of Ni-PET batteries is similar to those with Al current collectors, delivering capacity retention of 85.4% after 500 cycles at 0.5 C. In addition, Ni-PET can also act as a bipolar substrate due to the compatible stability of nickel metal and lithium metal. The polarization voltage of the internal bipolar battery is lower than the external bipolar configuration. The capacity retention of assembled bipolar batteries with Ni-PET is 95.4% after 250 cycles. Furthermore, the bending process decreases resistance, increasing capacity after 200 bending cycles. The coulombic efficiency of the bipolar battery is up to 99.8% during the dynamic bending test, showing great flexibility with PET-based current collectors.

In conclusion, this thesis offered effective strategies to improve the energy density of all-solid-state lithium metal batteries. The interfacial contact between the electrolyte and cathode was addressed by constructing the integrated structure. Fluorine-based polymer electrolytes enhanced the compatible stability with high-voltage cathodes.

Moreover, the bipolar configuration of solid-state batteries was optimized by introducing a Ni-PET current collector. The proposed strategies provide a solid foundation for industrial applications in the future.

LIST OF PUBLICATIONS

Published papers:

1. **Zhenyao Wei**[#], Tian Zhang[#], Man Wang, Wei Wu, Jun Wang, Shuai Li, Yusheng Zhao, Chaoyang Wang, Xiayin Yao*, Xiaoxiong Xu* and Yonghong Deng*. Formation of excellent cathode/electrolyte interface with UV-cured polymer electrolyte through *in-situ* strategy. **Journal of The Electrochemical Society**, 2021, 168: 020511.
2. Wei Wu[#], **Zhenyao Wei**[#], Jun Wang[#], Jian Shang, Man Wang, Shang-Sen Chi, Qingrong Wang, Leilei Du, Tian Zhang, Zijian Zheng and Yonghong Deng*. Enabling high-energy flexible solid-state lithium-ion batteries at room temperature. **Chemical Engineering Journal**, 2021, 424: 130335
3. Yufeng Luo, Lei Wang, **Zhenyao Wei**, Qiyao Huang, Yonghong Deng, Zijian Zheng*. Cracking-controlled slurry coating of mosaic electrode for flexible and high-performance lithium-sulfur battery. **Advanced Energy Materials**. 2023, 13: 2203621-2203629.
4. Shujing Wen, Chao Luo, Qingrong Wang, **Zhenyao Wei**, Yanxiang Zeng, Yidong Jiang, Guangzhao Zhang, Hongli Xu, Jun Wang, Chaoyang Wang, Jian Chang*, Yonghong Deng*. Integrated design of ultrathin crosslinked network polymer electrolytes for flexible and stable all-solid-state lithium batteries. **Energy Storage Materials**, 2022, 47: 453-461.

Papers in preparation

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LIST OF ABBREVIATIONS

ACN	acetone
Al	aluminum
AlF ₃	aluminum fluoride
ASSLMBs	all-solid-state lithium metal batteries
C	carbon
CC	current collector
CE	coulombic efficiency
CEI	cathode electrolyte interlayer
CPEs	composite polymer electrolytes
CV	cyclic voltammetry
DEMS	differential electrochemical mass spectrometry
DFT	density functional theory
DMAB	dimethylamine borane
DOL	1,3-dioxolane
DSC	differential scanning calorimetry
EDS	energy dispersive spectrometer
EIS	electrochemical impedance spectroscopy
EO	ether oxygen
ESW	electrochemical stable window
FT-IR	Fourier transform infrared spectra
HMPP	2-hydroxy-2-methylpropiophenone
METAC	2-methacryloyloxy)ethyl trimethylammonium chloride
MPTS	3-(trimethoxysilyl)propyl methacrylate
KPS	potassium persulfate
LATP	Li _{1.4} Al _{0.4} Ti _{1.6} (PO ₄) ₃
LCO	LiCoO ₂

LE	liquid electrolyte
LLTO	$\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$
LLZO	$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$
LMBs	lithium metal batteries
LMFP	$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$
LFP	LiFePO_4
LiClO_4	lithium perchlorate
LiNO_3	lithium nitrate
LiRAP	lithium-rich anti-perovskites
LiTFSI	lithium bis(trifluoromethane) sulfonilimide
Li-O ₂	lithium-air
Li-S	lithium-sulfur
LIBs	lithium-ion batteries
LISICON	lithium super ionic conductor
LSV	linear sweep voltammetry
LTO	$\text{Li}_4\text{Ti}_5\text{O}_{12}$
NASICON	Na superionic conductor
NCA	$\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Al}_{0.05}\text{O}_2$
NCM622	$\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$
NCM811	$\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$
Ni-PET	nickel coated PET
NMR	nuclear magnetic resonance
PAMD	polymer-assisted metal deposition
PAN	poly(acrylonitrile)
PBA	poly(acrylonitrile-co-butadiene)
PEGDA	poly(ethylene glycol) diacrylate
PEGDE	poly(ethylene glycol) diglycidyl ether
PEGDMEA	Poly(ethylene glycol) methyl ether acrylate
PEGMEMA	poly(ethylene glycol) methyl ether methacrylate

PEO	Poly(ethylene oxide)
PMA	poly(N-methyl-malonic amide)
PMMA	poly(methyl methacrylate)
PTFEMA	poly(2,2,2-trifluoroethyl methacrylate)
PVDF	poly(vinylidene fluoride)
PVDF-HFP	polyvinylidene fluoride-hexafluoropropylene
SEM	scanning electron microscopy
SEI	solid electrolyte interface
SPEs	solid polymer electrolytes
SS	stainless steel
SSEs	solid-state electrolytes
TFE	glycidyl 2,2,3,3-tetrafluoropropyl ether
TGA	thermogravimetric analysis
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
UV	ultraviolet

CHAPTER 1 INTRODUCTION

1.1 Background and Challenges

Lithium-ion batteries (LIBs) are commercialized in many fields ¹⁻³. However, safety problems hinder its further applications, resulting from the leakage of flammable liquid electrolytes. Besides, the lower theoretical capacity of the graphite restricts the energy density increase ^{4, 5}. The energy density could be enhanced with lithium metal anode replacing commercial graphite since the lithium metal can deliver 3860 mAh g⁻¹ in theory ⁶. In pursuit of higher energy density, extensive research has been focused on the lithium metal anode, such as lithium-air (Li-O₂), lithium-sulfur (Li-S), and other lithium metal batteries (LMBs) ^{7, 8}. However, many serious problems should be solved in practical applications. Firstly, internal short-circuit and capacity decline would result from dendrite growth due to non-uniform lithium plating/stripping on lithium metal electrodes ^{9, 10}. Secondly, severe reactions of lithium metal and organic liquid electrolyte result in solid electrolyte interface (SEI) layers. What's worse, the formed SEI layer is unstable, and the liquid electrolyte (LE) is consumed continuously; thus, the impedance of batteries increases, and coulombic efficiency (CE) decreases. Thus, it's urgent to develop novel electrolytes that stabilize lithium metal and suppress dendrite growth.

Compared to organic LEs, solid-state electrolytes (SSEs) are promising alternatives to stabilize the SEI layer and suppress the lithium dendrite growth due to their intrinsic features ^{11, 12}. Currently, there are three types of SSEs: oxide electrolytes, sulfide electrolytes, and solid polymer electrolytes (SPEs). Oxide electrolytes are relatively stable towards air and exhibit higher ionic conductivity ^{13, 14}. However, the oxide ceramic film is brittle, leading to poor interfacial contact with electrodes. By comparison, the sulfide electrolyte shows the highest ionic conductivity among SSEs, though they are costly and sensitive to air and humidity ^{15, 16}. The flexible SPEs could

provide excellent interfacial contact with electrodes^{17, 18}. However, the electrochemical performance does not meet the requirements for application, resulting from low ionic conductivity, poor compatibility with high-voltage cathodes, and low mechanical strength. The research on preparing block polymers and fabricating organic/inorganic composite polymer electrolytes (CPEs) can improve the mechanical strength and electrochemical performance of SPEs. Nevertheless, more attention should be paid to interfacial contact and compatibility with high-voltage cathodes.

Apart from the SSEs, optimization of battery configurations is another crucial advantage for all-solid-state lithium metal batteries (ASSLMBs). In commercial markets, the output voltage of electric vehicles is up to around 400 V, and the output voltage of an electric e-bike also reaches up to 48 V. In contrast, the output voltage of a unit cell is only about 3.6 V. Therefore, designing bipolar batteries is beneficial to promote the development of ASSLMBs¹⁹. For LIBs, the in-series configuration must be stacked with individual cells outside the package, ascribed to the fluidic feature of organic LEs. While for ALLSMBs, the internal bipolar configuration is easy to realize without ionic short-circuit²⁰.

Although some researchers have paid more attention to designing bipolar batteries through the inner in-series method, the battery performance is not good enough in the current stage. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is stable to aluminum (Al) for commercial cathode and anode active materials. In this way, the bipolar design can be realized easily^{21, 22}. However, replacing liquid electrolytes with solid-state electrolyte would enhance energy density. Using lithium metal anode, energy density on volumetric and gravimetric would increase by 70% and 40%, respectively²³. To introduce the lithium metal anode, another buffer layer was introduced to separate the two individual cells, leading to resistance increase and capacity fading^{24, 25}.

Notably, the characterization of the flexibility of solid-state batteries (SSBs) is rarely reported systematically. In current solid-state battery reports, the flexibility of batteries

is often mentioned. However, they show the demonstration of the pouch cell to illustrate the flexibility of solid-state batteries^{26, 27}. Moreover, some electrochemical properties are involved in reported works of literature, such as resistance change and cycle performance with fixed angles²⁸⁻³⁰. The blank area of flexibility for ASSLMBs should be filled up to adapt to the demands of wearable devices.

1.2 Research Objectives

This study focuses on enhancing the electrochemical performance of ASSLMBs by addressing the above challenges. The main strategy is synthesizing novel SPEs with unique functionalities. The detailed objectives are listed as follows:

- 1) ***In-Situ Polymerization of UV-Cured Polymer Electrolyte for $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ -based All-Solid-State Lithium Metal Batteries***
 - a) To synthesize the cross-linked SPEs through the UV-irradiation method;
 - b) To construct an “electrolyte-cathode” integrated structure for improvement of the interfacial contact.
- 2) ***Synthesis of fluorine-based polyether polymer electrolyte for high-voltage cathodes***
 - a) To synthesize the fluorine-based polymer electrolyte to improve the electrochemical stability with high-voltage cathodes;
 - b) To assemble in-situ solid-state batteries via thermal polymerization through fabricating porous substrate.
- 3) ***Highly flexible solid-state lithium batteries enabled by nickel-coated PET fabric***
 - a) To fabricate and characterize the textile-based current collector via the PAMD method;
 - b) To assemble internal bipolar solid-state batteries by connecting adjacent cells by sharing the nickel-coated PET (Ni-PET) as the current collector (CC).

1.3 Research Originality

In this research, we focus on the promotion of battery performance for SSBs, such as increasing the ionic conductivity of SPEs, improving interfacial contact between electrolyte and cathode, enhancing the compatibility with high-voltage cathodes, and optimizing the battery structure based on the feature of SPEs. Researchers previously reported literature paid more attention to the fabrication of organic/inorganic composite electrolytes and modifications on high-voltage cathode particles. Moreover, wearable devices' flexibility and application are rarely involved. The *in-situ* polymerizing method decreased the interfacial resistance between polymer electrolytes and electrodes. Besides, introducing fluorine-based molecules can facilitate the formation of stable SEI and cathode electrolyte interlayer (CEI) layers. Most importantly, the textile-based CC of Ni-PET provides excellent flexibility to SSBs and simplifies the fabrication of bipolar SSBs.

Firstly, cross-linked polymer electrolyte was synthesized through *in-situ* solvent-free polymerization. The precursor of SPEs can penetrate the cathode's inside and polymerize on the surface of the cathode layer. In this case, the polymerized SPE in the cathode can construct extra lithium-ion transport pathways and realize the “electrolyte-cathode” integrated structure, which benefits the lithium-ion transport across the interface. The results confirmed the enhancement of lithium-ion diffusion in the cathode, leading to better battery performance than in conventional layer-by-layer structures.

Secondly, fluorine-based SPE was synthesized by introducing fluorine-based molecules into the polymer matrix through *in-situ* thermal polymerization to enhance the battery performance with high-voltage cathodes. Introducing fluorine-based molecules enhances the electrochemical performance of SPEs. Formation of stable SEI on lithium anode enables the symmetric Li//Li cells to cycle for 2000 h under 0.2 mA cm^{-2} . The Li//LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (NCM622) battery with fluorine-based SPE exhibits excellent battery performance, charging to 4.3 V. Paring with LiFeO₄ (LFP), the battery cycles

up to 700 cycles stably. The XPS results prove that the LiF-rich SEI and CEI layers guarantee the battery performance of SSBs. Moreover, the assembled pouch cell shows great flexibility and capacity retention of 93.8% after 3000 bending cycles.

Finally, internal bipolar SSBs were assembled with the textile-based current collector. Ni-PET was fabricated with a 300 nm nickel metal coating layer through the PAMD method, exhibiting superior flexibility. The battery performance with Ni-PET was evaluated, indicating that Ni-PET is suitable for SSBs. Besides, the long-term cycle performance with Ni-PET is better than that with commercial Al foil. Moreover, Ni-PET CC is a promising alternative to stainless steel (SS) to connect the adjacent cells in bipolar SSBs since the contact resistance with SS is very high. The assembled bipolar batteries with Ni-PET show good cycle performance, delivering capacity retention of 92% after 250 cycles. Furthermore, the bipolar pouch cell demonstrates excellent flexibility with destructive bending conditions. The pouch cell can operate well under the dynamic bending process with a bending radius of 5.0 mm.

1.4 Outline of the Report

This thesis presents three strategies to improve the electrochemical performance of SSBs: (1) improving the interfacial contact, (2) introducing fluorine-based side chains into polymer electrolytes, and (3) constructing internal bipolar configuration. The thesis consists of the following contents:

Chapter 1 introduces the background and challenges of SSBs, including solid-state electrolytes and battery structures. And then, the research objectives and originality are involved.

Chapter 2 gives a compressive literature review on SSBs. Firstly, the necessity of SSBs, the research state of modification on SPEs and bipolar configurations, and the flexibility of SSBs.

Chapter 3 expresses the methodology used in this thesis, including materials preparation and characterization of structure and batteries.

Chapter 4 demonstrates the synthesis of cross-linked polymer electrolytes through the *in-situ* UV-Cured method. And then, the physical structure and electrochemical performance of SPE are conducted systematically. Finally, the battery performance with improved interface contact is evaluated.

Chapter 5 illustrates the synthesis of fluorine-based polyether polymer electrolytes through in-situ thermal polymerization. The characterization of structure, the effect of fluorous effect, and electrochemical performance are investigated. Moreover, the SEI and CEI layers are studied through XPS spectra in detail. Impressively, the flexibility of pouch cells is tested.

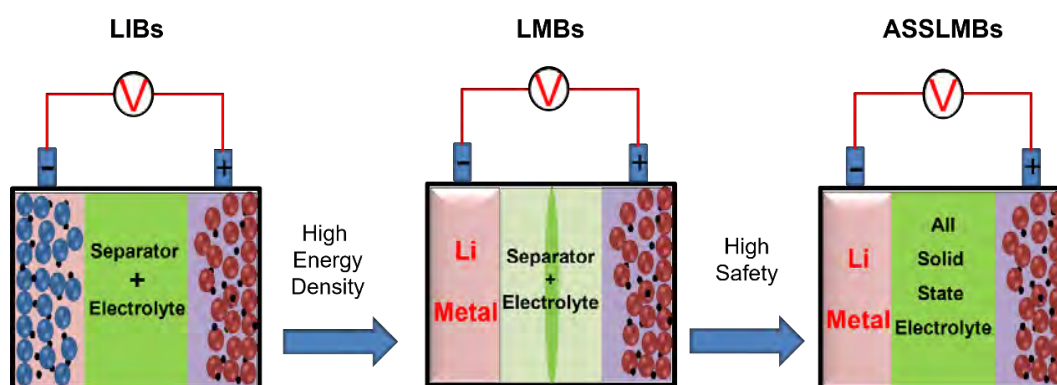
Chapter 6 demonstrates the fabrication of Ni-PET through the PAMD method. The battery performance employing Ni-PET as the current collector is evaluated in monopolar and bipolar cells. Besides, lithium-ion diffusion is compared between Ni-PET and Al foil. Notably, the flexibility of pouch cells for monopolar and bipolar cells is evaluated.

Chapter 7 summarizes the results of this thesis and provides the outlook for high-energy-density ASSLMs.

CHAPTER 2 OVERVIEW OF THE FLEXIBLE SOLID-STATE BATTERIES

In this chapter, a systematical review of high-voltage solid-state batteries is introduced. This section mainly contains four parts: 1) solid-state electrolytes, 2) polymer electrolytes for high-voltage cathode materials, 3) an overview of bipolar solid-state batteries, and 4) research progress of flexible batteries.

Lithium metal anode has been introduced into LIBs to meet the demands of high-energy-density batteries (**Scheme 2.1**). However, there are many issues in liquid battery systems. The leakage of flammable organic liquid electrolytes may cause fire hazards. The high reactivity of lithium metal and severe side reactions with liquid electrolytes lead to an unstable SEI layer, resulting in capacity decay during operation. For industrial design, the process of stacked modules is costly. By comparison, the solid-state features of SSEs enhance the safety properties. In addition, the side reactions are relieved between electrolytes and lithium metal. Significantly, the bipolar configuration for industrial modules can be considerably simplified.



Scheme 2. 1 Comparison of LIBs, LMBs, and ASSLMBs.

2.1 Solid-state Electrolytes

Over the past ten years, SSEs have emerged for energy storage systems. In the current research stage, there are three types of SSEs: oxide electrolytes, sulfide electrolytes,

and polymer electrolytes (shown in **Scheme 2.2**). The advantages of SSEs are different. The higher ionic conductivities of oxide and sulfide electrolytes lead to operating at room temperature. However, polymer electrolytes' device integration and industrial process cost are superior to others. Besides, the polymer electrolytes are pretty stable with lithium metal anode, stabilization during long-term performance. Significantly, based on the flexibility of polymer electrolytes, the excellent electrolyte-electrode interfacial contact benefits the battery's performance.

Oxide electrolytes (prepared in air)	Sulfide electrolytes (prepared in glove box)	Polymer electrolytes (prepared in glove box)
$\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}\text{P}_3\text{O}_{12}$ $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12}$ $\text{Li}_{6.28}\text{Al}_{0.24}\text{La}_3\text{Zr}_2\text{O}_{12}$ $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ $\text{Li}_{0.45}\text{La}_{0.55}\text{TiO}_3$ $\text{Li}_x\text{PO}_y\text{N}_z$	$\beta\text{-Li}_3\text{PS}_4$ $\text{Li}_7\text{P}_3\text{S}_{11}$ $\text{Li}_7\text{P}_2\text{S}_8\text{X}$, X=Br, Cl, I $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ $\text{Li}_6\text{PS}_5\text{Cl}$ $\text{Li}_2\text{S-P}_2\text{S}_5$ $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.76}\text{S}_{11.7}\text{Cl}_{0.3}$	Polymer matrix: PEO, PVDF, Polycarbonates Lithium salt: LiClO_4 , LiTFSI, LiFSI, LiDOFB Plasticizers: Ester, ether, oligomer Additives: SiO_2 , Al_2O_3 , Oxide and Sulfide Electrolytes

Scheme 2. 2 Three types of SSEs.

2.1.1 Oxide electrolytes

Initially, Na superionic conductor (NASICON) type Li^+ conductors were investigated as alternative solid-state electrolytes. The three-dimensional Li^+ conduction pathways allow fast Li^+ conduction³¹. The common oxide electrolytes are as follows: (i) perovskites, e.g., $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO)³², (ii) NASICON structures, e. g . , $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP)³³, (iii) garnet type electrolytes, e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)³⁴, (iv) Lithium-rich anti-perovskites (LiRAP), ClOLi_3 and $(\text{Cl}, \text{Br})\text{OLi}_3$ ³⁵.

For oxide electrolytes, there are two methods to enhance the ionic conductivity: (i)

chemical substitution with trivalent or pentavalent ions ³⁶ and (ii) incorporation of secondary phases in the fabrication step, tuning the microstructure and thus enhancing boundary conductivity ³⁷. For instance, by decreasing the particle size, Al-substituted LLZO exhibits higher total ionic conductivity of $5.2 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C with a relative density of 94% ³⁸. Using Nb and Ga as dopants, Garnet-structured oxides $\text{Li}_{6.8-3x}\text{Ga}_x\text{La}_3\text{Zr}_{1.8}\text{Nb}_{0.2}\text{O}_{12}$ ($x = 0, 0.1, 0.15, 0.2, 0.25, \text{ and } 0.3$) reaches the highest ionic conductivity of $1.42 \times 10^{-3} \text{ S cm}^{-1}$ at 50°C with the relative density of 93-95% ³⁹.

Among the above oxide electrolytes, LATP and LAGP are unstable with lithium metal due to the reduction of Ti^{4+} and Ge^{4+} . Garnet-based oxide electrolyte LLZO is the most investigated category. The main properties of cubic and tetragonal LLZO are shown in Table 2. 1:

Table 2. 1 Properties of cubic and tetragonal LLZO

	Cubic	Tetragonal
Space group	No.142 $I_{41/acd}$	No.230 I_{a3d}
Lattice parameters	$a=13.134 \text{ \AA}, c=12.663 \text{ \AA}$ ⁴⁰	$a=12.975 \text{ \AA}$ ⁴¹
Ionic conductivity	$10^{-6} \sim 10^{-5} \text{ S cm}^{-1}$	$10^{-4} \sim 10^{-3} \text{ S cm}^{-1}$
Activation energy	0.4 ~ 0.5 eV	0.3 ~ 0.4 eV
Li^+ distribution	$8a, 16f, 32g$	$24d, 96h$ partly occupied

The tetragonal phase is the product of the lack of symmetry of the cubic phase. The lattice parameters of the c axis become smaller, while the lattice parameters of the a and b axes become larger. The tetragonal unit cell is obtained by flattening the cubic unit cell. The conductivity of the cubic phase is two orders of magnitude higher than that of the tetragonal phase ⁴². Although the conductive properties of LLZO are excellent, there is also restriction to be addressed, including interfacial contact with electrodes and lithium dendrite growth.

2.1.2 Sulfide electrolytes

Sulfide-based SSEs exhibit the highest ionic conductivity of over 10^{-2} S cm⁻¹ at 25°C⁴³⁻⁴⁵. The comparable ionic conductivity to liquid electrolytes makes sulfide-based SSEs attract much attention. Compared with oxide electrolytes, the lower electro-negativity of sulfur leads to smaller bonding strength with Li⁺. The larger atom radius of sulfur contributes to faster Li⁺ transport than oxygen. Therefore, the giant migration channels for Li⁺ in sulfide electrolytes benefit the migration of Li⁺.

Thio-Lithium Super Ionic Conductor (thio-LISICON) (Li₁₀GeP₂S₁₂) exhibits a high ionic conductivity of 1.2×10^{-2} S cm⁻¹, an electrochemical stable window of up to 5 V and an activation energy of 0.24 eV⁴³. Argyrodite-type crystals Li₆PS₅X (X = Cl, Br or I)⁴⁶⁻⁴⁸ also present high ionic conductivities. In addition, some glasses electrolytes, such as 67(75Li₂S-25P₂S₅)-33LiBH₄⁴⁹ and 30Li₂S-26B₂S₃-44LiI⁵⁰, exhibit high ionic conductivities of around 2×10^{-3} S cm⁻¹ with lithium salts.

2.1.3 Polymer electrolytes

In 1973, the segmental motion of PEO chains was found to assist the Li⁺ transport in polymer matrix⁵¹. Then, other polymer electrolytes based on polycarbonate⁵², poly(acrylonitrile) (PAN)⁵³, poly(vinylidene fluoride) (PVDF)⁵⁴, and polysiloxane (POSS)⁵⁵ have been investigated for ASSLMs. Lithium ionic can be coordinated with the polar groups of the polymer, hopping from one coordinating site to another with the help of the segmental motion of polymer chains⁵⁶ (**Figure 2.1**). Generally, lithium bis(trifluoromethane) sulfonimide (LiTFSI) is the source of lithium ions due to its larger radius of anion, which benefits lithium ions transport⁵⁷. Among the SPEs mentioned above, PEO-based polymer electrolyte is considered as the most potential alternative to liquid electrolytes, owing to its excellent electrochemical performance with lithium metal electrodes. However, the poor electrochemical performance, such as low ionic conductivity at room temperature and stability with high-voltage cathodes,

hinders further applications.

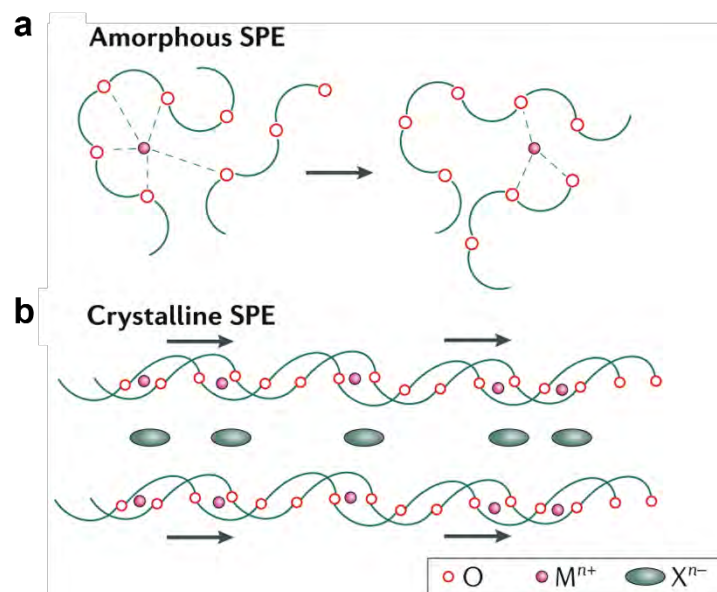


Figure 2.1 Ion conduction in solid polymer electrolytes. (a) Lithium-ion transport in amorphous SPE; (b) Lithium-ion transport in crystalline SPE¹².

2.2 Polymer Electrolytes for High-voltage Cathodes

Polymer electrolytes have been commercialized for many years. However, LiFePO₄ (LFP) cathode dominates the market for polymer-based SSBs, which operates at a low cutoff voltage than 4.0 V. To enhance the energy density of ASSLMs, high-voltage cathodes, such as LiNi_xCo_yMn_zO₂ (NCM), LiNi_{0.85}Co_{0.1}Al_{0.05}O₂ (NCA), and LiCoO₂ (LCO), should be employed for polymer-based batteries. Combining high-voltage cathodes with polymer electrolytes would result in new problems related to the chemical and electrochemical stability of cathodes and polymer electrolytes.

2.2.1 Decomposition of polymer electrolyte with high-voltage cathode

The battery performance for polymer electrolytes is related to the oxidative stability of polymer electrolytes and the reactivity of high-voltage cathodes. Taking poly(ethylene oxide) (PEO) as an example, the limited oxidative stability is ascribed to the labile lone pair on the ether oxygen (EO) atom of PEO chains⁵⁸. The degradation mechanism of EO is illustrated in **Figure 2.2**^{59, 60}. The whole process can be divided into three steps:

firstly, an electron from EO attacks the TFSI⁻ anion to form the radical cation. Afterward, the neutral HTFSI was generated by transferring a proton to TFSI⁻ anion (**Figure 2.2 a**). Secondly, the second electron transfer forms carbocation, anchoring a second TFSI⁻ anion (**Figure 2.2 b**). Finally, the HTFSI can attack other EO chains, causing cleavage of the PEO matrix (**Figure 2.2 c**). Furthermore, the HTFSI can also react with lithium metal anode to generate H₂ in batteries ⁶¹.

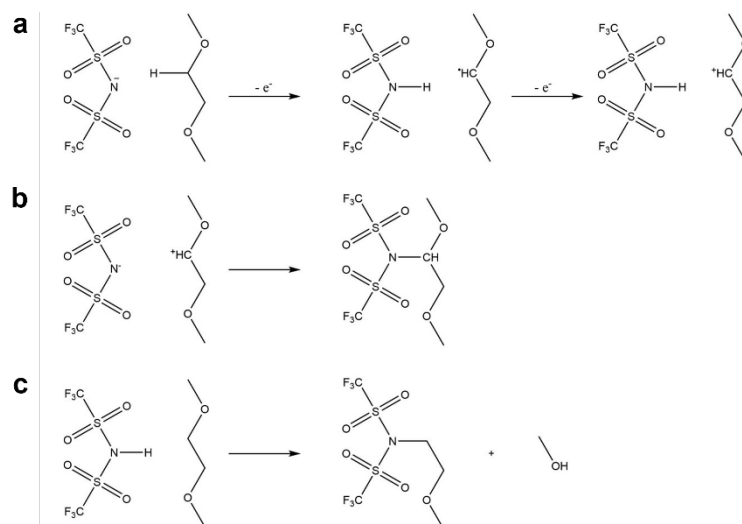


Figure 2.2 Simplified oxidation mechanism of EO with LiTFSI. (a) Oxidation of EO group; b) Anchoring of TFSI⁻ on the carbocation; c) Cleavage of EO by HTFSI.

The polymer host decided on the polymer electrolyte's electrochemical stable window (ESW). According to the calculation of density functional theory (DFT), the oxidation potential of PEO is below 4.0 V (vs. Li/Li⁺) ⁶². After making the polymer-salt complex, the ESW experienced a noticeable decline due to the shielding effect of salt anion in the polymer oxidized state. Therefore, the oxidation potential for PEO-based polymer electrolytes is influenced by the polymer matrix, polymer-salt complex, and the oxidation process of EO groups.

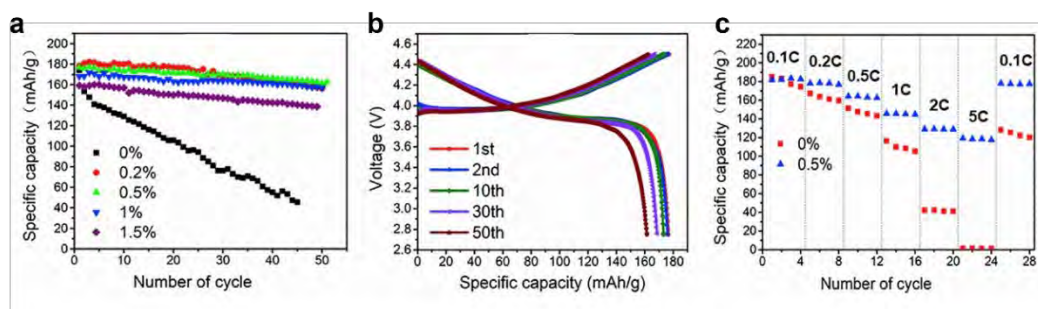


Figure 2.3 Battery performance of LATP-coated LCO batteries. (a) Cycling performance with different loading of LATP; (b) Charge/discharge profiles of 0.5wt% LATP-coated LCO; (c) Rate performance of pristine and 0.5wt% LATP-coated LCO.

Currently, the ESW of polymer electrolytes often was characterized by SS-blocking electrodes, which neglect the surrounding effect of materials. In this case, the ESW of the polymer electrolyte was overestimated significantly. In particular, two more factors should be considered: a) the reactivity of composite cathode materials and b) the chemical reactivity of active materials of cathodes. Performing linear sweep voltammetry (LSV) with the carbon-coated electrode, the oxidation potential decreases from 4.5 V to 3.8 V⁶³. The strong oxidation ability of cathode materials facilitates the oxidation process of polymer electrolytes. For example, the high oxidative ability of LCO results in poor cycling performance (**Figure 2.3**)⁶⁴. In contrast, coating LCO with or $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ (LATP) would effectively prohibit the decomposition of polymer electrolytes, which was accelerated by the electrochemical process. Thus, to enhance the oxidation stability of polymer electrolytes, effective modifications should be made to polymer electrolytes and cathode materials.

2.2.2 Molecular design of polymer electrolytes

There are several methods to improve the ESW of SPEs. In the reported literature, modification of the molecular structure of polymer and fabrication of inorganic/organic composite electrolytes can improve the electrochemical compatibility with high-voltage cathodes.

In LIBs, the fluorinated components can contribute to forming LiF-rich SEI to stabilize the long-term cycling performance. Besides, fluorine-based electrolytes can improve the stability with high-voltage cathodes, owing to the ultra-stability of generated LiF during operation ^{65, 66}. Hu *et al.* ⁶⁷ reported topological polymeric solid electrolyte (FMC-ASPE-Li) by combining PEO, β -Cyclodextrin, and poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) (**Figure 2.4 a**). The PTFEMA provides abundant Li⁺ coordination groups and stabilizes the long-cycling performance with high-voltage cathodes of NCM622 and NCM811. Lynden A. Archer *et al.* ⁶⁸ investigated the *in-situ* polymerized 1,3-dioxolane (DOL) in the presence of aluminum fluoride (AlF₃) in Li//NCM622 solid-state batteries. The AlF₃ plays a vital role in building fluorinated CEI, which protects the Poly-DOL from decomposition during cycling. In addition, the Al₂O₃ layer on Al foil avoids dissolution under the protection of formed LiF-contained CEI (**Figure 2.4 b**).

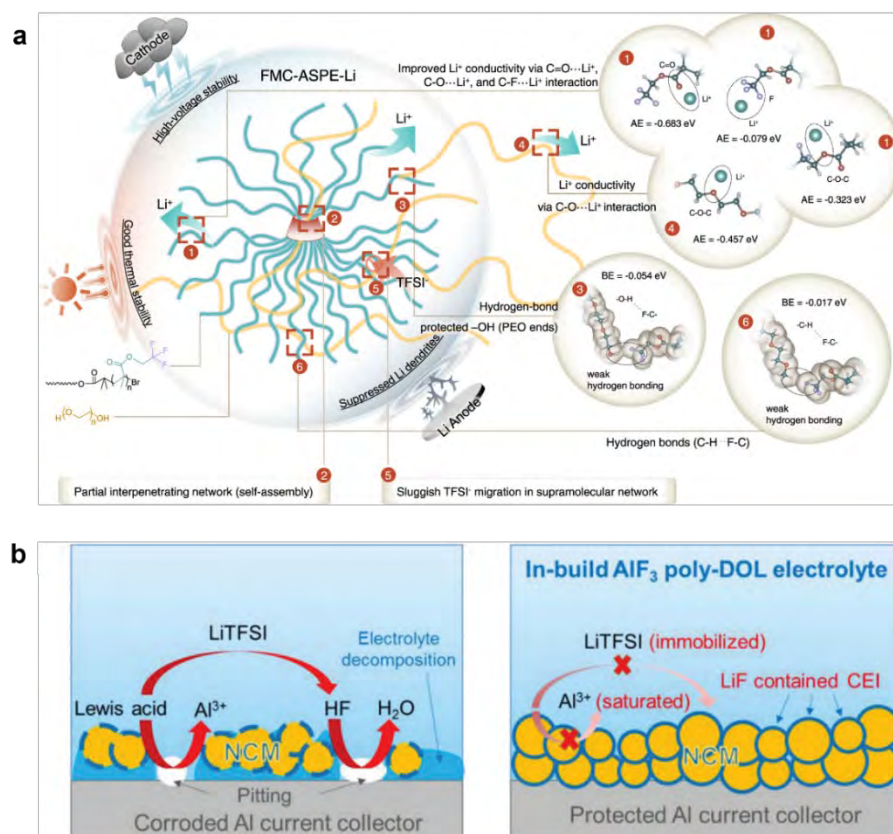


Figure 2.4 (a) Schematic interactions in FMC-ASPE-Li membrane; (b) Illustration of Al corrosion in electrolytes.

In addition, introducing inorganic electrolytes can enhance the electrochemical stability of PEO-based CPEs. The reported inorganic electrolytes, such as LLZTO, LAGP, and $\text{Li}_6\text{PS}_5\text{Cl}$, exhibit wider ESW over 4.5 V vs. Li/Li^+ . The primary mechanism in electrochemical stabilization is attributed to the Lewis acid-base interaction or dipolar interactions between PEO ether lone pairs and the surface groups of inorganic electrolytes. According to the degradation process of EO groups, the main task is to hinder the attack of TFSI⁻ anions. Binding salt anions on the surface of inorganic fillers would decrease the interaction of anions and PEO host, stabilizing PEO against oxidation^{69, 70}.

2.2.3 Asymmetric structure of polymer electrolytes

Fabricating double/multi-layer can also enhance the electrochemical stability of SPEs. Many research works have verified that PEO is relatively stable with lithium metal anode. Thus, searching for polymer electrolytes with high compatibility with high-voltage cathodes to design a double layer can increase the energy density of batteries. Goodenough *et al.*⁷¹ fabricated a double-layer polymer electrolyte of Poly(N-methyl-malonic amide) (PMA)-LiTFSI/PEO-LiTFSI. In principle, PMA-LiTFSI with a high dielectric constant shows high oxidation tolerance contacting the high-voltage cathode. PEO-LiTFSI contacts the lithium metal anode to improve the interfacial contact and suppress the dendrite growth (**Figure 2.5 a**). Li/PEO-LiTFSI/PMA-LiTFSI/LiCoO₂ cells maintain a capacity retention of 91.2% after 100 cycles with 0.2 C. Similar double-layer SSEs have been reported, such as PEO-SN/PAN-LATP⁷². Triple-layer SSEs are also fabricated to pair with high-voltage cathodes to take advantage of inorganic electrolytes. PEO-LATP-PAN sandwiched structure was fabricated for NCM622 cathode (**Figure 2.5 b**)⁷³. The designed SSE utilized the merits of each layer for wettability towards cathode and lithium dendrite suppression. Assembled cells demonstrated excellent cycling stability and high Coulombic efficiency.

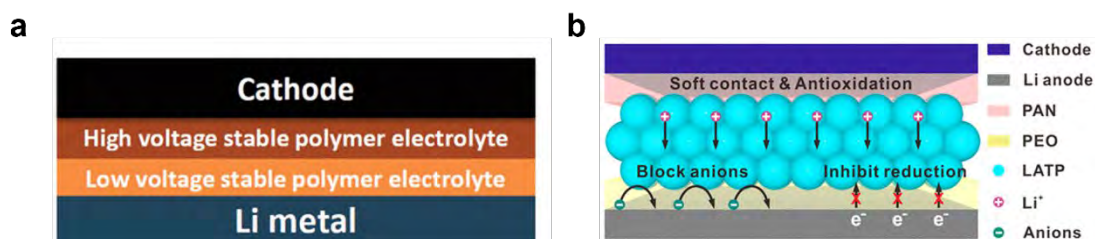


Figure 2.5 (a) Illustration of double-layer polymer solid-state electrolyte; (b) Schematic illustration of triple-layer solid-state electrolytes.

2.2.4 Modification of high-voltage cathodes

Besides modification on SPEs, coating strategy on high-voltage cathodes can also enhance the electrochemical compatibility with SPEs. Coating stable SSEs (organic or inorganic electrolytes) with high-voltage capability on the high-voltage cathode particles can solve the electrochemical compatibility with SPEs. Guo and co-workers reported a poly(acrylonitrile-co-butadiene) polymer (PBA) coating NCM622 cathode materials (**Figure 2.6 a**)⁷⁴. The PBA polymer plays dual functions in the cathode: a) the soft polymer can improve the physical contact between cathode materials and SPE; b) the coating layer can relieve the side reactions and ion diffusion across the cathode/electrolyte interface. Cells with PBA-coated NCM622 maintain capacity retention of 75% after 400 cycles, which is much higher than the control sample. The gas release behavior in Li/PEO-LiTFSI/LCO cell is observed at 4.2 V from differential electrochemical mass spectrometry (DEMS) results. By comparison, the oxidative ability was enhanced in Li/PEO-LiTFSI/LATP@LCO cells (**Figure 2.6 b**). The LATP layer delays the onset voltage of gas release to 4.5 V⁶¹. Therefore, the solution to postpone the decomposition of the PEO matrix is to modify the cathode materials or PEO molecule, leading to excellent compatibility of cathode materials and PEO-based SPEs.

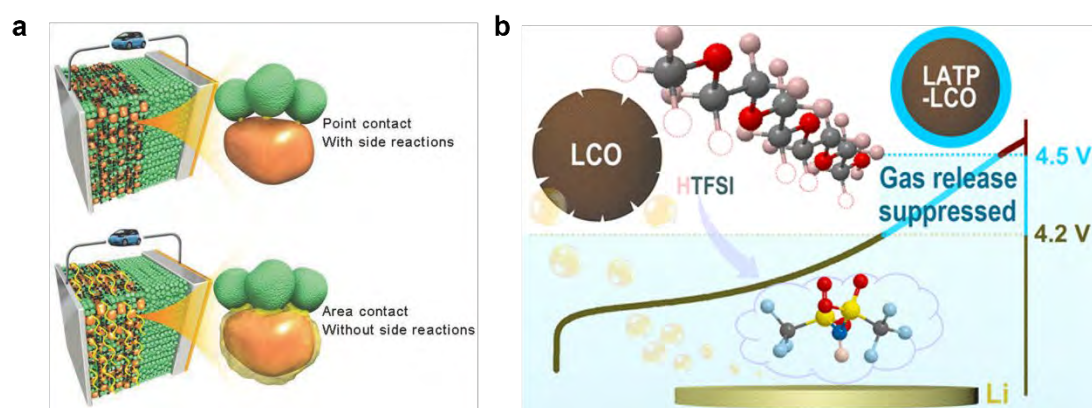


Figure 2.6 (a) Illustration of PBA-coated cathode materials; (b) Schematic effect of LATP coating layer.

2.3 Overview of Bipolar Batteries

The bipolar battery configuration was first emerging in lead-acid batteries in the 1920s. With technology development, the relevant cell configurations have been applied in lithium-ion batteries. The introduction of solid-state electrolytes makes bipolar configuration more convenient and brings many advantages to the battery system.

2.3.1 General structure of bipolar batteries

The battery system in commercial electric vehicles consists of several modules connected in-series or in-parallel to meet the energy or power density requirements for industrial applications. For example, the output voltage of commercial BYD is ~ 400 V, comprising ~ 110 LIB cells. Depending on how to connect the individual cells in the module system, the battery configuration can be divided into two types: monopolar configuration and bipolar configuration (**Figure 2.7**). As shown in **Figure 2.7 a**, the monopolar configuration represents the battery with liquid electrolytes, and external connectors connect the individual cells. For monopolar configuration, it consists of individual cells and external connectors. Obtaining higher output voltage, the individual cells are assembled and sealed, thereby presenting internal ion short-circuit due to liquid electrolyte leakage. During discharge, the electron flow is transferred through external connectors, leading to an extended pathway and resistance increase.

On the other hand, the bipolar configuration (**Figure 2.7 b**) represents the individual cells are connected directly inside only one package. This simple configuration benefits from the solid-state electrolyte, with no flowing inside the battery package. The electron flow is transferred through the connected area between two individual cells. Removing the external connectors and package reduces the overall resistance of the battery system, weight, volume, and cost. Therefore, the key advantages of bipolar configuration are simple architecture and easy voltage build-up, higher power and energy density, and low cost. The main technical challenges are internal short-circuit due to misalignment, low lithium-ion (Li^+) conductivity and poor interfacial contact, corrosion susceptibility of the bipolar substrate, and complicated fabrication process.

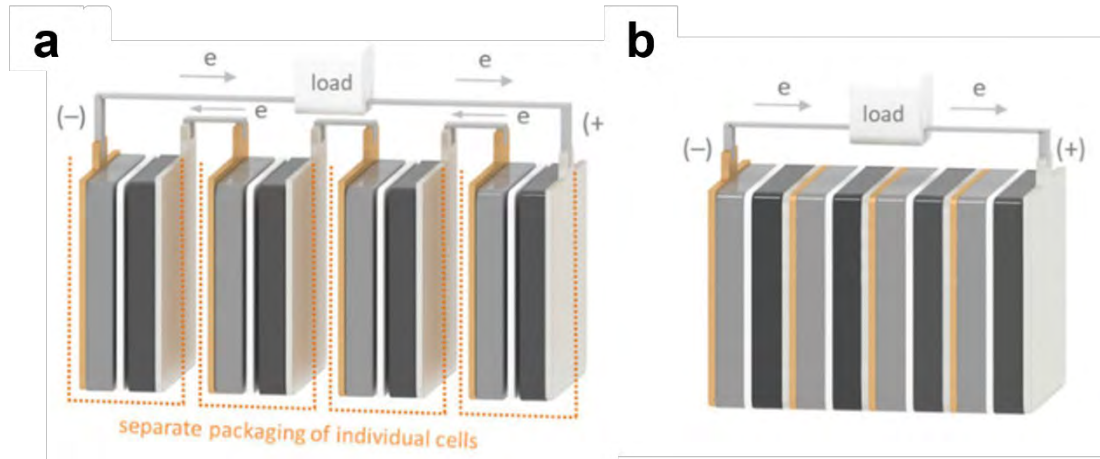


Figure 2.7 Schematic diagrams of (a) Monopolar design of current LIBs with liquid electrolytes and (b) Bipolar design of solid-state batteries⁷⁵.

2.3.2 Advantages of bipolar batteries

All the individual cells are integrated into one complex package with external connectors for industrial power systems ⁷⁶. Adapting the inner bipolar battery configuration, the energy density will increase by $\approx 40\%$ in volume and $\approx 20\%$ in weight. In this way, the process of assembling bipolar batteries will be simplified, and the thickness of the battery system will be equal to all the components without extra substrates and packages. The weight of the battery system also decreases. As we all know, the energy density of a battery is related to the capacity and voltage of batteries.

For bipolar batteries, the capacity is similar to that of individual cells, and the number of individual cells determines the output voltage ⁷⁷. Therefore, the gravimetric and volumetric energy density significantly increase due to less materials and thickness.

Moreover, the electrochemical performance will be enhanced as well. For the battery system, the whole resistance of the battery system is R:

$$R = R_{\text{electrolyte}} + R_{\text{am}} + R_{\text{separator}} + R_{\text{i, am/cc}} + R_{\text{cc}} + R_{\text{external connectors}}$$

Where $R_{\text{electrolyte}}$, R_{am} , $R_{\text{separator}}$, $R_{\text{i, am/cc}}$, R_{cc} , $R_{\text{external connectors}}$ represent the resistance of the electrolyte, active materials, separator, interface between active materials, current collectors, and external connectors, respectively. In the inner in-series bipolar configuration, the resistance of external connectors will be ignored since the cathode of one cell and the anode of another cell will share the same current collector. In this way, the current will pass through the current collectors instead of external connectors. Resistance decrease will lead to better battery performance.

2.3.3 Research progress of bipolar batteries

In bipolar battery configuration, the cathode current collector of one cell will contact the anode of another cell. Therefore, the choice of bipolar substrate for adjacent cells is crucial. The role of the bipolar substrate is to transfer the electron flow during the discharge process and collect current for the cells. For commercial lithium batteries, the typical current collector is Al, which is inexpensive, conductive, and stable to the cathodic active materials and electrolyte systems ^{78, 79}.

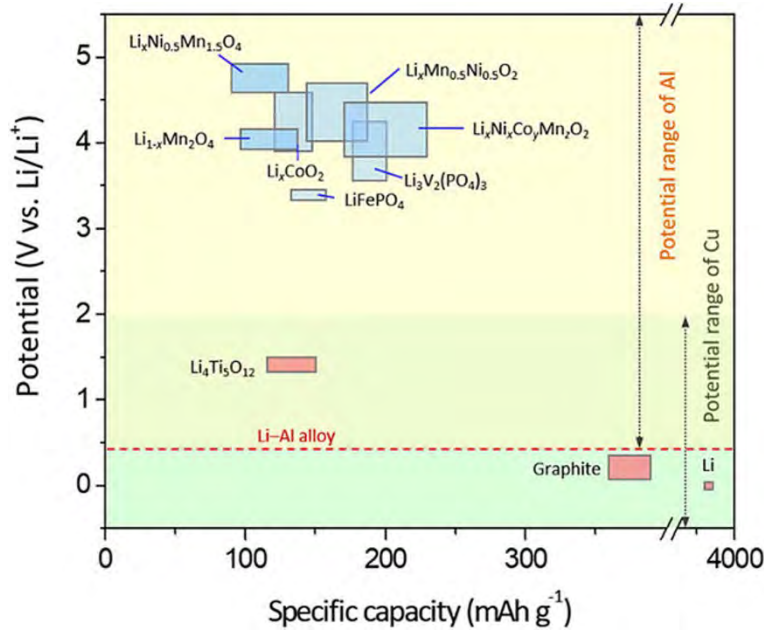


Figure 2.8 Potential ranges of Al and Cu Current collectors ⁷⁵.

As shown in **Figure 2.8**, for active materials, Al and Cu are suitable to act as current collectors for cathode and anode materials, respectively. However, LTO anode material can be cast onto Al CC to cycle batteries ⁸⁰. Therefore, Al CC can be chosen as the bipolar substrate to assemble bipolar batteries. However, lithium metal is considered a future anode material for high energy density. However, many issues should be addressed, such as current lithium dendrite growth and stability between the solid-state electrolyte and lithium metal. Considering the choice of anode materials and the instability of lithium metal, initial progress on bipolar configuration adopted the LTO as the anode and Al CC as the current collector, meaning the cathode and anode share the same current collector.

1. Al CC acting as the bipolar substrate

Commercial lithium-ion batteries with liquid electrolytes inherently process a higher output voltage for application ⁸¹. When the monopolar configuration changes to a bipolar configuration with a solid-state electrolyte, the bipolar configuration of LIBs becomes more competitive for application in electric and hybrid vehicles ¹⁹.

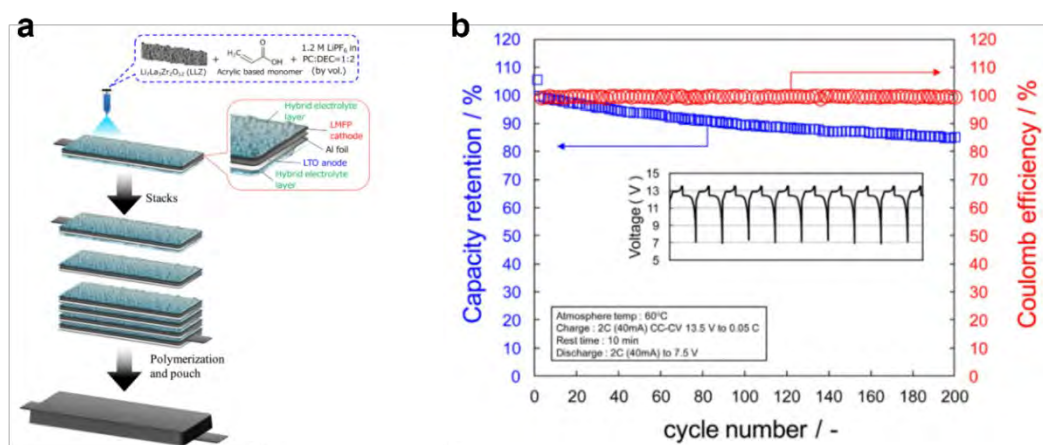


Figure 2.9 (a) Schematic process for the preparation of bipolar battery; (b) Cycle performance of the 12 V-class bipolar battery at 60°C.

Yoshima *et al.* adopted an *in-situ* method to fabricate bipolar batteries with gel electrolyte⁸² (**Figure 2.9**). In this work, individual cells were prepared and stacked into one package. Then, heating polymerization occurred for gel electrolyte formation. Only one kind of current collector is used in the bipolar battery since LTO is compatible with Al CC. The 12 V-class bipolar battery cycled at 60°C, delivering capacity retention of 85% after 200 cycles.

Besides typical casting methods, slurry printing processes are simple, low-cost, and easily scalable. The solid-state battery can be fabricated by printing electrode materials and electrolytes layer by layer. Sang-Young Lee *et al.* assembled bipolar solid-state batteries through a multi-stage printing process (**Figure 2.10 a**)^{21, 22}. The bipolar battery assembling process is to print another individual cell the same as the former one. The charge and discharge profiles of mono cells, two-cells, and three-cells are compared in **Figure 2.10 b**. As the cell number increased, the charge and discharge voltage nearly doubled and tripled. Due to the higher resistance of increased cells, the specific capacity decreases as cell number increases. The battery performance of two bipolar methods, in-series, and in-plane are investigated at the voltage range of 3.0-5.4. The charge and discharge process are very stable, with coulombic efficiency of 98% (**Figure 2.10 c**). The above results indicate that the printing process is versatile and

practical for multistage operations.

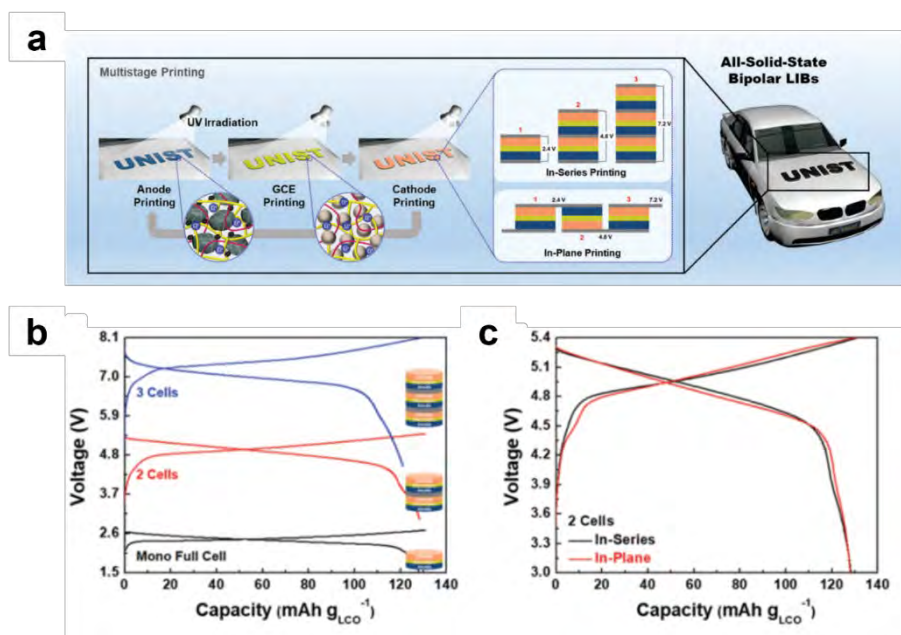


Figure 2.10 (a) Schematic illustration of bipolar batteries via multistage printing process; (b) The charge/ discharge profiles of the printed bipolar cells ;(c) Charge/ discharge profiles of the printed bipolar cells (in-series and in-plane).

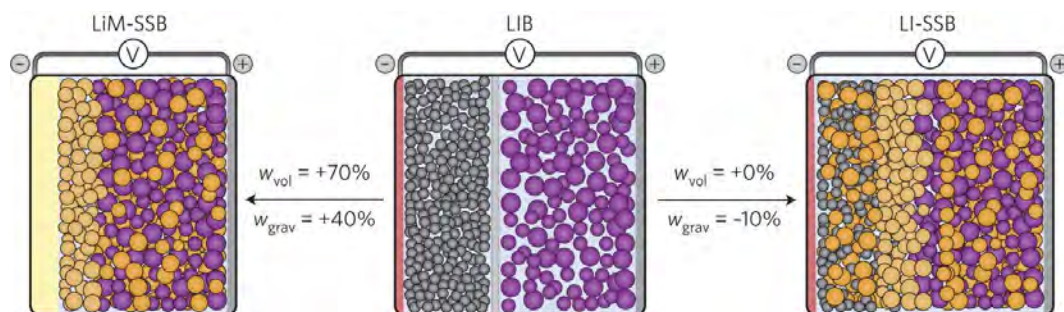


Figure 2.11 Battery configurations for lithium-ion and solid-state batteries ²³.

Although the bipolar configuration was realized with an LTO anode, the impact on the solid-state battery is insignificant. The main merit of a solid-state battery system is introducing lithium metal as the anode ⁸³. To calculate the energy density of the illustrated solid-state batteries in **Figure 2.11**, all the components, including electrolytes, active materials, and metallic foils, should be considered. Using liquid electrolytes in solid-state batteries keeps the volumetric energy density unchanged, and the gravimetric energy density decreases by 10%. Therefore, lithium metal as the anode is

crucial for solid-state batteries. In this case, the volumetric and gravimetric energy density is enhanced by 40% and 70%, respectively.

2. Introducing another buffer layer as the bipolar substrate

Introducing lithium metal anode into bipolar batteries could increase the energy density of SSBs. Getting the information from **Figure 2.8**, Cu can be chosen to act as a host for lithium metal. Jong-Won Lee *et al.* reported several articles on bipolar batteries with Cu hosting lithium metal^{25, 84}. The main structure (Cu-Li-SSE-NCM-Al||Cu-Li-SSE-NCM-Al) for bipolar configuration is shown in **Figure 2.12 a**. The bipolar battery cycled in the 9.2-12.0 V voltage range, successfully operating without ion or electron short-circuit. The capacity retention of the bipolar battery is 83% after 50 cycles (**Figure 2.12 b**).

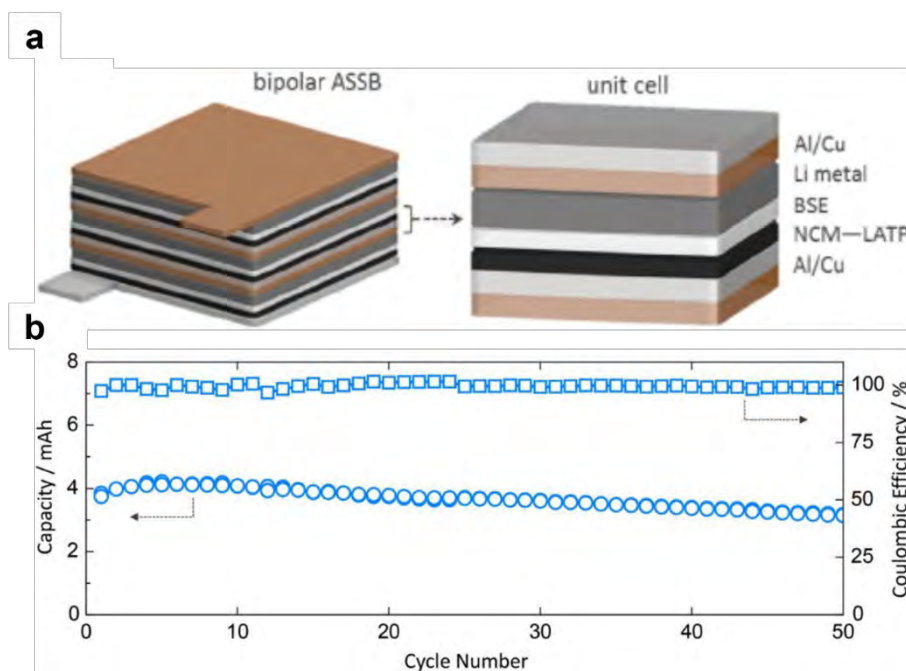


Figure 2. 12 (a) Illustration of the bipolar ASSB; (b) Cycling performance of bipolar ASSB⁸⁴.

In addition to Cu hosting lithium metal, stainless steel is compatible with lithium metal. From the CV curves of stainless steel, no significant change appeared to the potential of 5 V. Besides, no alloy reaction benefits negative materials, including lithium metal

⁸⁵. Therefore, stainless steel can also be introduced to host lithium metal for bipolar configuration.

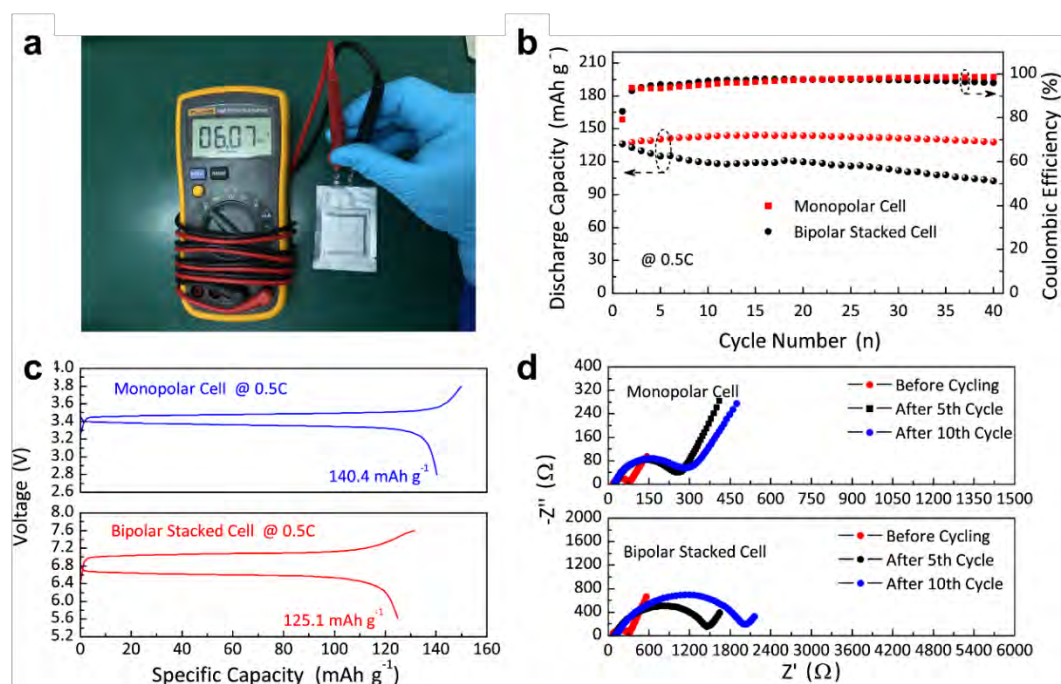


Figure 2.13 (a) Open-circuit voltage of the bipolar ASSLMb; (b) Cycling performance of monopolar and bipolar ASSLBs; (c) Charge/discharge profiles of monopolar and bipolar ASSLBs; (d) AC impedance of monopolar and bipolar ASSLBs ²⁴.

Xu *et al.* reported bipolar batteries with stainless steel as the buffer layer ^{24, 86}. In their research, an integrated electrode-electrolyte structure was fabricated, simplifying the assembling process for bipolar cells. Firstly, they assembled two individual cells and introduced another stainless steel as a buffer layer to separate them. After assembling, the open-circuit voltage of the bipolar cell is 6.07 V (**Figure 2.13 a**). The battery performance of monopolar and bipolar cells was evaluated under 0.5 C at 60°C. The retention of bipolar cells is only 76% after 40 cycles (**Figure 2.13 b**). The capacity fading may be attributed to resistance increases. Due to the higher polarization voltage, the discharge capacity is lower than the monopolar cell (**Figure 2.13 c**). The initial interfacial resistance of the bipolar battery was 236.78 Ω, larger than the monopolar cell of 55.027 Ω, as shown in **Figure 2.13 d**. Furthermore, the interfacial resistance of the bipolar cell increased significantly. By comparison, the interfacial resistances of

monopolar cells remain stable. The poor “solid-solid” interfacial contact is also responsible for the inferior cell performance.

In summary, from the above literature, introducing another metal foil as a buffer layer to separate the two individual cells is not a good choice. Because introducing another layer would lead to a resistance increase and the contact between solid metallic layers is poor, the state of the bipolar battery is not stable, and resistance keeps increasing, leading to low-capacity retention.

3. Stainless steel acting as the bipolar substrate

The sulfur cathode is equipped with a higher theoretical capacity of 1672 mAh g^{-1} , which is considered an ideal cathode material. Besides, the sulfur cathode is compatible with stainless steel. Sang-Young Lee *et al.*⁸⁷ reported the first sulfur-based bipolar solid-state battery with a printing process. As shown in **Figure 2.14 a**, two kinds of bipolar batteries with in-series and in-plane configurations were fabricated. The sulfur cathode and lithium metal share the same current collector of stainless steel. The unit cell, 2-stacked- and 3-stacked cells cycle stably (**Figure 2.14 a**). Due to the numbered cells, stacked batteries show higher polarization voltage and lower capacity. In-series and in-plane configurations deliver the same battery performance (**Figure 2.14 c, d**). The capacity retention of bipolar batteries is about 85% after 50 cycles.

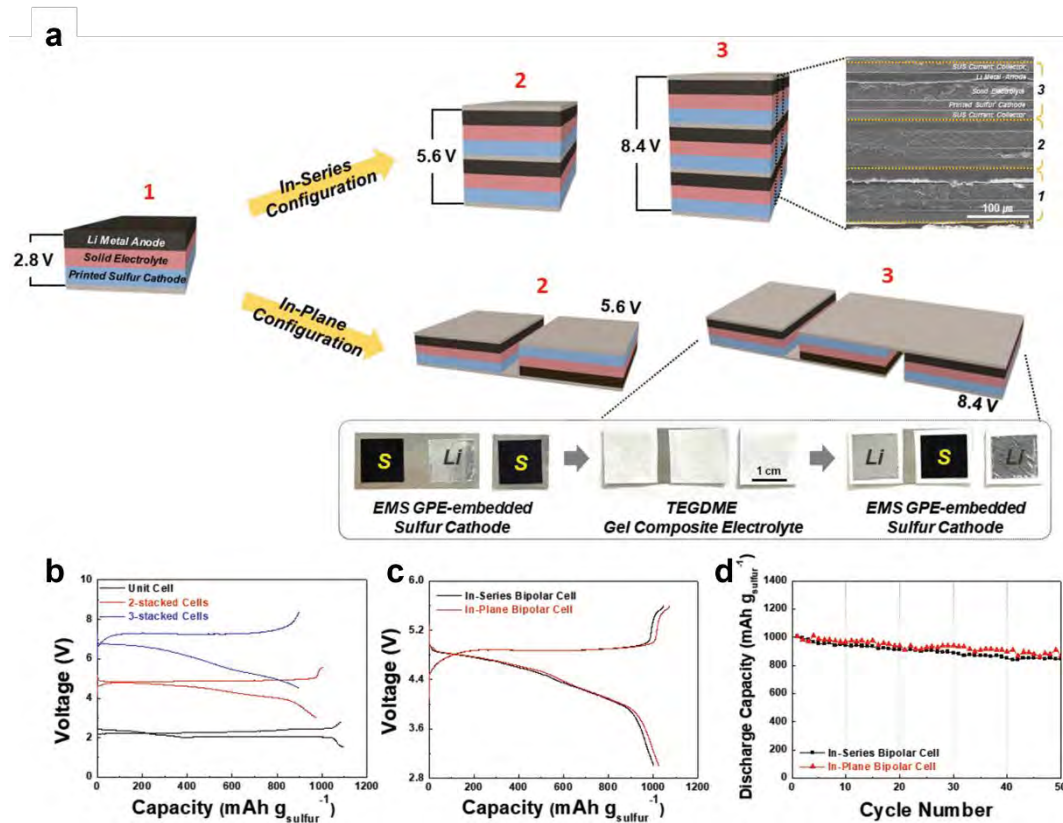


Figure 2.14 Fabrication and characterization of the printed bipolar ASSLSBs. (a) Schematic fabrication procedure of the printed bipolar ASSLSBs; (b) Charge/discharge profiles of the printed bipolar ASSLSBs; (c) Charge/discharge profiles and (d) Cycling performance of the printed bipolar ASSLSBs (in-series and in-plane).

The main problems for the reported literature are limited cycles and low-capacity retention. This poor battery performance may be attributed to the instability between the bipolar substrate and lithium metal anode^{88, 89}. Nickel is stable up to 4.5 V (vs. Li/Li⁺), after which the dissolution of Ni begins⁹⁰. Moreover, nickel-based current collectors are often reported for flexible LIBs^{91, 92}.

2.3 Research Progress of Flexible Batteries

2.3.1 Flexible lithium-ion batteries

Flexible devices such as roll-up displays, smartphones, and intelligent textiles have emerged daily. The demands for flexible power systems are also promising, integrating

flexible devices with flexible batteries together. Two strategies to realize high flexibility are soft structure strategy and soft materials strategy⁹³. The works that adopted these two strategies are shown in **Figure 2.15**. These representative proof-of-concept examples of FLBs are achieved by two primary techniques: 1) The engineering of the soft structure and 2) the use of soft material electrodes. They also reflect the enormous enthusiasm of both industrial and academic communities for developing FLBs for industrial applications⁹⁴.

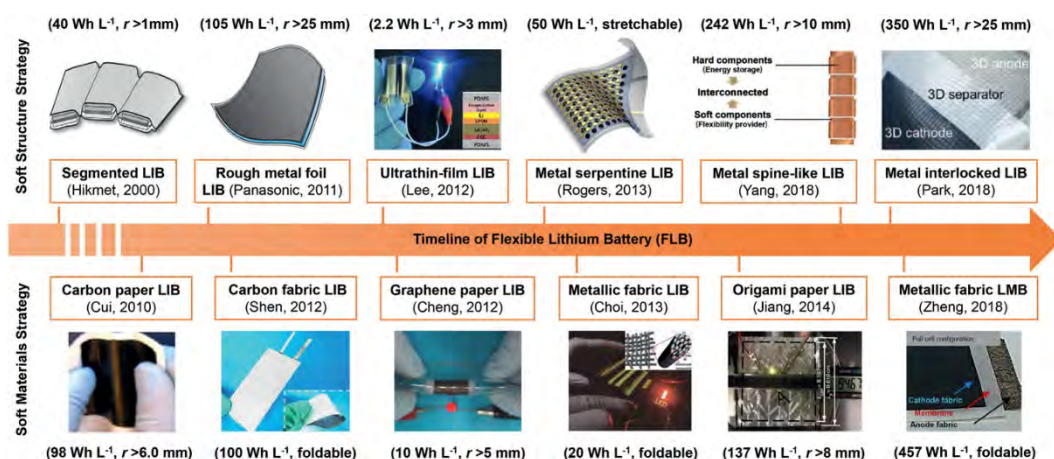


Figure 2.15 Timeline of developments in flexible lithium batteries.

A soft structure strategy means reconstructing the battery structure to achieve high flexibility. In 2013, Roger's group reported the stretchable lithium-ion batteries with "self-similar" interconnectors⁹⁵. Reducing the thickness of batteries can also improve the flexibility of cells due to the strain of bending being directly related to the thickness. The ultrathin of about 10 μm of flexible battery was reported with high flexibility (**Figure 2.16 a**)⁹⁶. The rate performance of the battery was evaluated with different bending radius. The capacity retention for non-bending batteries is about 97.3 % after 100 cycles. For bending tests, the capacity retention is 93% and 88.2% for the bending radius of 16.0 mm and 3.1 mm, respectively (**Figure 2.16 b**). The bending tolerance of the flexible lithium-ion batteries is over 2×10^4 cycles with the radius of 3.1 mm. The initial open circuit voltage is 4.071 V. After bending 2×10^4 cycles, the voltage decreases to 4.060 V, only 0.27%. The above results demonstrate the excellent flexibility of ultrathin battery (**Figure 2.16 c**).

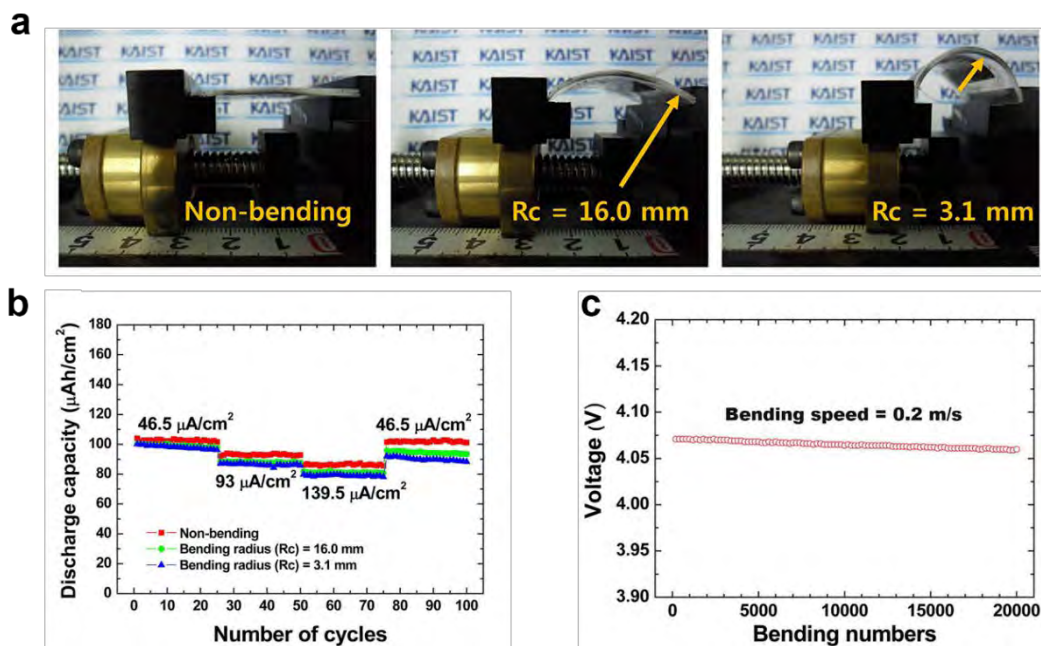


Figure 2.16 (a) Digital photographs in different states; (b) Rate performance at various rates: 46.5, 93, and 139.5 μAcm^{-2} ; (c) Voltage stability during the dynamic test.

Another strategy is to prepare soft materials to realize the flexible configuration. Based on the components of LIBs, the current collector's flexibility influences the whole battery's flexibility due to the rigid feature of metallic foils. For the preparation of flexible electrodes, CNTs and graphene meet all the requirements for flexible electrodes: mechanical properties, high electronic and ionic conductivity, stability in the electrolytes, and strong bonding to the active materials⁹³.

Graphene-based flexible electrodes were prepared for cathode and anode using pulsed laser deposition⁹⁷. The battery structure with V_2O_5 /graphene paper cathode and graphene paper anode is shown in **Figure 2.17 a**. The battery was measured with a current density of $10 \mu\text{A cm}^{-2}$ from 3.8 V to 1.7 V. The initial capacity is $\sim 15 \mu\text{Ah cm}^{-2}$, with a negligible first irreversible capacity (**Figure 2.17 b**). For further cycles, the capacity of the graphene-based battery shows highly reservable, though the capacity decreases slightly.

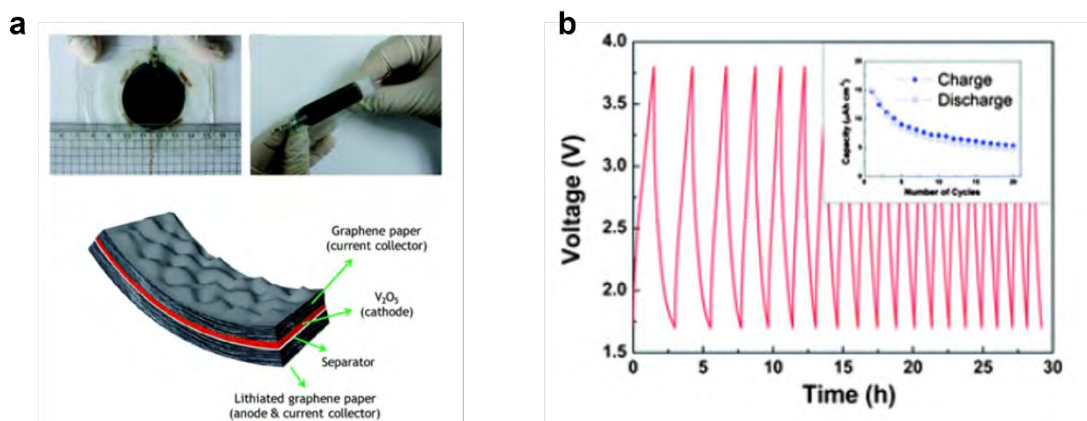


Figure 2.17 (a) Scheme of flexible Li battery; (b) Charge-discharge curves of the battery (inset: capacity vs. number of cycles) ⁹⁷.

Moreover, soft textiles can be modified for flexible current collectors as well. Nickel-coated textile-based current collector applying in LIBs exhibits great flexibility⁹⁸. The pouch cell with nickel-coated carbon fabric (NiCF) cycles well after bending 100 cycles with a radius of 7.5 mm and 5.0 mm (**Figure 2.18 a**). The Li-S pouch cell with a size of 4 cm² cycles stably after 40 repeating folds with a radius of <1 mm. In contrast, the conventional Li-S pouch cell can cycle normally in a pristine state. After bending 100 cycles with a radius of 5 mm, the pouch cell is out of work, and the capacity decreases rapidly. The comparison of NiCF-based Li-S pouch cells with conventional Li-S pouch cells demonstrates the great flexibility of textile-based current collectors (**Figure 2.18 b, c**)

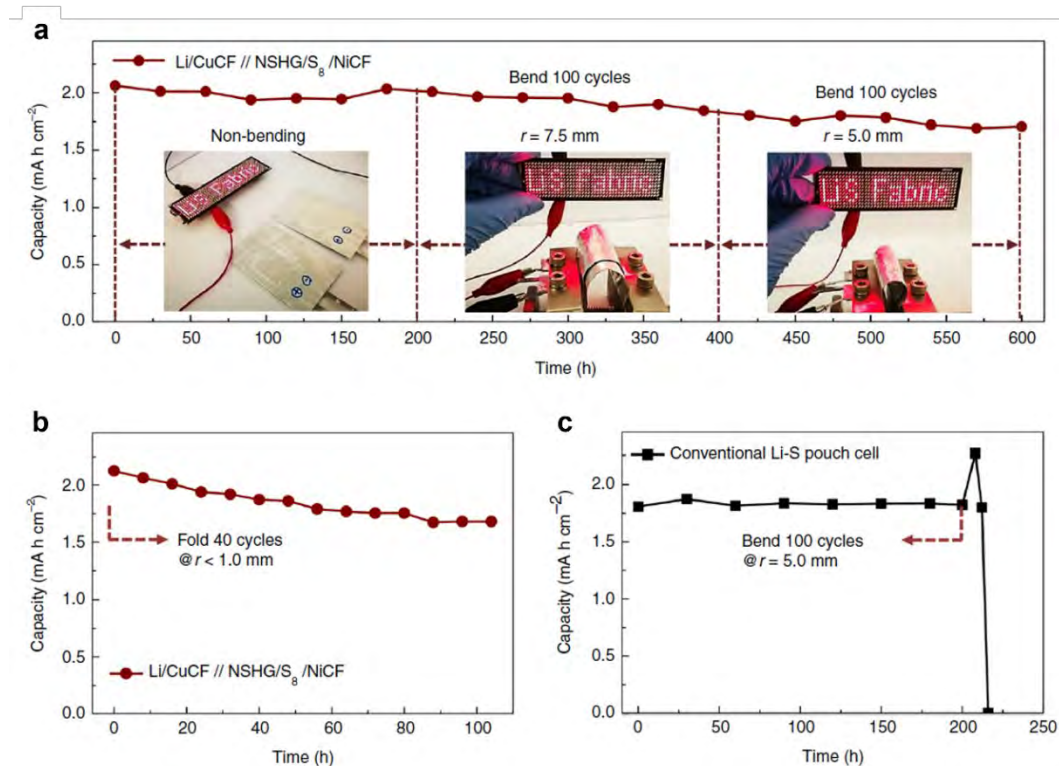


Figure 2.18 (a) Cycle performance of Li-S full cells during 200 bending cycles with the different bending radii; (b) Cycle performance of textile-based Li-S full cells; (c) Cycle performance of the conventional Li foil-based Li-S pouch cell.

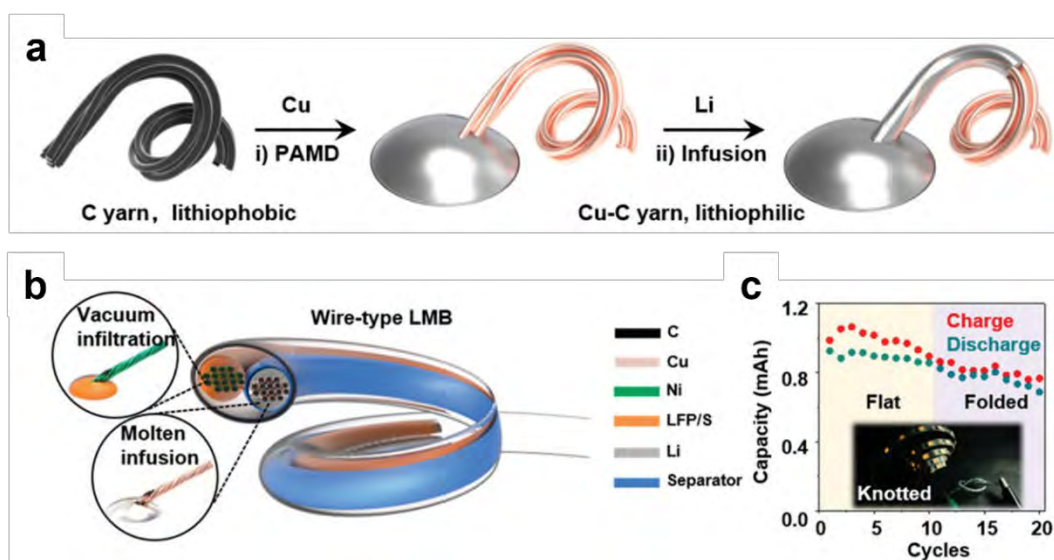


Figure 2.19 (a) Illustration of the lithium–metal composite yarn; (b) Scheme of the wire-type lithium metal battery; (c) Cycle performance of the wire-type LMB.

Apart from the typical flexible LIBs, textile-based fiber battery exhibits higher flexibility. The textile yarns can be modified to a fiber-based current collector using the

PAMD method (**Figure 2.19 a**)⁹⁹. The process includes fabricating conductive carbon (C) yarn *via* the PAMD method and infusing molten lithium into the Cu-coated C (Cu-C) yarn. The fiber-based cathode was prepared with vacuum infiltration. The assembled wire-type lithium metal battery is illustrated in **Figure 2.19 b**. The wire-type lithium metal battery cycles well after folding, powering 36 LED arrays (**Figure 2.19 c**). In principle, the composite electrodes' design rationale can be applied to various anodic and cathodic materials to realize durable, flexible, and wearing-comfortable e-textiles.

2.3.2 Flexible solid-state batteries

Solid-state batteries, as next-generation battery technology, need to develop compressively. Current research on batteries mainly focuses on materials preparation, battery performance enhancement, and no further flexibility for flexible devices^{12, 100, 101}. In reported literature^{26, 27, 102}, the demonstration was made to show the flexibility of solid-state batteries (**Figure 2.20 a**). Moreover, the electrochemical performance may be characterized to monitor the resistance changes. Lu *et al.* test the resistance of pouch cells at different folding angles from 0°-180°, indicating superior flexibility and stable ion conduction under the deformation process²⁸ (**Figure 2.20 c**).

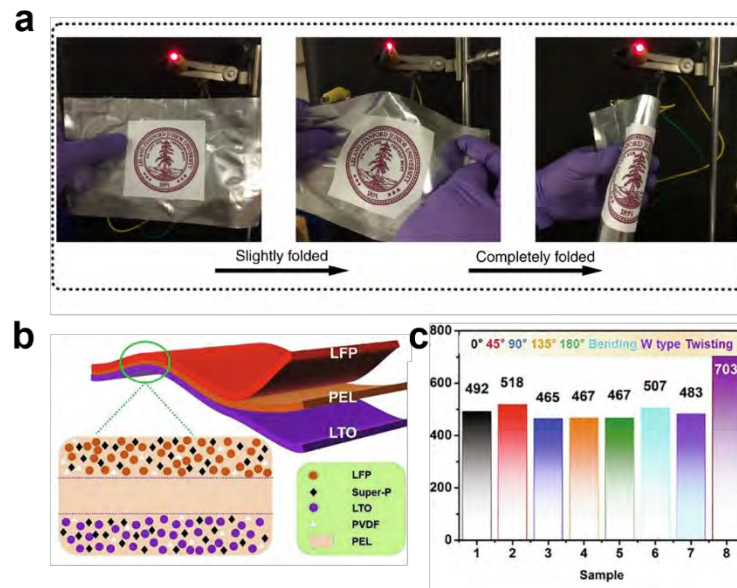


Figure 2.20 (a) Flexible display of Li/PI/PEO/LiTFSI/LFP pouch cell; (b) Scheme of LFP/PEL/LTO pouch cell; (c) Resistance of cells at various folding angles.

The battery performance must be evaluated for the characterization of flexible solid-state batteries. Rüdiger-A. Eichel *et al.*¹⁰³ fabricated flexible solid-state batteries with $\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, and PVDF-based polymer electrolyte. The charge and discharge profiles are shown in **Figure 2.21 a** to evaluate the assembled pouch cell's flexibility. Charge and discharge curves of bendable cells match well with initial data with a flat state. Yao Xiayin *et al.* also evaluated the solid-state battery performance with different bendable states³⁰. When the LFP//Li flexible battery experiences curling and several foldings, the pouch cell's cycle performance and potential remain unchanged, exhibiting nearly overlapped curves without capacity loss under different states (**Figure 2.21 b**).

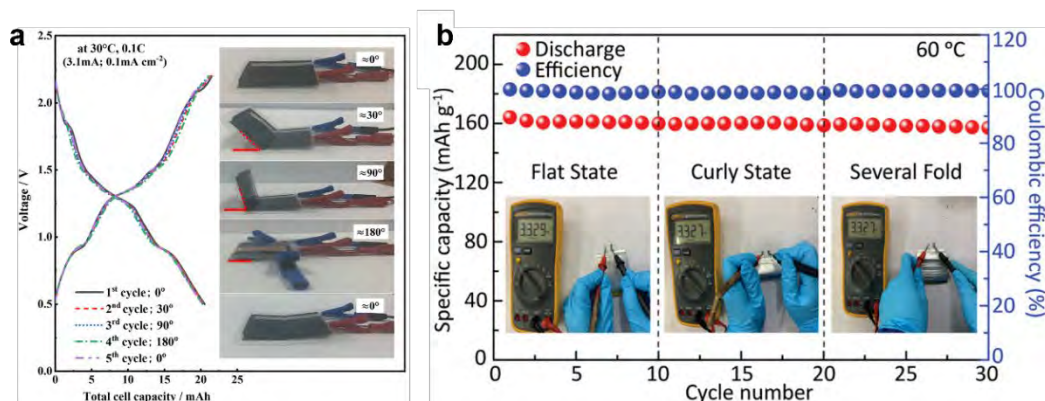


Figure 2.21 (a) Charge/discharge profiles of the pouch cell at different angles; (b) Cycle performance of LFP//Li pouch cell under normal and curled states.

For solid-state batteries, the bipolar configuration should be improved to enhance the battery performance since the current bipolar substrate is not compatible enough to get good battery performance. In addition, the investigation on the flexibility of solid-state batteries needs to fill up about the electrochemical changes after the bending process.

CHAPTER 3. METHODOLOGY

This chapter will introduce general experiments for materials preparation, textile-based current collector modification, coin cell assembly, pouch cell assembly, and characterization. In-situ methods are adapted to improve the interfacial contact between polymer electrolytes and electrodes through UV irradiation and thermal polymerization for synthesizing polymer electrolytes. The flexible textile-based current collectors could be fabricated through polymer-assisted metal deposition (PAMD) developed by our group. Besides, coin or pouch cells will evaluate the electrochemical performance of polymer electrolytes and batteries. The assembly methods for coin cells and pouch cells will be illustrated in this chapter.

3.1 Materials

Lithium bis (trifluoromethane) sulfonilimide (LiTFSI, 99.95% purity, Sigma-Aldrich), Deionized water (from own Lab), Lithium perchlorate (LiClO_4 , 99.99% trace metals basis, Sigma-Aldrich), Poly(ethylene oxide) (PEO, $M_v=60$ W, Sigma-Aldrich), Conductive agent (Super-P), polyvinylidene fluoride (PVDF, MTI), 1-methyl-2-pyrrolidinone (NMP, 99.5%, Aladdin), acetonitrile (ACN, 99.9%, J&K) are used without further treatment if no specification. The cathodes, including $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ (LMFP), LiFePO_4 (LFP), and single-crystal $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622), are supplied by Shenzhen Capchem Chemicals Co., Ltd. Carbon-coated aluminum foil (Al) was bought from Shenzhen Keijing Star Technology Company.

3.2 Experimental Sections

3.2.1 Cathodes preparation

In this thesis, all the cathodes are fabricated by the doctor-blading method.

Preparation of LMFP cathode: 70% LMFP particles and 10% Super-P are milled homogenously. Then, the above mixture, 10% SN-LiTFSI (-CN: $\text{Li}^+=20:1$) and 10%

PVDF binder, are dispersed and dissolved into NMP solvent, respectively. After stirring for 24 h, the slurry is coated on the carbon-coated Al foil. Subsequently, the electrode is moved to a vacuum oven for solvent evaporation for 12 h at 80°C.

Preparation of LFP cathode: Firstly, 20% PEO-LiClO₄ (EO: Li=18:1) is dissolved into ACN, followed by 70% LFP and 10% Super-P added. After stirring for 24 h, the slurry is coated onto the carbon-coated Al foil or textile-based current collector. Finally, the electrode is dried in the vacuum oven for 12 h at 60°C.

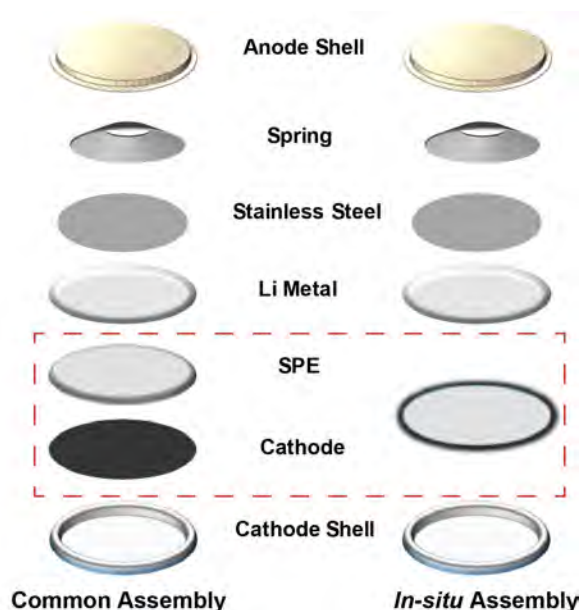
Preparation of NCM622 cathode: To construct an ion transport channel, 0.5 M LiTFSI in ionic liquid (IL) is prepared for cathodic slurry. 10% PVDF and 10% 0.5M LiTFSI-IL are dissolved into NMP solvent. After dissolving into the homogenous solution, 70% NCM622 and 10% Super-P are added to the above solution. After stirring for 24 h, the slurry is coated onto the carbon-coated Al in the glove box (H₂O, O₂ < 0.5 ppm). After solvent evaporation for 12 h at 80°C, the cathode is cut into dishes with a diameter of 12 mm.

3.2.2 Cell assembly

In this thesis, different types of cells are assembled to evaluate the battery performance according to specific conditions. The electrochemical performance of polymer electrolytes, including ionic conductivity, linear sweep voltammograms (LSV), lithium transference number (t_{Li}^+), cyclic voltammetry (CV), cycle, and rate performance for battery performance are evaluated using coin cells. The flexibility of a textile-based battery is conducted with pouch cells. All the cells are assembled in the glove box with Ar atmosphere (H₂O, O₂ < 0.5 ppm)

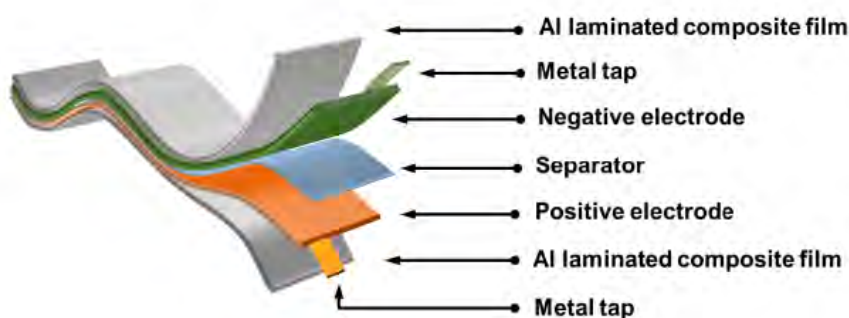
Coin cell assembly: The cathode dishes are placed on the cathode shell for the traditional assembling process (**Figure 3.1, left**). Then, the polymer electrolytes are covered on the cathode dishes, followed by putting lithium metal on polymer

electrolytes. After that, the stainless steel (SS), spring, and anode shell are placed individually. Finally, the coin cell is sealed through the standard crimper of the MSK-110 machine. The polymer electrolyte can be polymerized on the cathode layer or lithium foil for a modified in-situ process. In this way, the interfacial contact between electrodes and polymer electrolytes will be tight, beneficial to ion transport across the interface. Taking the integrated structure of the SPE-cathode as an example, the assembled process is illustrated in Figure 3.1 (right). Other steps are similar to the typical assembly process.



Scheme 3.1 Schematic illustration of the typical and *in-situ* assembly process.

Pouch cell assembly: The cathode and polymer electrolyte are tailored into a desirable size of 2 cm × 4 cm. Nickel tap and Al tap are attached to the lithium metal anode and cathode layer, respectively. The cathode, polymer electrolyte, and lithium metal are assembled and sealed with aluminum-plastic film. The structure of the pouch cell is illustrated in **Figure 3.2**.



Scheme 3.2 Schematic illustration of pouch cell.

3.3 Characterizations

3.3.1 Structural characterizations

Fourier transform infrared spectra (FT-IR): FT-IR (Nicolet iS50) is performed to characterize the structure of raw materials and polymer electrolytes over the range of 4000-500 cm^{-1} .

Thermogravimetric analysis (TGA): TGA (Mettler-Toledo) is conducted to detect the decomposition temperature with the heating rate of $10^{\circ}\text{C min}^{-1}$ from 25°C - 600°C under a nitrogen atmosphere.

Differential scanning calorimetry (DSC): DSC is used to confirm the glass transition temperature (T_g) of polymer electrolytes. It is characterized on DSC (Mettler-Toledo) with sealed Al pan hosting 5-10 mg samples. All the samples were cooled to -60°C first and then heated to 100°C with the cooling and heating rate of $5^{\circ}\text{C min}^{-1}$.

Scanning electron microscopy (SEM): FE-SEM (Tescan MIRA3) is used to investigate the morphology of samples, including polymer electrolytes and cathode. The polymer electrolytes should be sputtering conductive Pt for signal enhancement before testing.

Nuclear magnetic resonance (NMR): The chemical shift peaks for functional groups can justify the change before and after polymerization. The NMR spectra, including ^1H -NMR, ^{13}C -NMR, and ^{19}F -NMR, are performed on a Bruker 400 MHz spectrometer. For NMR samples, CDCl_3 is chosen to lock fields, and the measurements adapt to decoupling mode.

3.3.2 Electrochemical characterizations

The basic electrochemical properties of polymer electrolytes, including ionic conductivity, electrochemical stable window, and lithium-ion transference number, are evaluated on the Solartron electrochemical workstation. The electrochemical performance, including lithium stability and cycle or rate performance of batteries, are evaluated on Land or Neware battery testing systems.

Ionic conductivity: The ionic conductivity is measured by electrochemical impedance spectroscopy (EIS) using a perturbation signal of 10 mV over the frequency of 1 MHz to 10 Hz. The polymer electrolytes are sandwiched with stainless steel blocking electrodes with SS/SPEs/SS configuration. The ionic conductivity is calculated by the following equation:

$$\sigma = L / (S \cdot R)$$

Where L (cm) stands for the thickness of SPEs, S (cm^2) stands for the contact area of SS and SPEs, and R (Ω) represents the bulk resistance of blocking batteries obtained by EIS.

Linear sweep voltammograms (LSV): The electrochemical stable window of SPEs is evaluated by LSV measurement with Li/SPEs/SS configuration over the potential of 0.0 V - 6.0 V with a scanning rate of 0.5 mV s^{-1} at a specific temperature.

Lithium-ion transference number (t_{Li}^+): The lithium-ion transference number is investigated with the combination of AC impedance and DC polarization, using a symmetrical blocking electrode of Li/SPEs/Li configuration. AC impedance of

symmetrical cells is detected over the frequency of 1 MHz to 0.01 Hz by EIS. The voltage of DC polarization is 10 mV. The values of t^+ are calculated by the Bruce-Vincent-Evans equation:

$$t^+ = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})}$$

Where I_0 (A) and I_{ss} (A) represent the initial current and the stable current after polarization, respectively. ΔV (V) is the applied voltage of DC polarization. R_0 (Ω) and R_{ss} (Ω) stand for the interfacial resistance before and after polarization, respectively.

Electrochemical stability against lithium metal: The stability of polymer electrolytes is investigated with symmetric Li/SPEs/Li cells through galvanostatic cycling measurements at the constant current density. The cells are charged and discharged for 1 h.

Battery performance: The cells' long-term cycle and rate performance are evaluated on Land or Neware battery testing systems. The charge/discharge voltages for LMFP, LFP, and NCM622 are 3.0-4.25 V, 3.0-3.8 V, and 3.0-4.3 V (vs. Li^+/Li), respectively.

The flexibility of pouch cell: The flexibility of the pouch cell is investigated on the homemade machine with a four-probed bending test system (Keithley2400 SourceMeter). The pouch cell is fixed on the device (Flat status). Then, one side of the pouch cell will move close to the other with a specific speed until it reaches a particular bending radius.

CHAPTER 4 IN-SITU POLYMERIZATION OF UV-CURED POLYMER ELECTROLYTE FOR THE HIGH-VOLTAGE CATHODE

4.1. Introduction

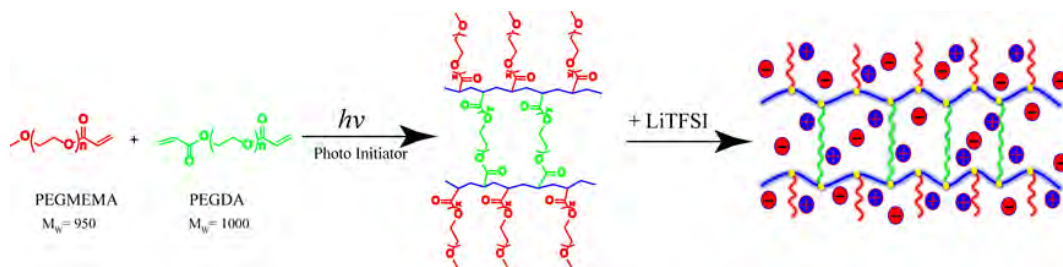
Commercial lithium-ion batteries, such as electric cars and energy storage systems, are widely commercialized in the market ¹⁻³. However, the low theoretical capacity of graphite and leakage of flammable liquid electrolytes result in lower energy density and safety concerns, restricting its further development in many commercial applications ³⁻⁵. Using lithium metal as an anode instead of graphite in LMBs would provide higher energy density due to the excellent intrinsic features of lithium metal, delivering 3860 mAh g⁻¹ in theory ⁶. Extensive research on Li-S, Li-O₂, and other LMBs has verified the higher energy density than LIBs ^{7, 8, 104}. However, non-uniform lithium plating/stripping would lead to continuous lithium dendrite growth, causing short-circuit and capacity decline ^{10, 105}. Besides, severe side reactions of lithium metal with the liquid electrolyte would consume organic electrolytes to form SEI layers, causing cell impedance increase and coulombic efficiency decrease. Finally, thick and unstable SEI layers affect the cycle performance ¹⁰⁶.

Fortunately, ASSLMs using lithium metal electrodes would relieve the challenges mentioned above. Nonflammable SSEs are extremely stable with lithium metal, settling safety concerns ^{107, 108}. Inorganic ceramic electrolytes and SPEs are the best alternatives to liquid electrolytes ^{14, 109, 110}. Among these SSEs, inorganic ceramics exhibit higher ionic conductivity and thermal stability ¹¹¹. In comparison, the poor interfacial contact with electrodes for oxide electrolytes and chemical stability for sulfide electrolytes hinder their further applications ¹⁶. For SPEs, excellent interfacial contact and scalable device integration contribute to their promising applications in ASSLMs ¹¹².

Among the SPEs mentioned above, the excellent electrochemical performance of PEO-

based polymer electrolytes makes them the most promising alternatives to liquid electrolytes. Self-supporting SPE films were prepared by dissolving the polymer in the organic agent and evaporating the solvent at a high temperature. Therefore, fabricating SPE membranes by *in-situ* thermal and photopolymerization is more competitive. *In-situ* plasticized SPEs with a double network were fabricated through facile polymerization. The prepared SPE exhibits enhanced electrochemical performance, such as ionic conductivity, wide electrochemical stable window, high thermal stability, and dendrite suppression²⁶. Besides, *in-situ* photo-polymerization has more advantages than thermal polymerization, such as conducting at room temperature and initiating polymerization with lower activated energy. In our previous works^{24, 86, 113}, an integrated “electrolyte-cathode” structure was fabricated through photo-polymerization, simulating the liquid electrolyte penetrating inside the cathode. In this way, the polymer electrolyte in the cathode provides ionic transport channels and acts as a binder to bond cathode particles.

Herein, UV-cured SPE (UV-SPE) was synthesized *via* copolymerizing poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) and poly(ethylene glycol) diacrylate (PEGDA) (**Scheme 4.1**). UV-SPE shows excellent electrochemical properties and electrochemical compatibility with lithium electrodes. Besides, the ability of dendrite suppression was investigated by contrasting with conventional separators. Furthermore, the cell performance of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ (LMFP)//Li with an integrated “electrolyte-cathode” interface is also evaluated. Therefore, the novel UV-SPE can be applied in next-generation energy devices.



Scheme 4.1 Synthetic route of UV-SPE.

4.2. Experimental Sections

4.2.1 Preparation of UV-cured SPE

LiTFSI was dissolved in the mixture of PEGMEMA and PEGDA. After getting the homogenous solution, the photoinitiator of 2-hydroxy-2-methylpropiophenone (HMPP, 2 wt. %) was added to the sample bottle to get a homogenous and transparent solution. And then, the photo-polymerization process was conducted in a Teflon plate under a UV lamp for 20 mins. Finally, free-standing polymer electrolyte membranes were obtained and abbreviated as “UV-SPE”.

4.2.2 Characterizations

Structural characterization: The structure of UV-SPE was confirmed with FT-IR and X- XRD measurements. The thermal properties of UV-SPE were performed on DSC and TGA. Morphology and EDS mappings of UV-SPE were investigated by FE-SEM, S-4800.

Electrochemical characterization: All the electrochemical measurements, including ionic conductivity, CV, LSV, and t_{Li}^+ were performed on the Solartron electrochemical workstation. The symmetric Li/UV-SPE/Li cells were employed to evaluate the electrochemical stability with lithium metal through galvanostatic cycling measurements. The electrolyte and separator for the control sample are 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC = 1:1:1 (by volume)) and Celgard 2400, respectively.

In-situ LMFP//Li Battery evaluation: LMFP is fabricated through a typical doctor-blading method for cell evaluation. Afterwards, the precursor of UV-SPE is poured onto the cathode layer to construct an integrated cathode with polymer electrolyte, as in our previous work ^{24, 86, 113}. Finally, CR-2025 coin cells are assembled for battery

performance. The mass loading of LMFP is around 2.0 mg cm^{-2} . The battery performance was investigated on Land charge/discharge instruments (LAND CT2001A). The potential range of LMFP//Li batteries was 3.0-4.25 V.

4.3. Results and Discussions

4.3.1 Physical Properties and Micromorphology

Initially, the precursor of UV-SPE is the liquid state. After UV-curing at ambient temperature, the liquid precursor became solid, as shown in **Figure 4.1 a**. Structural characterization was conducted through FT-IR. The characteristic peak of -C=C- from PEGDA and PEGMEMA is located at 1674 cm^{-1} ²⁴. The characteristic peak for the C-C double bond disappears after UV-curing (**Figure 4.1 b**). The results indicate that the precursor was polymerized entirely without residual monomers¹¹³. Moreover, the XRD spectrum in **Figure 4.1 c** demonstrates that the prepared UV-SPE exhibits an amorphous state. In contrast, the PEO-based SPE has both amorphous and crystalline states¹¹⁴.

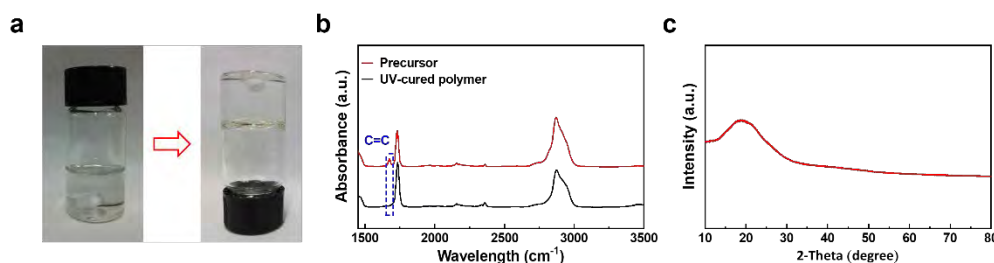


Figure 4.1 (a) Digital photographs of the precursor and polymerized state; (b) FT-IR characterization of precursor and polymer; (c) XRD spectrum of prepared SPE.

As shown in **Figure 4.2 a**, the UV-SPE film is transparent, and the logo of “SUSTech” behind the film is clear. In addition, the inset photograph shows the high flexibility of UV-SPE. To observe the micro-structure of prepared UV-SPE, the scanning electron microscope was carried out, showing a smooth surface without any pores (**Figure 4.2 b**). The dense and continuous polymer matrix is beneficial to lithium-ion transport. The Inset of **Figure 4.2 b** is the cross-section of UV-SPE, showing that the thickness is about

175 μm . The distribution of elemental mapping of carbon, fluorine, oxygen, and sulfur in **Figure 4.2 c** is uniform, demonstrating homogeneously LiTFSI dissolving in the polymer matrix.

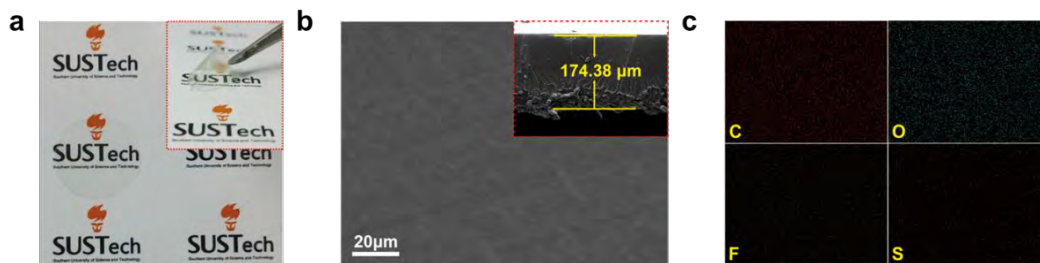


Figure 4.2 (a) Optical photograph of prepared UV-SPE (inset: flexible state of UV-SPE); (b) SEM images of UV-SPE (inset: cross-section of UV-SPE); (c) EDXS elemental mapping of UV-SPE.

4.3.2 Thermal properties of UV-SPE

Thermal properties are essential for battery operation in practical applications. TGA thermograms of UV-SPE were investigated within the temperature range from 30°C to 600°C. The result in **Figure 4.3 a** demonstrates that the decomposition temperature for UV-SPE is around 321.94°C, and the weight loss of 5% as reference. Besides, the second weight loss temperature of around 400°C is attributed to the decomposition of LiTFSI¹¹⁵. The thermal stable UV-SPE enables the batteries using this polymer electrolyte to cycle stably at high temperatures. Moreover, the glass transition temperature (T_g) of UV-SPE was characterized to be -44.9°C according to the phase transition behavior in **Figure 4.3 b**. Besides, no other endothermic peaks indicate the amorphous structure of the UV-SPE. The amorphous domain benefits the enhancement of ionic conductivity.

In addition, the thermal stability of UV-SPE and commercial Celgard separator were all investigated in **Figure 4.3 c**. The commercial Celgard separator shows a slight shrink when put in the heating plate at 100°C for 1 hour. And it rolled up entirely at 150°C. By

contrast, UV-SPE kept its shape during the whole process, indicating UV-SPE exhibits excellent thermal stability compared to the commercial Celgard separator.

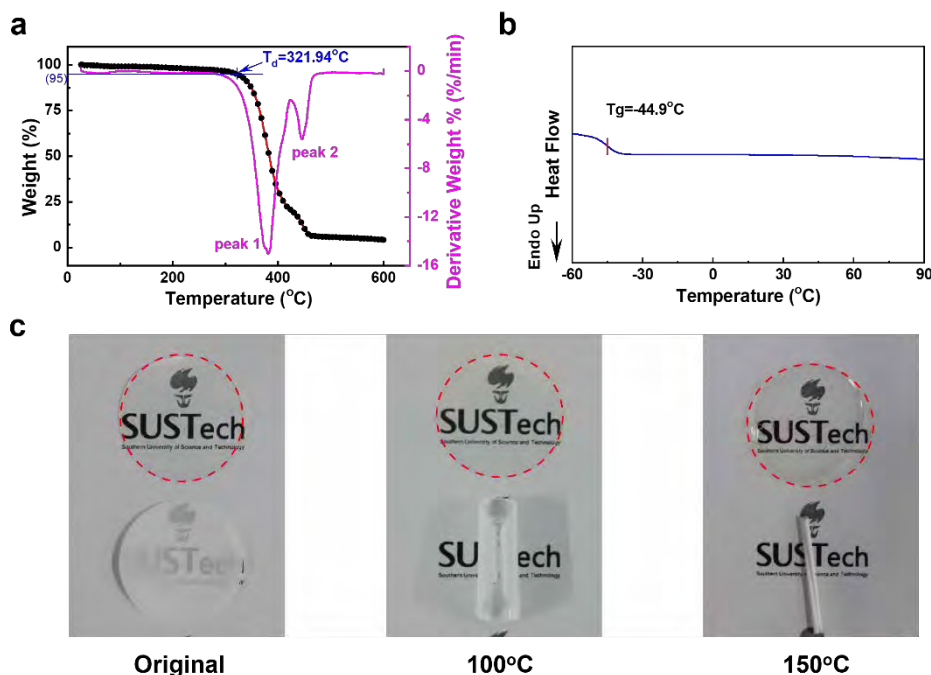


Figure 4.3 TGA (a) and DSC (b) curves of UV-SPE; (c) Photographs of thermal shrinkage of UV-SPE (top) and Celgard separator (bottom) at different temperatures.

4.3.3 Electrochemical properties of UV-SPE

The free Li^+ influences the lithium conduction in polymer electrolytes, with Li^+ coordinating with polar groups along with the segmental motion. The molar ratio of EO/Li^+ was fixed as 20:1, showing the highest ionic conductivity²⁴. The AC impedance of UV-SPE at different temperatures is shown in **Figure 4.4 a**. According to the calculation, the ionic conductivity at 30°C is $2.95 \times 10^{-5} \text{ S cm}^{-1}$, much higher than the reported PEO/LiTFSI polymer electrolyte¹¹⁶. With the temperature increasing, the ionic conductivity increases in **Figure 4.4 b** since the segmental motion of polymer chains becomes faster. The amorphous state of UV-SPE contributes to enhanced ionic conductivity. Besides, the temperature-dependent ionic conductivity meets with the Vogel-Tamman-Fulcher (VTF) empirical equation (**Figure 4.4 c**)¹¹⁷.

$$\sigma = A T^{-1/2} \exp\left(\frac{-E_a}{k(T-T_0)}\right) \quad (1)$$

Calculating from equation (1), the value of E_a for UV-SPE is 0.04 eV, much lower than PEO/LiTFSI-based SPE¹¹⁸, indicating faster lithium-ion transport in the UV-SPE.

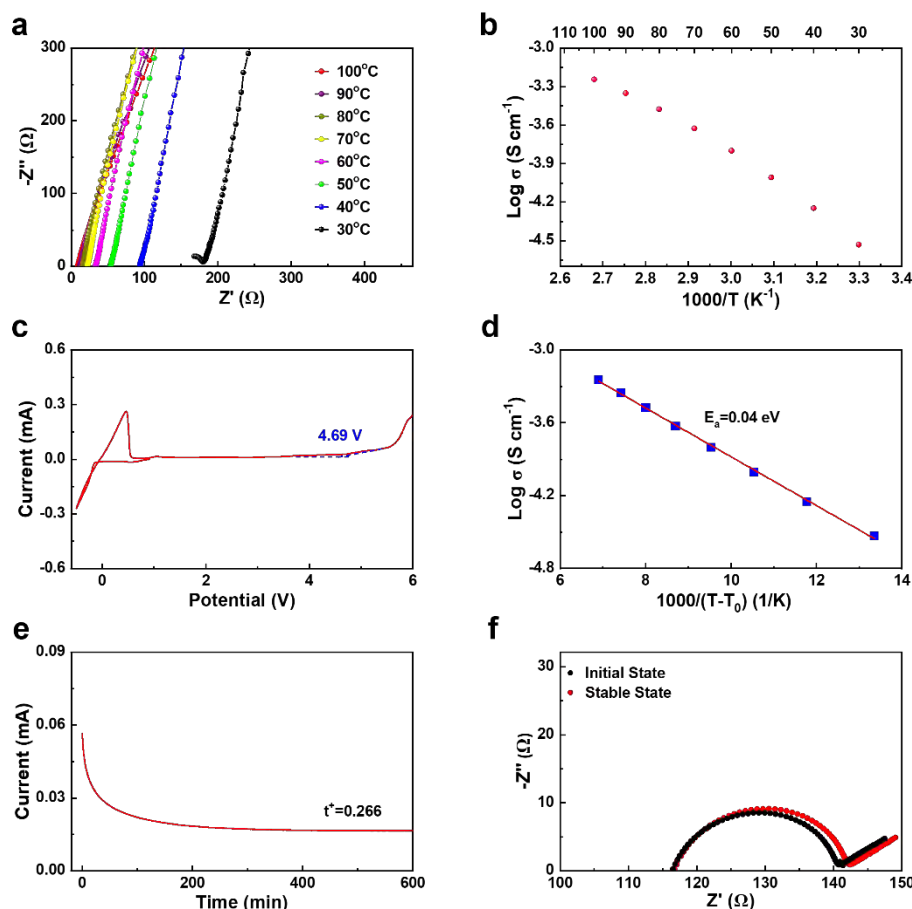


Figure 4.4 Electrochemical properties of prepared UV-SPE. (a) AC impedance of UV-SPE at different temperatures; (b) Ionic conductivities of UV-SPE over the temperature range of 30–100°C; (c) VTF fitting of temperature-dependent ionic conductivities; (d) CV and LSV curves of SPE; (e) Polarization curve of Li/UV-SPE/Li symmetric cell at ambient temperature; (f) The EIS spectra before and after polarization test.

Taking the glass transition temperature as T_0 , the ionic conductivities of the prepared UV-SPE at different temperatures agree well with the VTF equation. After fitting with the VTF equation, the linear equation is ($y = -0.201x - 1.870$), and the standard deviation is 0.9988. Moreover, the ESW of SPEs affects the battery performance in further practical applications. The CV and LSV curves in **Figure 4.4 d** determine the electrochemical stable window of UV-SPE. The CV curve demonstrates the lithium

plating/stripping behavior on the stainless steel electrode.^{119, 120} In the LSV curve above the open-circuit, the current remains unchanged until up to 4.69 V, indicating electrochemical stability over the potential range of 0-4.69 V (vs. Li/Li⁺). Then, the current increases rapidly, implying the decomposition of the polymer framework.

Moreover, the t_{Li}^+ represents Li⁺ dissociation in the polymer electrolyte matrix, related to the cell cycle performance¹¹¹. The polarization of symmetric cell Li/UV-SPE/Li with the potential of 10 mV is presented in **Figure 4.4 e**. After direct-current polarization, the interfacial resistance increased, as shown in **Figure 4.4 f**. Calculating from polarization and EIS plots before and after polarization, t_{Li^+} is 0.266, according to Bruce Vincent Evans (BVE) equation¹²¹. The BVE equation is as follows:

$$t_{Li}^+ = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})} \quad (2)$$

Higher t_{Li}^+ of UV-SPE than the PEO/LiTFSI polymer electrolyte is ascribed to the amorphous state of the polymer electrolyte. The larger free-moving space of polymer chains benefits faster Li⁺ conduction, resulting in higher ionic conductivity and lithium transference number¹²².

4.3.4 Electrochemical stability with the lithium metal anode

The lithium metal plating/stripping behavior was investigated during the long-term cycle performance at a current density of 0.1 mA cm⁻² at 60°C (**Figure 4.5**). The SEI layer was formed with lithium plating/stripping at initial cycles¹¹⁷. The polarizing voltage of the Li/UV-SPE/Li cell retains 0.6 V in **Figure 4.5 a**. Benefiting from the formed stable SEI layer, the Li//Li symmetric cell can operate over 800 h stably, demonstrating excellent electrochemical stability with the lithium metal anode.

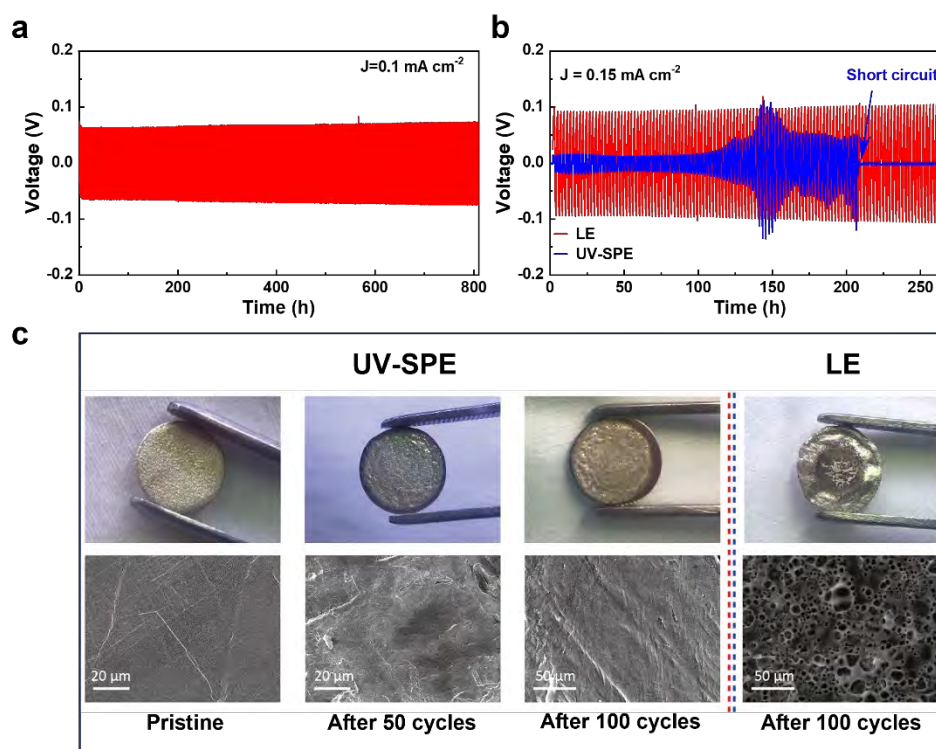


Figure 4.5 Electrochemical compatibility of UV-SPE with lithium metal anode. (a) Long-term cycle performance of Li/UV-SPE/Li at 0.1 mA cm^{-2} ; (b) Comparison of Li/UV-SPE/Li with Li/Separator–Liquid Electrolyte/ Li symmetrical cells at 0.15 mA cm^{-2} ; (c) Photographs and SEM images of Li//Li symmetric cells with UV-SPE and liquid electrolyte at 0.15 mA cm^{-2} .

In addition, the deposited morphologies of lithium metal were compared with symmetric cells using UV-SPE and the liquid electrolyte at a current density of 0.15 mA cm^{-2} at 60°C , shown in **Figure 4.5 b**. At the beginning of tests, the potential of Li/UV-SPE/Li is much larger than that of the Li/ Separator–Liquid Electrolyte /Li cell, which is attributed to the lower ionic conductivity and higher interfacial resistance. The potential of the Li/UV-SPE/Li cell remains unchanged without fluctuation. By comparison, the potential of the Li/ Separator–Liquid Electrolyte /Li cell shows a sharp increase after 100 lithium plating/stripping cycles, resulting from continuous side reactions of the liquid electrolyte and lithium metal ¹²³. Moreover, the smooth surface of the lithium metal anode was deteriorated by uneven lithium deposition, thus causing serious lithium dendrites growth (**Figure 4.5 c**). In contrast, the surface of cycled lithium with UV-SPE remains smooth, indicating stable lithium plating/stripping under

the protection of a stable SEI layer. Therefore, UV-SPE is compatible with lithium metal anode at higher temperatures, stabilizing lithium metal anode for battery operation.

4.3.5 Integrated interface between cathode and UV-SPE

In-situ construction of an integrated “electrolyte-cathode” interface can decrease interfacial resistance, thus improving battery performance. According to a special design for the polymer electrolyte, combining the polymer electrolyte and cathode can contribute to the integrated structure of “electrolyte-cathode”, UV-curing the precursor of the polymer electrolyte on the surface of the cathode layer. The contact between the polymer electrolyte and cathode is strengthened in this case. The interfacial resistance decreased by facilitating lithium-ion transport across the interface. Besides, the polymer electrolyte in the cathode layer can connect the particles of active materials and provide extra lithium-ion transport pathways ²⁴.

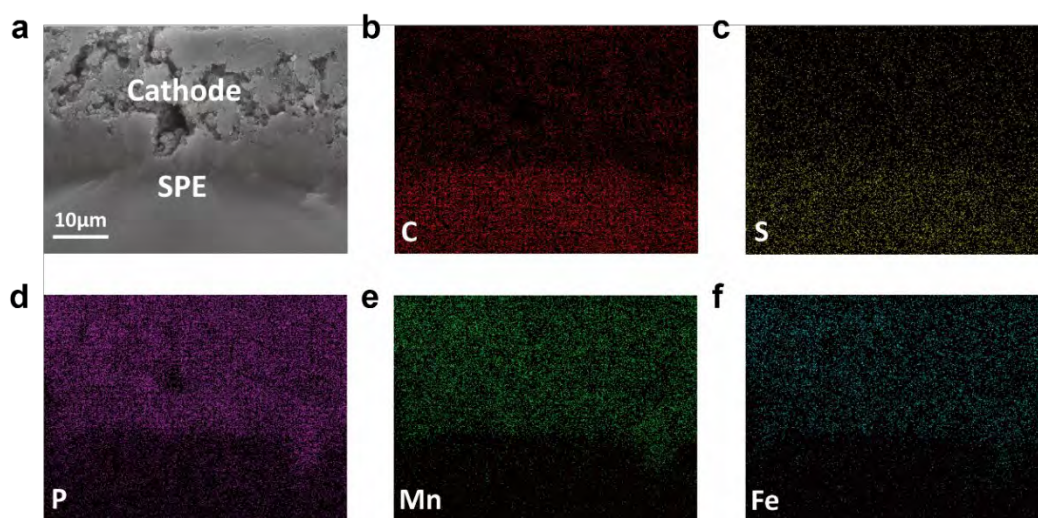


Figure 4.6 (a) SEM image of the integrated “electrolyte-cathode” interface; EDS mapping image for (b) C, (c) S, (d) P, (e) Mn, and (f) Fe.

The integrated “electrolyte-cathode” structure is shown in **Figure 4.6 a**, with no gaps between the polymer electrolyte and the cathode. The thickness of electrolyte in in-situ polymerization is around 150 μm, which is consistent with the thickness of SEM image in **Figure 4.2 b**. The EDS elemental mapping images in **Figure 4.6 b-f** provide

convincing evidence for the effective integrated “electrolyte-cathode” interface, signal of sulfur coming from UV-SPE.

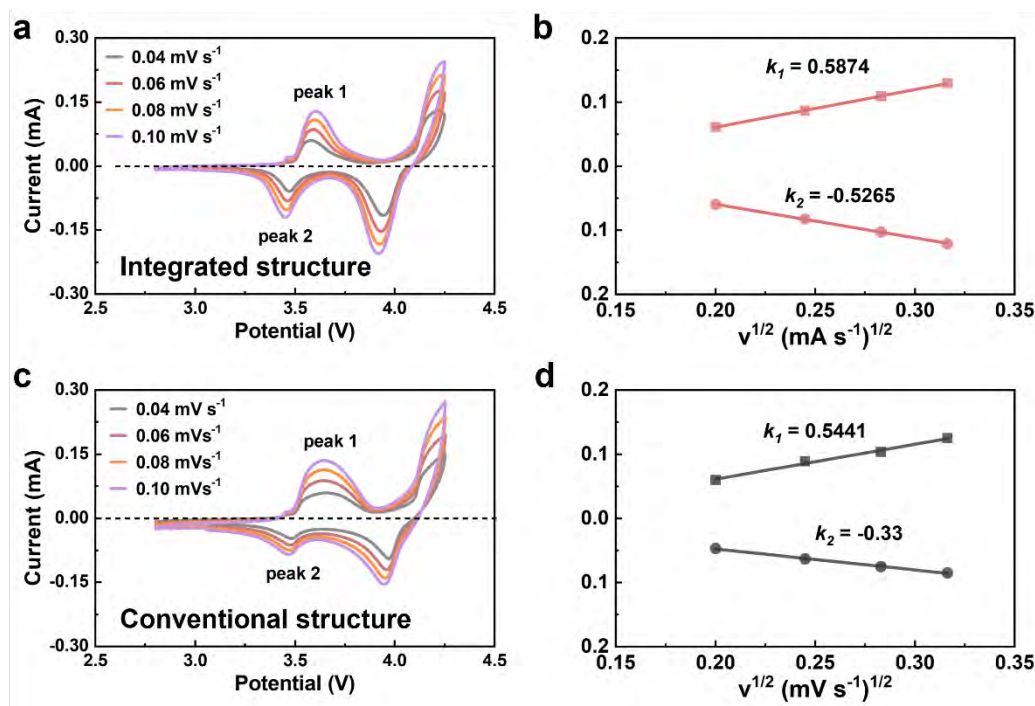


Figure 4.7 Analysis of lithium-ion diffusion. (a, c) CV profiles of the integrated and conventional cell; (b, d) The corresponding relationship between peak current and the square root of scanning rate ($v^{1/2}$).

Moreover, the lithium-ion diffusion in the cathode layer was further analyzed with LMFP/UV-SPE/Li batteries through CV curves over 2.8-4.25 V by the Solartron 1470E electrochemical workstation. The polarization voltage at different scanning rates reflects the speed of lithium-ion transport in the cathode. Lower scanning speed corresponds to faster lithium-ion transport. The polarization voltage becomes larger with the scanning rate increasing, causing lower Li⁺ transport in **Figure 4.7 a**. Compared to the CV curves of the conventional cell (shown in **Figure 4.7 c**), the polarization voltage of the integrated cell is lower, demonstrating its faster Li⁺ transport in both the cathode and cathode/electrolyte interface. To verify the more rapid Li⁺ diffusion in the integrated cathode/electrolyte interface, Randles-sevick equation (3)¹²⁴ was adopted to calculate the Li⁺ diffusion coefficient (D_{Li}).

$$i_p = 2.68 \times 10^5 n^{3/2} A (D_{Li})^{1/2} C_{Li} v^{1/2} \quad (3)$$

The value of D_{Li} is related to the slope of $i_p/v^{1/2}$. For the integrated cells, the slope value of peaks 1 and 2 is 0.5874 and 0.5265, respectively. By comparison, the slope value of peaks 1 and 2 is only 0.5441 and 0.33, respectively (**Figure 4.7 b and d**). The results demonstrate a faster Li^+ diffusion coefficient in the integrated cells than in conventional cells. The higher ratio of k_2/k_1 indicates higher reversible capacity during battery operation.

4.3.6 Battery performance and safety evaluation of LMFP//Li cells

The battery performance was evaluated with the high-voltage cathode of LMFP (4.25 V) (shown in **Figure 4.8**). The batteries are assembled by constructing a “cathode-polymer electrolyte” integrating structure according to our previous work^{86, 113}. Assembled batteries are stored for 2 h at 60°C before cycling tests. The rate performance of LMFP/UV-SPE/Li cells is presented in **Figure 4.8 a** from 0.1 C to 1.0 C. The initial discharge capacity and coulombic efficiency of the integrated cell are 147.4 mAh g⁻¹ and 84.5%, respectively. After activating lithium-ion transport channels in the initial cycles, the discharge capacity increases to 164.7 mAh g⁻¹¹²⁵. The reversible discharge capacity of LMFP//Li at 0.2 C, 0.5 C, and 0.1 C is 157.9, 147.4, and 124.6 mAh g⁻¹, respectively. Besides, the discharging capacity increases to 162.5 mAh g⁻¹ after the C-rate returns to 0.1 C, showing excellent rate performances. Charge/discharge profiles with different C-rates are shown in **Figure 4.8 b**. The voltage plateaus correspond to oxide and redox reactions of Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} ¹¹³. With the current densities increasing, the polarization voltages of LMFP/Li cells increase due to lithium-ion concentration polarization.

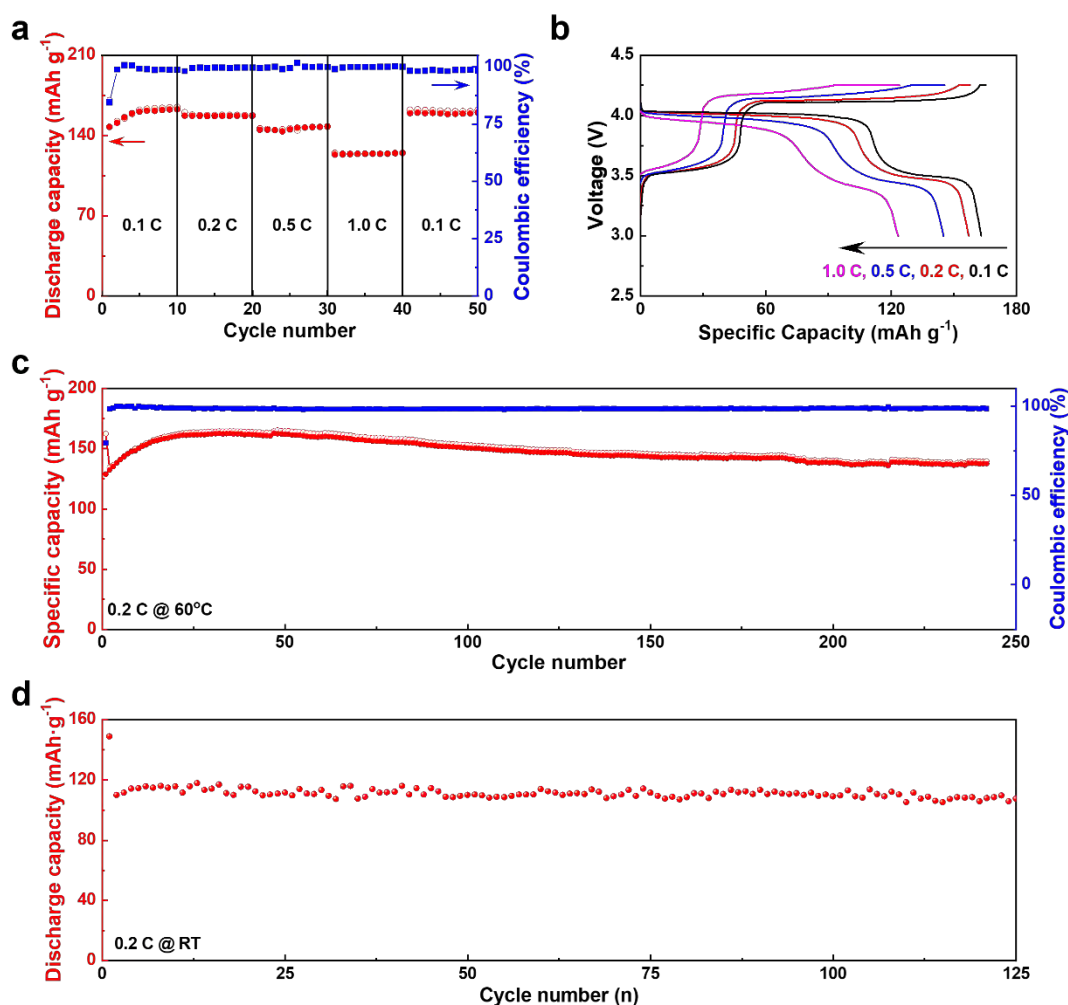


Figure 4.8 Cell performance of LMFP//Li battery. (a) Rate performance at 60°C; (b) Charge/discharge profiles with different C-rates; (c) Long-term cycle performance under 0.2 C at 60°C; (d) Cycle performance of LMFP//Li cell at room temperature.

Furthermore, the long-term cycle performance of the LMFP//Li cell was investigated under 0.2 C at 60°C (**Figure 4.8 c**). The initial discharge capacity and coulombic efficiency are 125.9 mAh g⁻¹ and 79.38%, respectively. The maximum discharge capacity increases to 158.8 mAh g⁻¹. The discharge capacity after 240 cycles still retains 134.4 mAh g⁻¹. Notably, the LMFP//Li cell delivers a reversible capacity of 115 mAh g⁻¹ under 0.2 C (**Figure 4.8 d**). The perfect integrated structure contributes to the superior battery performance^{24, 86}.

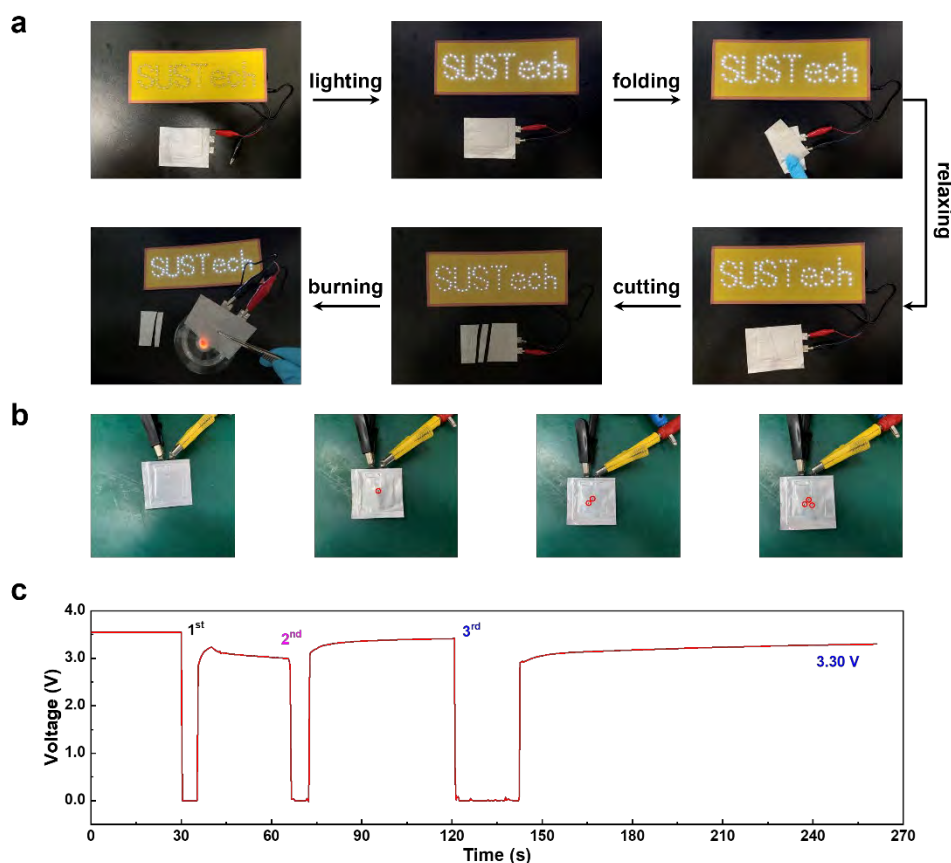


Figure 4.9 Safety evaluation of LMFP//Li battery. (a) Operation under destructive conditions; (b) Photographs of soft-packed battery after nail penetration test; (c) Open circuit changes after puncturing three times continuously at room temperature.

Safety concerns are essential in ASSLMBs, mainly for industrial applications in energy storage systems¹²⁶. In this case, the safety properties were evaluated with a soft-packed battery with UV-SPE. As shown in **Figure 4.9 a**, a soft-packed battery could light up a series of LED lamps with the logo of “SUSTech”. After being folded, the battery keeps in good shape and has stable capacity output. Moreover, LED lamps are still lightened with a piece of battery cutting from the soft-packed battery. The cut piece from the battery can still turn on the LED lamps when it is burnt in the fire. The results demonstrate a soft-packed battery equipped with high flexibility and safety. The three continuous nail penetration tests in **Figure 4.9 b and c** prove short-circuit prevention, and the battery is in good shape without flame and explosion. These results provide robust evidence for *in-situ* UV-curing SPE with excellent safety.

4.4. Conclusion

In summary, a novel polymer electrolyte (UV-SPE) was synthesized under UV irradiation without any solvent. The chemical structure was confirmed with FT-IR and XRD spectra. The UV-SPE shows excellent electrochemical performance, including ionic conductivity of $2.95 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and the stable electrochemical window of 4.69 V (vs. Li/Li⁺). Besides, the electrochemical compatibility with lithium metal anode was superior to liquid electrolytes at higher temperatures. Moreover, the lithium-ion diffusion was enhanced by constructing the integrated “electrolyte-cathode” structure. Furthermore, LiMn_{0.8}Fe_{0.2}PO₄/Li cells were assembled for battery evaluation. The capacity retention of LMFP//Li cell at 0.2 C is 84.6% after 240 cycles. It was demonstrated that this UV-cured SPE has potential applications in ASSLMBs.

CHAPTER 5 SYNTHESIS OF FLUORINE-BASED POLYETHER POLYMER ELECTROLYTE FOR HIGH-VOLTAGE CATHODES

5.1 Introduction

Lithium-ion batteries (LIBs) have been commercialized in the market, such as smart electronics, electric vehicles, and energy storage systems¹²⁷⁻¹²⁹. The demands of higher energy density motivated the introduction of lithium metal, replacing commercial graphite as the anode because the lithium metal was equipped with a higher theoretical specific capacity of 3860 mAh g⁻¹ and a lower redox potential of -3.04 V¹³⁰. However, highly reactive Li metal would react with liquid electrolytes, resulting in the unstable SEI layer and further lithium dendrite growth, causing the battery to short-circuit and explosions. Therefore, SSEs are promising alternatives to liquid electrolytes for lithium metal batteries^{12, 101}. However, for polymer-based ASSLMBs, the research has mainly focused on the LiFePO₄ cathode, lower operation voltage, and energy density compared with commercial LIBs^{24, 29, 131-134}. To achieve higher energy density, high-voltage cathodes with higher theoretical capacity and operating voltage should be employed for ASSLMBs^{67, 135, 136}.

Solid polymer electrolytes (SPEs) have attracted more attention based on the advantages of flexibility and easy-processability. PEO-based polyether electrolytes have been studied for decades because of their excellent solubility to lithium salt, detailed transport mechanism of lithium-ion coordinating with ether oxygen, and excellent interface contact with electrodes^{27, 137}. PEO-based polymer electrolytes have been commercialized in electric vehicles based on their advantages. However, many inherent limitations hinder its applications, such as poor chemical/electrochemical

compatibility with high-voltage cathode and capacity decay during long-term cycling^{61, 64}. Many efforts have been made to improve the circumstances. Modifications on SPEs could enhance the electrochemical window and oxidation stability under high cut-off voltage, including mixing with functional polymers and fabricating inorganic-organic composite electrolytes^{67, 138-140}. Constructing a robust layer on the surface of high-voltage cathode particles with $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ (LATP) can also relieve the decomposition of PEO resulting from delithiated LiCoO_2 with strong oxidation ability^{61, 141}. Moreover, fabricating asymmetric polymer electrolytes can also enable PEO-SPE to match with high-voltage cathodes for stable cycling^{71, 73, 142}. However, the long-term cycling stability is still limited, although PEO-based polymer electrolytes can work with high-voltage cathodes after modification.

In liquid electrolyte systems, fluorine-based molecules can contribute to LiF-rich components formation in the interface of both lithium metal anode and high-voltage cathode, thus improving the long-life cycle performance^{66, 143}. Based on the mechanism of LiF formation in lithium-ion batteries, combining fluorine-based polymer or other inorganic particles with PEO-based polymer electrolytes can also promote the enrichment of LiF particles in the interface, which is equipped with ultra-high electrochemical stability with high-voltage cathode⁶⁷. Besides, adding fluorine-based components can decrease the bonding energy of lithium-ion to polymer, indicating a higher lithium-ion transference number⁶⁵. Unfortunately, the investigation has not been reported on the one-step synthesis of fluorine-based polyether polymer electrolytes paired with the high-voltage cathode in solid-state lithium metal batteries.

In this work, fluorine-based polyether polymer electrolyte was synthesized through *in-situ* cation open-ring polymerization, poly(ethylene glycol) diglycidyl ether (PEGDE) copolymerizing with glycidyl 2,2,3,3-tetrafluoropropyl ether (TFE) to generate PEGDE-co-TFE polymer electrolyte (named as Poly(PEGDE-co-TFE)). We demonstrated that introducing TFE could increase the ion conductivity of homo-

polymerization of PEGDE [Poly(PEGDE)], widen the electrochemical stable window, and increase the lithium-ion transference number. Moreover, TFE segments can contribute to LiF formation in the interface of lithium metal anode and high-voltage cathode. Lithium plating/stripping behavior can stabilize for over 2000 h at 0.2 mA cm^{-2} . Compared with Poly(PEGDE), fluorine-based Poly(PEGDE-co-TFE) can tolerate the high-voltage cathode of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622 - 4.3 V) with capacity retention of 72.3% after 200 cycles. Li/Poly(PEGDE-co-TFE)/ LiFePO_4 (LFP) batteries show stable long-term cycling performance capacity retention of 73.3% after 700 cycles. Moreover, the assembled pouch cell shows excellent flexibility after bending 3000 cycles with a bending radius of 4 mm. This work verified that introducing fluorine-based components into a polyether polymer structure can achieve stable long-term cycling batteries with high-voltage cathodes.

5.2 Experimental Sections

5.2.1 Preparation of materials

Preparation of SSEs: LiTFSI (99.5% Capchem) and LiBF_4 (Initiator, 2.0 wt%) were dissolved into the monomer of PEGDE and TFE, subsequently stirring for 1 h to obtain a homogenous solution. According to previous work, EO: Li^+ was controlled at 18:1, exhibiting the highest ionic conductivity. Then, the solution was poured into a PTFE holder with a sealed lid. After heating for 8 h at 60°C , the membranes can be peeled from the PTFE holder and get the self-supporting SPEs.

Preparation of PVDF-HFP substrate: Lithium nitrate (LiNO_3) and polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) were dissolved into acetone (ACN) and stirred until getting a homogenous solution. The weight ratio of ACN, LiNO_3 , and PVDF-HFP is 90:5:5. Subsequently, the solution was cast and peeled from the aluminum-plastic film. Finally, the porous PVDF-HFP film (PPH) was dried in the vacuum oven at 80°C .

Flexible pouch cell assembly: To evaluate the flexibility of the pouch cell with Poly(PEGDE-co-TFE), the pouch cell with a textile-based current collector is assembled for testing. Firstly, the flexible cathode is prepared by coating the slurry of the cathode on the prepared Ni-PET fabric. Secondly, the flexible lithium metal anode is prepared by rolling with flexible Cu-PET fabric. Subsequently, the PPH film is sandwiched with a cathode and lithium anode, injecting the Poly precursor (PEGDE-co-TFE). Finally, the pouch cell is sealed with a vacuum.

5.2.2 Characterizations

Structural characterizations: The structures of Poly(PEGDE) and Poly(PEGDE-co-TFE) are confirmed by NMR (including ^1H -NMR, ^{13}C -NMR, and ^{19}F -NMR), FT-IR, and XPS. TGA and DSC characterize the thermal properties. The morphology of polymer electrolytes cycled lithium metal anode and cycled cathodes are visualized by FE-SEM and TEM.

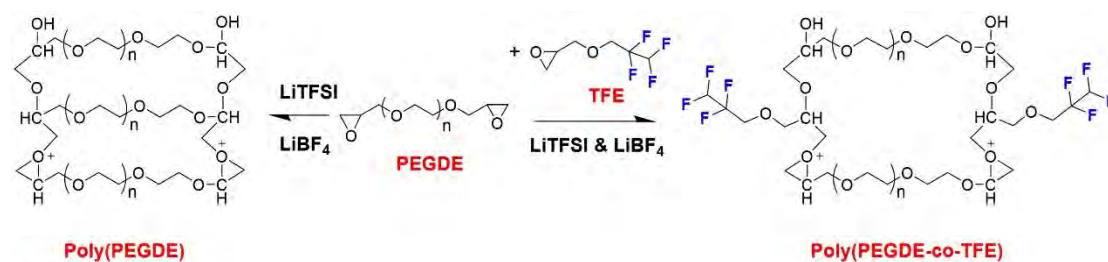
Electrochemical characterizations: The ionic conductivity, lithium-ion transference number, electrochemical stable windows, and electrochemical floating analysis paring with NCM622 cathode are evaluated on Solartron electrochemical workstation. The electrochemical compatibility with lithium metal and battery performance, including cycle and rate capability, are conducted on the Neware battery testing system.

5.3 Results and Discussions

5.3.1 Structural characterization of polymer electrolytes

Two kinds of polymer electrolytes were heat-polymerized with monomer (PEGDE with/without TFE), the lithium salt of LiTFSI and initiator of LiBF_4 , named Poly(PEGDE) and Poly(PEGDE-co-TFE) (**Scheme 5.1**). Cationic polymerization initiated by LiBF_4 can explain the reaction mechanism. The LiBF_4 would be

decomposed to BF_3 and LiF with a trace of H_2O under heating conditions. Subsequently, the BF_3 can be combined with a trace of H_2O to generate $\text{H}^+(\text{BF}_3\text{OH})^-$, attaching to the oxygen atom of the epoxy groups and initiating the open ring polymerization process^{144, 145}. The digital pictures in **Figure 5.1 a** show that the original liquid precursor transformed into a transparent, solid product after heating for 8 h.



Scheme 5.1 Schematic illustration of the synthetic route of polymer electrolytes.

To confirm the successful polymerization of Poly(PEGDE) and Poly(PEGDE-co-TFE), FT-IR, and NMR, including ^1H -NMR, ^{13}C -NMR, and ^{19}F -NMR were conducted to analyze the chemical structure. The FT-IR spectrum of PEGDE, TFE, Poly(PEGDE), and Poly(PEGDE-co-TFE) are shown in **Figure 5.1 b**. The peaks for epoxy groups in PEGDE and TFE are prominent at 911 cm^{-1} . After polymerization, the peaks of epoxy groups disappear in Poly(PEGDE) and Poly(PEGDE-co-TFE) samples. The peak at 1190 cm^{-1} is attributed to asymmetric stretching of C-O-C. The intensity in Poly(PEGDE) and Poly(PEGDE-co-TFE) is much higher than in PEGDE and TFE. The peaks at around 1100 cm^{-1} belong to the symmetric stretching of C-O-C in PEGDE and TFE. After LiTFSI is added, the peaks shift to 1050 cm^{-1} in Poly(PEGDE) and Poly(PEGDE-co-TFE), indicating interactions between LiTFSI and EO groups. Due to the open-ring polymerization of epoxy groups, the intensity of bending vibration of C-H at 1350 cm^{-1} and asymmetric stretching of $-\text{CH}_2$ increase in Poly(PEGDE) and Poly(PEGDE-co-TFE). The above results demonstrate the successful open-ring polymerization of PEGDE and TFE.

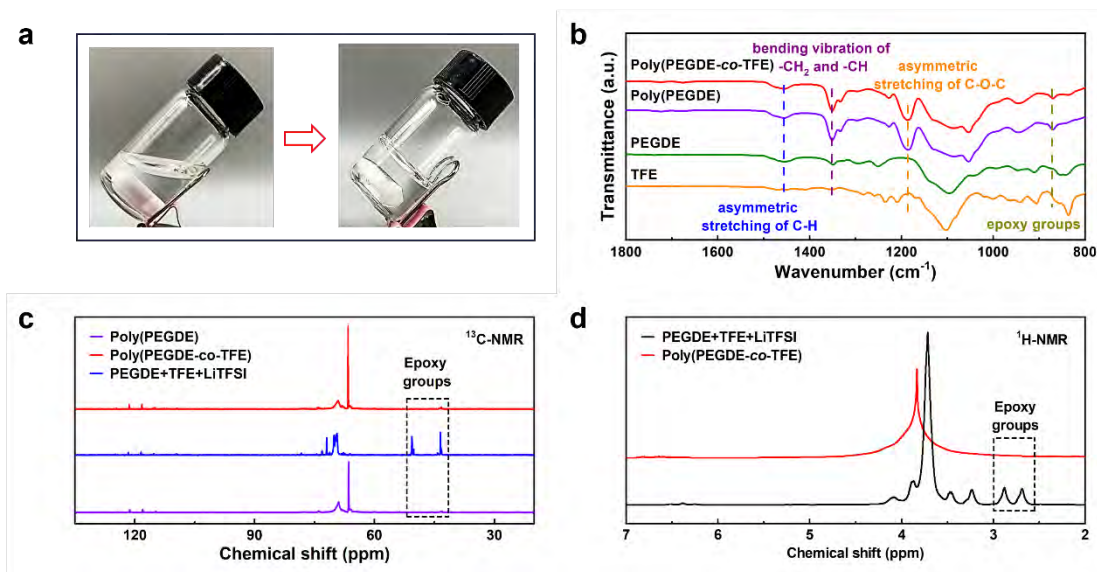


Figure 5.1 (a) Digital photographs of Poly(PEGDE-co-TFE) before and after polymerization; (b) FT-IR spectra of Poly(PEGDE) and Poly(PEGDE-co-TFE); (c) ¹³C-NMR and (d) ¹H-NMR spectra of Poly(PEGDE) and Poly(PEGDE-co-TFE)

Figure 5.1 c shows the ¹³C-NMR of Poly (PEGDE), Poly(PEGDE-co-TFE), and its precursor without LiBF₄. In ¹³C-NMR spectra, the peaks at 43.3 ppm and 50.6 ppm belong to -CH₂- and -CH- of epoxy groups, respectively. By comparison, such signals of epoxy groups in Poly (PEGDE) and Poly(PEGDE-co-TFE) disappear after polymerization. The peak at 66.5 ppm was assigned to the carbon of -CH₂- connecting the two PEGDE skeletons. The peaks of -CH₂- in main chains at 69.6 ppm were broadened after polymerization. The ¹H-NMR in **Figure 5.1 d** demonstrates that the chemical shift of -H in epoxy groups disappears after polymerization. The peaks for -CH₂- in main chains significantly transformed to one massive broadened peak. According to the integral of reacted hydrogen atoms in epoxy groups and residual hydrogen atoms of epoxy groups, the conversion of monomer to polymer is around 96.3%. The ¹³C-NMR and ¹H-NMR measurements confirmed the successful polymerization. High polymerization conversion could alleviate the side reactions between monomer and lithium metal anode.

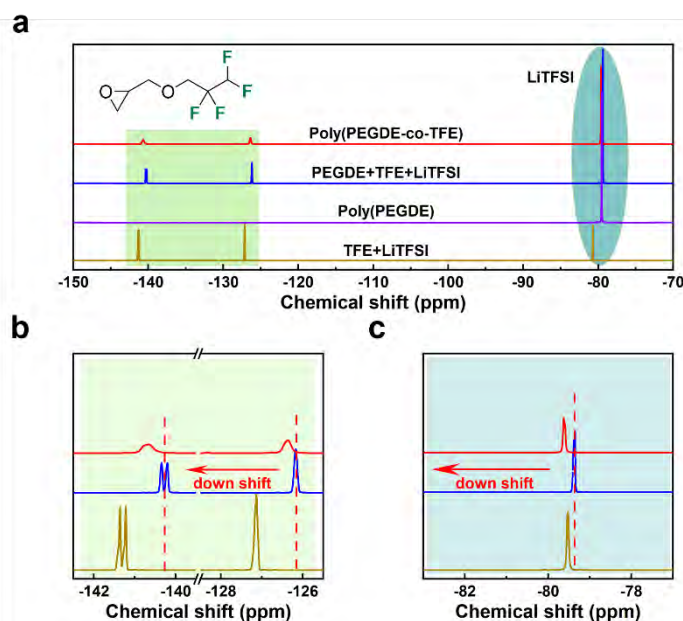


Figure 5.2 The relationships between TFE and chemical shift. (a) ^{19}F -NMR spectra of TFE-LiTFSI, Poly(PEGDE), precursor, and Poly(PEGDE-co-TFE); Comparison of chemical shift in ^{19}F -NMR of F-signal from (b) TFE and (c) LiTFSI.

^{19}F -NMR in **Figure 5.2 a** was conducted to distinguish the coordination interactions between Li^+ and F-groups in Poly(PEGDE) and Poly(PEGDE-co-TFE). For Poly(PEGDE), the peaks at -79.5 ppm and 153.02 ppm resulted from LiTFSI and LiBF_4 ¹⁴⁵. By contrast, two more peaks from TFE in Poly(PEGDE-co-TFE) were located at -126.3 ppm and -140.6 ppm. Initially, the F-signals of TFE are located at 141.19 ppm and 127.13 ppm. After adding the PEGDE monomer, two large downshifts of 1.02 ppm and 0.97 ppm are shown in the precursor of Poly(PEGDE-co-TFE) (in **Figure 5.2 b**), indicating decreased coordination interaction with Li^+ . This phenomenon is probably attributed to the Li^+ coordinating with oxygen groups in PEGDE. Once the TFE was bounded on the Poly(PEGDE-co-TFE), slight up-shifts of 0.43 ppm and 0.19 ppm happened, indicating stronger coordination interaction with Li^+ ^{146, 147}. Besides, it should be noted that the -F peak at -140.2 ppm in the precursor is two separate peaks. After polymerization, it transformed into one broadened peak, reflecting the successful polymerization of TFE. The lower chemical shift of ^{19}F in TFSI⁻ anions for

Poly(PEGDE-co-TFE) represents a stronger shield effect of Li nuclei than that of Poly(PEGDE) (**Figure 5.2 c**). The results confirm that introducing TFE can accelerate the process of LiTFSI dissociating to TFSI⁻ anions and free Li⁺, promoting Li⁺ transport in Poly(PEGDE-co-TFE).

It's reported that Li-ion prefers to transport in amorphous areas of polymer electrolytes. DSC and TGA were conducted to evaluate the thermal properties of Poly(PEGDE) and Poly(PEGDE-co-TFE). As shown in **Figure 5.3 a**, there is only one peak for the glass transition temperature (T_g). The crosslinking framework inhibited the crystalline region. The T_g of Poly(PEGDE) and Poly(PEGDE-co-TFE) is -53.71°C and -54.73°C, respectively. Lower T_g of Poly(PEGDE-co-TFE) represents higher ionic conductivity than Poly(PEGDE). The thermal stability of polymer electrolytes is also crucial for further operation in battery systems (**Figure 5.3 b**). Taking 5% weight loss as the standard, the decomposing temperature of Poly(PEGDE-co-TFE) is around 174°C, which is lower than that of Poly(PEGDE) (267°C). Adding TFE would decrease the crosslinking degree of Poly(PEGDE-co-TFE). A higher crosslinking degree of Poly(PEGDE) presents higher thermal stability. The weighting loss around 400°C and 450°C is attributed to the decomposition of LiTFSI and LiBF₄, respectively.

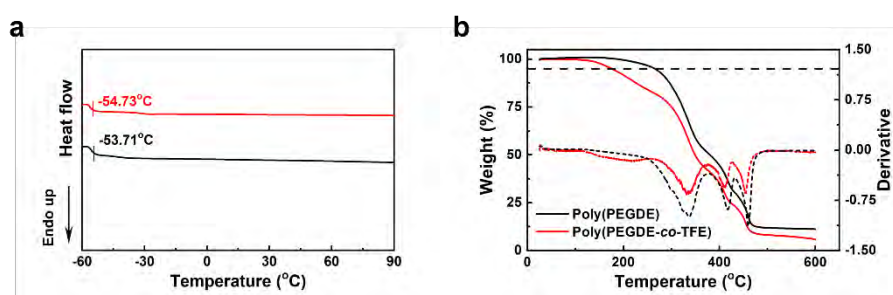


Figure 5.3 Thermal properties of Poly(PEGDE) and Poly(PEGDE-co-TFE). (a) DSC curves and (b) TGA curves

5.3.2 Optimization of composite electrolytes

In-situ assembling solid-state batteries can improve the interfacial contact between

polymer electrolytes and electrodes since the precursor of polymer electrolytes can penetrate inside the electrodes and attach the electrodes to the polymer electrolytes. In this work, we compare three types of substrates to evaluate the capability of the precursor. The micromorphology of substrates is shown in **Figure 5.4 a-c**. The prepared PPH film voids are larger than Celgard 2500 and PI film. The resistance compares the effect of substrates with symmetric Li//Li cells. As shown in **Figure 5.4 d**, the bulk resistance of Li/PI/Li cells is the lowest due to hosting more polymer electrolytes. However, because of the rigid structure of PI film, the interfacial contact between PI-polymer electrolyte and lithium metal is poor, leading to large interfacial resistance. By comparison, the prepared PPH film is soft and beneficial to improve interfacial contact, resulting in low interfacial resistance. The size of the pores in PPH film is around 2 μm . Prepared PPH film is more suitable for hosting polymer electrolytes for battery *in-situ* assembly. The polymerization heating time was investigated in symmetric stainless steel (SS)//SS cells to get high precursor conversion. The AC impedance after different heating hours shows that the resistance is almost unchanged after 8 h heating (**Figure 5.4 e**). Therefore, all the electrochemical properties with *in-situ* assembled cells are conducted after heating 8 h in the oven.

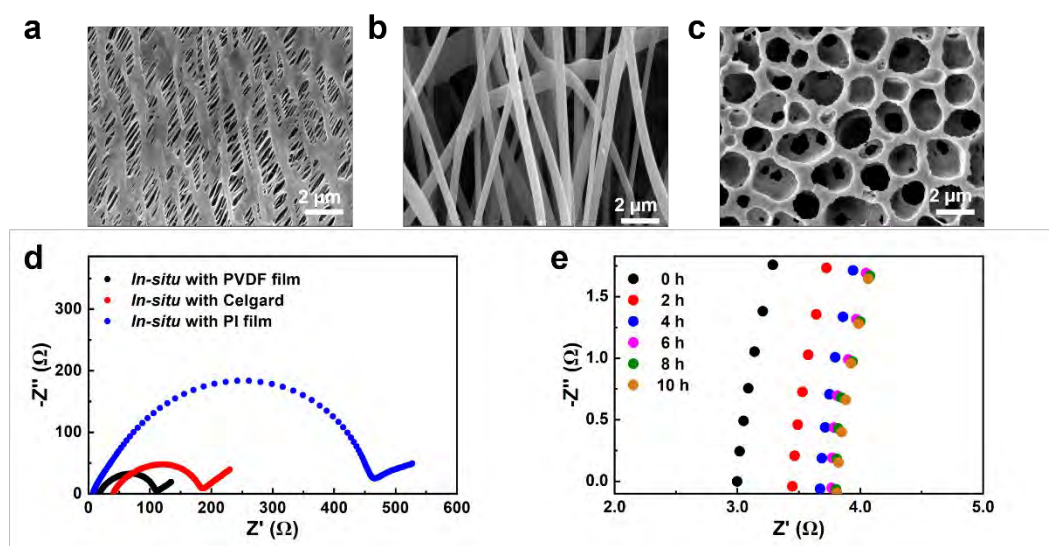


Figure 5.4 SEM images of (a) PPH film, (b) Celgard 2500, and (c) PI film; (d) Comparison of symmetric Li//Li batteries with different supporting substrates; (e) Resistance of symmetric SS//SS cell with Poly(PEGDE-co-TFE) after heating different hours.

The distribution of voids in PPH film is uniform, as shown in **Figure 5.5 a**. A composite polymer electrolyte was prepared to inject the precursor into the PPH film, and thermal polymerized it in a sealed mold. Scanning Electron Microscope (SEM) image visualizes the microstructure of composite polymer electrolyte in **Figure 5.5 b**. It demonstrates that the polymer electrolyte fills in the pores of PPH film entirely after polymerization, supported by the energy dispersive spectrometer (EDS) mapping images in **Figure 5.5 c-e**. C, F, and S elements stand for Poly(PEGDE-*co*-TFE), PPH film, and LiTFSI, respectively. C, F, and S uniform distribution represents the Poly(PEGDE-*co*-TFE) covering the PPH film uniformly. The continuous polymer matrix favors Li-ion transport and prevents inside micro-short circuits during battery operation. The composite polymer electrolyte was semi-transparent and flexible (**Figure 5.5 f**). The thickness of the composite polymer electrolyte is around 12 μm , equal to the PPH film.

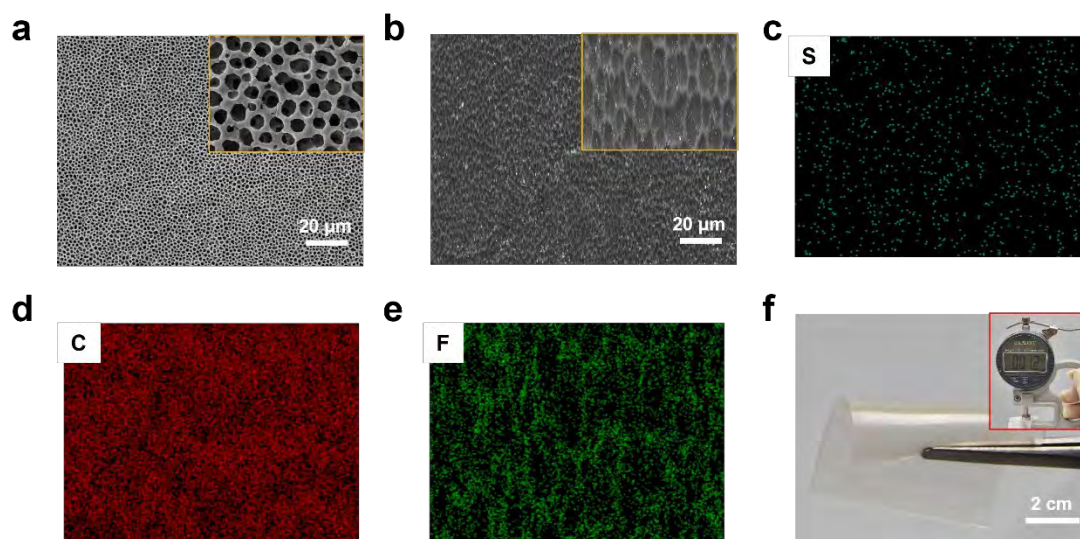


Figure 5.5 (a) SEM images of PPH film; (b) SEM image of composite polymer electrolyte with PPH supporting Poly(PEGDE-*co*-TFE); EDS mapping images of (c) Sulfur, (d) Carbon, (e) Fluorine for Poly(PEGDE-*co*-TFE); (f) Digital photograph of composite polymer electrolyte.

5.3.3 Electrochemical performance of composite electrolytes

For the electrochemical properties of Poly(PEGDE-*co*-TFE), the ionic conductivities were evaluated by adding different TFE ratios at room temperature (**Figure 5.6 a**). The

Poly(PEGDE) shows all cross-linked structures in theory with ionic conductivity of $5.9 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. Li-ion can coordinate with EO groups, hopping from one coordinating site to another with the help of the segmental motion of polymer^{148, 149}. Introducing TFE into Poly(PEGDE) could decrease the degree of crosslinking, resulting in more segmental motion of the polymer and promoting Li-ion transport. Moreover, apart from the EO groups, the polar groups of C-O-C and C-F in TFE could help transport Li-ion and enhance ionic conductivity^{18, 67}. As optimized, The Poly(PEGDE-co-TFE) with 35 mol% TFE exhibits the highest ionic conductivity of $8.15 \times 10^{-5} \text{ S cm}^{-1}$. Adding more TFE in Poly(PEGDE-co-TFE) would decrease the concentration of EO groups, although the C-F groups would increase. The decreasing ionic conductivity with more TFE indicates that EO groups provide better Li-ion transport pathways than C-F groups in TFE.

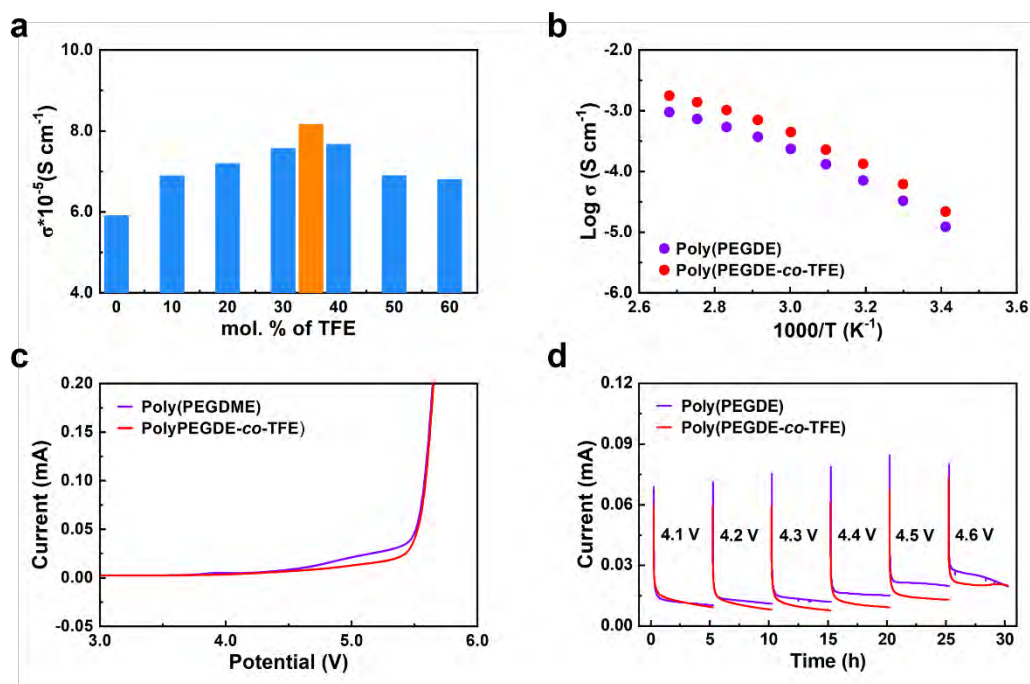


Figure 5.6 Electrochemical performance of composite polymer electrolytes. (a) Optimization of ionic conductivity with the different ratio of TFE; (b) Ionic conductivity at the temperature range of 20~100°C; (c) Linear sweep voltammetry (LSV) profiles for polymer electrolytes at the scanning rate of 0.5 mV s^{-1} ; (d) Electrochemical floating analysis in the assembled Li//NCM622 batteries.

The temperature-dependent ionic conductivities of Poly(PEGDE) and Poly(PEGDE-co-TFE) were recorded with temperatures of 20°C-100°C in **Figure 5.6 b**. Introducing TFE could promote ionic conductivity over the whole temperature range of 20-100°C. The ionic conductivity reached $1.32 \times 10^{-4} \text{ S cm}^{-1}$ and $2.28 \times 10^{-4} \text{ S cm}^{-1}$ for Poly(PEGDE) and Poly(PEGDE-co-TFE) at 50°C, respectively. The following electrochemical performance was investigated at 50°C

The electrochemical stable window of polymer electrolytes is an important parameter to judge their possibilities for matching with high-voltage cathodes. Linear sweep voltammetry (LSV) measurements are performed on the electrochemical workstation to monitor the oxidative process of Poly(PEGDE) and Poly(PEGDE-co-TFE). In **Figure 5.6 c**, choosing the current of 10 μA as a reference for oxidation potential, the oxidation potential of Poly(PEGDE) is 4.59 V vs. Li^+/Li . In contrast, the oxidation potential of Poly(PEGDE-co-TFE) increased to 4.83 V vs. Li^+/Li . The increased oxidation potential is mainly attributed to the strong electron-withdrawing effect of fluorine, shifting away from EO groups¹⁵⁰. The formation of a TFE-rich area separates the EO groups and electrode surface, protecting C-O-C from decomposition at high voltage. Therefore, the wide electrochemical stable window of Poly(PEGDE-co-TFE) can ensure the battery cycling with high-voltage cathodes. The electrochemical floating analysis using NCM622 cathode provides solid evidence for oxidation stability (**Figure 5.6 d**). The leakage current under a fully charged state reflects the oxidative stability of electrolyte¹⁵¹. In this experiment, the Li//NCM622 cells are charged at a 4.2-4.7 V voltage and maintained for 5 h. A similar leakage current was observed for both composite electrolytes, indicating similar oxidation stability at 4.2 V. Once the batteries are charged over 4.3 V, the leakage current for Poly(PEGDE)-based battery is increasing higher than Poly(PEGDE-co-TFE)-based battery, implying severe side reaction happening in Poly(PEGDE)-based battery. The key reason is probably that stable interfaces are formed on the lithium metal anode and NCM622 cathode, resulting in stable long-term cycling performance.

Li-ion transference number (t_{Li}^+) is another crucial parameter for polymer electrolytes because it relates to battery performance. t_{Li}^+ of Poly(PEGDE) and Poly(PEGDE-co-TFE) were measured through chronoamperometry combined with AC impedance spectroscopy. **Figure 5.7 a, b** shows the i - t curve of Poly(PEGDE) under the direct current of 10 mV and AC impedance spectra before and after chronoamperometry over the frequency range of 10^6 Hz - 0.01 Hz. The calculated t_{Li}^+ for Poly(PEGDE) is 0.296, according to Bruce-Vincent-Evans equation. Similarly, the t_{Li}^+ for Poly(PEGDE-co-TFE) is 0.368, calculated through **Figure 5.7 c-d**. The higher t_{Li}^+ for Poly(PEGDE-co-TFE) is attributed to two aspects: larger motion volume and “fluorous effect”^{150, 152}. On the one hand, the grafted TFE in Poly(PEGDE) benefits the polymer's segmental motion and provides more free-moving volume for Li-ion transport. In addition, the strong interactions between TFSI⁻ anions and TFE reduce their mobility. The delocalization of electron density decreases the binding strength of Li⁺ to oxygen atoms, facilitating Li⁺ transport across the Poly(PEGDE-co-TFE)¹⁵². The synergistic effect of the above two aspects results in higher t_{Li}^+ of Poly(PEGDE-co-TFE).

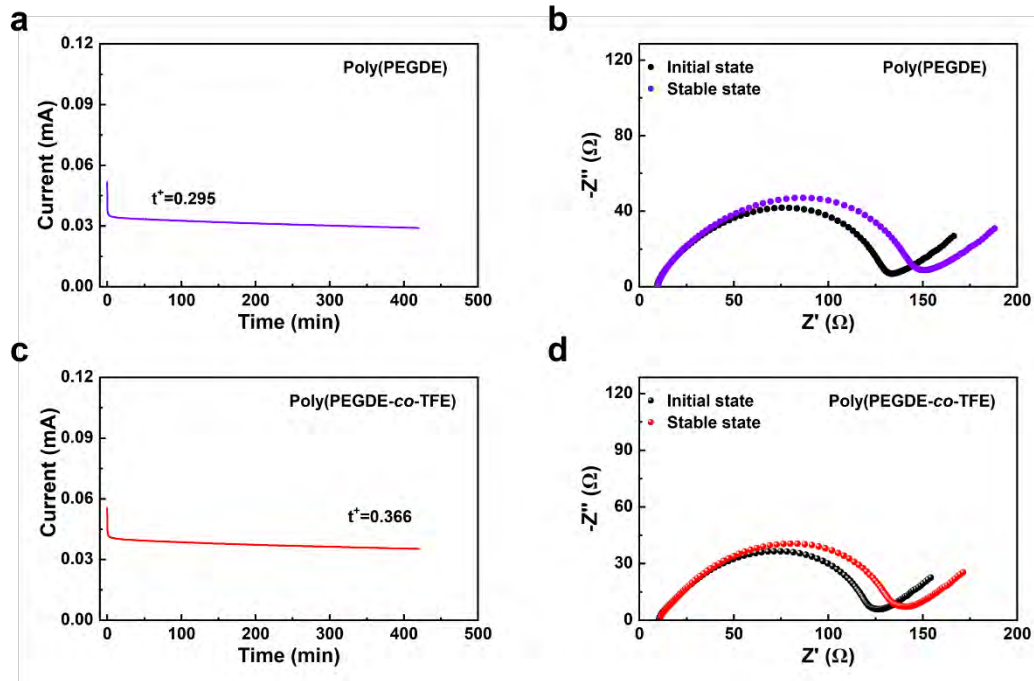


Figure 5.7 (a) Polarization curve of Poly(PEGDE); (b) AC impedance before and after polarization; (c) Polarization curve of Poly(PEGDE-co-TFE); (d) AC impedance before and after polarization.

5.3.4 Interfacial stability with lithium metal anode

The electrochemical stability against lithium metal anode affects the lifetime of battery cycling performance. Chronopotentiometry tests were conducted through symmetric Li//Li cells with Poly(PEGDE) and Poly(PEGDE-co-TFE). Firstly, the plating/stripping behavior was investigated under different current densities in **Figure 5.8 a**. For the Li/Poly(PEGDE)/Li symmetric cell, voltage oscillation appears at 0.3 mA cm^{-2} . Further, an increase in current density causes rapid voltage increase and, finally, short-circuit occurring at 0.5 mA cm^{-2} , suggesting the formation of unstable SEI¹⁵³. In sharp contrast, the plating/stripping behavior is relatively stable with different current densities up to 0.6 mA cm^{-2} , meaning the construction of a stable SEI layer. Subsequently, long-term cycling performance was evaluated at 0.2 mA cm^{-2} .

Figure 5.8 b shows that Poly(PEGDE-co-TFE) exhibits stable lithium plating/stripping for 2000 h without voltage fluctuation, indicating effective dendrite suppression. By comparison, the Poly(PEGDE) can only cycle stably for less than 500 h. Afterward, a severe voltage increase happened, and a short circuit occurred around 600 h. The AC impedance of symmetric cells further confirms the superior stability of Poly(PEGDE-co-TFE) against lithium metal. The resistance for Li/Poly(PEGDE)/Li cell continuously increases with cycling cycles, resulting from side reactions of Poly(PEGDE) to lithium metal (**Figure 5.8 c**). By comparison, the Li//Li symmetric cell with Poly(PEGDE-co-TFE) demonstrates relatively stable resistance after 5 cycles (**Figure 5.8 d**). The above results indicate that Poly(PEGDE-co-TFE) exhibits superior stability against lithium metal anode during long-term cycle performance.

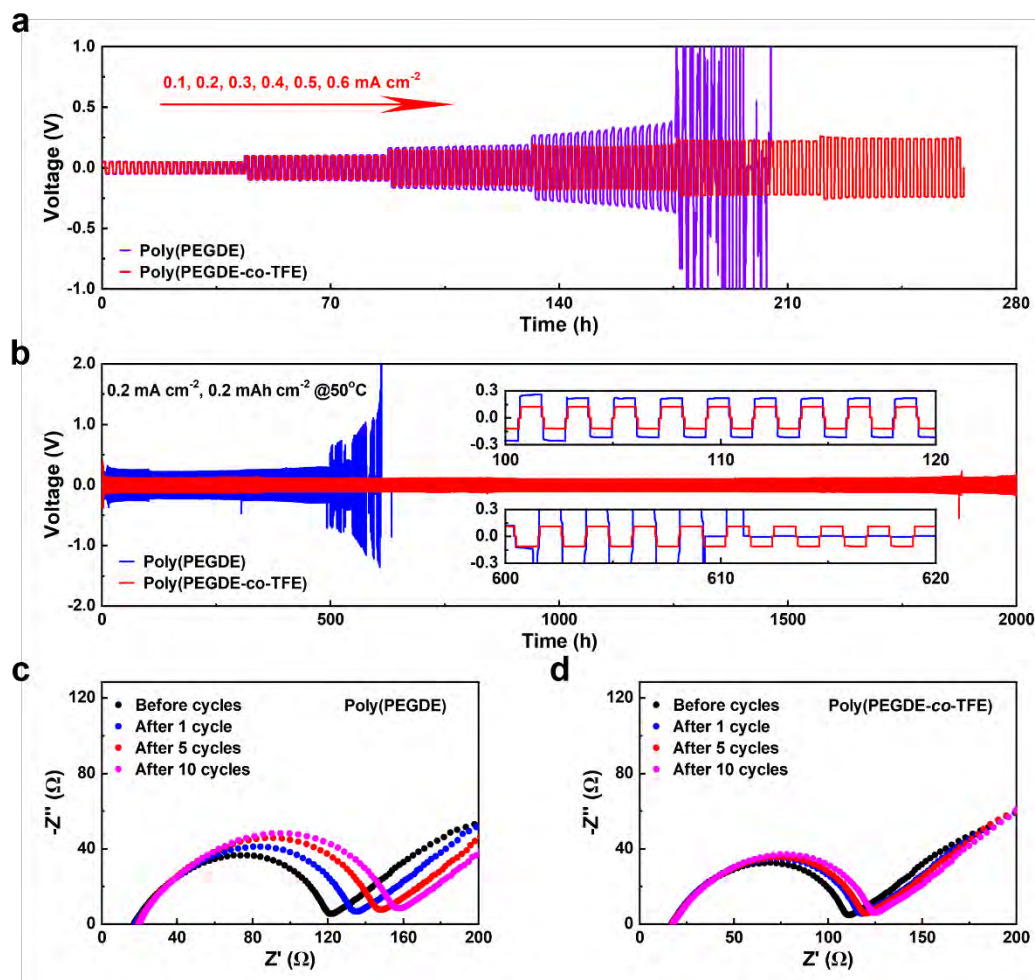


Figure 5.8 Lithium metal plating/stripping performance using symmetric Li//Li batteries with Poly(PEGDE) and Poly(PEGDE-co-TFE). (a) Rate performance of Li//Li batteries at different current densities from 0.1 mA cm⁻² to 0.6 mA cm⁻² at 50°C; (b) Cycling performance of Li//Li batteries at 0.2 mA cm⁻²; AC impedance of cycled symmetric Li//Li batteries after different cycles with (c) Poly(PEGDE) and (d) Poly(PEGDE-co-TFE).

To further compare the difference in lithium metal morphology during the plating/stripping process, cycled symmetric Li//Li cells with Poly(PEGDE) and Poly(PEGDE-co-TFE) were tested. SEM images of cycled lithium metal with Poly(PEGDE) in **Figure 5.9 a** show uneven and random deposition on the surface of lithium metal after 20 cycles at 0.2 mA cm⁻². By comparison, uniform deposition of nano-spheric lithium metal particles was observed on the surface of cycled lithium

metal with Poly(PEGDE-co-TFE) (**Figure 5.9 b**). Apart from the effect of Poly(PEGDE-co-TFE), polar PVDF-HFP can redistribute the Li-ion flux through the strong interactions between polar functional groups of PVDF-HFP and lithium metal. The aligned F atom in PVDF-HFP enhances the interaction of C-F and Li metal, favoring the lithium metal deposition¹⁵⁴. These results indicate that the abundant fluorine in Poly(PEGDE-co-TFE) contributes to the formation of stable SEI, supporting the hypothesis of fluorine moiety stabilizing the lithium plating/stripping process.

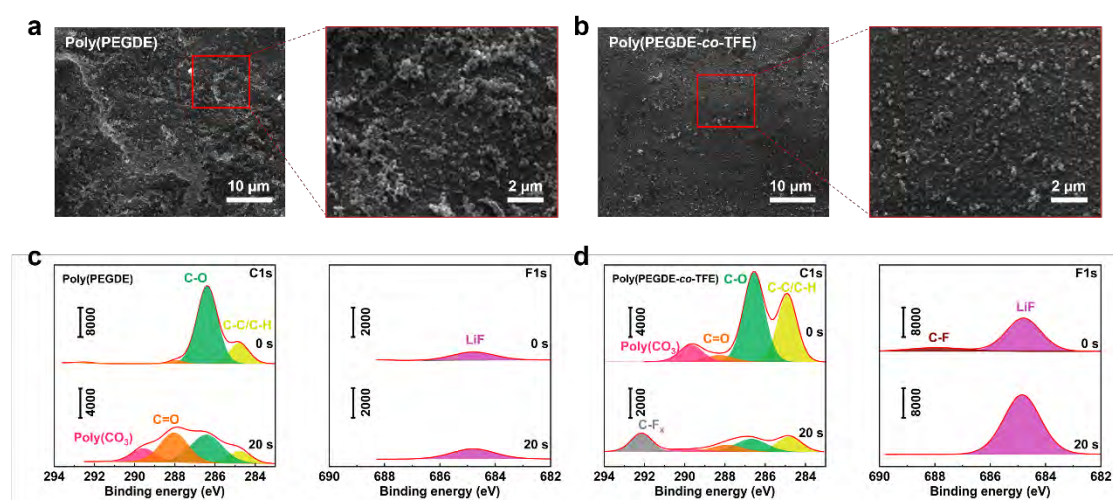


Figure 5.9 Surface of deposited lithium metal with (a) Poly(PEGDE) and (b) Poly(PEGDE-co-TFE) after 20 cycles; XPS spectra with etching depth profiles of cycled lithium metal with (c) Poly(PEGDE) and C 1s and (d) Poly(PEGDE-co-TFE) after 20 cycles.

Furthermore, XPS results confirmed the formation of the SEI layer by Poly(PEGDE) and Poly(PEGDE-co-TFE) after lithium plating/stripping for 20 cycles. For the SEI layer formed by Poly(PEGDE), the outmost layer composition in C 1s spectra (**Figure 5.9 c**) is mainly C-C/C-H at 284.8 eV, C-O at 286.5 eV and C=O at 288.1 eV¹⁵⁵. The C-O originated from RCO, such as RCOLi, and C-C-O from Poly(PEGDE). The C=O belongs to O-C=O of RCO₂Li. The inorganic components for LiF are located at 684.8 eV in F 1s. For the innermost layer of SEI etching for 20 s, the organic compounds, including C-C/C-H and RCOLi, declined. The apparent peak for Poly(CO₃) appears at

289.9 eV, decomposing from Poly(PEGDE). The increased LiF signal for the innermost layer suggests that inorganic compounds are in the innermost layer of SEI, indicating organic compounds on the outmost layer. By comparison, Poly(CO₃) exists in the outmost layer of SEI formed by Poly(PEGDE-co-TFE) (**Figure 5.9 d**). By sharp contrast, the intensity of LiF is much stronger than that in Poly(PEGDE), implying a higher percentage of inorganic compounds in the outmost layer. Meanwhile, the C-F peak at 688.2 eV was detected, indicating Poly(PEGDE-co-TFE) undergoing an electrochemical reaction with lithium metal to form SEI. In the in-depth profiles of the Poly(PEGDE-co-TFE) system, the organic components decrease along with the enhancement of LiF inorganic compounds. Inorganic compounds dominate the SEI layer in depth for the Poly(PEGDE-co-TFE) system. The results are consistent with the coordination interaction of -CF species with Li⁺. Therefore, the LiF-rich inorganic SEI layer enables the long-term lithium plating/stripping process in the Poly(PEGDE-co-TFE) system.

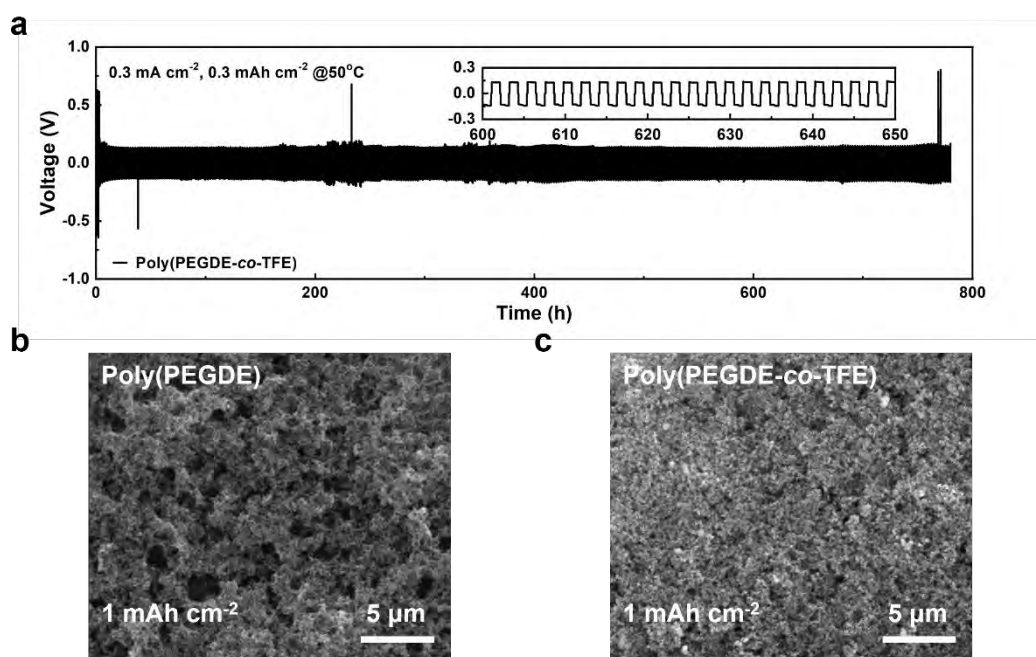


Figure 5.10 (a) Cycling performance of Li/Poly(PEGDE-co-TFE)/Li battery at 0.3 mA cm⁻²; Morphology of deposited lithium metal with (b) Poly(PEGDE) and (c) Poly(PEGDE-co-TFE).

Based on the stable SEI for Poly(PEGDE-*co*-TFE)-based symmetric Li//Li batteries, the cycle performance under a high current density of 0.3 mA cm^{-2} was evaluated. The symmetric cell with Poly(PEGDE-*co*-TFE) shows stable plating/stripping behavior up to 750 h (**Figure 5.10 a**). The above results confirm that Poly(PEGDE-*co*-TFE) exhibits stable lithium plating/stripping behavior during long-term cycling. In addition, a more dense structure of deposited lithium metal particles was obtained with Poly(PEGDE-*co*-TFE) for a capacity loading of 1.0 mAh cm^{-2} (**Figure 5.10 b**). By comparison, loose deposited lithium metal particles and large-scale voids were seen with Poly(PEGDE) (**Figure 5.10 c**).

5.3.5 Formation of stable CEI layer

Apart from the stable SEI on the lithium metal anode, Poly(PEGDE-*co*-TFE) can also promote the formation of LiF-riched cathode electrolyte interphase (CEI) on the high-voltage cathode of NCM622. The CEI components on NCM622 after 50 charge/discharge cycles were characterized with SEM and high-resolution TEM measurements. The SEM image in **Figure 5.11 a** shows that the cycled NCM 622 particle with Poly(PEGDE) maintains a smooth surface with less LiF coating. The TEM image in **Figure 5.11 b** demonstrates that a non-uniform and thick CEI layer is formed due to the excessive decomposition of Poly(PEGDE). In contrast, the prominent protective LiF-rich layer covers the cycled NCM622 in Poly(PEGDE-*co*-TFE), suppressing cracks during charge/discharge cycles(**Figure 5.11 c**). TEM image of cycled NCM622 with Poly(PEGDE-*co*-TFE) also confirmed the uniform CEI layer ($\sim 8 \text{ nm}$) after 50 charge/discharge cycles (**Figure 5.11 d**). The elemental analysis of cycled NCM622 through SEM confirmed the much higher contents of F in the Poly(PEGDE-*co*-TFE) system, leading to the LiF-rich CEI layer.

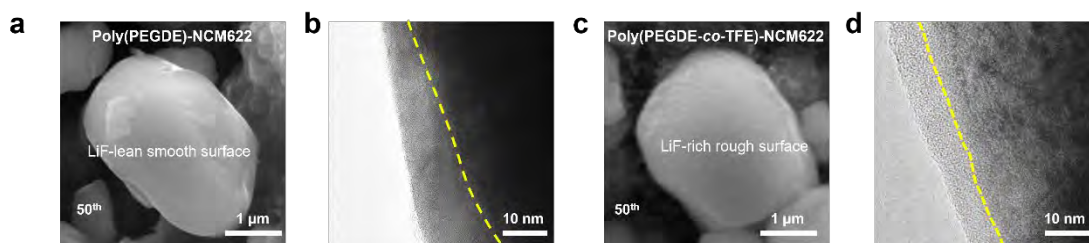


Figure 5.11 (a) High-resolution TEM and (b) SEM images of cycled NCM622 with Poly(PEGDE); (c) High-resolution TEM and (d) SEM images of cycled NCM622 with Poly(PEGDE-co-TFE).

An XPS investigation was conducted on the surface of cycled NCM622 with Poly(PEGDE) and Poly(PEGDE-co-TFE) to further analyze the chemical states and components of CEI layers after 50 cycles. Etching depth profiles in **Figure 5.12** evaluated the distribution of elements in the CEI layer on cycled NCM622 particles along with the depth. The percentage of C and F for Poly(PEGDE) varies randomly with etching depth, indicating organic species and LiF distributing non-uniformly (**Figure 5.12 a**). The non-uniform CEI in the cathode would lead to cracks and reconstructions during the charge/discharge process, resulting in the decomposition of Poly(PEGDE). However, the CEI layer of the Poly(PEGDE-co-TFE) system shows a steady trend of C and F elements distribution with a much higher atomic percent of 46% after etching 5 s (**Figure 5.12 b**). The steady trend of C, F, Li, and O in the Poly(PEGDE-co-TFE) system demonstrates that a homogenous CEI layer is formed and promotes electrolyte compatibility with NCM622 for long-term cycling stability at high-voltage regions^{65, 155}. In addition, the S content in Poly(PEGDE) is higher than that in Poly(PEGDE-co-TFE), meaning more TFSI⁻ ion decomposition during operation.

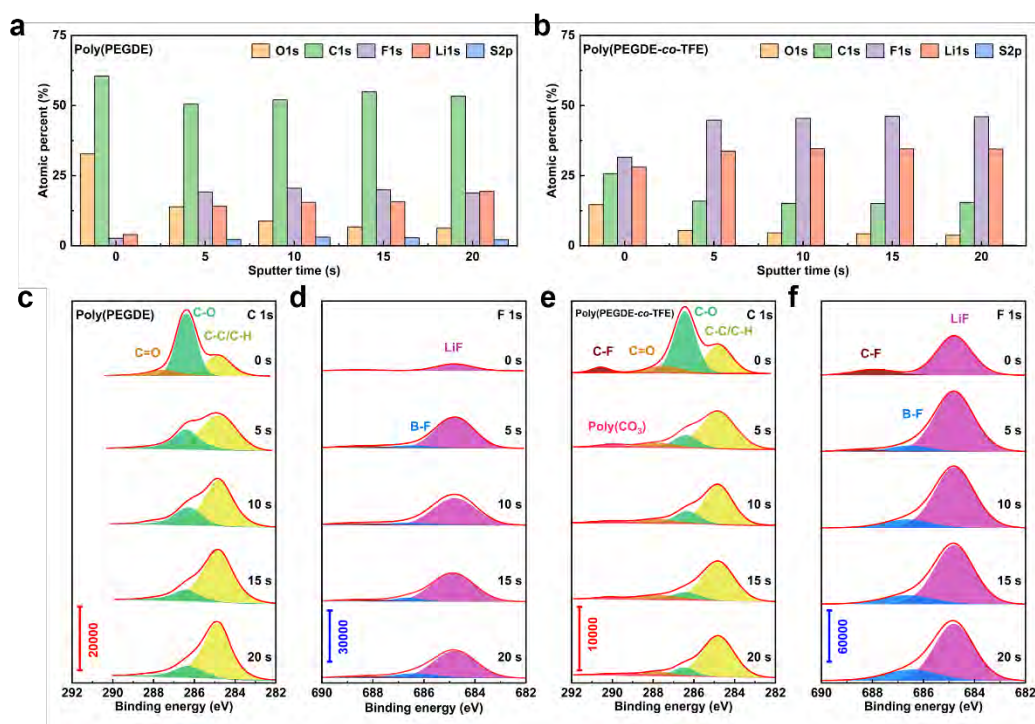


Figure 5.12 *Ex-situ* interface characterization of cycles NCM622 cathode. XPS elemental depth profiles of cycled NCM622 with (a) Poly(PEGDE) and (b) Poly(PEGDE-co-TFE); (c) C 1s and (d) F 1s XPS spectra of cycled NCM622 for Poly(PEGDE) after etching 5 s, 10 s, 15 s, and 20 s; (e) C 1s and (f) F 1s XPS spectra of cycled NCM622 for Poly(PEGDE-co-TFE) after etching 5 s, 10 s, 15 s and 20 s.

In the C 1s spectra of Poly(PEGDE), the common species of C-C/C-H (284.8 eV), C-O (286.5 eV), and C=O (288.1 eV) are presented in **Figure 5.12 c**. The organic species keep stable, though the percentage varies along the etching depth. In F 1s spectra, there is less LiF in the outmost CEI layer. However, the intensity of LiF shows a significant increase. A new peak for B-F was detected at 686.5 eV after etching 5 s, demonstrating more inorganic components participating in the formation of CEI^{156, 157} (**Figure 5.12 d**). By comparison, additional signals of Poly(CO₃) (290.1 eV) and C-F (290.6 eV) are detected in the Poly(PEGDE-co-TFE) system (**Figure 5.12 e**). The existence of C-F mainly resulted from the decomposition of TFE, supported by F 1s spectra in **Figure 5.12 f**. Except for the different species, the intensity of carbon-based substances in CEI components for Poly(PEGDE-co-TFE) is only half of that in the Poly(PEGDE) system.

While in F 1s spectra, the intensity of LiF and $\text{Li}_x\text{BO}_y\text{F}_z$ (attributed to B-F at 686.5 eV) is much higher in the Poly(PEGDE-co-TFE) system. The intensity of organic or inorganic species remains stable along the etching depth, consistent with the depth profiles of CEI in **Figure 5.12 b**. The results demonstrated that the CEI layer for Poly(PEGDE-co-TFE) is inorganic species-dominated components, organic species-dominated for Poly(PEGDE). The robust inorganic CEI layer ensures stable long-term cycling with a high-voltage NCM622 cathode for Poly(PEGDE-co-TFE).

5.3.6 Battery performance with different cathodes

The systematic electrochemical performance of Poly(PEGDE) and Poly(PEGDE-co-TFE) was evaluated with lithium metal as anode and single-crystal $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622) or LiFePO_4 (LFP), as cathodes. According to the above-mentioned wide electrochemical stability window, excellent compatibility with NCM622, and stable CEI layer, the battery performance of Li//NCM622 with the cutoff voltage of 4.2 V and 4.3 V was investigated in **Figure 5.13** and **Figure 5.14**. Setting the cutoff voltage to 4.2 V, the initial discharge capacity of Li/Poly(PEGDE-co-TFE)/NCM622 cell is 134.19 mAh g⁻¹ at 0.2C at 50°C (**Figure 5.13 a**). After the 5-cycle activation process¹²⁵, the highest discharge capacity increased to 142.95 mAh g⁻¹. The capacity retention of Li/Poly(PEGDE-co-TFE)/NCM622 cell is 76.0% after 300 cycles, higher than 42.8% for Poly(PEGDE)-based cell, indicating more stable long-term cycling performance. The initial discharge capacity of Li/Poly(PEGDE-co-TFE)/NCM622 cell at 0.1 C is 156.64 mAh g⁻¹ with initial coulombic efficiency (CE) of 87.57%, increasing to the highest capacity of 167.31 mAh g⁻¹ after 3 cycles. When the C-rate increased to 0.2 C, 0.5 C, and 1 C, the discharge capacity was 149.5 mAh g⁻¹, 126.5 mAh g⁻¹, and 98.92 mAh g⁻¹, respectively. The discharge capacity recovered to 165.83 mAh g⁻¹ when the C-rate returned to 0.1 C, implying superior cycling capability with different C-rate (**Figure 5.13 b**). By comparison, for Li/Poly(PEGDE)/NCM622 cells, the initial discharge capacity (153.69 mAh g⁻¹) and CE (80.89%) is relatively lower than that of Poly(PEGDE-co-TFE). The discharge capacity can only recover to 147.43 mAh g⁻¹

after C-rate cycling. Besides, the discharge capacity at a higher C-rate of 0.2 C, 0.5 C, and 1 C is much lower. The charge/discharge profiles of Poly(PEGDE-co-TFE)-based battery are shown in **Figure 5.13 c**. Furthermore, based on the high tolerance for higher current density, the cycle performance of Poly(PEGDE-co-TFE) is investigated at 0.5 C, delivering capacity retention of 77.6% after 200 cycles (**Figure 5.13 d**). Therefore, the long-term cycle and rate performance for Poly(PEGDE-co-TFE)-based cells are superior to Poly(PEGDE)-based cells.

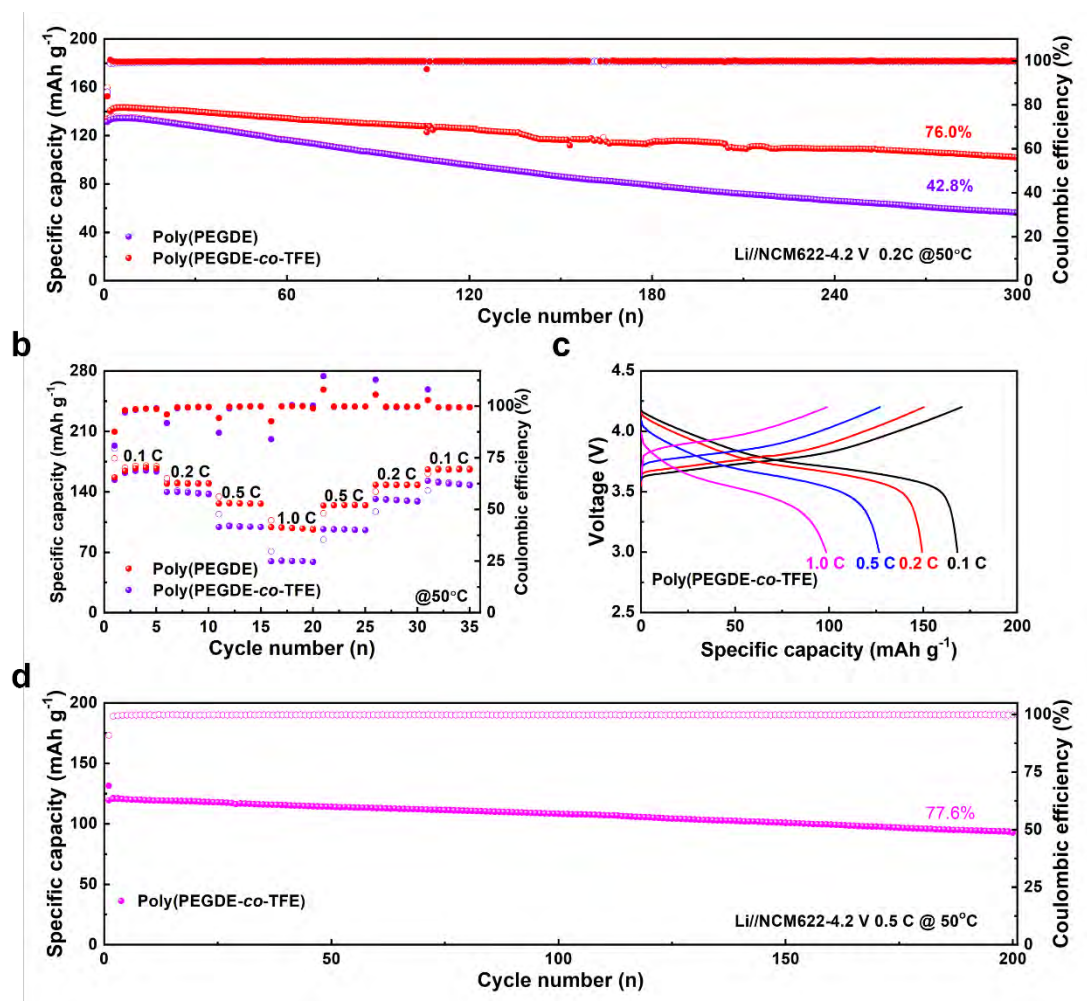


Figure 5.13 Battery performance of all-solid-state lithium metal batteries with NCM622 at 50°C (Cutoff voltage: 4.2 V). (a) Long-term cycle performance at 0.2 C; (b) Rate performance and (c) charge/discharge profiles of Poly(PEGDE-co-TFE) under different C-rate; (d) Long-term cycle performance of Poly(PEGDE-co-TFE) at 0.5 C.

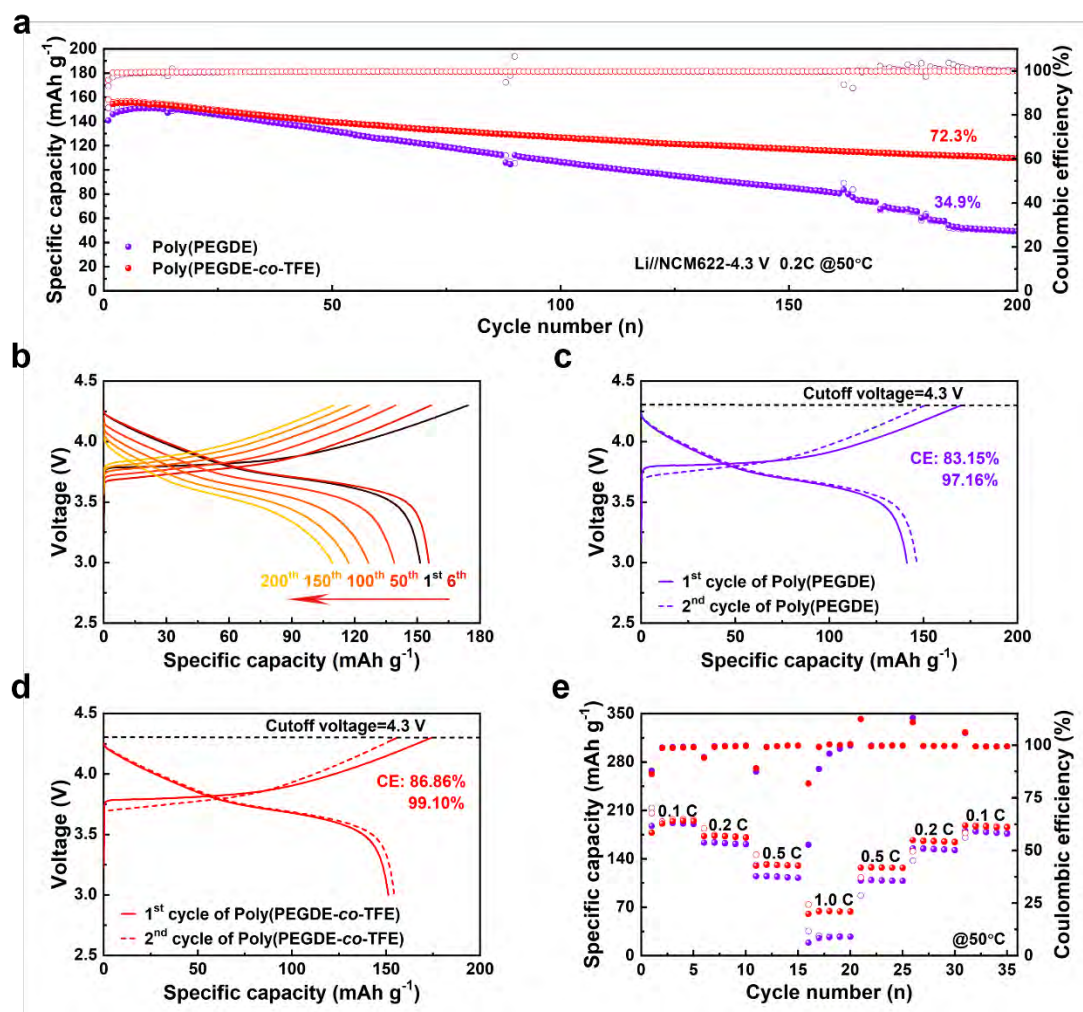


Figure 5.14 Battery performance of all-solid-state lithium metal batteries with NCM622 at 50°C (Cutoff voltage: 4.3 V). (a) Long-term cycle performance at 0.2 C, (b) Charge/discharge profiles after different cycles; The charge/discharge profiles of first two cycles for (c) Poly(PEGDE) and (d) Poly(PEGDE-co-TFE); (e) Rate performance.

The oxidation stability and compatibility with NCM622 at high voltage were further evaluated by increasing the cutoff voltage to 4.3 V. The initial discharge capacity of Li/Poly(PEGDE-co-TFE)/NCM622 cell rose to 151.23 mAh g⁻¹ with coulombic efficiency of 86.86%, higher than 140.78 mAh g⁻¹ with CE of 83.15% for Li/Poly(PEGDE)/NCM622 cell (**Figure 5.14 a**). The CE of Poly(PEGDE-co-TFE)-based cell increased to 99.10% after the second cycle (**Figure 5.14 b**). However, the CE of the Poly(PEGDE)-based cycle after the second cycle is only 97.16% (**Figure**

5.14 c). The enhancement of CE demonstrates that the formation of stable CEI for Poly(PEGDE-co-TFE) enables the cell to reach the steady cycling state earlier than Poly(PEGDE). The capacity retention of Li/Poly(PEGDE-co-TFE)/NCM622 cell at 0.2 C is 72.3% after 200 cycles, higher than 34.9% for Poly(PEGDE)-base cell. The charge/discharge profiles after different cycles are shown in **Figure 5.14 d**.

The rate performance with the cutoff voltage of 4.3 V was also evaluated at 50°C (**Figure 5.14 e**). The initial discharge of Li/Poly(PEGDE-co-TFE)/NCM622 cell at 0.1 C is much higher than that with the cutoff voltage of 4.2 V, delivering 177.86 mAh g⁻¹ with CE of 86.32%. The highest discharge capacity at 0.1 C is 194.79 mAh g⁻¹. When the current density increased to 0.2 C, 0.5 C, and 1.0 C, the discharge capacity declined to 173.08 mAh g⁻¹, 131.15 mAh g⁻¹ and 64.34 mAh g⁻¹, respectively. The discharge capacity would recover to 188.09 mAh g⁻¹ when the C-rate returns to 0.1 C, indicating excellent rate performance. For Poly(PEGDE)-based cells, the discharge capacity is 187.29 mAh g⁻¹, 163.28 mAh g⁻¹, 114.67 mAh g⁻¹, 25.12 mAh g⁻¹ at 0.1 C, 0.2 C, 0.5 C, and 1.0 C, respectively. The capacity can only recover to 180.67 mAh g⁻¹ at 0.1 C after the rate performance test, which is lower than the initial discharge capacity. It should be noted that there is an increased capacity gap at a higher C-rate of 1.0 C for these two electrolytes, which coincides with the better lithium stability of Poly(PEGDE-co-TFE) under high current density.

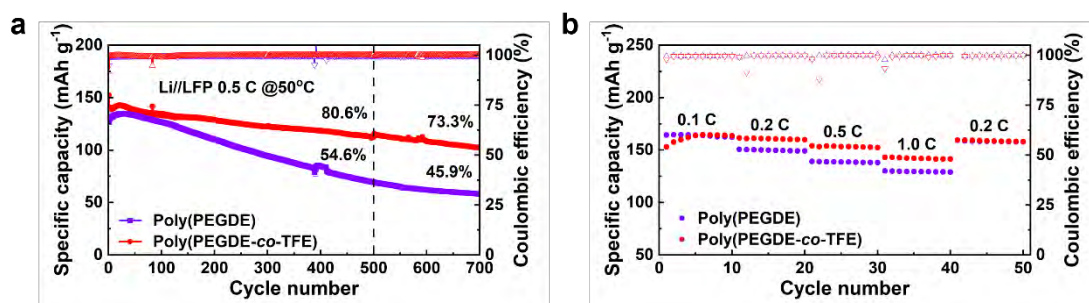


Figure 5.15 Battery performance with LFP cathode. (a) Cycle performance and (b) Rate performance.

Furthermore, the long-term cycle stability of electrolytes pairing with LFP was also investigated. As shown in **Figure 5.15 a**, the capacity retention of Li/Poly(PEGDE-co-TFE)/LFP is 80.6% and 73.3% after 500 cycles and 700 cycles, respectively. In sharp contrast, the capacity retention of Li/Poly(PEGDE)/LFP cells is only 45.9% after 700 cycles, suggesting excellent lithium stability endorsing batteries' long-term stable cycling performance. The rate performance with LFP cathode verified the better battery performance of Poly(PEGDE-co-TFE) at higher C-rate conditions (**Figure 5.15 b**).

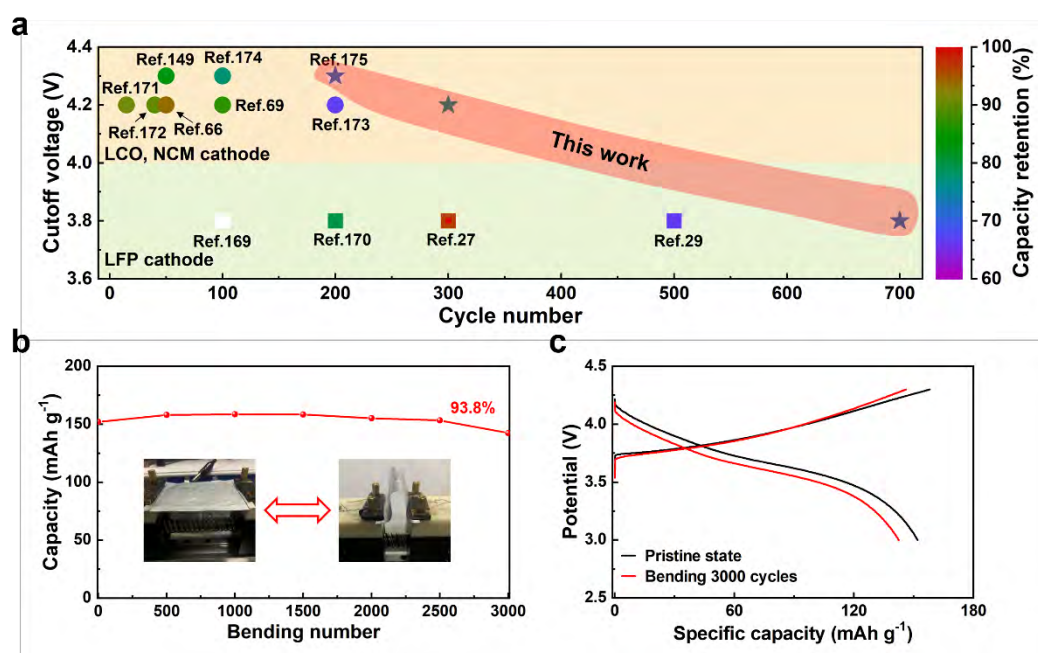


Figure 5.16 (a) Comparison of cycling performance with reported literature; (b) Flexibility of assembled pouch cell under the radius of 4.0 mm; (c) Charge/discharge profiles before and after bending test.

To highlight the excellent oxidation stability of Poly(PEGDE-co-TFE) with the high-voltage cathode of NCM622, the cutoff voltage of the cathode, cycle number, and capacity retention were compared with previously reported polyether electrolyte-based batteries (**Figure 5.16 a**)^{27, 29, 64, 67, 138, 158-164}. The assembled Poly(PEGDE-co-TFE)-based batteries show the most prolonged cycles pairing with LFP cathode. For the high-voltage cathode of NCM622, the Poly(PEGDE-co-TFE) can tolerate 300 cycles at 4.2 V and 200 cycles at 4.3 V, respectively. The capacity retention is higher than reported

work after the same cycles ¹⁶⁴. Impressively, the flexibility of Li/Poly(PEGDE-co-TFE)/NCM622 was evaluated with a textile-based pouch cell (**Figure 5.16 b**). The capacity retention is 93.8% after 3000 bending cycles with a radius of 4 mm. The charge/discharge profiles in **Figure 5.16 c** confirmed the capacity decreasing to 152.52 mAh g⁻¹, compared to the pristine state of 151.96 mAh g⁻¹. Therefore, the *in-situ* polymerized Poly(PEGDE-co-TFE) enhances compatibility with the high-voltage cathode, providing higher energy density and broadening the application in all-solid-state flexible lithium metal batteries.

5.4 Conclusion

We have proposed an effective strategy to enhance the compatibility with high-voltage cathodes for all-solid-state lithium metal batteries using fluorine-based polyether polymer electrolyte (Poly(PEGDE-co-TFE)). The increased coordination interaction of TFE with Li ions provides high conductivity, the wide electrochemical stable window, and excellent oxidation stability against the high-voltage cathode. Besides, Poly(PEGDE-co-TFE) shows remarkable long-term cycling stability at 0.2 mA cm⁻² for 2000 h during the lithium metal plating/stripping test. Based on the stable LiF-rich inorganic-dominated CEI layer, as-assembled all-solid-state lithium metal batteries (with NCM622 cathode) demonstrated outstanding cycling stability and capacity retention of 76.0% after 300 cycles. Moreover, the assembled textile-based pouch cell exhibits excellent flexibility with a capacity retention of 93.8% with a radius of 4 mm. Finally, introducing a fluorine-based component can facilitate the formation of stable SEI and CEI layer, supporting cycling stability with high-voltage cathodes.

CHAPTER 6 HIGHLY FLEXIBLE SOLID-STATE LITHIUM BATTERIES ENABLED BY NICKEL-COATED PET FABRIC

6.1 Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used in smart devices, electric cars, and energy storage systems in recent years^{165, 166}. However, the output voltage of the unit cell is around 3.0 V, much lower than the required voltage of devices. Therefore, high-voltage modules for large-scale energy storage devices must pack the unit cells in-series together to reach the high output voltage¹⁶⁷. For the LIBs system, the bipolar design should be conducted outside the unit cells, connecting in series by external wires after the individual is sealed and packed. The external connecting is mainly attributed to the leakage of liquid electrolytes, causing internal ions to short-circuit. By comparison, in a solid-state system, the solid-state electrolytes having no fluidic feature enable the bipolar design to realize the inner battery package without sealing and packaging individual cells^{84, 168}. There are three main advantages of internal bipolar configuration. Firstly, eliminating extra current collectors, individual packages, and externally connected wires can enhance volumetric and gravimetric energy density^{169, 170}. Besides, the polarization potential is related to the resistance of stacked modules. In a solid-state bipolar system, the resistance only includes the electrolytes, electrodes, and interface of electrode/electrolytes compared to the extra resistance of external connectors in a liquid battery system¹⁷¹. Furthermore, the current and electron can flow through the stacked cells vertically instead of the small terminal taps of unit cells. Current and electron distribution over the surface of electrodes can suffer from higher current density and avoid overheating, which would cause fire and safety concerns¹⁷¹⁻¹⁷⁴.

According to the advantages mentioned above of internal bipolar configuration, the

solid-state battery system with lithium metal anode is the best choice to realize the ideal concept^{23, 175}. Many efforts have been made to implement the bipolar configuration¹⁷⁶⁻¹⁷⁸. Since the electrochemical alloy reaction between commercial Al foil and lithium metal, researchers studied the bipolar solid-state batteries using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as the anode, including polymer and inorganic electrolytes^{21, 22, 82, 177, 179, 180}. Promoting the development of bipolar configuration in solid-state batteries, a suitable bipolar substrate should be applied to prevent the internal short circuit between adjacent cells. The bipolar substrates feature high electronic conductivity and chemical/electrochemical stability against reductive lithium metal and oxidative cathodes. Surficial passivated stainless steel (SS) is widely used in coin-type cells, which are relatively stable with lithium metal anode^{24, 86, 181}. So, SS was introduced to connect unit cells for assembling bipolar batteries, though leading to higher contact resistance and capacity decays rapidly^{25, 182-184}. Apart from SS, the Cu current collector can also support lithium metal to connect adjacent cells⁸⁴. The extra bipolar substrates increase the resistance of whole bipolar batteries and result in poor battery performance²⁴. The cathode slurry coated on the surface of SS and connected to the lithium metal anode of adjacent cells can simplify fabricating bipolar batteries. This way, the cathode materials and lithium metal can share the same current collector in bipolar batteries⁸⁷. Such approaches have improved the electrochemical performance of bipolar batteries. However, SS has a relatively high contact resistance passivation layer, decreasing the conductivity of the electrode materials. Besides, the element of Fe may diffuse into the cathode and cause a capacity decline significantly^{79, 185}. These shortcomings of SS lead to the limitation of long-term cycle stability.

According to our previous work, types of metal such as Cu, Ni, and Ag can be deposited on the textile fabric through polymer-assisted metal deposition (PAMD) methods^{91, 186, 187}, promoting strong adhesion between fabrics and metal particles. Nickel metal has been used for negative electrodes and can stabilize up to 4.5^{90, 188}. The textile-based metallic fabric as a current collector suppresses lithium dendrite growth in LIBs and could endow the batteries with excellent flexibility^{99, 189}. Because of the rigid current

collector, evaluating the flexibility of solid-state batteries is restricted to performed systematically. Only a few pieces of literature characterized the flexibility under different bending angles without the bending process on pouch cells^{29, 30, 103}. Employing a metallic fabric current collector in solid-state batteries could provide mechanical strength and excellent flexibility for application in wearable devices.

Herein, a PET-based current collector (Ni-PET) was fabricated through the PAMD method, nickel nanoparticles growing on the fiber of PET chemically. The thin nanolayer of 300 nm metallic nickel retains excellent flexibility and resistance unchanged during 10000 bending cycles under a bending radius of 5.0 mm. The assembled monopolar solid-state battery exhibits similar rate performance and superior long-term performance at 0.5 C, with capacity retention of 85.4% after 500 cycles. Given the excellent compatibility between Ni-PET and lithium metal, internal bipolar solid-state batteries are fabricated by connecting adjacent unit cells directly without any bipolar substrates. In this case, the bipolar batteries deliver 126.0 mAh g⁻¹, with a capacity retention of 92% after 250 cycles. The flexibility of bipolar pouch cells is evaluated systematically. Due to resistance declining, the discharge capacity slightly increases after bending 200 cycles with a bending radius of 5.0 mm. The pouch cell can usually cycle during dynamic bending tests. Therefore, using Ni-PET as a current collector in solid-state batteries not only simplifies the process of bipolar pouch cell assembly but also provides excellent flexibility for application in wearable devices.

6.2 Experimental Sections

6.2.1 Materials and instruments

Materials: The major agents used in the research project are listed as follow: 3-(trimethoxysilyl)propyl methacrylate (MPTS, 98%, Sigma-Aldrich), acetic acid (100%, Acros), [2-methacryloyloxy)ethyl] trimethylammonium chloride solution (METAC, 75wt %, Sigma-Aldrich), potassium persulfate (KPS, 99.5%, Uni-Chem),

ammonium tetrachloropalladate(II) (Pb 37%, Alfa Aesar), tri-Sodium citrate dihydrate (99.5%, Fisher Chemicals), Nickel (II) Sulfate (AR, Uni-Chem), dimethylamine borane (98%, J&K), L(+)-Lactic acid (90%, Acros), Ethyl Alcohol, sodium hydroxide (97%, Uni-Chem), copper(II) sulfate pentahydrate (99.0%, Uni-Chem), potassium sodium tartrate tetrahydrate (99.5%, Sigma-Aldrich), formaldehyde solution (37% - 41%, BDH), Poly(ethylene glycol) methyl ether acrylate ($M_n=480$, PEGDMA, Sigma-Aldrich), 2-Hydroxy-2-methylpropiophenone (HMPP, 97%, Sigma-Aldrich),

Instruments: UVP high-intensity UV lamps (100 W, Analytic Jena) for polymer electrolyte UV-polymerization, Slurry casting machine (MSK-AFA-HC100, Shenzhen Kejing) for casting slurry on the current collector, Argon-filled Glove boxes (H_2O and $O_2 < 0.5$ ppm, Vigor) for assembling batteries, Battery testing system (Neware) for battery performance testing, Compact Vacuum Sealer (MSK-115A-S, Shenzhen Kejing) for pouch cell assembling, CHI600E electrochemical workstation for electrochemical properties testing, Keithley 2400 for resistance monitoring and recording; Scanning Electron Microscope (Tescan VEGA3) for morphology observing, X-ray Diffractometer (9 kW, Rigaku SmartLab) for structure verifying. Instron 3365 instrument for mechanical characterization testing of substrates. Translation stage (TSA50-C, ZOLIX INSTRUMENTS CO., LTD) for flexibility test.

6.2.2 Experiments

Preparation of nickel-coated PET fabrics (Ni-PET): The available PET fabric was pretreated in 2 M NaOH for 2 h at 80°C to improve hydrophilic properties. Then, the treated PET fabric was washed to neutral with DI water, followed by four steps PAMD process. Firstly, the treated PET fabric was immersed into 4% (v/v) 3-(trimethoxysilyl) propyl methacrylate solution (solvent: 95% EtOH, 1% acetic acid, and 4% DI water) for 1 h at room temperature. After washing three times with DI water, the siliconized PET fabric was put into the mixture of [2-(methacryloyloxy)ethyl]trimethyl ammonium chloride (METAC) (20% v/v in water), adding potassium persulfate (2 g L^{-1}) as initiator.

Afterward, the branched polymer was grafted onto the PET fabric at 80°C for 1h. After washing, the PET fabric was dipped into a 5 mM (NH₄)₂PdCl₄ solution in a dark place for 30 min for an ion-exchange reaction to coat [PdCl₄]²⁻ catalyst on the substrate. The [PdCl₄]²⁻ loaded PET was immersed into an electroless deposition bath consisting of solutions A (NiSO₄·6H₂O, 40 g L⁻¹; sodium citrate, 20 g L⁻¹; lactic acid, 10 g L⁻¹) and solution B (DMAB, 1 g L⁻¹). Solution B was dropped into solution A slowly until the resistance of the sample was about 1.0 Ω.

Preparation of polymer and composite solid-state electrolyte: The specific amount of LiTFSI was dissolved into the monomer of PEGDMEMA, and then 2 wt% HMPP as a photoinitiator was added into the precursor. The molar ratio of LiTFSI and EO functional groups is 1:20. After stirring to get a homogeneous solution, the precursor solution was poured onto the Teflon plate and UV-polymerized with the irradiation of UV Lamps for 2 h. Finally, a free-standing polymer electrolyte membrane was obtained for electrochemical characterization. The LLZTO powder was introduced after LiTFSI dissolved into the PEGDMEMA for organic and inorganic composite electrolytes. After stirring overnight, 2 wt% HMPP was added, a UV-polymerized process was conducted, and a free-standing composite electrolyte was obtained for further characterization.

Assembling typical monopolar battery and bipolar battery: First, the cathode was prepared with the Ni-PET current collector. 0.018 g LiClO₄ and 0.132 g PEO were dissolved into 4.5 g ACN. After getting a homogenous solution, 0.075 g Super-P and 0.525 g LFP were added to the above solution. After stirring overnight, the slurry was cast onto the Ni-PET. Then, the sample was put in a vacuum oven at 60°C overnight. Then, the CR-2025-coin cells are assembled to evaluate the battery performance. The bipolar battery was built with two individual monopolar cells, and the cathode of the upper one was connected with the anode of the bottom one directly. The battery performance was evaluated on the Neware testing system.

Preparation of flexible pouch cell: Several pouch cells were assembled to investigate

the flexibility of PET-based solid-state batteries. As the limitation of the flexibility of lithium foil, Cu-PET hosting lithium metal composite anode was prepared through electrochemical deposition. After the composite anode was washed and dried, the PET-based pouch cells were assembled to evaluate the flexibility.

6.3 Results and Discussions

6.3.1 Organic/inorganic composite polymer electrolyte

The concentration of lithium salt in polymer electrolytes affects the ionic conductivity. The molar ratio of EO: Li⁺ was first studied. As shown in **Figure 6.1 a**, the polymer electrolyte with EO: Li⁺=20:1 was equipped with the highest ionic conductivity of $5.14 \times 10^{-5} \text{ S cm}^{-1}$. The mechanism is that EO functional groups assist the lithium-ion transport. For polymer electrolytes, the segmental motion of polymer chains assists in the migration of lithium-ion, hopping from one coordination site to another ¹⁹⁰. A moderate concentration of lithium salt contributed to the highest ionic conductivity. The coordinating site is more than the free lithium-ion when the EO: Li⁺ is lower than 20:1. Increasing lithium salt leads to more coordinating lithium-ion. Once the lithium salt exceeds critical mass, more free lithium-ion would aggregate, and lithium-ion is trapped into the polymer chains, leading to lower ionic conductivity.

The ionic conductivity of composite electrolytes with different mass ratios is depicted in **Figure 6.1 b**. The optimized composite polymer electrolyte is achieved with an LLZTO content of 10%, exhibiting the highest ionic conductivity of $9.1 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. As reported in literature ¹⁹¹, the dispersed LLZTO oxide particles can facilitate the segmental motion of polymer chains, increase lithium-ion mobility, and decrease the crystalline region of the polymer electrolytes. After introducing the ceramic LLZTO particles, the Li⁺ in LLZTO can be absorbed by the polymer, considering that the polymer may dilute the lithium salt by as much as 50 wt%. This effect increases the lithium-ion vacancies, which are mobile carriers on the surface of

LLZTO, thus increasing the overall ionic conductivity in combination with the highly conducting LLZTO bulk. As a result, the percolation effect is believed to play an important role in enhancing ionic conductivity.

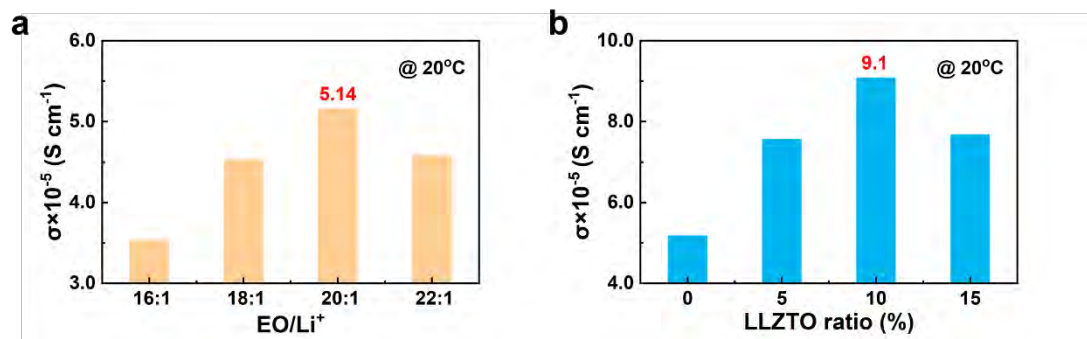


Figure 6.1 The electrochemical properties of composite polymer electrolyte. (a) Optimization of ionic conductivity with different concentrations of lithium salt; (b) Optimization of ionic conductivity with varying ratios of the weight of ceramic electrolyte LLZTO.

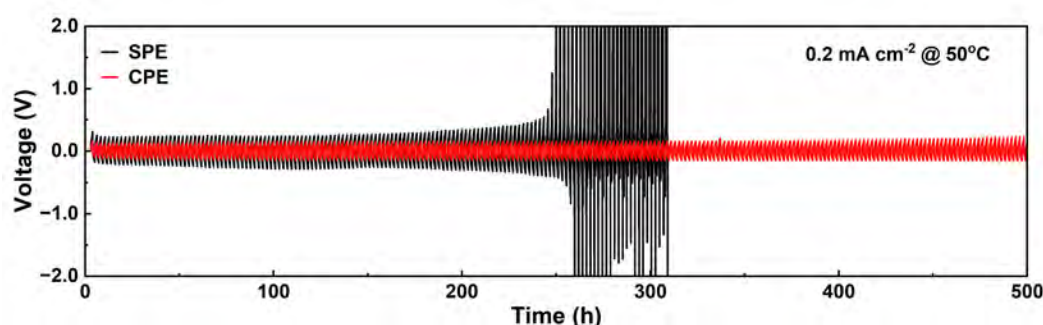


Figure 6.2 Lithium depositing and stripping of batteries with pure polymer electrolyte and composite polymer electrolyte under a current density of 0.2 mA cm⁻².

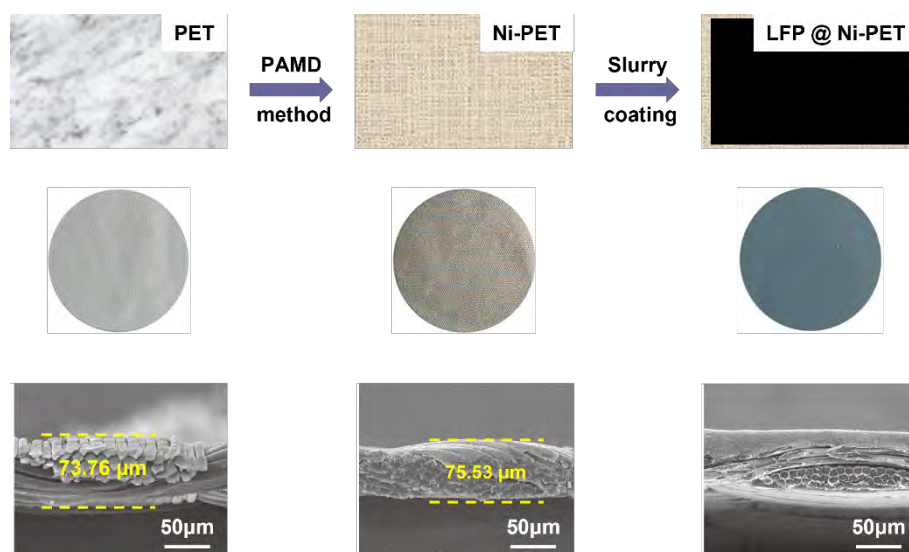
Subsequently, the galvanostatic long-term cycling performance of the symmetric batteries with pure polymer electrolyte and composite polymer electrolyte was evaluated at $J=0.2 \text{ mA cm}^{-2}$ (**Figure 6.2**). Long-term cycling performance is to assess the compatibility of solid-state electrolytes with lithium metal anode. Lithium ions are deposited on or stripped from lithium metal during cycling, forming a solid electrolyte interface. In the initial cycles, the potential of CPE and SPE stabilize at 0.07 V and 0.113 V, respectively. After cycling 200 h, the potential of the battery with SPE

increases continuously and reaches 5 V, meaning ultra-high resistance. In contrast, the potential of the battery with CPE stabilizes below 0.2 V after 550 h cycles. The results indicate that CPE is more compatible with lithium metal anode than SPE.

6.3.2 Fabrication of Ni-PET-based cathode

The current collector is an essential component of lithium batteries. In conventional battery systems, aluminum foil is the best substrate for host cathode materials due to its highly conductive nature. However, commercial aluminum foil is rigid, and its flexibility is restricted. Searching for highly flexible substrates is urgent for flexible batteries. Poly (ethylene terephthalate) (PET) is a woven textile fabric with high flexibility and mechanical strength after metal coating. Therefore, metal-coated PET fabric is an excellent alternative to commercial aluminum foil for flexible batteries^{192,}

193.



Scheme 6.1 Schematic illustration of fabricating Ni-PET-based cathode.

The optical photographs of PET fabric and Ni-PET substrate are shown in **Scheme 6.1**. The pristine PET fabric is white and well-woven parallel and vertically. The fabric yarns pass under and over the neighboring yarns. After nickel coating through the PAMD method¹⁸⁶, the substrate is fully covered with nickel particles, showing a metallic color. Apart from the macroscopical color changes, the weaving structure remains unchanged.

In order to confirm the metallic nickel layer on the fiber's surface, SEM testing was conducted to detect the thickness of change before and after nickel coating. The thickness increases to 75.53 μm from 73.76 μm of the PET fabric. Due to the dense weaving structure of PET fabric, the LFP cathode slurry would coat the surface of the Ni-PET current collector.

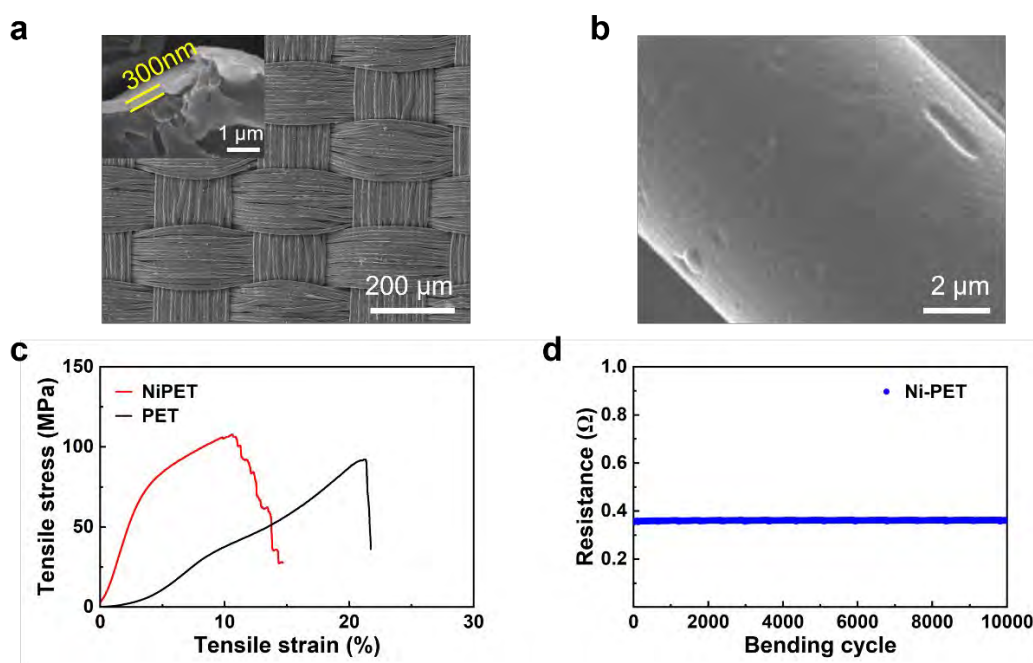


Figure 6.3 Physical characterization of Ni-PET. (a) SEM image of Ni-PET (inset: cross-section of coated fiber); (b) SEM image of fibers on the Ni-PET fabric; (c) Tensile stress-strain curves of pristine PET and Ni-PET; (d) Resistance change of Ni-PET after different bending cycles with the radius of 5 mm.

As shown in **Figure 6.3 a**, the weaving structure is stable after the PAMD process. The thickness of the Ni layer on the PET fabric is around 300 nm. The nano-nickel particles are deposited on the surface of PET fibers (**Figure 6.3 b**). The mechanical properties of Ni-PET are an essential parameter for battery current collectors. The tensile stress-strain of PET and Ni-PET fabrics were characterized. As shown in **Figure 6.3 c**, the tensile strain of pristine PET is about 21.3%, and the tensile stress is around 92.2 MPa. After metallic coating, the tensile strain of Ni-PET decreases to about 10.6%, and the tensile stress increases to 103.4 MPa. Although the tensile strain decreases slightly, the

tensile stress increases, leading to Young's modulus increasing to 2013.3 MPa from 601.8 MPa of pristine PET fabric. Young's modulus increases three times a lot. Apart from the mechanical enhancement, the Ni-PET substrate shows excellent electrochemical stability after a series of bending cycles. As shown in **Figure 6.3 d**, the resistance of Ni-PET is stable, and there is no increase after bending 10000 cycles with a radius of 5 mm. The above results indicate that Ni-PET is an excellent alternative to commercial aluminum foil acting as a current collector in the battery system.

6.3.3 Comparison of battery performance with Ni-PET and Al CC

The electrochemical performance of batteries employing Ni-PET and Al current collectors, LFP as cathode and Li metal as anode, were evaluated at 50°C. **Figure 6.4** shows the rate performance of two kinds of current collectors within the voltage range of 3.0 V ~ 3.8 V from 0.1 C to 1.0 C. The maximum discharge capacity is 154 mAh g⁻¹ for Ni-PET and Al CC. It should be pointed out that the battery with Ni-PET CC needs more cycles to activate the lithium-ion transport pathway. Current density increasing, the discharge capacity of Ni-PET based battery is 149 mAh g⁻¹, 138 mAh g⁻¹, and 118 mAh g⁻¹ at 0.2 C, 0.5 C, and 1.0 C, respectively. After the activation process, the discharge capacity of Al is similar to Ni-PET-based batteries. Furthermore, when the current density returns to 0.2 C, the discharge capacity can go back to 147.10 mAh g⁻¹ for a Ni-PET-based battery, slightly higher than that of an Al-based battery (146.03 mAh g⁻¹). The results above show that Ni-PET and Al CC batteries deliver similar discharge capacities. After undergoing rate cycles, the battery performance of Ni-PET CC is better than Al CC.

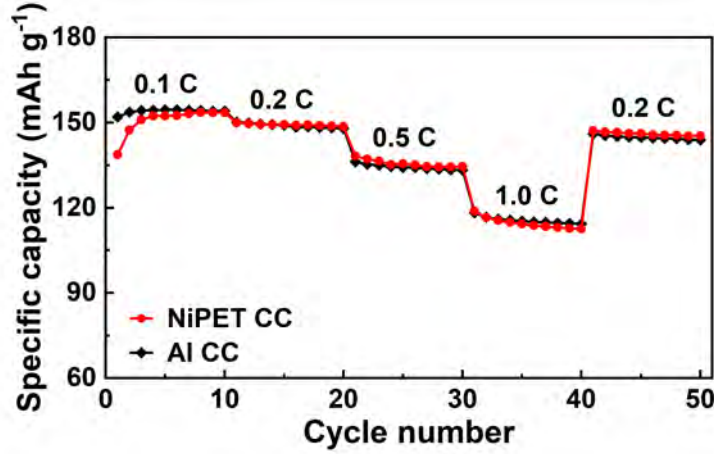


Figure 6.4 Rate performance of batteries with Ni-PET and Al current collector.

Based on the longer activation process of Ni-PET CC, the kinetic analysis of batteries with Ni-PET and Al foil was carried out to demonstrate the advantages of porous Ni-PET fabric. CV curves of batteries with Ni-PET and Al current collectors were characterized with various sweep rates of 0.02-0.10 mV s⁻¹ in the 2.8-3.8 V range at 50°C (**Figure 6.5 a, d**). The peak current and polarizing voltage increase with the scanning rate increasing for all the batteries. To compare the lithium-ion diffusion more correctly, the lithium-ion diffusion coefficient (D_{Li}) is calculated according to the Randles-Sevick equation ¹²⁴:

$$i_p = 2.68 \times 10^5 n^{3/2} A (D_{Li})^{1/2} C_{Li} v^{1/2}$$

According to the equation, the value of D_{Li} is related to the slope of $i_p/v^{(1/2)}$. The larger the slope is, the higher D_{Li} is. In the charging process, the slope of the battery with Ni-PET is the same as that with Al. It means that, for the oxidation process, the lithium-ion diffusion is constant after changing to a porous Ni-PET current collector (**Figure 6.5 b, e**). For the discharging cycle, the value of slope for the Al current collector is higher than that with Ni-PET. The above results indicate that lithium-ion diffuses faster with Al current collector than Ni-PET.

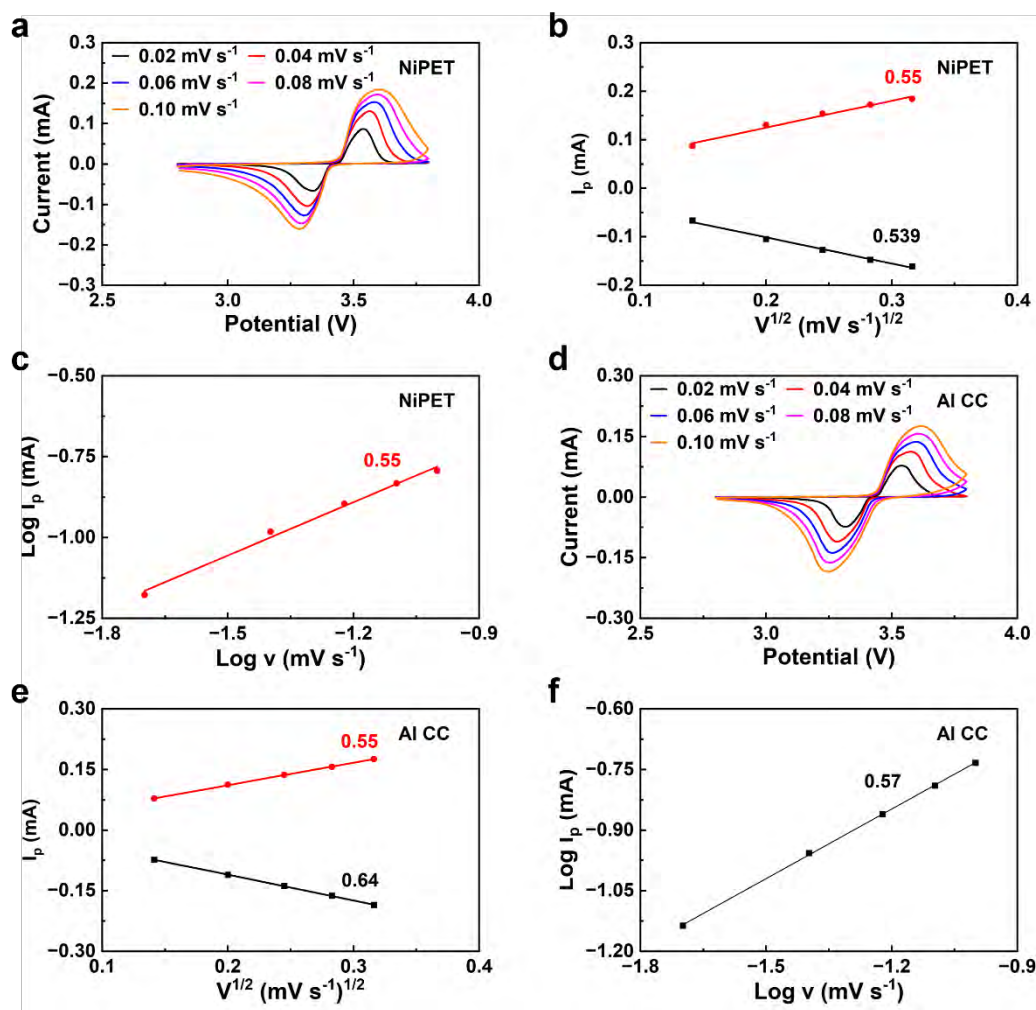


Figure 6.5 CV curves of (a) Ni-PET and (d) Al current collector at different scanning rates; the corresponding relationship between peak current and square root of scanning rate for (b) Ni-PET and (e) Al foil; the linear fitting plot of log (peak current) vs. log (scanning rate) for (c) Ni-PET and (f) Al foil.

The difference in kinetics can be further analyzed by the power law equation ¹⁹⁴:

$$\text{Log}(i_p) = b \log(v) + \log(a)$$

In the equation, the meaning of i_p and v is the same as the Randles-Sevick equation. a and b are the fitting parameters. The b value of 0.5 represents a diffusion-controlled behavior (intercalation process), while the value of 1.0 represents the surface-mediated behavior (capacitive process). For the two kinds of current collectors, the b values are all higher than 0.5, indicating surface-mediated electrochemical reaction kinetics. According to the results above, the lithium-ion diffusion coefficient for Ni-PET and Al

is the same. The b value mainly compares corresponding to the discharging process. The b value for Al current collector is higher than that of Ni-PET (**Figure 6.5 c, f**). Therefore, the cathodic reaction is faster with the Al current collector under operation. The cathode materials would penetrate the pores for a porous Ni-PET current collector, and the lithium-ion transport method is limited.

According to the rate performance, the batteries with Ni-PET CC need more cycles to activate to maximum capacity. Therefore, the cycle performance of Ni-PET and Al CC batteries was investigated to reveal the activation process at different current densities. As shown in **Figure 6.6 a, b**, the initial discharge capacity is 151 mAh g^{-1} with an initial coulombic efficiency of 96.16% for Al CC, while the initial discharge and coulombic efficiency is 138 mAh g^{-1} and 85.73% for Ni-PET CC. After the activation process, the batteries with Ni-PET and Al CC all reach the same highest discharge capacity. However, it takes 8 cycles to activate Ni-PET, just 5 cycles for Al CC.

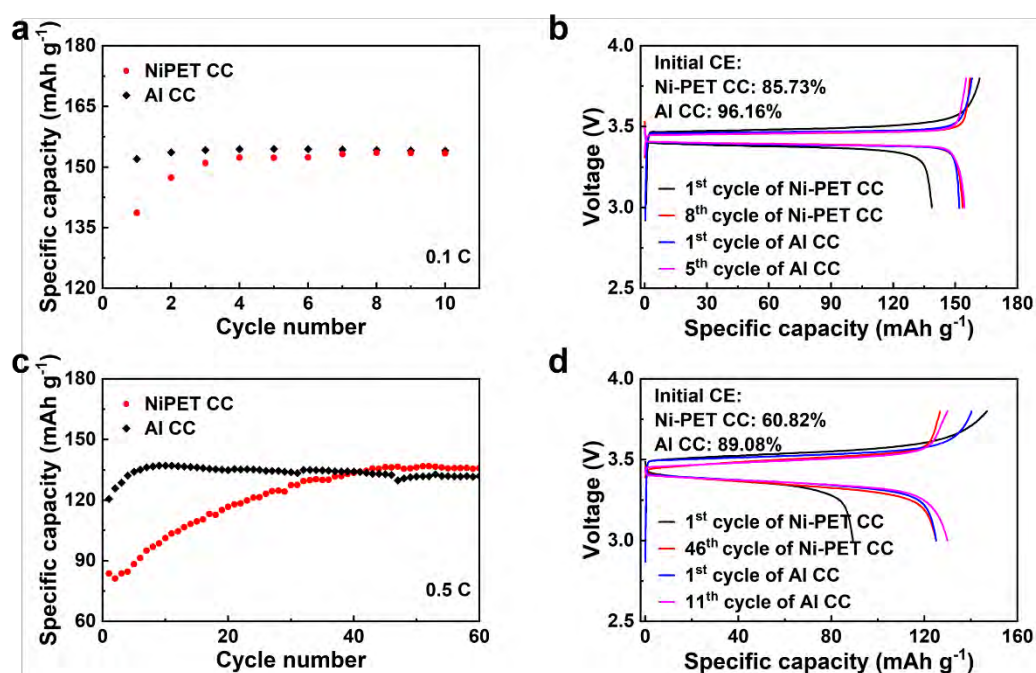


Figure 6.6 Cycle performance of Ni-PET and Al CC. (a) Discharge capacity at 0.1 C; (b) Charge/discharge profiles at 0.1 C; (c) Discharge capacity at 0.5 C; (d) Charge/discharge profiles at 0.5 C.

When the current density increased to 0.5 C, the initial discharge capacity and coulombic efficiency were 128 mAh g⁻¹ and 89.08% for Al CC, much lower than that at 0.1 C. For Ni-PET CC, the initial discharge capacity is only about 90 mAh g⁻¹, with an initial coulombic efficiency of 60.82% (**Figure 6.6 c, d**). Afterward, the discharge capacity increases continuously until up to 132 mAh g⁻¹, with coulombic efficiency of nearly 100%. The results indicate that the battery with Ni-PET CC takes more cycles to activate the lithium-ion transport pathway. This activation process may be attributed to the porous structure of Ni-PET CC, in which the cathode penetrates inside the pores, and the connection between particles is incontinuous. After the activation process, the lithium-ion transport pathway was well constructed, and the battery performance is the same as that with Al CC ¹²⁵.

The long-cycle performance of batteries with Ni-PET CC is vital for solid-state batteries. The cycle performance of batteries with two kinds of current collectors is shown in **Figure 6.7**. For batteries with Ni-PET CC, though the initial discharge capacity is only about 90 mAh g⁻¹ at 0.2C, the discharge capacity increases in subsequence. After the activation process, the discharge capacity increases to 126 mAh g⁻¹. The capacity retention is about 98.2% after 150 cycles, according to the highest discharge capacity. While for the battery with Al CC, the initial discharge capacity is 123 mAh g⁻¹, which is much higher than that with Ni-PET CC. After several cycles of activation, the discharge capacity reaches the highest capacity of 129.8 mAh g⁻¹. However, the discharge capacity fades away slightly. After 150 cycles, the capacity retention is 82.3%, slightly lower than Ni-PET CC's (**Figure 6.7 a**). The cycle performance at 0.5 C confirms the cyclic stability of batteries with Ni-PET CC, delivering capacity retention of 90.3% and 73.1%, respectively, after 250 cycles (**Figure 6.7 b**). The stable long-term performance is probably attributed to the strong adhesion of LFP to the Ni-PET current collector.

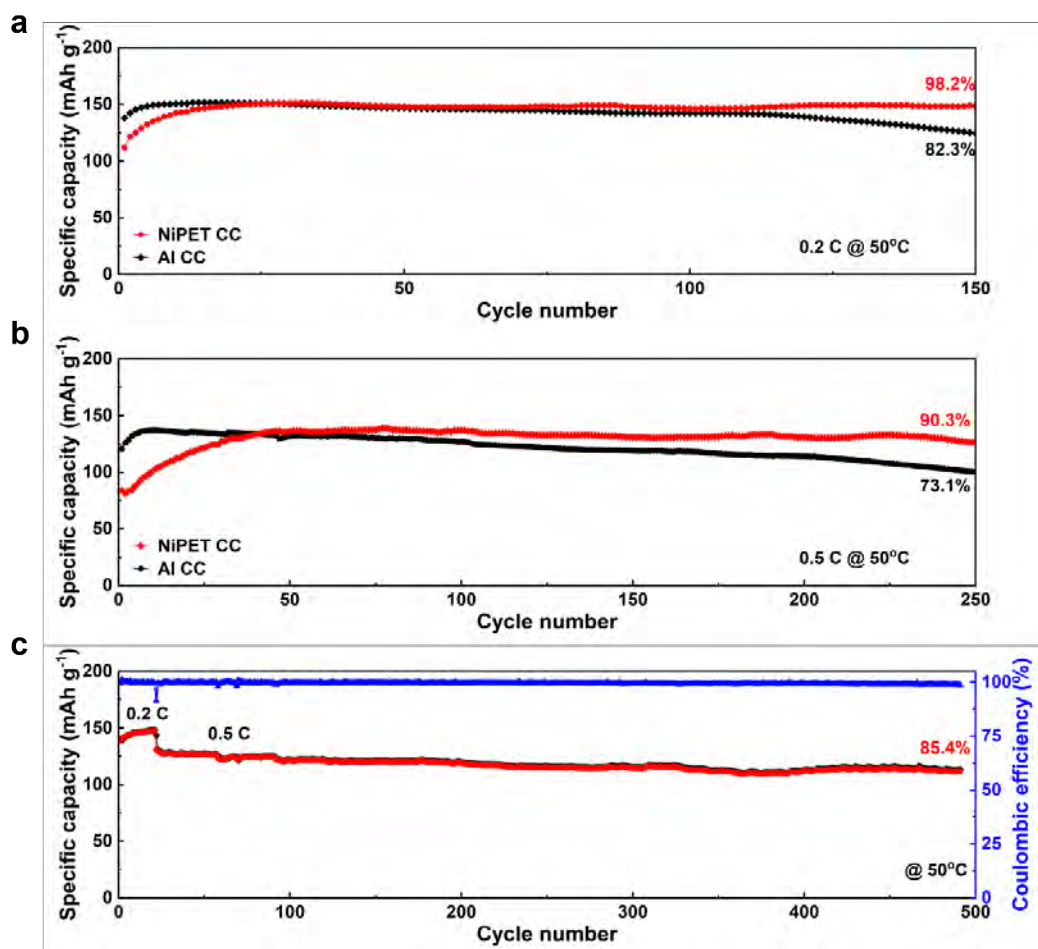


Figure 6.7 Battery performance with Ni-PET CC. Comparison of cycle performance of batteries with Ni-PET and Al CC at (a) 0.2 C and (b) 0.5 C; (c) Long-term cycle performance of battery with Ni-PET CC at 0.5C.

As aforementioned, it takes more cycles to activate the lithium-ion transport pathway for batteries with Ni-PET CC. In this way, the battery cycling at a higher current density should first cycle with a lower density of 0.2 C. The battery with Ni-PET CC delivers about 150 mAh g⁻¹. After changing the current density to 0.5 C, the discharge capacity decreases to 136.4 mAh g⁻¹. The capacity retention at 0.5 C is about 85.4% after around 500 cycles (**Figure 6.7 c**). The above results indicate that Ni-PET CC is suitable for acting as a solid-state battery system current collector.

6.3.4 Flexibility of pouch cell with Ni-PET CC

Introducing Ni-PET CC endows the cathodic electrode flexibility compared to the commercial Al CC. For solid-state battery systems, rare literature systematically reported pouch cell flexibility. They only investigated the battery performance with specific bendable angles. To evaluate the flexibility of the battery with Ni-PET CC, a pouch cell with a size of 2×3 cm was assembled. Firstly, the pouch cell cycles with 0.2 C at 50°C, delivering about 140 mAh g⁻¹ for initial discharge capacity with coulombic efficiency of 85.9%. After several cycles of the activation process, the discharge capacity increases to 151.8 mAh g⁻¹ and then cycles stably. The bending process was exerted on the pouch cell after 20 cycles. The bending radius of the flexible experiment is 5.0 mm. After bending 200 cycles, the pouch cell was placed in the oven for 5 h. Afterward, the strain of the pouch cell was released and set for another 20 cycles. Interestingly, the discharge capacity shows a slight increase. The discharge capacity increased from 151.75 mAh g⁻¹ to 153.93 mAh g⁻¹ (**Figure 6.8 a**). By comparing the charge and discharge profiles before and after the bending test, the polarizing voltage decreases to 0.105 V from 0.117 V (**Figure 6.8 b**). Looking into the underlying reason, the AC impedance of the pouch cell before and after the bending test was performed on the electrochemical workstation. As shown in **Figure 6.8 c**, the starting point of the EIS curves is the same, indicating the bulk resistance of the pouch cell is unchanged. While for the first semicircle, representing the SEI resistance of the cell, the curves are coincident. The only difference between the two EIS curves is the second semicircle. The value of the pouch cell after bending cycles decreases. That is, the resistance for charge transfer decreases slightly. The change of resistance explains the discharge capacity increase. The interfacial contact between the polymer electrolyte and electrode becomes denser due to compression during the bending process.

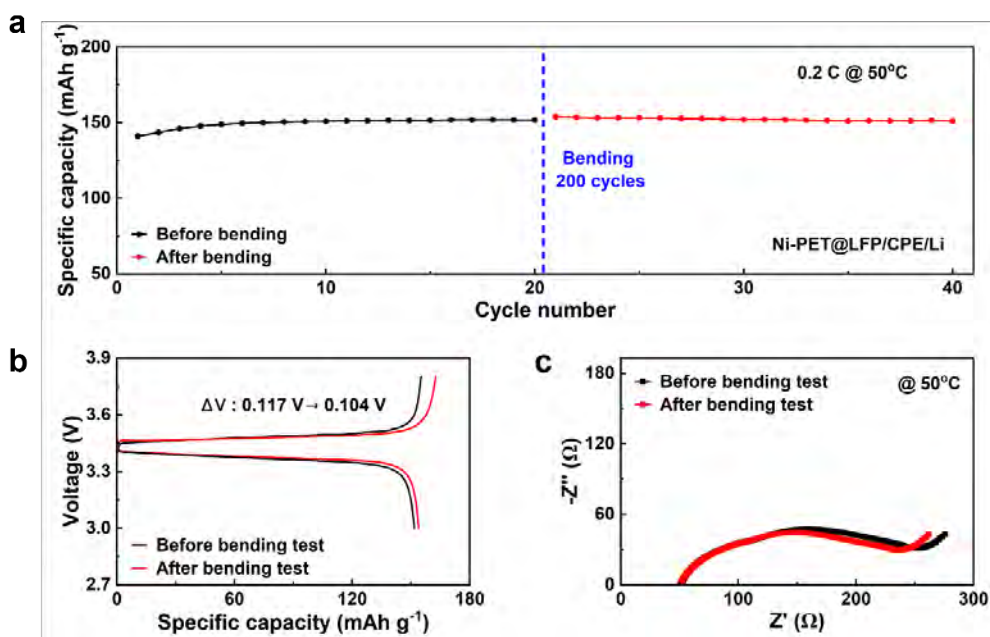


Figure 6.8 The characterization of flexibility for the pouch cell with Ni-PET CC. (a) Cycle performance before and after bending cycles; (b) Charge/discharge profiles before and after bending test; (c) AC impedance spectrum before and after bending test.

In the reported literature, the flexibility of the pouch cell mainly focuses on the battery performance before and after the bending process. In contrast, for flexible devices, whether the battery can power the devices during operation under destructive conditions. In this research, the battery performance was evaluated during the dynamic bending process, which means that the battery can keep charging and discharging during the bending process. A severe bending experiment was performed with commercial lithium foil (**Figure 6.9 a**). In the first stage, the charging process of the pouch cell is normal. Afterward, the voltage changes frequently, and the charging process becomes unstable. However, by stopping the bending process, the pouch cell can charge and discharge normally again. The remarkable phenomenon implies the mechanical strength of lithium foil is not good enough to undergo the destructive process. Even if some cracks occur on the surface of lithium foil, the connection between cracks can be repaired after stopping the bending process due to the soft feature of lithium foil (**Figure 6.9 b**). Therefore, lithium foil is not suitable for destructive flexible experiments.

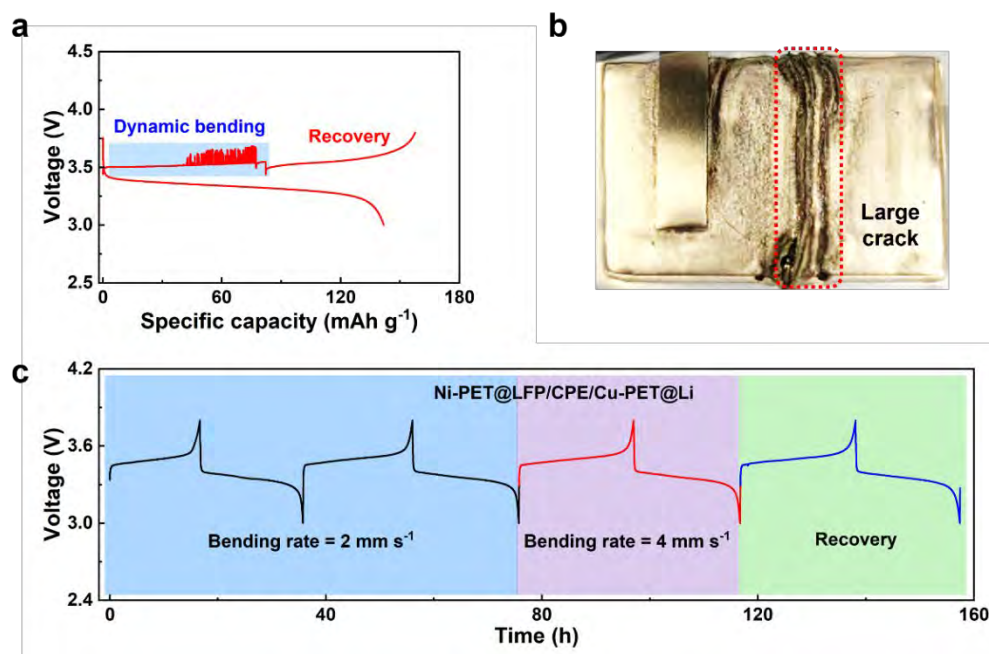


Figure 6.9 Dynamic flexibility of pouch cell with Ni-PET CC. (a) Charge/discharge profiles of pouch cell with lithium foil as anode; (b) Optical photograph of lithium foil anode after bending process; (c) Charge/discharge profiles with flexible anode under different bending rates for dynamic flexibility.

The above battery charge and discharge profiles indicate that a flexible host with strong mechanical strength is essential for continuous bending. A composite lithium anode consisting of the flexible host (Cu-PET) and lithium metal anode was fabricated by rolling Cu-PET and lithium metal together (Cu-PET@Li). Then, the pouch cell with a size of 2×3 cm was fabricated, including Ni-PET hosting LFP cathode, Cu-PET hosting lithium metal anode, and polymer electrolyte. As shown in **Figure 6.9 c**, the pouch cell charges and discharges typically with a setting bending speed of 2 mm s⁻¹. It should be noted that the discharge capacity exceeds the charge capacity during the bending process. The increase in capacity is consistent with the above conclusion about resistance decrease. The excellent battery cycle performance under the bending process demonstrates that the flexibility of composite lithium anode is better than that of commercial lithium foil. The bending speed of pouch cells also plays a vital role in device usage. After accelerating the bending speed to 4 mm s⁻¹, the pouch cell can also cycle well with a coulombic efficiency of 99.5%. Furthermore, by stopping the bending

process, the charge and discharge profiles remain stable with a flat state. Therefore, the textile-based pouch cell with metallic PET fabric hosting cathode and lithium metal is flexible for flexible devices. The systematic investigation of the flexibility of solid-state batteries fills in the current gaps and proposes an advanced approach to enhance the flexibility of solid-state pouch cells.

6.3.5 Comparison of monopolar cell and bipolar cell

As introduced bipolar design inside solid-state batteries has many merits, including energy density enhancement, polarization voltage decreases, and safety improvement. Compared to the current bipolar substrate, Ni-PET CC is compatible with lithium metal and LFP cathode. In this chapter, organic/inorganic composite polymer electrolyte (CPE) was prepared to enhance the electrochemical properties (including ionic conductivity and stability to lithium metal) and mechanical properties. Then, the bipolar solid-state battery was fabricated through direct contact between two-unit cells (the structure of bipolar battery as shown in **Figure 6.10 a**). The NiPET CC is quite stable with lithium metal, no new peaks appearing after connecting with lithium metal for hours (**Figure 6.10 b**). In contrast, the alloying reaction between the common cathodic current collector of Al and lithium metal anode makes it difficult to assemble internal bipolar cells directly^{195, 196} (**Figure 6.10 c**). Moreover, the oxidative and reductive stability in bipolar cell was evaluated with CV curves (**Figure 6.10 d**). There are no obvious oxidation/reduction peaks over the potential of 5.6-7.6 V (vs. Li^+/Li), suggesting the electrochemical stability of NiPET CC. The advantages of inside bipolar design were demonstrated by comparing polarization voltage. The long-term cycle performance and flexibility of bipolar batteries were also investigated systematically.

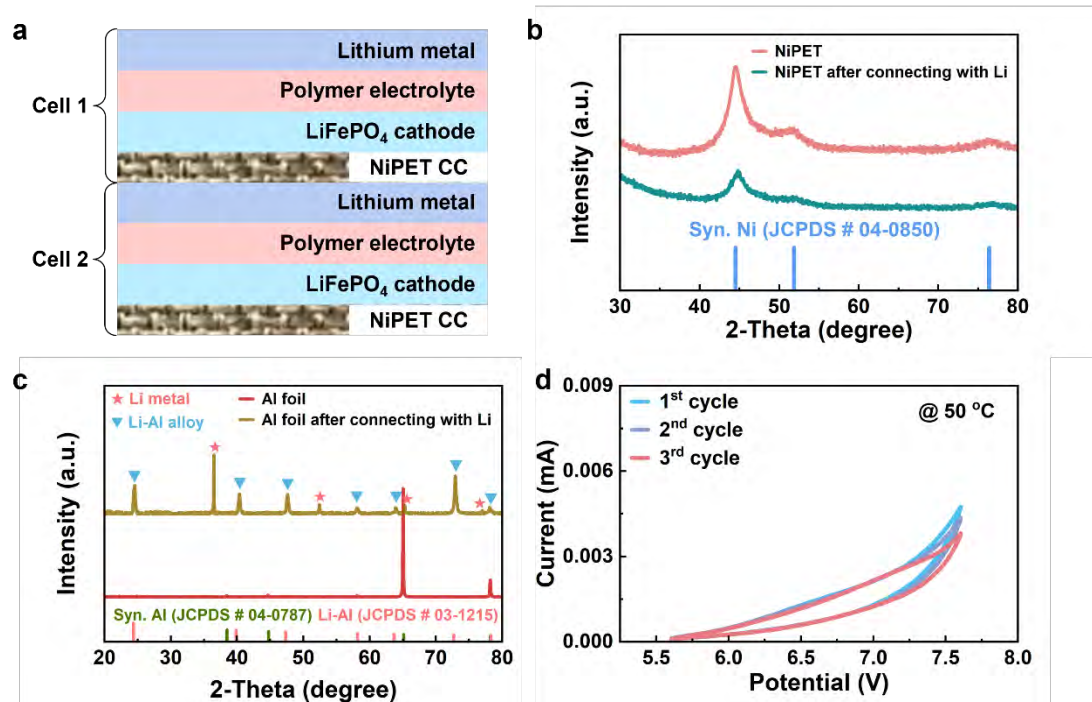


Figure 6.10 (a) The inner structure of bipolar cell with NiPET; The XRD results of NiPET (b) and Al (c) before and after connecting Li; (d) CV curve of bipolar cell over the potential of 5.6 – 7.6 V.

The high output voltage of the power system is realized through an in-series of monopolar cells. The polarization voltage of bipolar and external connection cells is demonstrated in **Figure 6.11 a, b**. CV curves of bipolar and external connection cells were studied with 0.1 mV s^{-1} at 50°C . The bipolar and external connection cells were conducted in three cycles, and the first cycle is mainly related to the SEI formation process. The following two cycles coincide perfectly. As calculated, the polarization voltage of a bipolar cell is 0.517 V, 0.582 V for an external connection cell. By comparison, the polarization voltage of bipolar cell is lower than external connection cell's, indicating that the inner in-series connection is better than the external in-series connection. The resistance of bipolar and external connection cells was also investigated (**Figure 6.11 c**). The resistance of bipolar cell is lower than external connection cells, which is consistent with the results of polarization voltage. Besides, the charge/discharge profiles of bipolar and monopolar cells were compared in **Figure 6.11 d**. Calculating from charge and discharge profiles, the polarization voltage of a

bipolar cell is 0.28 V, which is also smaller than two times 0.1588 V for a monopolar cell. When a bipolar cell is seen as one individual cell, the polarization voltage of a bipolar is higher than that of the monopolar cell, leading to lower discharge capacity.

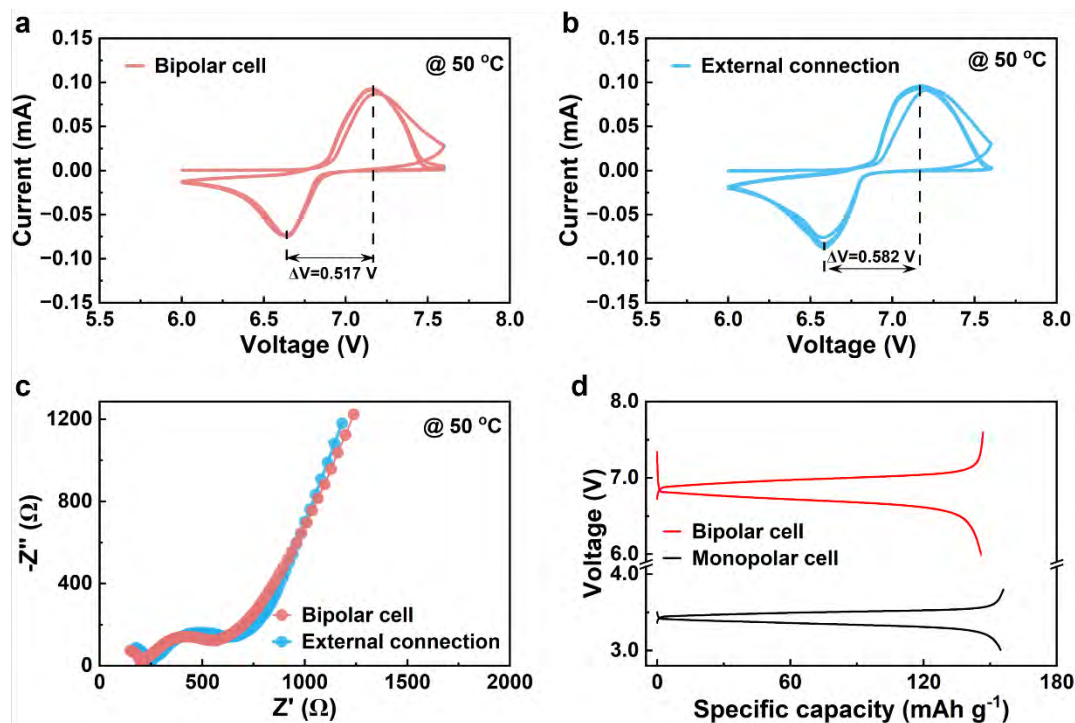


Figure 6.11 Comparison of polarization voltage of bipolar cell (a) and external connection cells (b) with CV curves; (c) EIS plots of bipolar and external connection cells; (d) Charge/discharge profiles of bipolar and monopolar cell.

6.3.6 Battery performance of bipolar batteries

The electrochemical performance reflects the effect of Ni-PET acting as a bipolar substrate. The cycle performance of bipolar cells with the structure of Ni-PET/LFP//CPE//Li || Ni-PET/LFP//CPE//Li is shown in **Figure 6.12 a**. For the first cycle, the discharge capacity is 112.3 mAh g⁻¹, with an initial coulombic efficiency of 77.1%. For the following cycles, the discharge capacity increases gradually, with coulombic efficiency of nearly 100%. After 20 activation cycles, the discharge capacity reaches the maximum capacity of 138.6 mAh g⁻¹. Afterwards, the battery cycles stably, and the discharge capacity keeps around 138 mAh g⁻¹. The stable long-term cycle performance of bipolar cells confirms the excellent compatibility of Ni-PET CC with

lithium metal anode since the two parts contact directly. The discharge capacity fades away after 210 cycles, with decreased coulombic efficiency lower than 99.9%. The discharge capacity retention is around 92% after 250 cycles. In sharp contrast, the capacity of external connection cell fades away rapidly after 30 cycles. In addition, the rate performance of bipolar and external connection cells was evaluated under 0.2 C, 0.5 C, 1.0 C and 0.5 C (shown in **Figure 6.12 b**). The discharge capacity of bipolar cell under 0.2 C, 0.5 C and 1.0 C is 156.44 mAh g⁻¹, 152.21 mAh g⁻¹ and 138.44 mAh g⁻¹, respectively. In comparison, the discharge capacity is 151.52 mAh g⁻¹, 143.65 mAh g⁻¹ and 129.61 mAh g⁻¹, respectively, which is lower than external connection cell. Moreover, compared with the reported literature, Ni-PET-based bipolar cells, including quasi-solid-state battery systems, display excellent battery performance (**Figure 6.12 c**).

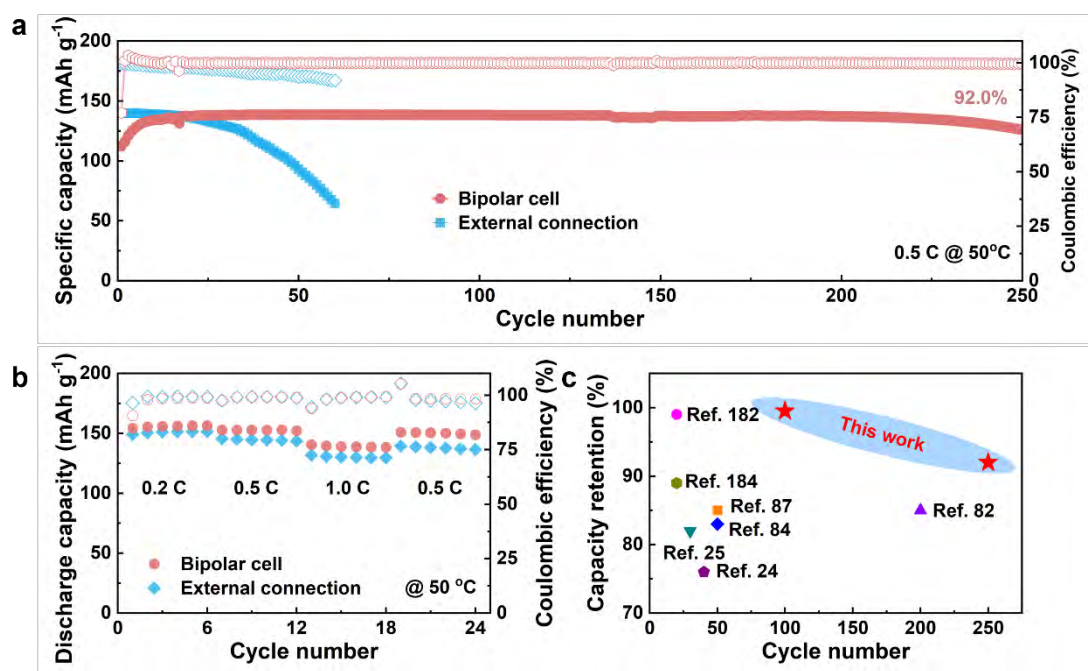


Figure 6.12 Battery performance of bipolar cells. (a) Cycle and (b) rate performance of bipolar and external connection cells under 0.5 C at 50°C; (c) Comparison of capacity retention and cycle number with reported literature.

The battery performance of bipolar cells with Ni-PET CC was compared with the reported literature in **Table 6.1**. Using lithium metal as an anode would achieve higher

energy density for solid-state battery systems. In bipolar cells of reported literature, the researchers used quasi-electrolytes for better battery performance. However, introducing another buffer layer to separate the two individual cells would lead to higher overall resistance. The cycle life is no more than 50 cycles, and the capacity retention is also lower. By contrast, using Ni-PET CC as a bipolar substrate contributed to stable cycle performance and higher capacity retention of 92% after 250 cycles. This is mainly attributed to the dense contact between lithium metal and Ni-PET CC. Therefore, this work addresses several problems in bipolar assembly. Firstly, using lithium metal as anode is the first principle in a solid-state system. Besides, the Ni-PET is compatible with lithium metal and cathode materials concurrently, Ni-PET replacing two types of current collectors. Furthermore, flexible Ni-PET can endorse the battery's excellent flexibility, which will be discussed later.

Table 6. 1 Comparison of battery performance with literature

Battery Structure	Cycle number	Retention	Ref.
LCO/QSE/ LTO-AI-LCO /QSE/LTO ²²	NA.	NA.	22
LMFP/QSE/ LTO-AI-LMFP /QSE/LTO ⁸²	200	85	82
LFP/QSE/ Li-Cu-AI-LFP /QSE/Li ²⁵	30	82	25
NCM/CPE/ Li-Cu-AI-NCM /CPE/Li ⁸⁴	50	83	84
LFP/SPE/ Li-SS-AI-LFP /SPE/Li ²⁴	40	76	24
NCM/QSE/ Li-SS-AI-NCM /QSE/Li ¹⁸²	20	99	182
LFP/ISE/ Li-SS-AI-LFP /ISE/Li ¹⁸⁴	20	89	184
S/QSE/ Li-SS-S /QSE/Li ⁸⁷	50	85	87
LFP/CPE/ Li-Ni-PET-LFP /CPE/Li	250	92	This work

Notes: CPE: composite polymer electrolyte

QSE: quasi-solid electrolyte

SPE: solid polymer electrolyte

ISE: inorganic solid electrolyte

6.3.7 Flexibility of bipolar pouch cell with Ni-PET CC

The flexibility of monopolar pouch cells has been investigated before. However, for

bipolar pouch cells, the thickness of batteries doubled, and the flexibility needs to be studied again. Firstly, the cycle performance under the bending test was evaluated. As shown in **Figure 6.13 a**, the initial discharge capacity is about 135 mAh g⁻¹, and the maximum discharge capacity reaches 145 mAh g⁻¹ after 10 cycles. After that, the discharge capacity stabilized at around 145 mAh g⁻¹. After cycling 20 cycles, the bending process was performed for 200 cycles under a bending radius of 5.0 mm. And then, the bipolar pouch cell was set to recycle. The discharge capacity increases to 153.6 mAh g⁻¹, slightly higher than before the bending test. The charge/discharge profiles in **Figure 6.13 b** show capacity increases after the bending test.

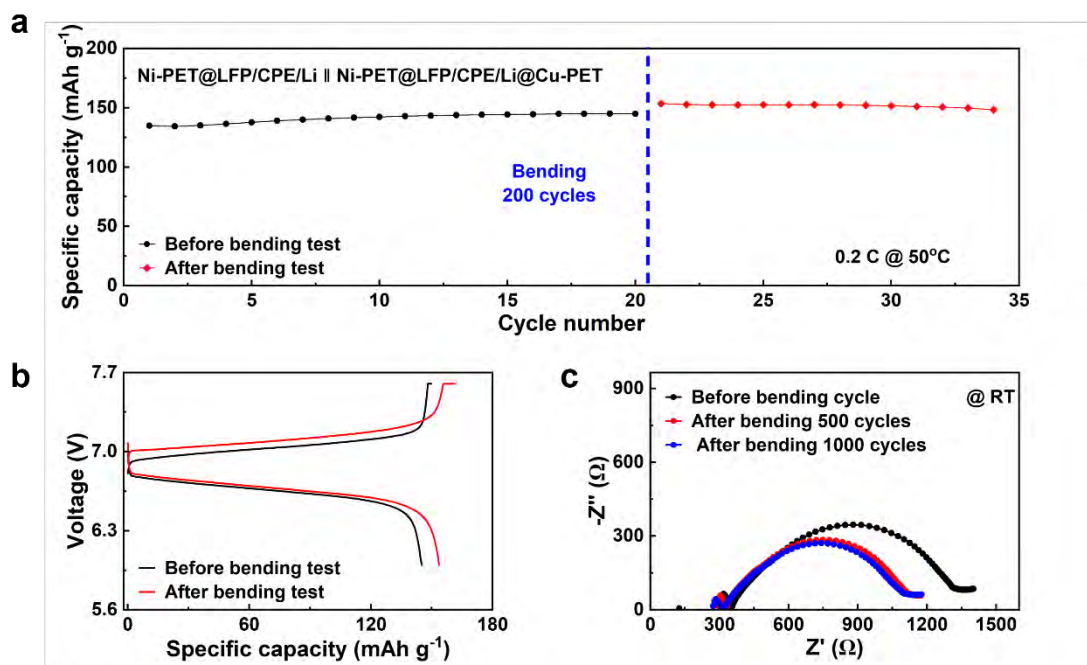


Figure 6.13 Flexibility of bipolar pouch cell. (a) Cycle performance of bipolar pouch cell before and after bending 200 cycles under bending radius of 5.0 mm; (b) Charge/discharge profiles before and after bending test; (c) AC impedance of bipolar pouch cell before and after different bending cycles at room temperature.

Subsequently, the AC impedance was first detected before and after different bending cycles in **Figure 6.13 c**. Before the bending test, the initial bulk resistance of the bipolar pouch cell is about 354 Ω, and the overall interfacial resistance is about 964 Ω at ambient temperature. Afterwards, the bending process was exerted onto the bipolar cell.

The bulk resistance is similar to the initial state, while the interfacial resistance decreases to 781.4 Ω . Furthermore, another 500 bending cycles were performed, and the EIS curves almost coincided with that after 500 bending cycles. The result indicates that the bending process enhances the interfacial contact between individual layers, decreasing resistance. Once the resistance drops to some extent, the bipolar pouch cell becomes stable, and the overall resistance remains unchanged. The declined resistance explained the increasing discharge capacity after the bending test.

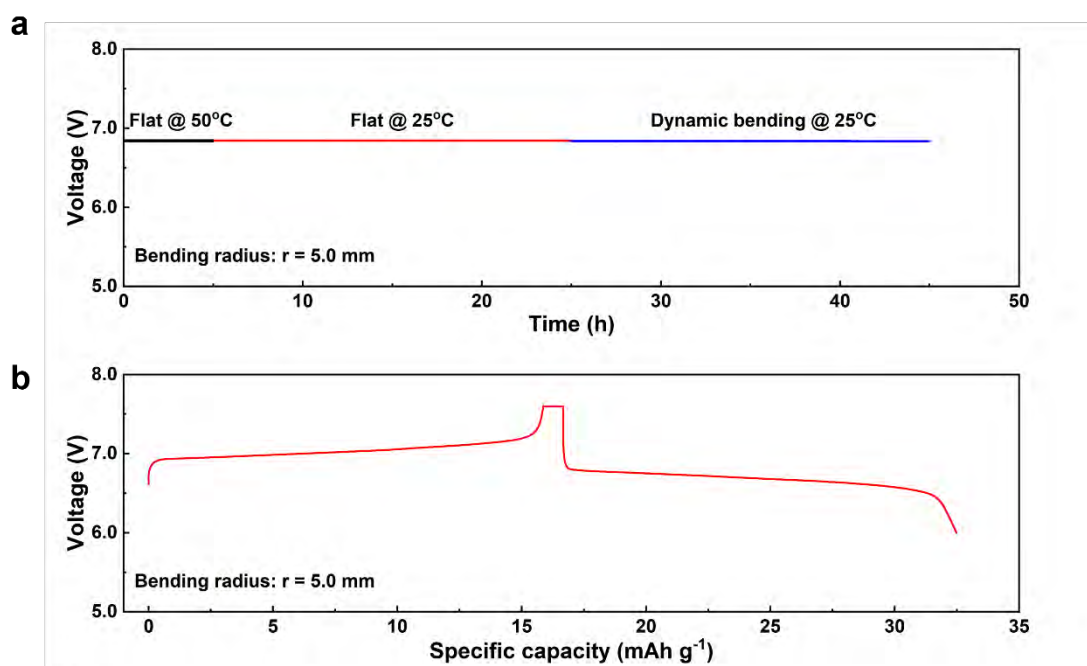


Figure 6.14 (a) Voltage stability of bipolar pouch cell at different temperatures and during dynamic bending test; (b) Charge/discharge profiles of bipolar pouch cell at 0.05 C under bending rate of 2 mm s⁻¹.

To evaluate the flexibility of bipolar cells, the voltage stability of bipolar cells should be verified during dynamic bending. **Figure 6.14 a** shows the voltage stability of bipolar pouch cells at different states with 50% depth of charge (DOC). After 50% DOC, the voltage plateau stabilized at 6.83 V at 50°C. Putting the pouch cell at 25°C, the voltage plateau was unchanged. Moreover, the voltage plateau is also stable by bending the pouch cell with a bending radius of 1 cm. The above results indicate that the bipolar structure is stable and in close contact during dynamic bending. Later, the

charging/discharging profiles will be tested during the dynamic bending process.

Dynamic bending experiment is stricter for bipolar pouch cells due to more layers and higher thickness. The destructive bending cycles were implemented to the bipolar pouch cell continuously along with battery charge and discharge with a bending rate of 2 mm s^{-1} (**Figure 6.14 b**). To ensure the stability of the lithium metal anode, the composite anode was fabricated by rolling flexible Cu-PET with lithium foil. The bipolar pouch cell cycles stably, and the coulombic efficiency is nearly 100% at 0.05 C at ambient temperature. The above results demonstrate that the bipolar pouch cell with Ni-PET CC hosting LFP cathode and Cu-PET hosting lithium metal as the anode is equipped with high flexibility.

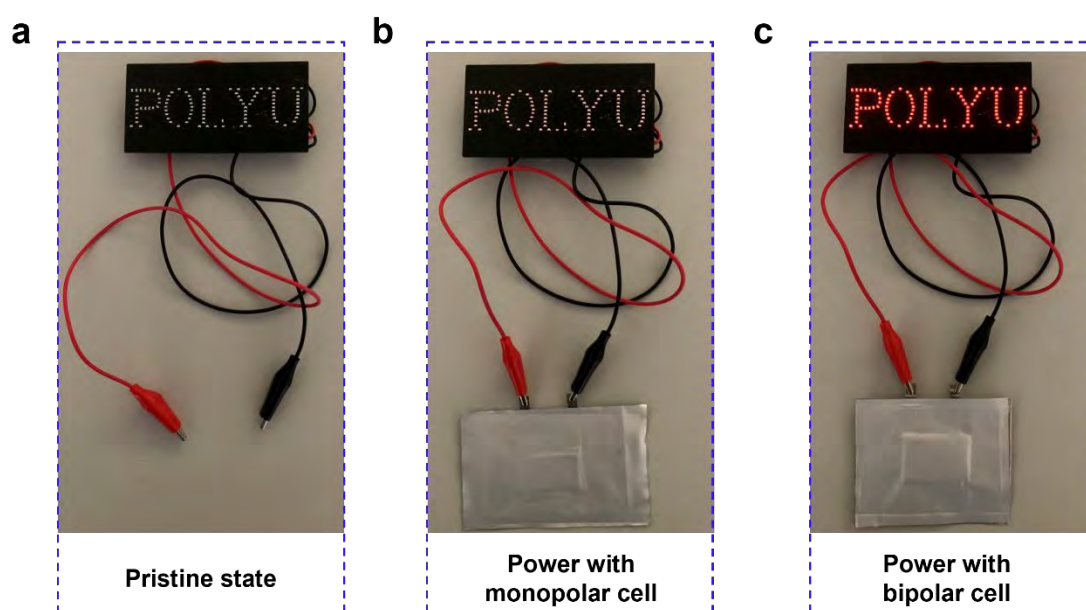


Figure 6.155 (a) Demonstration of LED device at pristine state; (b) Monopolar cell power the LED device; (c) Bipolar cell power the LED device.

To demonstrate the essential of the bipolar cell to high-voltage devices, the comparison was made with monopolar and bipolar cells. The LED lights are white in a pristine state without a power system (**Figure 6.15**). Afterwards, LED lights can be powered with monopolar cells, although the brightness is very low. Once they were powered with bipolar cells, the brightness was very strong, and the LED lamps showed red colors.

The illustration demonstrates that a high-voltage battery is necessary for some devices.

6.4 Conclusion

In summary, the Ni-PET current collector was fabricated through the PAMD method, introducing and endorsing the solid-state battery's excellent flexibility. The electrochemical properties acting as the current collector are similar to commercial Al foil in the monopolar battery system. Due to the porous structure of the Ni-PET current collector, it takes more cycles to activate the lithium-ion transport pathway according to current density. The capacity retention of the Ni-PET-based battery is 90.3% after 250 cycles, which is much higher than the Al foil-based battery of 73.1%. Besides, the long-term cycle performance is improved, with capacity retention of 85.4% after 500 cycles under 0.5 C. Moreover, based on the compatibility of Ni-PET with lithium metal and cathode, the bipolar solid-state battery was assembled by sharing Ni-PET as a current collector for the anode and cathode. The capacity retention is 92% after 250 cycles, much higher than the reported literature. Furthermore, the bending process would compress the bipolar solid-state battery and lead to excellent interfacial contact, resulting in lower resistance and higher discharge capacity. Therefore, textile-based current collectors endorse the solid-state battery's superior flexibility and realize simplified fabrication of bipolar battery configurations.

CHAPTER 7 CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

7.1 Conclusions

The solid-state battery has attracted more and more attention for next-generation technology. Replacement of liquid electrolytes with solid-state electrolytes would enhance the safety. Besides, introducing lithium metal as an anode would further increase the energy and power density. In recent decades, many researchers have focused on preparing novel solid-state electrolytes and improving electrode interfacial compatibility. In this thesis, we developed strategies to enhance the electrochemical performance of solid-state batteries. Firstly, a kind of cross-linked polymer electrolyte was synthesized through in-situ UV-cured on the surface of the cathode. In this way, the obtained integrated “polymer electrolyte-cathode” facilitates lithium diffusion across the electrolyte/electrode interface. Secondly, a polyether-based polymer electrolyte with a wide electrochemical stable window was synthesized by introducing fluorine-based side chains, enhancing the compatibility with high-voltage cathodes. Finally, to meet the requirements for high-voltage devices, a bipolar battery configuration was fabricated, sharing Ni-PET as a current collector for the anode and cathode. Furthermore, the assembled bipolar battery exhibits excellent flexibility under the dynamic bending test.

In Chapter 4, a novel polymer electrolyte (UV-SPE) was synthesized by copolymerizing poly(ethylene glycol) methyl ether methacrylate and poly(ethylene glycol) diacrylate under UV irradiation without any solvent. The chemical structure was confirmed with FT-IR and XRD spectra. The UV-SPE shows excellent electrochemical performance, including ionic conductivity of $2.95 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and the stable electrochemical window of 4.69 V (vs. Li/Li⁺). Besides, the electrochemical compatibility with lithium metal anode was superior to liquid electrolytes at higher

temperatures. Moreover, the lithium-ion diffusion was enhanced by constructing the integrated “electrolyte-cathode” structure. Furthermore, $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4//\text{Li}$ cells were assembled for battery evaluation. The capacity retention of LMFP//Li cell at 0.2 C is 84.6% after 240 cycles. It was demonstrated that this UV-cured SPE has potential application in all-solid-state lithium and sodium metal batteries.

In Chapter 5, we designed and synthesized a fluorine-based polymer electrolyte with poly(ethylene glycol) diglycidyl ether (PEGDE) copolymerizing with glycidyl 2,2,3,3-tetrafluoropropyl ether (TFE) for safe and stable all-solid-state lithium batteries. Introducing TFE increases the ionic conductivity to $8.15 \times 10^{-5} \text{ S cm}^{-1}$, enhances the electrochemical compatibility with high-voltage NCM62, and improves the stability of the lithium metal anode. Moreover, the constructed LiF-rich solid electrolyte interface ensures the symmetric lithium metal cell cycling for 2000 h under 0.2 mA cm^{-2} . The assembled all-solid-state lithium batteries paired with $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ demonstrate outstanding capacity retention after 300 cycles with coulombic efficiency of 99.95% and long-term charge/discharge stability with LiFePO_4 for 700 cycles. Notably, the assembled pouch cell exhibits excellent flexibility with a capacity retention of 93.8% after 3000 bending cycles under a radius of 4.0 mm. Introducing fluorine-based components into polymer structure provides an effective strategy to stabilize high-voltage cathode during long-term operation.

In Chapter 6, PET-based current collectors (Ni-PET and Cu-PET) were prepared through the PAMD method. For the Ni-PET current collector, the nickel coating layer was deposited on the fibers of PET homogenously, and the thickness of the nickel layer is about 300 nm. After nickel coated, the young's modulus increased three times that of pristine PET substrate. In the employment of Ni-PET in solid-state batteries, the capacity retention is 90.3% under 0.5 C after 250 cycles, higher than 73.1% of Al-based batteries. Besides, the long-term cycle stability was improved with capacity retention of 85.4% after about 500 cycles. Moreover, optimization of battery structure with bipolar configuration could further enhance the energy density of the solid-state battery,

resistance decreasing, and materials saving. Considering compatibility with lithium metal, Ni-PET is a good candidate to act as a bipolar substrate, cathode, and anode sharing the same current collector. The long-term cycle performance of bipolar batteries with Ni-PET was also evaluated, delivering 140 mAh g⁻¹ and capacity retention of 92% after 250 cycles. Furthermore, though the thickness of the bipolar battery becomes larger, the flexibility is also great. After bending 200 cycles, the resistance decreases, and the capacity increases slightly. Last but not least, bipolar battery cycles well during dynamic bending test with a radius of 5.0 mm.

7.2 Suggestions for Future Research

This thesis addressed the compatibility with high-voltage cathode by introducing fluorine-based side chains. We fabricated the flexible bipolar solid-state batteries with the flexible textile-based current collector. However, many aspects should be investigated to promote the industrialization of solid-state batteries:

1. **Enhancement of ionic conductivity:** Currently, the operation temperature of polymer-based solid-state batteries is higher than room temperature under the restriction of ionic conductivity lower than 10⁻⁴ S cm⁻¹. Based on the synthesized polymer electrolytes, inorganic solid-state electrolytes (LLZTO, LATP, LPSCl, *et al.*) can be introduced to enhance the mechanical strength and electrochemical properties due to the high ionic conductivity. Moreover, increasing the overall dielectric constant can also facilitate lithium-ion transport by introducing P(VDF-TrFE)-based terpolymer or BaTiO₃ particles with a high dielectric constant.
2. **Employment of high-nickel cathodes:** In this thesis, the fluorine-based polyether polymer electrolytes can match with the high-voltage cathode of NCM622. However, the capacity decays with increasing the cutoff voltage to 4.3 V. The compatibility with the high nickel-based cathode of NCM811 needs to be improved for higher energy density. According to the literature, fabricating artificial CEI on a cathode can also relieve the decomposition of polymer electrolytes. Therefore,

fluorine-based molecules and artificial CEI could synergistically enhance the battery performance with high nickel-based cathodes.

3. ***Optimization of bipolar configuration:*** Due to the porous structure of Ni-PET, the lithium-ion diffusion was restricted in initial cycles compared to Al foil-based solid-state batteries. The mechanism of lithium-ion transport should be investigated systematically. A more detailed comparison of in-series and external in-series should be made in resistance, polarization voltage, and cycle performance. The requirements of cathode and polymer electrolytes for every individual cell in the bipolar configuration are strict, which leads to a high standard in assembly. In this thesis, the thickness of shared Ni-PET substrate is around 75 μm , much heavier than commercial Al foil. The lighter current collector would result in higher energy density.

Overall, there is a long way to go for the industrialization of solid-state batteries. For example, increasing ionic conductivity at room temperature, employing a high-voltage cathode, and increasing the mass loading in solid-state batteries are urgent to solve in the future.

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