

Application of Single-ion conducting polymer electrolytes
(SICPEs)

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ABSTRACTS

Polymer electrolytes have been widely studied as a potential candidate for next generation batterie with improved safety and higher energy density. Especially, single-ion conducting polymer electrolytes (SICPEs) have attracted significant attention due to their almost unity lithium-ion transport number, which is believed to help suppress lithium dendrite growth and extend battery cycle life. However, there is still a long way to go before they can be practically applied in batteries, due to their relatively low ionic conductivity at ambient temperature. Therefore, the main goal of this work is to explore various methods that can improve the ionic conductivity of SICPEs at ambient temperature, together with the investigation of the effect of ion transport number on battery performance.

In this dissertation, a SICPE with a “soft” poly(dimethylsiloxane) (PDMS) backbone and poly(ethylene oxide) (PEO) side chains was designed. The obtained SICPE exhibits accelerated segmental dynamics, improved lithium-ion conductivity at ambient temperature (4.7×10^{-6} S/cm), and good electrochemical stability with the lithium metal electrode.

Then, a detailed investigation of SICPEs copolymerized with different neutral units possessing either flexible or polar structures are presented. The results emphasize the important role of miscibility between plasticizing neutral units and ionic conductive units, while the polarity of sidechains has limited influence on ion dissociation. This work suggests that polyanions with a strongly delocalized charge would be a promising structure to achieve sufficient ionic conductivity.

Lastly, plasticized polymer electrolyte membranes containing either SICPE or dual-ions lithium salt were employed to investigate the transport number's effect on battery performance by fixing other parameters, such as mechanical robustness and chemical composition. Even with a relatively lower conductivity, the sample with a high lithium-ion transport number demonstrated the best performance in a Li/Li symmetric cell, which is ascribed to the uniform deposition of lithium and the formation of a stable solid electrolyte interface (SEI) layer. A full cell test with the configuration of LiFePO_4 (LFP)/Li is still under investigation. Knowledge gained from the research in this thesis provides a deeper understanding of the mechanism of lithium-ion transport in SICPEs and can guide the design of SICPEs to improve ionic conductivity.

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INTRODUCTION

With the increasing demand for personal electronics and the popularity of electric vehicles in the automobile industry, the global lithium-ion battery market has expanded dramatically over the past several decades. Commercially available lithium-ion batteries (LIBs) are mainly used with liquid electrolytes and have potential safety problems due to the existence of flammable organic solvents. In addition, commercial LIBs have almost reached the limit of their obtainable energy density. Therefore, solid polymer electrolytes (SPEs) have been studied as a potential candidate to realize next generation battery technology with enhanced safety and breakthrough in energy density.

Among the various polymer matrices studied, polyethylene oxide (PEO)-based structures are the most promising. The beauty of PEO is its unique capability to solvate lithium-ions and facilitate fast ion transport by ethylene oxide bonds. However, the rate of ion transport within the polymer matrix is still much slower than in liquid electrolytes. As a result, the ionic conductivity of SPEs is still below the required value for practical application ($\sim 10^{-3}$ - 10^{-4} S/cm at ambient temperature). Therefore, it is critical to find polymeric structures that will enable high ionic conductivity at ambient temperature.

Another problem for conventional PEO-based polymer electrolytes is the low lithium-ion transport number, which would result in severe cell polarization, increased internal impedance, and lithium dendrite growth. According to theoretical models, a high lithium-ion transport number is helpful to suppress lithium dendrite growth and extend battery life. Therefore, a type of SPE with the charge centers immobilized on a polymer matrix was proposed: single-ion

conducting polymer electrolytes (SICPEs), which possess an almost unity lithium-ion transport number. Lithium dendrite growth is a complicated process influenced by the mechanical property, chemical composition, ionic conductivity, and transport number. Therefore, a systematic study focused on the effect of transport number on battery performance is essential.

In this dissertation, various strategies that can improve ambient temperature ionic conductivity of SICPEs are explored. Firstly, a polydimethylsiloxane (PDMS) based SICPE was designed to achieve accelerated segmental dynamics. The significantly improved ionic conductivity emphasizes the importance of fast segmental dynamics and indicates the applicability of this concept to other types of polymer electrolytes. Then to explore potential structure that may substitute PEO, a copolymer type SICPE with different neutral units was synthesized. The conductivity of the synthesized SICPEs was found to be mainly controlled by glass transition temperature (T_g), in which the one with PEO still had the highest ionic conductivity.

Additionally, the results emphasize the necessity to design polyanions having reduced Coulombic interaction with lithium-ions. To investigate the sole effect of transport number on battery performance, plasticized crosslinked PEO membranes were prepared as a SICPE or SPE with different concentrations of dual-ions lithium salt, i.e., lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Our results clearly demonstrate that a high lithium-ion transport number could afford homogenous lithium deposition and form a stable SEI layer on the lithium metal surface, potentially improving the electrochemical stability of polymer electrolytes. The dissertation has the following organization.

Introduction gives the organization of this dissertation.

Chapter 1 gives a brief overview of the mechanisms for ionic conductivity in SPEs and the background of SICPEs.

Chapter 2 describes the experimental techniques employed in this work. This chapter includes the fundamental mechanisms and instrumentation of techniques used to characterize structure, composition, thermal property, mechanical property, as well as conductivity and battery tests.

Chapter 3 presents a strategy to improve ionic conductivity through the incorporation of a soft “PDMS” backbone with flexible PEO side chains. The thermal property, rheological behavior, morphology analysis, molecular dynamics simulation, conductivity and battery performance have been evaluated. The obtained SICPEs presented accelerated segmental dynamics, significantly improved ionic conductivity and good electrochemical stability with the lithium metal electrode.

Chapter 4 presents a detailed investigation of new SICPEs copolymerized with PEO units and other types of neutral units possessing either flexible or polar structures. The results emphasize the importance of miscibility between neutral units and conductive components, while the polarity of sidechains have limited influence on ion dissociation. Moreover, we conclude that the design of polyanions with strongly delocalized charge is another promising method to improve ionic conductivity of SICPE.

Chapter 5 evaluates the battery performance of polymer electrolytes having different lithium-ion transport number and ionic conductivity. The system only focusses on the effect of transport number by fixing other parameters, such as the chemical composition and mechanical

property. The Li/Li symmetric cell of plasticized polymer electrolytes with SICPE (pSI-20) presented a stable lithium stripping/plating process for over 2200 hours, while the cells with dual-ions salt LiTFSI (pDI) already failed before 2000 hours of cycling at the same current density. Based on the SEM and XPS results, we conclude that high lithium-ion transport number benefits the uniform lithium electrodeposition process and forms stable SEI layer. Both pDI-50 and pDI-100 presented rapid capacity fading in full cell test with LiFePO_4 (LFP)/Li configuration, while there's no significant difference in specific capacity between pDI-20 and pSI-20 till now, which suggests longer time battery test, or even higher C-rate, is required.

Lastly, the conclusions are summarized, and future work are presented.

Chapter I

Historical Background

Based on a report published by Polaris Market Research in 2020, the global lithium-ion battery market is expected to reach \$83.6 billion by 2027, with a compound annual growth rate of 12.6%.¹ The increasing demand for personal electronics is the main driving source for the growth of the market. In addition, the popularity of electric vehicles (EV) in the automobile industry has helped to expand the market size. Commercially available lithium-ion batteries (LIBs) are composed of three primary functional parts: cathode, anode, and electrolyte. Conventional liquid electrolytes consist of various lithium salts dissolved in organic solvents, such as LiPF_6 in ethylene carbonate. This combination possesses fast lithium-ion transport and good contact with solid electrodes. However, the usage of flammable organic solvents may also cause some safety problems.^{2, 3} Over the charge/discharge cycles of the battery, mossy structures of lithium may sprout from the surface of electrodes and spread across the electrolyte. These dendrite structures may penetrate through the whole system and cause both short circuit and leakage of the electrolyte.⁴⁻⁷ Since the resulting short circuit would lead to overheating, the organic solvent may catch fire and even cause an explosion.

Therefore, to eliminate the above safety problems, various alternative materials have been explored. Solid-State Electrolytes (SSEs) are expected to realize next generation battery technology with enhanced safety due to their resistance to the volume changes caused by lithium dendrite growth during cycling. By 2016, state-of-the-art LIBs reached energy densities up to 770 Wh/l, or 260 Wh/kg, and may soon reach their theoretical limit.⁸ As a comparison, SSEs commonly have a higher average output voltage and reduced volume. At the same time,

SSE enables the use of lithium metal as the anode, with a theoretical energy density of 3680 mA/g, which is limited for liquid electrolytes. Combined with the use of high-voltage cathodes and high-capacity materials, SSE may dramatically increase the achievable energy densities (Figure 1.1).^{9, 10} In addition, a battery with SSE has better thermal and electrochemical stability, enabling a longer cycle life and ability to perform under relatively critical condition.

Up to now, SSEs can be simply categorized as two main types: inorganic solid electrolytes and organic/polymer electrolytes. Compared with inorganic solid electrolytes, polymer electrolytes have better processibility, improved compatibility with electrodes and better economic availability.¹¹⁻¹⁴ For large-scale manufacturing of solid-state electronic devices, the polymer electrolyte should satisfy several criteria. The most important one is to have high lithium ionic conductivity close to that of current liquid electrolytes ($\sim 10^{-3} - 10^{-4}$ S/cm at ambient temperature), with no or limited electronic conductivity.¹⁵⁻²⁰ Moreover, the polymer electrolyte needs to possess high thermal, mechanical, and electrochemical stability against the electrodes within the working temperature range for long-term battery performance.

1.1 Mechanism of conductivity

To break through the fundamental limitations of ionic conductivity in polymer electrolytes, we should have a comprehensive understanding on the mechanisms of their ion transport.²¹ For simplicity, we may define the conductivity (σ) of an electrolyte having independent ion migration as:

$$\sigma = \sum p_i q_i \mu_i \quad (1.1)$$

in which p , q , and μ is the concentration, charge, and electrical mobility of free ions. $q_+ = -q_-$.

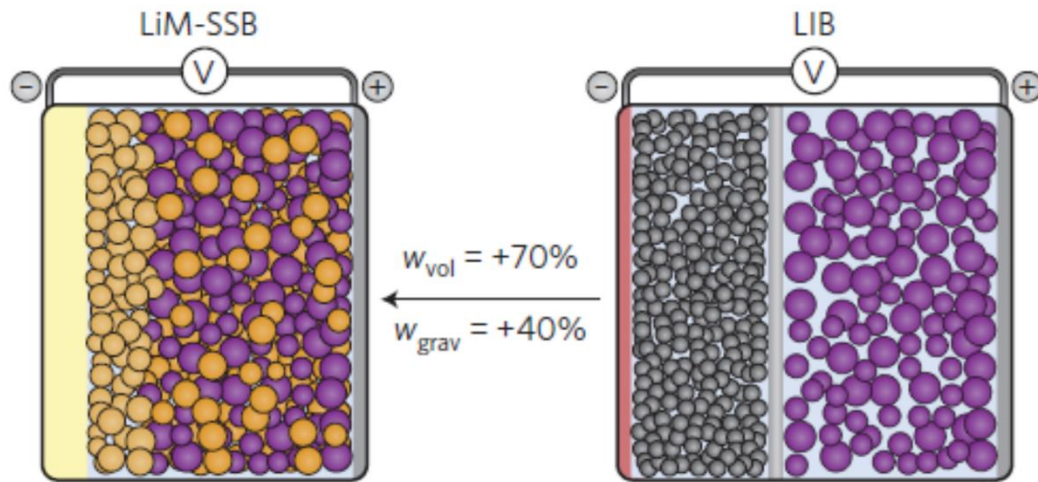


Figure 1.1 Typical battery architectures for the lithium-ion with solid state electrolyte (left) and liquid electrolyte (right). The volumetric and gravimetric energy densities are represented by w_{vol} and w_{grav} , respectively.¹⁰

since the studied system in this work consists of lithium-ion and a singly charged anion. Furthermore, the average mobility of cations and anions is applied for the simplicity of study. Therefore, $\sigma = p q \mu$ is used for the following discussion. This equation is valid when the electrolyte is completely or almost completely dissociated, such as in a strong electrolyte at dilute concentrations. Based on Einstein relation about the diffusion of charged particles, the mobility can also be expressed as:

$$\mu = \frac{qD}{k_b T} \quad (1.2)$$

where D is the diffusivity of the ions, k_b is the Boltzmann constant, and T is temperature. Therefore, combining both equations, the conductivity is defined as:

$$\sigma = \frac{p q^2 D}{k_b T} \quad (1.3)$$

For liquid electrolytes, we can further assume the validity of the Stokes-Einstein relation:

$$D = \frac{k_b T}{C \eta r} \quad (1.4)$$

where C is ion-solvent interactions determining constant, η is the medium viscosity and r is the hydrodynamic ion radius. Therefore, we have $\mu \sim \frac{T}{D} \sim \frac{1}{\eta}$.

1.2 Relation of segmental relaxation and conductivity

Upon super cooling, amorphous material may undergo a reversible transition process named glass transition, in which the material transforms from a rubbery state to a relatively brittle or “glassy” state. This transition process is featured with glass transition temperature, T_g , in which the properties of polymers dramatically change near T_g , such as viscosity and mechanical

properties. For example, viscosity smoothly increases with decreasing temperature and approaches a constant value in the vicinity of T_g . In this regime, the temperature dependence of viscosity deviates from a linear Arrhenius equation and follows Vogel-Fulcher-Tammann (VFT) equation:

$$\eta = \eta_0 \exp\left(\frac{B}{T-T_0}\right) \quad (1.5)$$

where η_0 , B and T_0 are all empirical material-dependent parameters. Various models have been proposed to explain VFT equations, while most of them are phenomenological and still have limitations to interpret the nature of this temperature dependence. For example, the free volume approach assumes that an empty volume is needed for molecular motion, which decreases with decrease in temperature. However, the unreasonable parameters of free volume may be required to describe certain materials. Since this equation is also valid to describe other properties influenced by glass transition, such as segmental relaxation time and diffusion rate, other methods can be used to define T_g . For example, T_g can also be defined as the temperature when segmental relaxation time reaches 100~1000s.

1.2.1 Coupled segmental relaxation and ionic conductivity

For most polymer electrolytes, the lithium-ion is solvated by polymer segments rather than the whole chain. Thus, the local viscosity should be applied instead of the macroscopic viscosity used in liquid electrolytes. The empirical Walden rule can express this relation:

$$\Lambda \tau_s = \text{constant} \quad (1.6)$$

in which Λ is the molar conductivity, and τ_s is the segmental relaxation time. This strong coupling effect between conductivity and segmental relaxation is observed for most of the studied polymer electrolytes, such as polyethylene oxide (PEO) or polypropylene oxide (PPO) based polymer electrolytes (Figure 1.2(a)).²² In such systems, the lithium-ions are strongly coordinated with the oxygen atoms, in which lithium-ion transport is controlled by the movement of chain segments. Therefore, fast segmental relaxation improves lithium-ion conductivity, which can be achieved by increasing the temperature. Otherwise, polymer electrolytes with low T_g are essential. Polymer matrices with low T_g , such as poly(dimethylsiloxane) (PDMS) and poly(olefin), have been widely studied. However, the poor capability to solvate lithium-ions limits their practical application. Actually, it is almost impossible for dry polymer electrolytes to possess ambient temperature ionic conductivity comparable to that of liquid electrolytes, due to the fundamental limitations of the coupled ion transport mechanism. Therefore, other strategies need to be proposed.

1.2.2 Decoupled effect of ion transport

The decoupled effect of ion transport was firstly reported by Sasabe and coworkers in 1972, in which they found that the ionic conductivity is less sensitive to the change of temperature than segmental relaxation (Figure 1.2(b)).²³ In this case, the Walden rule may change to:

$$\Lambda \tau_s^\alpha = \text{constant} \quad (1.7)$$

in which α is a parameter that characterizes the degree of the decoupled effect. This decoupled effect is more obvious when we plot the molar ionic conductivity over structural relaxation time in a double logarithmic scale. A representative Walden plot analysis is presented in Figure 1.3.

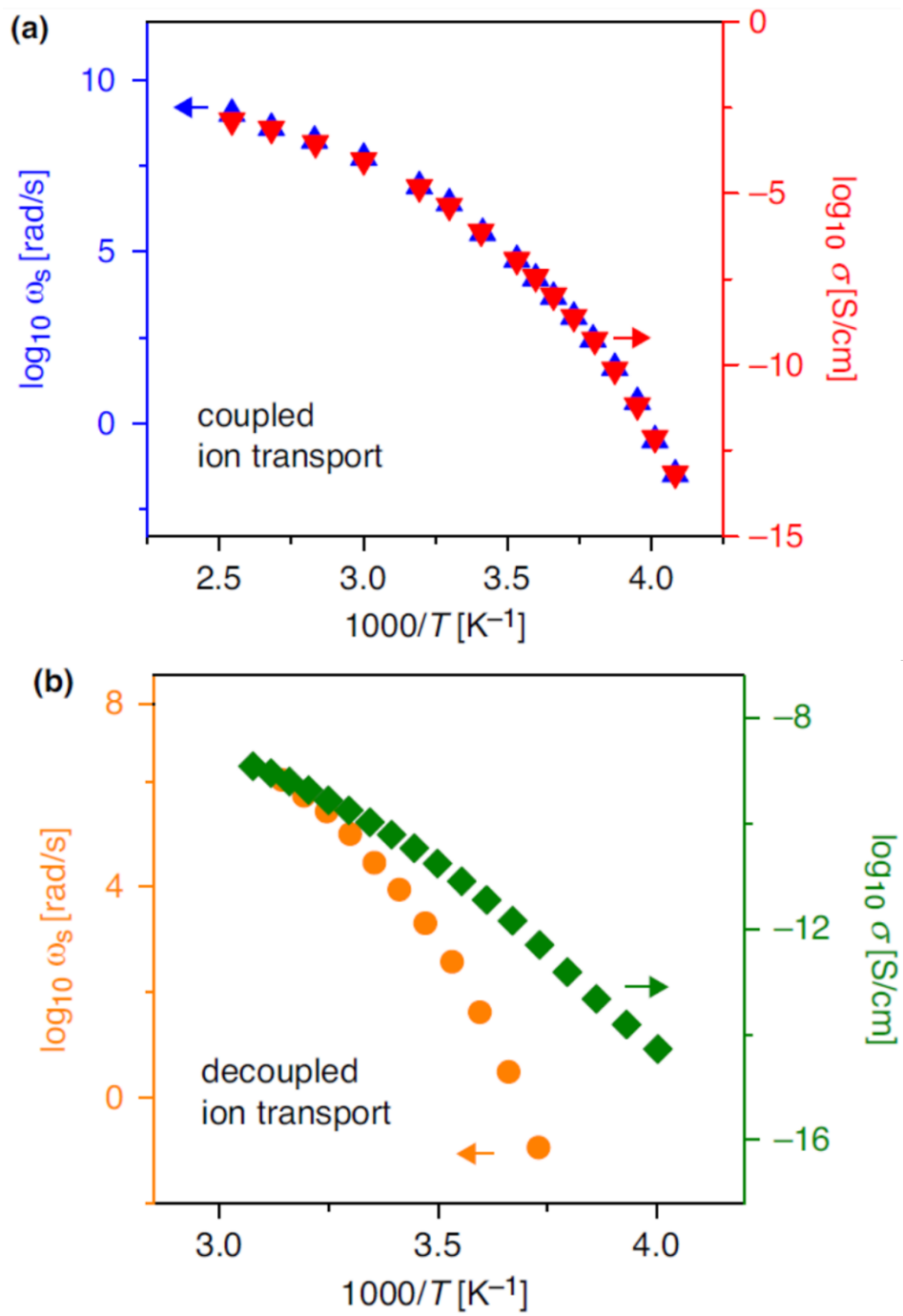


Figure 1.2 Temperature dependence of segmental relaxation frequency and dc conductivity for (a) coupled and (b) decoupled polymer electrolytes.²⁴

Commonly, a dilute solution, such as LiCl in propylene carbonate (PC) or water, is used as a reference to draw a standard line with a slope of one. For strongly coupled systems, the slope of their lines would also be one, i.e., $\alpha=1$ (Figure 1.3(a)).²¹ On the other hand, the slope would be smaller than one for a decoupled system, which indicates that ion diffusion is faster than structural relaxation. Therefore, they're also called superionic conductor (Figure 1.3(b)).

The decoupled effect is commonly observed in some rigid polymers, such as polyvinyl chloride (PVC), whose T_g is mostly above room temperature.²⁵ Therefore, to improve ambient temperature ionic conductivity with a decoupled system, it is important to analyze ion transport below T_g , in which ion motions can be described as ion hopping within frozen structure over an energy barrier. In this case, the activation energy of conductivity (E_σ) is mainly controlled by electrostatic interactions ($E_{\text{electrostatic}}$) and elastic forces (E_{elastic}). Different models have been proposed to predict this energy barrier for conductivity, in which most of them differ in the elastic force contribution. Anderson and Stuart proposed a model to describe ion transport within superionic ceramics.²⁶ This model featured the elastic force contribution by introducing an “ill-defined” volumetric parameter R_d to characterize the “free volume” within polymers:

$$E_\sigma = E_{\text{electrostatic}} + E_{\text{elastic}} = \frac{\beta q_1 q_2}{4\pi\epsilon_0\epsilon(R_1 + R_2)} + G4\pi R_d(R_1 - R_d)^2 \quad (1.8)$$

in which β is the “Madelung” constant, R_1 is the radius of the mobile ion with charge q_1 , R_2 is the radius of the matrix ion with charge q_2 , ϵ is the dielectric constant, and G is the high frequency shear modulus. A minor change has been made by McElfresh and Howit, who substitute R_d with ion jump length λ for a better approximation.²⁷ In addition, a similar idea was

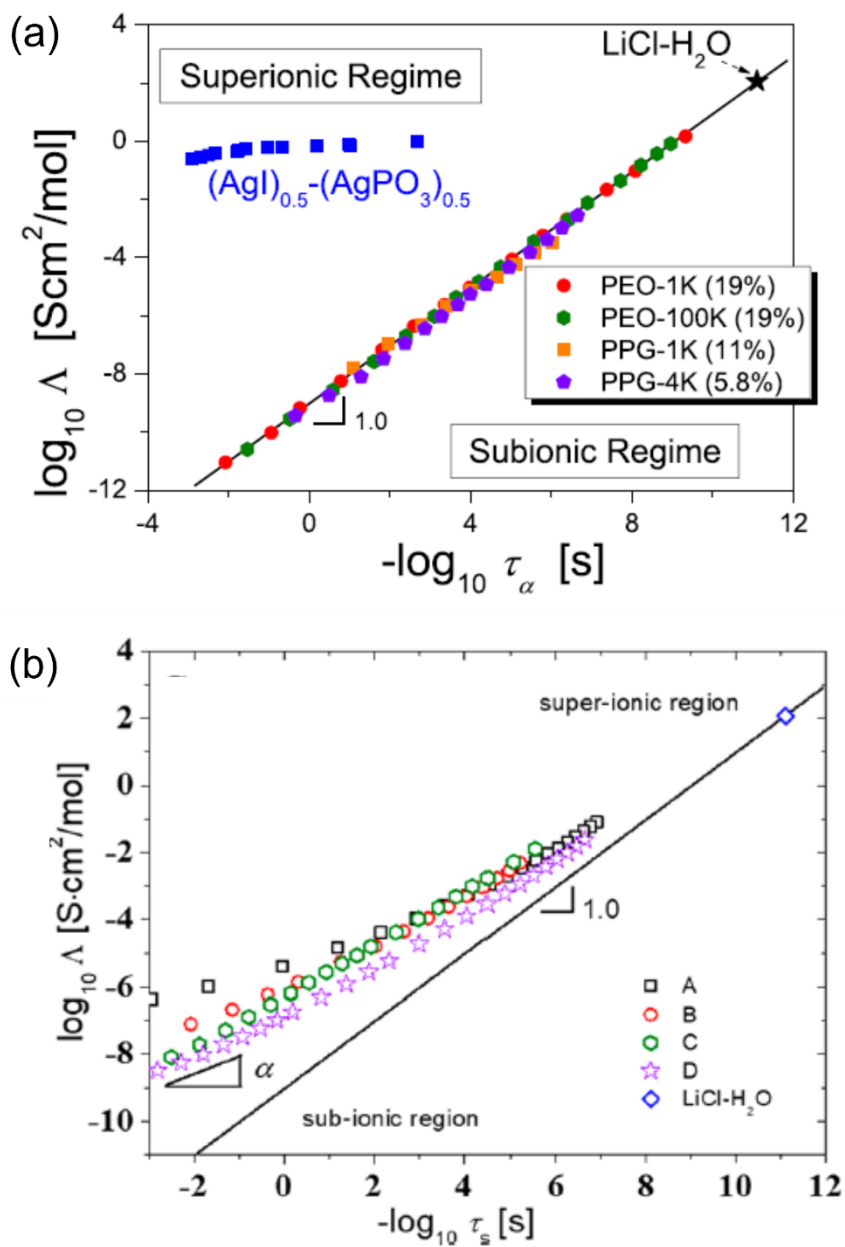


Figure 1.3 Walden plot presenting molar conductivity vs segmental relaxation rate for (a) coupled systems: PEO- and PPG-based polymers with different molecular weights (given by numbers in kg/mol) and weight fractions of Li salt (wt % in parentheses). (b) decoupled systems.²¹

also proposed by our group, which presents similar predictions.²⁸ Herein, a shoving model was employed to describe elastic forces:

$$E_{\sigma} = \frac{\beta q_1 q_2}{4\pi\epsilon_0\epsilon(R_1+R_2)} + \alpha G V_{ion} \quad (1.9)$$

in which V_{ion} is the volume of moving ions and α is a material-related constant ($\alpha < 1$). This model has been successfully applied to analyze single-ion conducting polymer electrolytes (SICPEs), whose definition is included in section 1.5. The reason to select SICPE is due to its single-ion conductor property, which excludes the complex contributions from various ions. Figure 1.4 presents the estimated activation energy of conductivity below T_g for the SICPE synthesized by our group together with data from other literatures. It reveals that the main driving force of ion diffusions in decoupled systems is different based on the size of the mobile ions. Particularly, the elastic force dominates the activation energy for the large ions, such as TFSI⁻ and PF₆⁻, in which the frustration of chain packing created more free volume for ion hopping.^{24, 28-30} As a comparison, Figure 1.4 clearly presents the dominating role of Coulombic interactions for small ions, like Li⁺ and Na⁺. In other words, to realize high lithium-ion conductivity in a decoupled system, alternative methods that can reduce Coulombic interactions would be helpful, such as developing a polymer matrix with a high dielectric constant or employing anions with delocalized charge. This part will be mainly discussed in Chapter 4.³¹ At the same time, since the decoupled effect was commonly observed for a polymer with a rigid structure and high T_g , their ionic conductivity is relatively low at ambient temperature, which needs further investigation. Overall, how to achieve high lithium-ion conductivity in polymer electrolytes remains a puzzle.

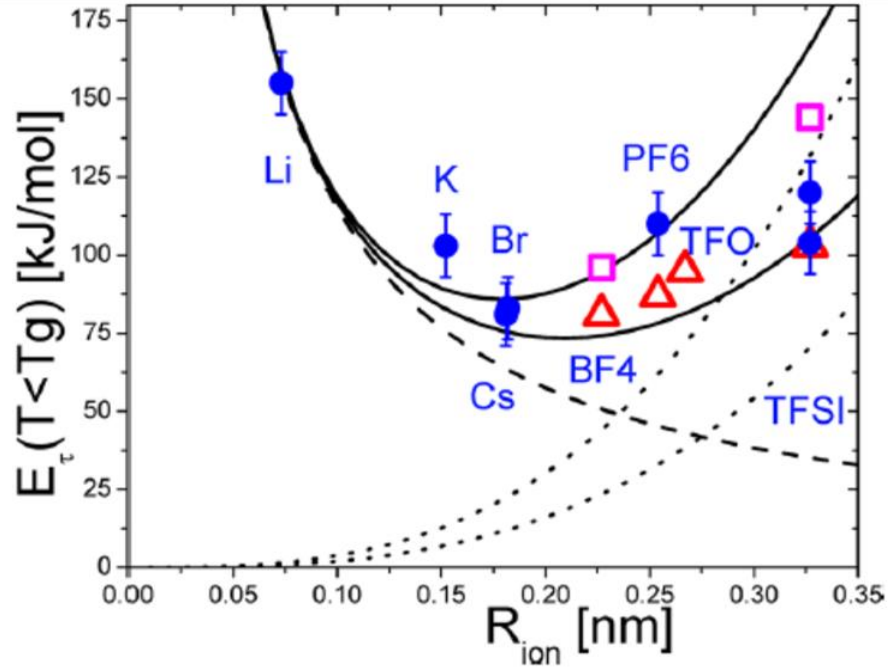


Figure 1.4 Activation energy for conductivity below T_g vs. the ion radius (blue circles). TFO corresponds to mobile anion CF_3SO_3^- . The dashed line presents Coulombic contribution with $\epsilon = 6$, while the dotted lines present elastic contribution with $\alpha G = 1$ and 1.5 GPa. The solid lines present the model predictions as a sum of the elastic and Coulombic contributions to the activation energy.²⁸

1.3 Polymer Electrolyte

Generally, polymer electrolytes are defined as a macromolecular system doped with ions, which exhibit significant ionic conductivity. In 1973, Peter Wright first discovered the reasonable conductivity from the complexes of polyethylene oxide (PEO) with alkali metal ions.³² After decades of study, the family of polymer electrolytes has been expanded from the simple mixture of polymers and salts (Figure 1.5). There are different ways to classify polymer electrolytes, and one of them is proposed here: classical polymer electrolyte, gel polymer electrolyte, polymeric ionic liquids (PolyILs), and composite polymer electrolyte.³³⁻⁴⁶

After the discovery of the first SPE material, a large number of classical polymer electrolytes have been studied,^{47, 48} such as polyacrylonitrile (PAN),^{49, 50} polyvinyl alcohol (PVA),⁵¹ polyvinylchloride (PVC),⁵² and polyvinylidene fluoride (PVDF)⁵³ (Table 1.1). Among them, the majority works focus on PEO mixed with a variety of lithium salts LiX, where $X^- = ClO_4^-$, $CF_3SO_3^-$ and PF_6^- , etc.^{54, 55} In order to minimize the undesirable anion migration, X can be anions with a bulky structure and delocalized charge, such as bis(trifluoromethyl-sulfonyl)imide (TFSi) and bis-(trifluoromethyl sulfonyl)-methide (TFSM). The main reason that PEO is attractive in this area is due to its unique structure. Firstly, the polar ether groups coordinate well with lithium-ions, which provides good dissociation from the anions. At the same time, the flexible structure also results in relatively low T_g and fast segmental dynamics, which assists in rapid charge transport. However, the crystallization of PEO at ambient temperature mostly freeze segmental dynamics and block lithium-ion mobility. Therefore, most PEO-based polymer electrolytes only work above the melting temperature of PEO (~50- 60°C). Different strategies have been

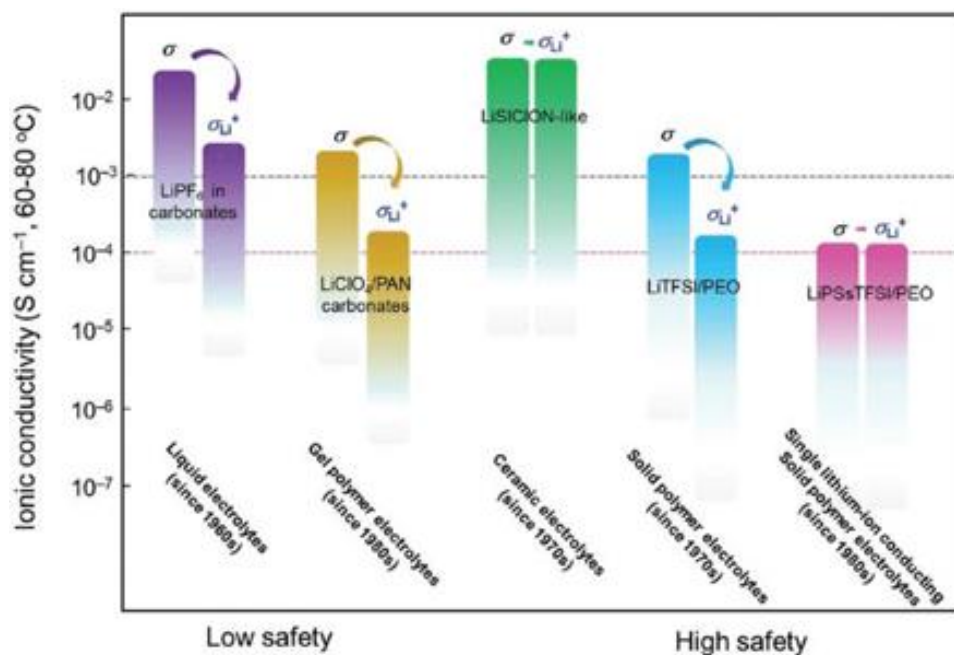


Figure 1.5 Roadmap for the development of Li-ion conducting electrolytes for rechargeable lithium and Li-ion batteries. The requirements of total ionic conductivity (σ) and individual Li^+ conductivity (σ_{Li^+}) for battery operation are shown as gray and pink dashed lines, respectively.⁵⁶

Table 1.1 Examples of solid polymer electrolytes.

Polymer matrix	Repeating Units	Reference
Polyethylene oxide(PEO)	$\text{CH}_2\text{CH}_2\text{O}$	Ref ^{54, 55}
Polyacrylonitrile (PAN)	$\text{CH}_2\text{CH}(\text{CN})$	Ref ^{49, 50}
Polyvinyl alcohol (PVA)	$\text{CH}_2\text{CH}(\text{OH})$	Ref ⁵¹
Polyvinylchloride (PVC)	CH_2CHCl	Ref ⁵²
Polyvinylidene fluoride(PVDF)	CH_2CF_2	Ref ⁵³

employed to increase the ratio of amorphous PEO within the system, such as a linear copolymer having short PEO chains or a comb polymer with PEO grafting as sidechains, which all show improved ionic conductivity at ambient temperature.^{57, 58}

After decades of studies, researchers are still struggling to achieve the required room temperature lithium-ion conductivity with dry polymer electrolytes. For the system with coupled ion dynamics, it is almost impossible to realize the required rate of ion transport due to the sluggish segmental dynamics of polymer matrix at room temperature. In this case, it was very tempting to use plasticizers to form gel polymer electrolytes (GPEs), which aims to accelerate segmental dynamics, decrease T_g and hence improve ionic conductivity at room temperature.^{7, 59} Plasticizers are commonly selected from solvents with low volatility and high dielectric constant to dissolve lithium salts, such as ethylene carbonate (EC), propylene carbonate (PC), and diethyl carbonate (DEC). Although many GPEs exhibit outstanding ambient temperature ionic conductivity values in the range of $\sim 10^{-4}$ - 10^{-3} S/cm, the use of plasticizers would weaken the mechanical property and bring back safety problems caused by organic solvents. In the case of decoupled dynamics, the energy barrier has to be dramatically reduced to ~ 25 kJ/mol. Otherwise, the rate of ion hopping would be too slow.²¹ It is noteworthy that the activation energy for ionic conductivity below T_g is commonly above 120 kJ/mol for most systems with lithium-ions, which indicates the importance of developing new polymer structures, such as polymer matrix with a high dielectric constant or anions with a strongly delocalized charge.

1.4 Mechanical properties of SPE

As discussed above, lithium dendrite growth is one of the main obstacles to realize a lithium-based battery with extended cycle life. One potential method is to employ a mechanically strong and confined structure. According to the model proposed by Monroe and Newman, for a polymer material with Poisson's ratio similar to PEO, interfacial roughening is mechanically suppressed when the separator shear modulus is about twice that of lithium ($\sim$ GPa).⁶⁰ Similar results have also been observed in other works, which emphasize the important role of mechanical pressure, which can reduce the height of dendrite protrusions through plastic deformation and hence obtain uniform lithium electrodeposition (Figure 1.6).^{61, 62} Therefore, using SSEs is an alternative strategy. Unlike inorganic glassy electrolytes or ceramics, it is hard to meet the criterion of mechanical property for polymer electrolytes. For example, the elastic modulus of a PEO-based electrolyte is commonly two to three orders lower than lithium metal. Additionally, to improve their ionic conductivity, polymer electrolytes are often doped with a plasticizer or operated at elevated temperatures, further decreasing mechanical strength, and increasing the tendency of dendrite piercing.

Various methods have been studied to solve the problem, one of which is to employ block copolymer.⁶³ Polystyrene-co-polyethylene oxide (PS-PEO) matrix attracted lots of attention in block copolymer electrolytes, since the PS block improves mechanical strength while the PEO regions facilitates lithium-ion transport. As a state-of-the-art, the PS-PEO copolymer blended with LiTFSI may reach an ionic conductivity of $\sim 10^{-3}$ S/cm at 90 °C, while the shear modulus is on the order of 0.1 GPa at the same temperature.^{64, 65} Although the electrolyte maintains 80%

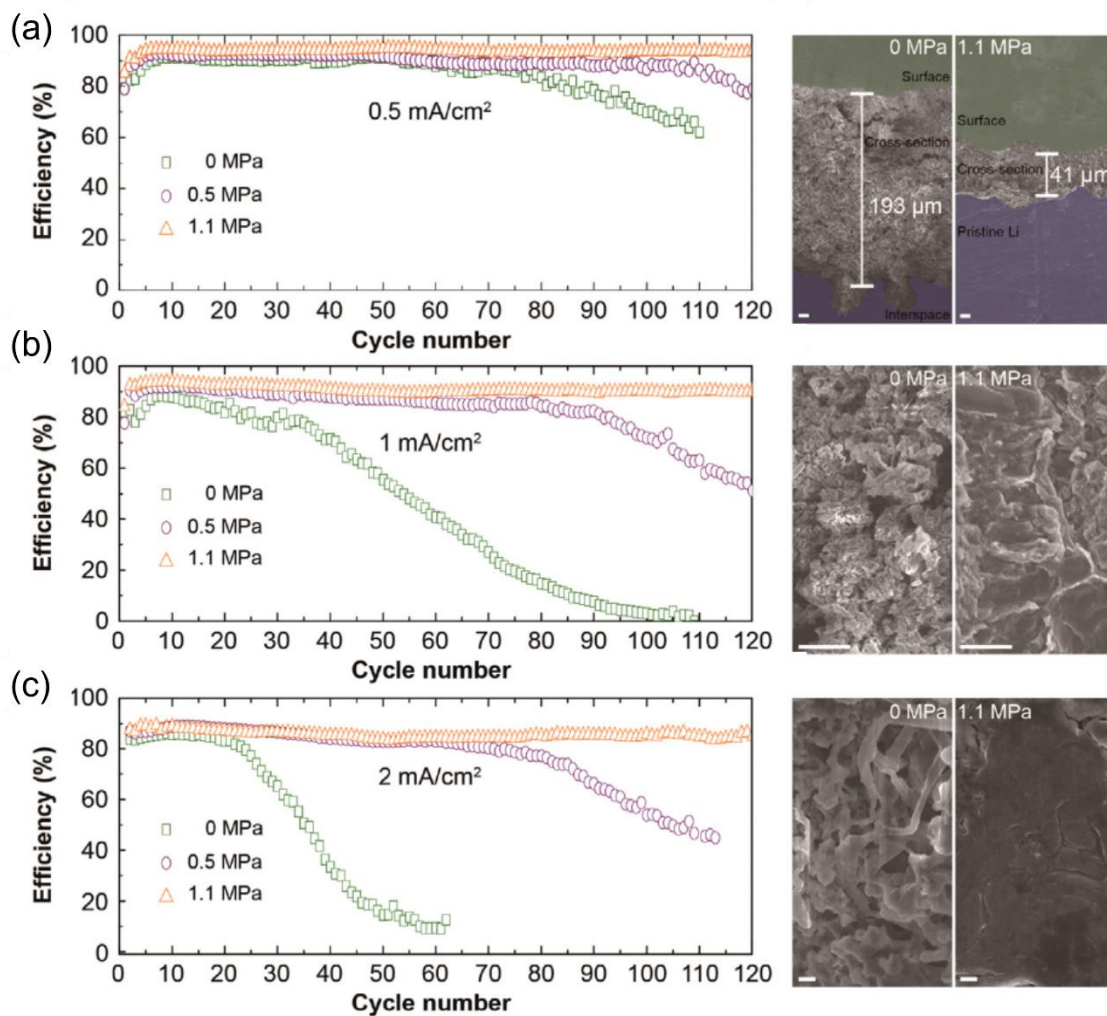


Figure 1.6 Cycling behaviors of Li-metal with and without external pressure. Cycling Coulombic efficiency of lithium metal under a pressure of 0 MPa, 0.5 MPa and 1.1 MPa and cross-section SEM images of Li foil after cycling at a current density of (a) 0.5 mA/cm², (b) 1 mA/cm² and (c) 2 mA/cm².⁶¹

of its original capacity after 300 hours of cycling, the crystallization of PEO limits its performance at room temperature. Another method is to build a crosslinking membrane. Compared to a linear polymer which may flow and lose mechanical property at high temperature, a crosslinking polymer electrolyte will maintain mechanical stability at the same condition.⁶⁶ However, this method has limited improvement on mechanical property, mostly up to 100 MPa.

Therefore, the addition of inorganic fillers has been widely studied.^{67, 68} For example, Guang and coworkers reported a PEO-based composite electrolyte with a woven glass fiber, with a high elastic modulus of up to 2.5 GPa over a broad temperature range.⁶⁹ Even being doped with plasticizer, the elastic modulus of membrane was still above 0.1 GPa with high ambient temperature conductivity ($\sim 10^{-4}$ S/cm). Assembled in a Li/Li cell, it exhibits a stable lithium cycling for over 3000 hours while maintaining a smooth lithium metal surface (Figure 1.7). Unlike inert components that are almost lithium-ion insulative, the addition of lithium-ion conducting ceramics may enhance both mechanical property and ionic conductivity at the same time. For example, Fu and coworkers prepared a garnet-type ceramic-LLZAO network infiltrated with a PEO/LiTFSI electrolytes. The composite membrane demonstrated better mechanical property and reached a high ambient temperature ionic conductivity (2.5×10^{-4} S/cm) due to the existence of long-range lithium-ion conductive pathways. The electrolyte also exhibited a stable voltage profile for 1000 hours with a current density of 0.5 mA/cm² (Figure 1.8).⁷⁰ It is noteworthy that the addition of an inorganic filler may introduce extra interfaces, voids, or defects, where dead lithium may deposit, accumulate, and then sprout out during battery cycling. Therefore, further investigation about structure distribution and Li deposition

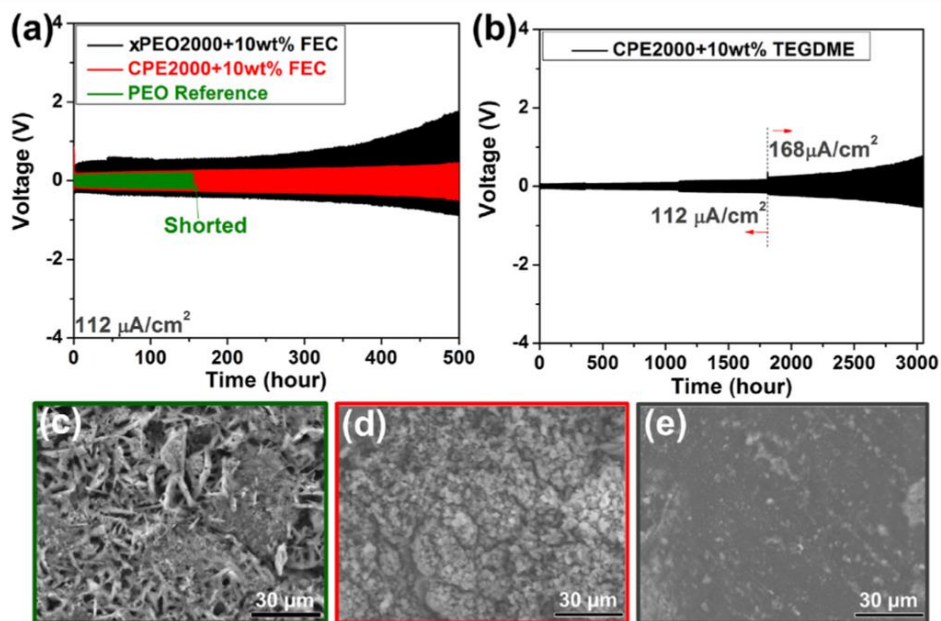
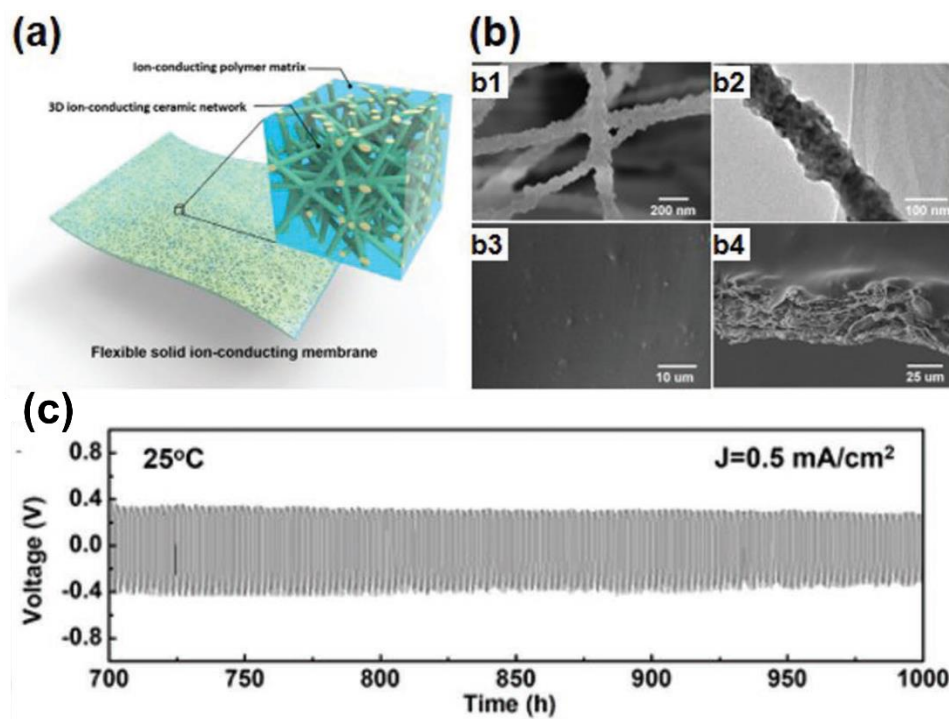


Figure 1.7 Electrochemical performance of various crosslinked membranes evaluated using a symmetric Li/Li cell at 70 °C. Voltage profile of lithium plating/stripping cycling for (a) membranes with 10wt% FEC with a current density of 112 $\mu\text{A}/\text{cm}^2$ and (b) xPEO2000 plasticized with 10wt% TEGDME with a current density of 112 $\mu\text{A}/\text{cm}^2$ for the first 1811 h and 168 $\mu\text{A}/\text{cm}^2$ for the subsequent 1269 h. SEM micrograph showing the surface morphology of the cycled Li electrode for (c) linear PEO electrolyte, (d) CPE2000 + 10wt% FEC, and (e) CPE2000 + 10 wt% TEGDME, respectively. ⁶⁹



behavior is also required.

1.5 Single-ion conducting polymer electrolytes (SICPEs)

Polymeric ionic liquids (PolyILs) are a class of polyelectrolytes with ionic liquid species chemically attached to the polymer matrix.^{56, 71-73} Depending on the type of the mobile ion, PolyILs can be categorized as polycations, polyanions, polyzwitterions and ionic copolymers. For the application in lithium-ion batteries, various polyanions with mobile lithium-ion have been widely studied.⁷⁴⁻⁸⁵

1.5.1 Transport Number vs. Transference Number

“Transport number” is one of the important factors that influence the ionic conductivity of polymer electrolyte. However, many works have wrongly used “transference number” to characterize the same property, which actually has a different definition. Therefore, it is important to clarify these two parameters before further discussion.⁸⁶ “Transport number” is defined as the fraction of total current carried by a specific ion in the electrolyte, with the symbol t^+ or t^- refers to the transport number for cation or anion. The differences in transport number arise from the differences of mobilities for ions:

$$t^+ = \frac{\mu_+}{\mu_+ + \mu_-} \quad (1.10)$$

Based on the definition of conductivity in section 1.2, we may also express transport number by partial conductivities or diffusion coefficient:

$$t^+ = \frac{\sigma_+}{\sigma_+ + \sigma_-} = \frac{D_+}{D_+ + D_-} \quad (1.11)$$

Typically, the cation transport number is lower than the anion transport number, especially for lithium-ion containing system. For example, t_{Li}^+ is $\sim 0.2-0.3$ for traditional PEO based polymer electrolytes. This low t_{Li}^+ is because lithium-ion is commonly surrounded by solvent molecules, or coordinated with polymer segments, to form a “shell” structure, while the anion has minimal interaction and more freedom to move.

As a comparison, transference number is defined as the number of moles of lithium transferred by migration per Faraday of charge. To better differentiate this parameter from transport number, we may take a generic lithium salt, LiX, as an example. Other than Li^+ and X^- , the partial dissociation of lithium salt may result in the existence of neutral ion pair LiX , or even ion triplets like Li_2X^+ and LiX_2^- . In this case, the lithium transference number, T_{Li}^+ , will be:

$$T_{Li}^+ = t_{Li}^+ + 2t_{Li_2X^+} - t_{LiX_2^-} \quad (1.12)$$

In other words, T_{Li}^+ features the net transference of all lithium-ion containing species. For an ideal case, like in a very dilute solution, lithium salt may fully dissociate and only produce Li^+ and X^- . In this case, $T_{Li}^+ = t_{Li}^+$. It is imperative to keep in mind that both parameters are not interchangeable for most cases. Another difference is the threshold. According to the definition, a transport number can only be between 0 and 1 for any species, while there's no limit for transference numbers. This may theoretically happen when the mobility of negative triplets LiX_2^- is so fast that overall lithium-ions move in the opposite direction of the current. In addition, the neutral ion pair LiX has no contribution to the transference number, since the net transference is zero. As a result, the transference number is commonly smaller than the transport number for lithium-ion.

Different methods have been used to measure these two parameters, which are discussed in detail in section 2.5.2. Vincent and Bruce proposed a method combining a DC polarization test and AC impedance spectroscopy to achieve transport number, although this method was originally targeted to measure transference number. To measure real transference number, Hittorf designed a relatively complex cell set up, which includes an additional reference section to exclude the influence of a concentration gradient. Since the Vincent-Bruce method is convenient, it has almost become a standard method to characterize new materials, although many recent works wrongly referred to it as “transference number”. We will also use this method in the following works.

1.5.2 Advantage of high transport number

The lithium-ion transport number, t_{Li^+} , is our main concern for lithium-ion batteries, since the lithium-ion should be the potential transporting ions. However, most commercially available electrolytes, both polymer electrolytes and liquid electrolytes, exhibit low t_{Li^+} , which means that the majority of conductivity is contributed by the anions. By grafting the anion on the polymer matrix, the mobility of the anion is significantly suppressed, which results in t_{Li^+} close to the unity. Therefore, PolyILs are also referred to as single-ion conducting polymer electrolytes (SICPEs).

Many computational results have demonstrated the significance of SICPEs in improving the electrochemical performance and prolonging the cycle life of lithium-ion batteries.⁸⁷⁻⁹⁶ With applied current in a binary electrolyte, there exists a moment when the salt concentration at electrode surface decreases to zero and uniform electrodeposition becomes unstable. This

dendrite initiation time is described as “Sand’s time” when self-amplifying lithium dendrite growth start to propagate. Based on the model proposed by Chazalviel et al., “Sand’s time” is proportional to t_{Li^+} , in which the velocity of lithium dendrite growth is close to that of anions extracted from the working electrodes.^{94, 97} This idea is consistent with the model proposed by Tikekar et al. that a certain fraction of immobilized anions would slow down the growth of Lithium dendrites, especially under high overpotential or with high current densities (Figure 1.9(a)).⁹⁵ Thus, tethered anions can improve the stability of the electrodeposition process on metal surfaces, suppressing dendritic growth, and lengthening battery cycling lifetime.

The high t_{Li^+} can also reduce the tendency to form ion concentration gradients. Otherwise, the significant gradient will cause strong polarization in the cell and increase internal impedance, which may slow down the charge-discharge process. Additionally, it is demonstrated that a high lithium-ion transport number can lead to the uniform reaction of active materials at the electrodes, which is especially favorable for fast charging applications. For example, a specific cell containing the Li/polymer/LiV₆O₁₃-composite electrode was modeled by Newman et al (Figure 1.9(b)).^{92, 98} Their best-available polymer electrolytes (a random copolymer of methylpolyethylene glycol acrylate and lithium sulfonated diethylene glycol acrylate, “non-unity” t_{Li^+}) and ionomer electrolytes (oxymethylene-linked polyethylene glycol with lithium bistrifluoromethyl-sulfonylimide, “unity” t_{Li^+}) were selected to determine the influence of transport number on long-term battery performance. The results indicated that the cell with ionomer electrolytes could obtain a high energy density without losing active materials on the electrodes, especially at high charge/discharge rates, even with an order of magnitude lower conductivity than polymer electrolytes. In addition, the benefits of high t_{Li^+} were also quantified

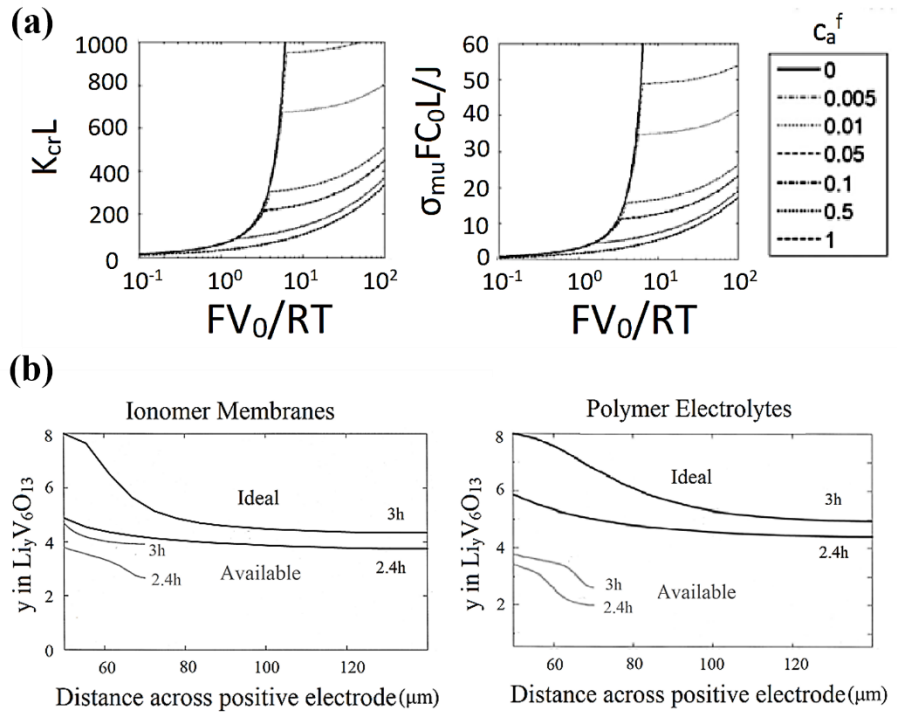


Figure 1.9 (a) Two important parameters of the stability analysis: critical wavenumber, K_{cr} , and growth rate of most unstable mode at varying overpotentials for different fixed anion fractions.⁹⁵ Note, V_0 is overpotential, F is Faraday's constant, L is the distance to lithium electrode interface, C_a^f is the fraction of immobilized anions, C_0 represents the total concentration of anions at equilibrium, σ_{mu} refers to the conductivity when the growth rate of perturbation is at maximum. (b) Active material utilization (expressed as y in $Li_yV_6O_{13}$, where y range from 0 to 8) across the positive electrode for the best-available and ideal ionomers (unity t_{Li^+}) and polymer electrolyte (non-unity t_{Li^+}) after 2.4 and 3 h of discharge at the optimum current density.⁹²

by a dual lithium-ion insertion cell model, in which the electrolytes have various conductivities and transport numbers.⁹⁹ The influence from other parameters, like the solid electrolyte interphase (SEI) layer and ionic impedance, are excluded in this model. In this case, the attainable state of charge (SOC) for an electrolyte, which denotes the currently available capacity relative to its rated capacity, increased with t_{Li}^+ at a high charge rate. In other words, the battery with a high t_{Li}^+ can obtain the same SOC with less time and hence benefiting fast charging applications.

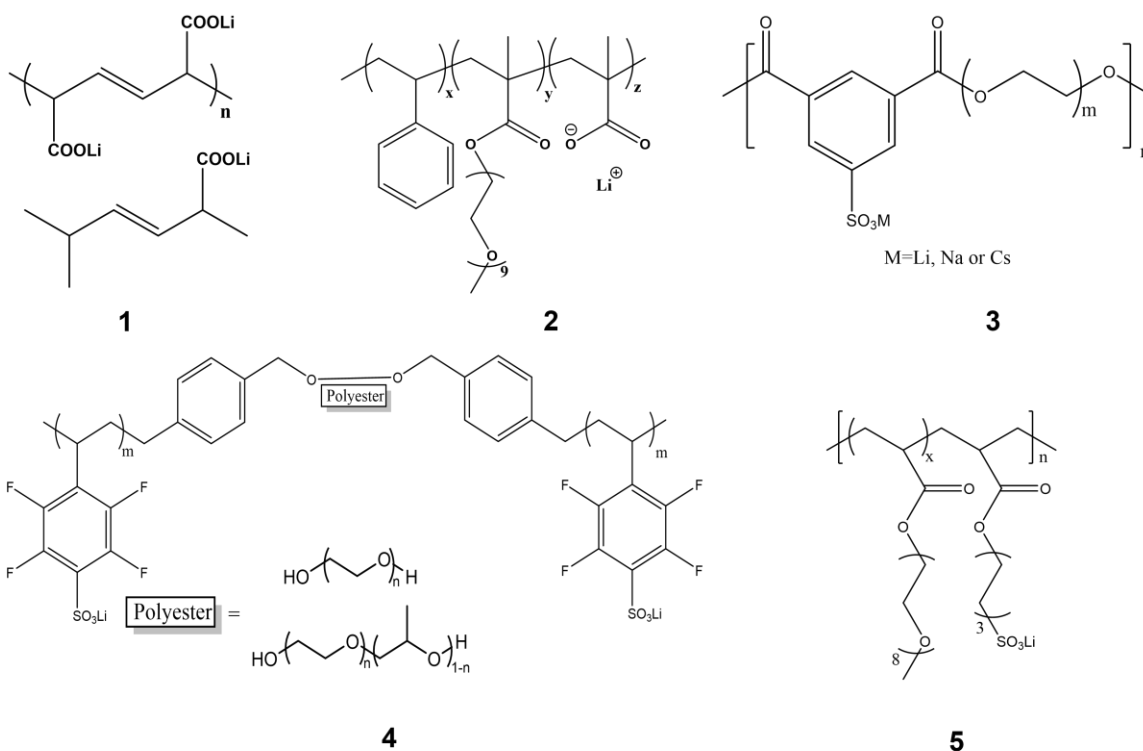
1.6 Review of Structure and conductivity value for SICPEs

1.6.1 Anionic group: carboxylate and sulfonate group

The anionic group is a key factor that controls the property of PolyILs used in lithium-ion batteries (Table 1.2). PolyILs with the carboxylate anion were firstly applied in this area (Scheme 1.1). Kubo and coworkers presented a physically blended membrane of polyether and polyethylene oxide together with a polyanion lithium salt having a carboxylate anionic group (**1**).¹⁰⁰ Due to the crystallization of PEO, the membranes were characterized at 80°C, where the conductivity varied from 10^{-4} to 10^{-5} S/cm depending on the concentration of lithium-ions. After adding Lewis acid-boron trifluoride etherate ($BF_3 \cdot OEt_2$) into the system, the conductivity at 80°C was improved up to two orders of magnitude while t_{Li}^+ was also relatively high (0.45~0.88). The author concluded that $BF_3 \cdot OEt_2$ not only accelerates dynamics as a plasticizer, but also induces delocalization of the anionic charge by forming a complex with the carboxylate group, hence improving lithium-ion dissociation. A similar improvement was also observed from work by Gohy, in which a copolymer with a single-ion conducting block poly(lithium methacrylate-co-

Table 1.2 Summary of various SICPEs with transport number and conductivity.

No.	Structure	t_{Li^+}	Ionic conductivity (S/cm)
1	Polyether, polyethylene oxide blended with SICPE	0.45~0.88	$10^{-4} - 10^{-5}$ at 80 °C (dry)
			up to 10^{-3} with $BF_3 \cdot OEt_2$
2	Block copolymer of poly(ethylene glycol methacrylate), polystyrene and poly (lithium methacrylate)	0.84	$10^{-8} - 10^{-11}$ at 25 °C (dry)
			up to 10^{-5} with $BF_3 \cdot OEt_2$
3	PEG ionomers with sulfonate anion	N/A	6.27×10^{-7} at 25 °C
4	Triblock SICPE with PEO, PPO and poly(lithium 2,3,5,6-tetrafluorostyrene-4-sulfonate)	N/A	10^{-6} S/cm at 20 °C
5	Comb-shaped copolymer of PEO and sulfonate monomer	N/A	2.0×10^{-7} at 25 °C (dry)
			1.4×10^{-4} with carbonate
6	Block copolymer of LiMTFSI and PEO	0.83	2.3×10^{-6} at 25 °C
7	Random copolymer of LiSTFSI and PEGMEA	> 0.9	7.6×10^{-6} at 25 °C
8	PDMS backbone grafted with LiPSI	0.89	7.2×10^{-4} at R.T. with carbonate
9	PEO blended with LiSsTFSI	>0.9	1.35×10^{-4} at 90 °C
10	Copolmer of polyethylene and LiAFSI	0.91	5.84×10^{-4} at 25 °C
11	Block copolymer of PEO and LiSTFSI	0.87-0.99	$10^{-4} - 10^{-7}$ at 60 °C
12	Polysiloxane ionomers with cyclic carbonate and three different borate monomers	N/A	10^{-7} at 25 °C
13	Homopolymer poly(PEOMA-TFSI ⁻ Li ⁺)	0.97-0.99	$10^{-4} - 10^{-5}$ at 90 °C



Scheme 1.1 Examples of SICPEs with carboxylate group (**1-3**) and sulfonate group (**4,5**).

ionomer, the ionic conductivity was drastically enhanced with the length of the PEO spacer. For example, the ionic conductivity at ambient temperature could be increased by four orders of magnitude to reach 10^{-6} S/cm , when M_n of PEO spacer was increased from 400 to 900. oligoethylene glycol methacrylate) and polystyrene block was presented (**2**).¹⁰¹ By adding BF_3 into the system, the ionic conductivity could reach 10^{-5} S/cm at room temperature.

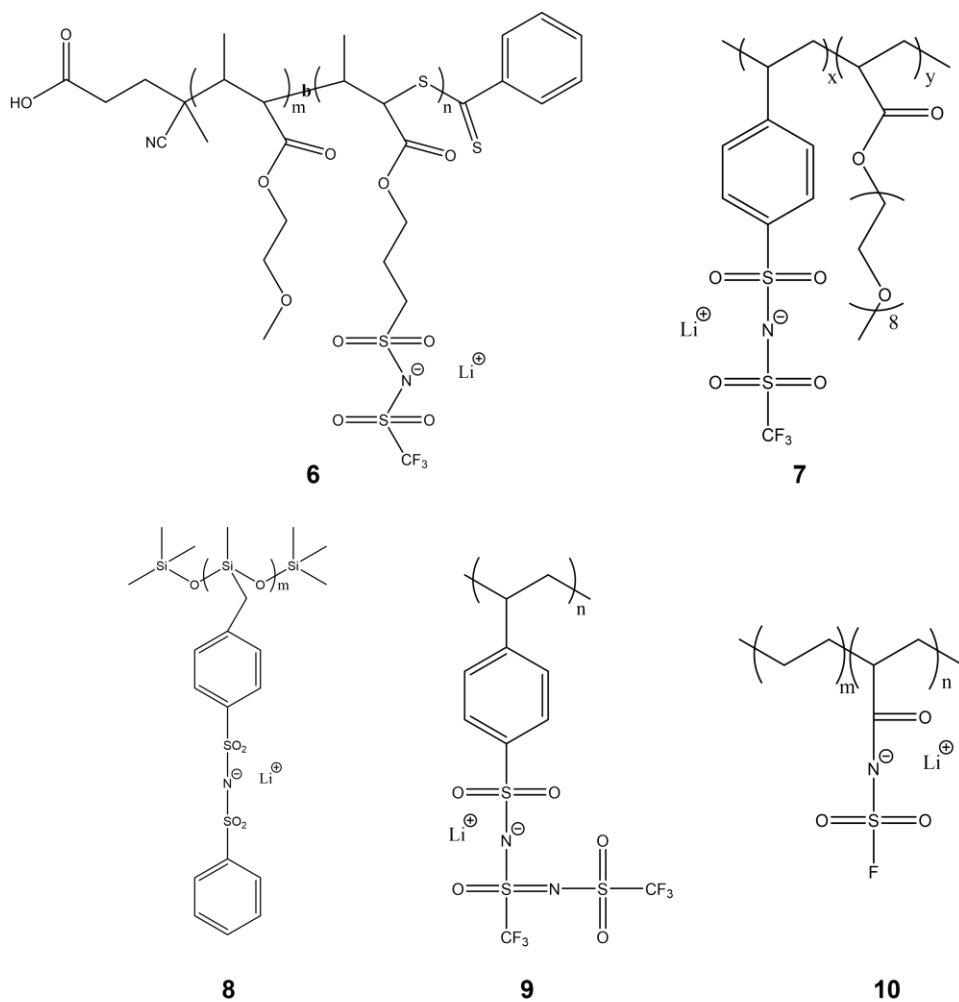
Compared to the carboxylate group, another commonly used anionic group- sulfonate, has weaker pairing strength with the lithium-ion. The conductivity and morphological property of SICPEs composed of sulfonated ionomers with different cations and PEO spacers in the backbone have been studied by Colby and coworkers (**3**).^{102, 103} The use of flexible PEO spacers was to take advantage of its ability to solvate small cations and facilitate ion transport. For Li

However, a further increase in the length of the PEO spacer results in the crystallization of PEO segments at ambient temperature, which results in a significant decrease in ionic conductivity. In this case, samples with longer PEO spacers had to work at higher temperatures to reach the required ionic conductivity.

To exclude the influence of PEO crystallization, different methods have been applied. Rather than using long range of ordered PEO segments, a random copolymer of PEO and PPO was selected to form triblock SICPEs with poly(lithium 2,3,5,6-tetrafluorostyrene-4-sulfonate) by Jannasch (4).⁸⁰ Without crystallization, the PEOPO materials with a ratio of EO/Li=18: 1 could reach the highest conductivity above 10^{-6} S/cm at 20 °C, while the conductivity of a PEO-based block polymer was still limited by the crystallinity of PEO (3.0×10^{-8} S/cm). Another method is employing short PEO segments as sidechains. A comb-shaped copolymer of PEO and sulfonate monomer have been studied by Sun (5).¹⁰⁴ In addition to being copolymerized within the system, PEO trimers were connected to the sulfonated monomer as a spacer, which also increased the mobility of sulfonate group. The highest conductivity of 2.0×10^{-7} S/cm was obtained with a ratio of EO/Li=40 at 25°C. In addition, this work used carbonate solvent mixture as a plasticizer to further improve ionic conductivity. Doped with 50wt% PC/EMC (1/1 v/v), the ionic conductivity can reach 1.4×10^{-4} S/cm at ambient temperature, while this gel polymer electrolytes also exhibited stable Li/Li cycling under the current density of 0.1 mA/cm² at 85 °C.

1.6.2 Sulfonyl(trifluoromethane-sulfonyl)imide (TFSI) group and its derivative

To have a better dissociation between anion and lithium-ions, the anion with a delocalized charge would be favorable. A main method is to have a bulky conjugation of anionic units or



Scheme 1.2 Examples of SICPEs with sulfonyle(trifluoromethane-sulfonyl)imide (TFSI^-) anion (**6,7**) and its derivatives (**8-10**).

attaching strong electron-withdrawing groups. Therefore, the anion units with structure similar to ionic-liquid, e.g., sulfonyle(trifluoromethane-sulfonyl)imide ($\text{SO}_2-\text{N}^-(\text{SO}_2-\text{CF}_3)$) and (fluorosulfonyl)-imide ($\text{N}^-(\text{SO}_2-\text{F})$), have dominated this research area (Scheme 1.2).¹⁰⁵⁻¹⁰⁸

Porcarelli prepared a block copolymer of lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethane-sulfonyl)imide (LiMTFSI) and PEO sidechains by reversible addition-fragmentation chain transfer (RAFT) polymerization (**6**).¹⁰⁹ The synthetic SICPEs exhibit decent

ionic conductivity up to 2.3×10^{-6} S/cm at 25 °C. As the SICPE is viscous liquid at ambient temperature, the cell was characterized at 70°C to have better wettability over the electrodes, in which good electrochemical stability (up to 4.5 V vs. Li^+/Li) and high transport number ($t_{\text{Li}^+}=0.83$) were obtained. In addition, a high charge/discharge efficiency and excellent specific capacity (up to 130 mAh/g) at C/15 rate was obtained with lithium–metal battery prototypes, which emphasize the advantage of high lithium-ion transport (Figure 1.10). Later on, they add a plasticizer, PC, into the same sample to further improve ionic conductivity by two orders of magnitude (10^{-4} S/cm), keeping the transport number still high ($t_{\text{Li}^+}=0.86$).

Another widely studied monomer is lithium 4-styrenesulfonyl(trifluoromethane-sulfonyl)-imide (LiSTFSI). Since the conductivity of the homopolymer at room temperature is heavily limited by their high T_g , different methods have been employed to improve the performance. A homopolymer of LiSTFSI was synthesized by two different methods, i.e., free radical polymerization and polymer modification, and physically blended with PEO matrix by Armand and coworkers.¹¹⁰ Above the melting temperature of PEO, the conductivity of polymer electrolytes with homopolymer by free radical polymerization (10^{-5} S/cm) is almost an order higher than the other one, which suggests the importance of synthesis method and the purity of sample. Similar to LiMTFSI, LiSTFSI has also been copolymerized with short PEO sidechains poly(ethylene glycol) methyl ether acrylate, PEGMEA, which the highest conductivity can reach 7.6×10^{-6} S/cm at 25 °C and 10^{-4} S/cm at 60 °C along with $t_{\text{Li}^+}>0.9$ (7).¹¹¹ This significant improvement was ascribed to the highly amorphous PEGMEA segments and low T_g of polymer matrix.

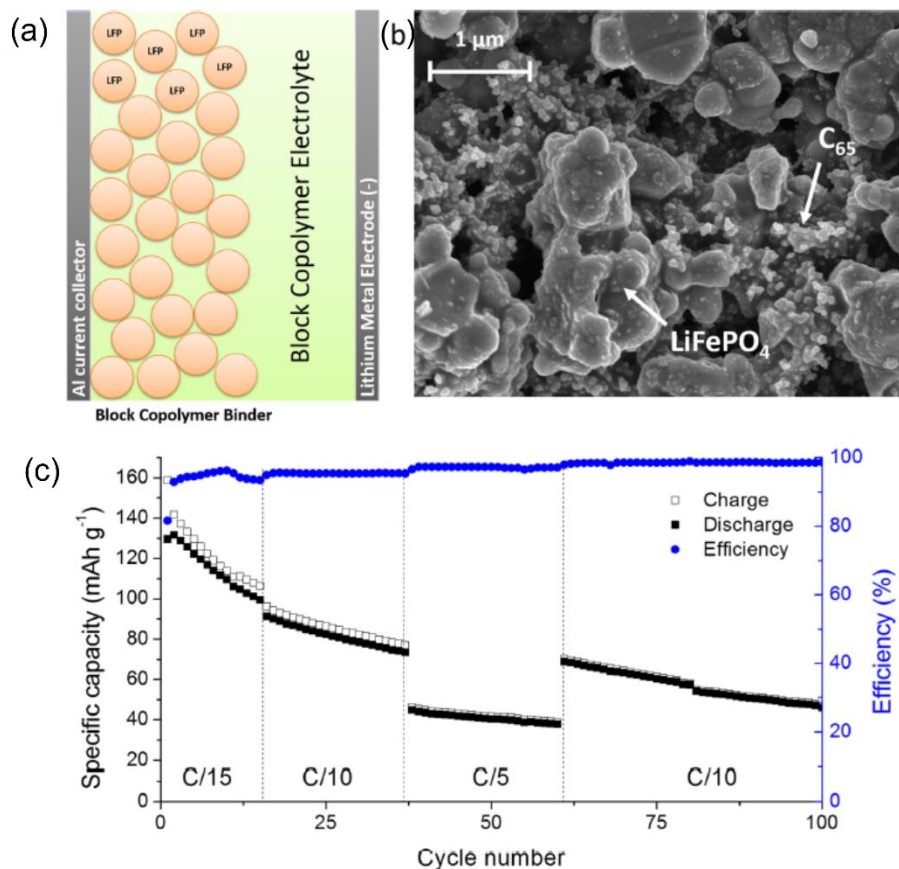


Figure 1.10 (a) Sketched representation of the cell assembly, where the percolation of the polyelectrolyte in the whole electrode structure is clearly evidenced. (b) SEM image of the composite electrode. (c) Specific capacity versus cycle number profile of the Li/LiBC-1/LiFePO₄ cell at different charge/discharge rates at 70 °C.¹⁰⁹

To further enhance the delocalization of the anion, LiTFSI can be substituted with additional electron withdrawing groups. Single-ion monomer lithium 4-Styrenesulfonyl(phenylsulfonyl)-imide (LiSPSI) with two benzen rings on both ends (**8**) was grafted on a PDMS backbone by Cheng and co-workers.¹¹² The extremely flexible PDMS backbone enabled fast chain dynamics, which results in high transport number ($t_{Li^+}=0.89$) and remarkable ambient temperature ionic conductivity of 7.2×10^{-4} S/cm after being soaked in the EC/PC (1:1 volume ratio) solvent mixtures. Lithium 4-styrene-sulfonyl(trifluoromethyl(S-trifluoromethylsulfonylimino)-sulfonyl)imide (LiSsTFSI) having =O replaced by another =NSO₂CF₃ (**9**) was also synthesized.¹¹³ Blended with a PEO matrix, the ionic conductivity of LiSsTFSI can reach 1.35×10^{-4} S/cm at 90 °C, which was comparable to the classic LiTFSI/PEO system at same temperature.

Additionally, Kim and coworkers proposed a novel SICPE containing acrylic (fluoro sulfonyl)imide anion (AFSI), which substituted -CF₃ terminal groups with single fluorine (**10**).¹¹⁴ In this work, the solvent free copolymer electrolyte of AFSI and polyethylene presented an impressive ambient temperature conductivity (5.84×10^{-4} S/cm at 25 °C), together with a high $t_{Li^+}=0.91$ (Figure 1.11). This enhancement in ionic conductivity suggested that the reduced interaction between AFSI⁻ anion and lithium-ions is the main driving force. Moreover, this new material also exhibited certain capability to self-healing and outstanding thermal stability.

1.6.3 Dominating usage of PEO structure

The structure of the polymer matrix is another important factor that influences ion transport and decides the mechanical property and thermal stability of SICPEs. Similar to traditional polymer electrolytes, the utilization of PEO dominates most of works (Scheme 1.3). Other than

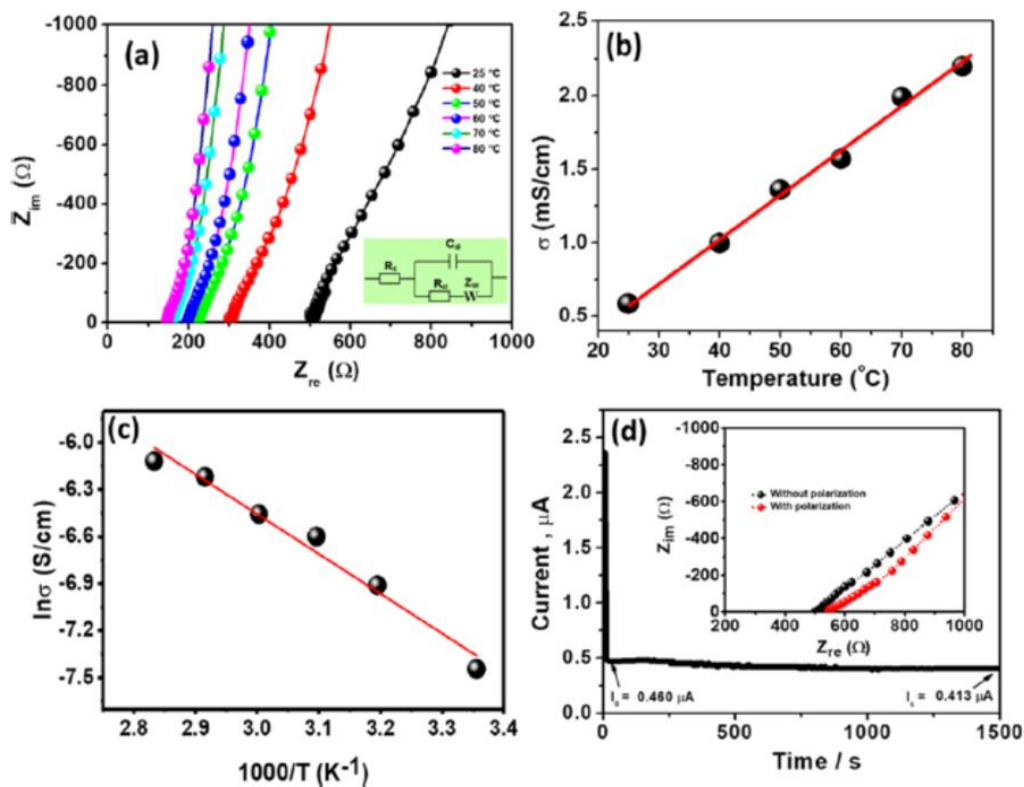
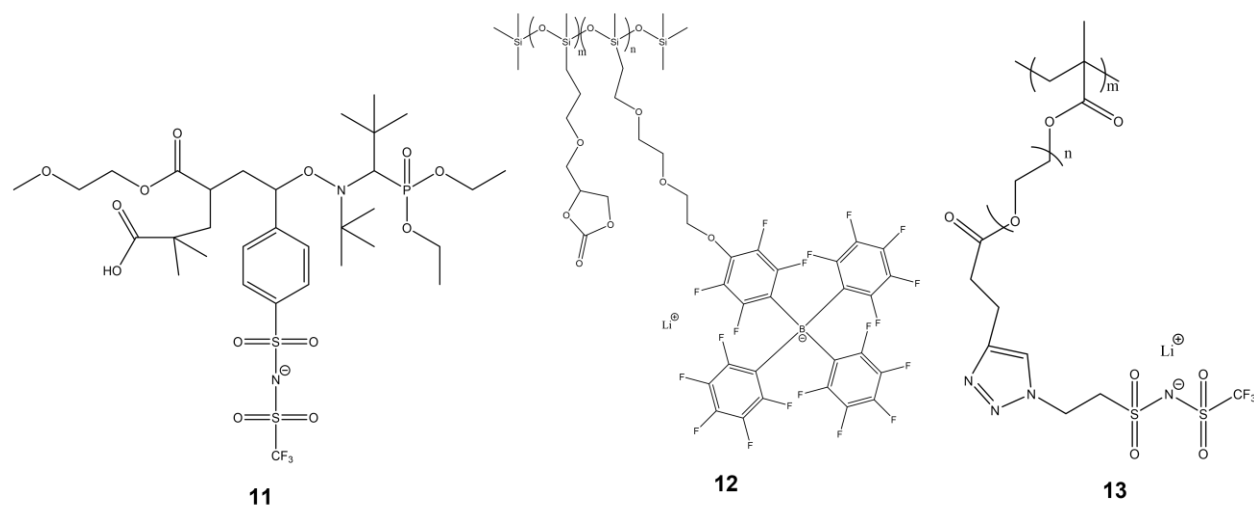


Figure 1.11 (a) Nyquist plots of the self-healed electrolyte-based SS/PEALiFSI/SS symmetrical cell in the temperature range of 25-80 °C under open-circuit condition. Inset: Randles equivalent circuit diagram to fit the Nyquist plots, where R_{CT} , R_s , Z_w , and C_{dl} are the charge-transfer resistance during the electrochemical reactions, bulk resistance due to the movement of Li^+ , Warburg diffusion resistance, and the double-layer capacitance, respectively. Plots of (b) Li^+ conductivity vs temperature and (c) $\ln(Li^+$ conductivity) vs. the inverse of absolute temperatures. (d) Chronoamperometric polarization plot of the self-healed electrolyte-based Li/PEALiFSI/Li cell at 10 mV for 1000 s (inset: Nyquist plots of the cell before and after polarization).¹¹⁴



Scheme 1.3 Examples of SICPEs containing PEO structure (**11-13**).

physical blending with SICPEs (**1,9**),^{115, 116} linear PEO with high molecular weights has been chemically grafted on the both sides or one side of SICPEs.^{74, 85, 117-123} For example, the ionic conductivity and morphology of PEO-b-PLiSTFSI block copolymer have been deeply studied by Balsara and coworkers (**11**).^{117, 118} Depending on the molecular weight, the block copolymer may exhibit microphase separation. In this case, the ionic conductivity at ambient temperature was strongly affected by the crystallinity of PEO, where lithium-ions were trapped in the glassy PSLiTFSI-rich microphases as ion clusters at low temperature. While ionic conductivity was increased abruptly by several orders of magnitude above the melting temperature, since the obtained amorphous PEO facilitates lithium-ion transport. Although crystalline PEO could enhance mechanical property, it strongly suppresses ionic conductivity and limits their application, especially at room temperature. To suppress or even eliminate the crystallinity, PEO chains with low molecular weights were copolymerized with monomers of SICPEs, which has been discussed above (**5-7**). With high content of amorphous PEO region, they could achieve a much higher ionic conductivity at ambient temperature (almost 10^{-5} S/cm).

Alternatively, PEO units can also be incorporated as the spacer between different structures.

Colby and coworkers proposed a polysiloxane ionomers with cyclic carbonate and three different borate monomers (**12**).¹²⁴ When bulky lithium triphenylstyryl borate anion was connected to the polymer backbone by PEO spacer, the compatibility between different segments were improved. Together with lower T_g and higher dielectric constant, the ionic conductivity at ambient temperature was also improved. In addition, when anion group was substituted with more delocalized perfluorinated phenyl rings, the highest ionic conductivity at ambient temperature was achieved ($\sim 10^{-7}$ S/cm). The similar improvement was also observed by Matyjaszewski and coworkers, which reported a homopolymer SICPEs with poly(poly(ethylene oxide) methacrylate lithium sulfonyl(trifluoromethyl-sulfonyl)imide), poly(PEOMA-TFSI-Li⁺) (**13**).¹²⁵ With PEO spacer between the single-ion conducting units and polymer backbone, SICPE had accelerated segmental dynamics, together with the formation of an amorphous and lithium-ion conducting phase. As a result, it presented high ionic conductivity (10^{-5} – 10^{-4} S/cm at 90 °C), high transport number (0.97–0.99) and stable lithium plating/stripping for over 300 cycles with current density ≥ 0.1 mA/cm² at 90 °C.

1.7 Research Goals

The development of solid polymer electrolyte (SPEs), with good mechanical flexibility and processibility, is important to realize for the next generation battery technology with enhanced safety and high energy density. However, the shortcomings of SPEs, such as relatively low conductivity at ambient temperature and low lithium-ion transport number (t_{Li^+}), limit their practical application. Single-ion conducting polymer electrolytes (SICPEs) have been proposed

to obtain an almost unity transport number, while the conductivity is still far below the required values ($\sim 10^{-4}$ to 10^{-3} S/cm at ambient temperature). Other than t_{Li^+} , battery performance is also strongly influenced by other parameters, such as mechanical property and chemical composition. Therefore, a point-to-point experimental result that can demonstrate the contribution only from t_{Li^+} on battery performance is required.

With above goals in mind, this work will focus on the following problems. Firstly, we will develop an SICPE having accelerated segmental dynamics that presents improved ionic conductivity. Then, we will explore potential neutral units to substitute PEO that has been widely used in the research of polymer electrolytes. Lastly, we will build up a system to investigate the effect of t_{Li^+} on battery performance by fixing other parameters.

Chapter II

Experimental Section

2.1 Characterization of Structures

2.1.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear Magnetic Resonance Spectroscopy (NMR) is a technique that monitors the transition of nuclei spin states in an applied magnetic field. When the energy matches the difference between nuclei spin levels, the nuclei would adsorb the energy from external magnetic field for the spin orientation, which can be characterized by the resonance radio-frequency pulse. As a key parameter of NMR measurement, this resonant frequency relative to a standard in a magnetic field is defined as chemical shift. The position, numbers and amplitude of chemical shifts would provide detailed information about functional groups of probed molecules. Probed by NMR, different molecules exhibit obviously different signals, while the same type of molecules but within different local chemical environments would also be distinguishable. Therefore, NMR is a definitive method to identify chemical structure of organic molecules, especially for small molecules. In addition, NMR has also been widely used to verify chemical composition of polymers. Different from the sharp peaks for small molecules, the width of peaks is typically broader for polymers due to poor molecular rotation and repeating units being situated in different chemical environments.¹²⁶ In addition, NMR may also be used to estimate an average degree of polymerization (DP_n) based on the integration value of featured peaks.^{81, 127} A representative NMR spectrum of POSS nanoparticles grafted with different ratios of polyethylene oxide and reversible addition fragmentation chain transfer agent (RAFT-CTA) is

shown in Figure 2.1. A certain ratio of single-ion monomer 4-styrenesulfonyl(trifluoromethanesulfonyl)imide lithium (STF-Li⁺) was attached through RAFT polymerization. The DP_n of poly(STF-Li⁺) was calculated to be 31.1 based on the comparative integration of the signals derived from the terminal methyl group in RAFT-CTA (0.5 -1.0 ppm) and the benzyl group in the monomer (6.0 -8.0 ppm).

The most common types of NMR are ¹H and ¹³C NMR spectroscopy, though it is applicable to any sample with nuclei spin, like ¹⁵N and ¹⁹F. For aqueous solution, it is mainly composed of solvent molecules, which is commonly hydrocarbons. Therefore, to avoid dominating proton NMR signal from solvent molecules, samples are usually dissolved in deuterated solvents based on solubility.

2.1.2 Fourier Transform-Infrared Spectroscopy (FT-IR)

Fourier Transform-Infrared Spectroscopy (FTIR) is a technique to obtain absorption of radiation by samples in the infrared range. Rather than applying a monochromatic radiation, FT-IR shines a light with various frequencies on the sample and records the amount of absorbed light at different wavelengths. To do that, the light is altered by a moving mirror and guided through an interferometer. After the first scan, the light would be modified to different combinations of frequencies and record the data again. After multiple scans, the data would be processed by Fourier transform technique and produce an IR spectrum in terms of the absorption at each wavelength. Since different functional groups possess different vibrational modes, the intensity and position of characteristic absorption bands would also be different. Therefore, FT-IR is a simple and reliable method used to identify chemical structures. Table 2.1 includes the

Table 2.1 Examples of Characteristic IR Absorption Frequencies for Organic Functional Groups.

Functional groups	Characteristic Absorptions (cm ⁻¹)*	Intensity
C-H (alkane)	s: 2850-3000; b: 1360-1480	strong
O-H (alcohol)	s: 3200-3600	strong, broad
C=O(carbonyl,ester)	s: 1670-1820	strong
C-O(ether)	s: 1000-1300	strong
N-H(amine)	s: 3100-3500; b: 1600	medium
C-N(nitrile)	s: 2210-2260	medium

* s: stretching mode, b: bending mode.

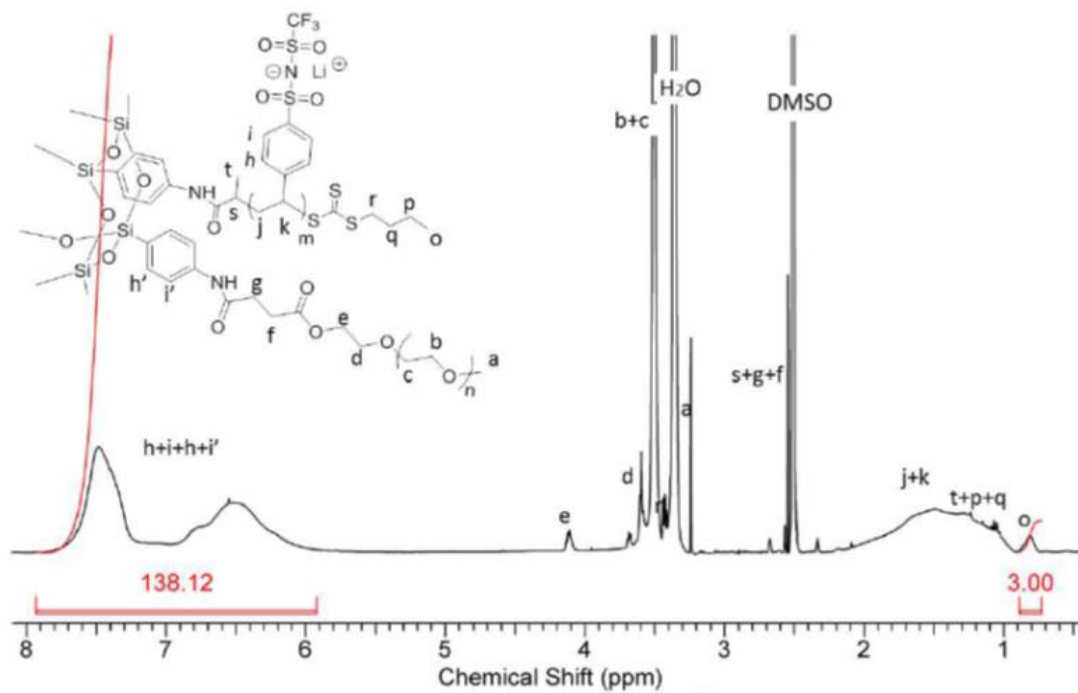


Figure 2.1 ^1H NMR spectrum of POSS-PEO_{5.3}-PSTF_{2.3}.⁸¹

absorption frequencies for some commonly seen functional groups for polymers.

Attenuated total reflection (ATR) is a sampling technique applied in FT-IR, which directly enables measurement of solid or liquid sample without further preparation. The infrared light is passed through an ATR crystal, like germanium and diamond, to form evanescent wave that extends into the sample. Since the penetration depth of light is only about 1~2 micrometers within sample, it not only has minimal requirement of sample thickness, but also prevents strong attenuation of IR signal for highly absorbing media, like aqueous solutions.¹²⁸

2.1.3 X-ray Scattering

X-ray scattering technique is a powerful method to reveal the information about crystal structure and physical properties of materials. After hitting the materials with X-ray beam, the resulting scattered intensity is recorded as a function of scattering angle, polarization or energy. The method is non-destructive and usually requires tiny amount of sample in either liquid or solid state, though the significant X-ray exposure may still damage the samples and should be avoided.

There are two scattering techniques commonly used to characterize polymeric materials: small-angle x-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS). Based on Bragg's equation:

$$n\lambda = 2d\sin(\theta) \quad (2.1)$$

In which θ is scattering angle, λ is the X-ray wavelength, d is the spacing distance between structures, it is obvious that the narrower scattering angle, the larger featured structures are

available to be probed. With scattering angle below 10° , SAXS could determine the structure in the nanometer to micrometer range in terms of parameters such as averaged sizes, shapes and distributions of ordered structure. Therefore, SAXS technique provide unique opportunities to study morphology factors of copolymers or blends.¹²⁹ Due to the different compatibility between components, the units within block copolymers or grafting copolymers tend to form phase separated structure spontaneously, which would present different scattering of X-rays, i.e., scattering length density. Typically, multiple SAXS peaks would be observed due to these long range periodic microdomains, whose shapes could be clarified based on the ratio of relative peak position. For example, Figure 2.2 presents an example of SAXS spectra for a hybrid materials composed of poly(isoprene-*block*-ethylene oxide) block copolymers (PI-*b*-PEO) and ceramics.¹³⁰ By changing the components of hybrid materials, the morphology would also change correspondingly. Herein, the pure block copolymer PP5 possess a sphere morphology, with the ratio of the peak positions in the wave vector space $1, \sqrt{2}, \sqrt{3}$. After introducing ceramic particles, the morphology may transit to hexagonal morphology (PP5/2), in which the ratio of peaks would be $1, \sqrt{3}, \sqrt{7}, \sqrt{9}$. With even higher loading of ceramic, it could further change to lamellae structure (PP5/3), when this ratio is 1,2,3,4. Instead of multiple peaks with specific spatial relations, a single broad peak or even shoulder may also be observed for certain systems. Compared to SAXS, WAXS is a complementary method to monitor sub-nanometer-sized ordered structure, like crystallization, within materials or the so-called short-range order, i.e., distances between various atoms and molecules. The samples are commonly measured with increasing angle, i.e., concentrating on 2θ larger than 10° , from closer distance to the detector. In addition, WAXS can also be used to determine the phase composition of thin film,

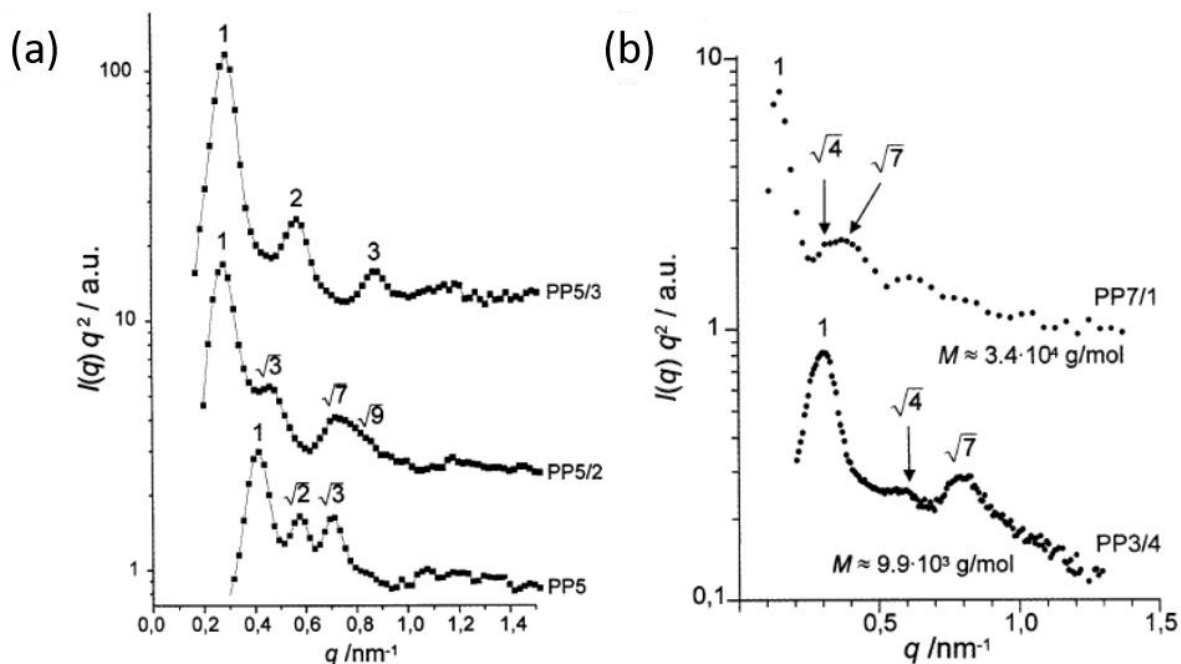


Figure 2.2 SAXS patterns of hybrid materials: (A) Block copolymer PP5 ($M = 1.4 \times 10^4$ g/mol, $f_{\text{PEO}} = 0.13$; bcc) with different amounts of inorganic material, $w_{\text{INORG}} = 0.32$ (PP5/2; hex), and $w_{\text{INORG}} = 0.45$ (PP5/3; lam). (B) Effect of block copolymer molecular weight on hexagonal morphology at a given amount of inorganic material, $w_{\text{INORG}} = 0.31$, $M = 9.9 \times 10^3$ g/mol (PP3/4), and $M = 3.4 \times 10^4$ g/mol (PP7/1) (hex). Angular positions of higher order peaks with respect to the first-order maximum are indicated for each curve.¹³⁰

the texture of film and presence of film stress, which will not be discussed in detail.

2.2 Thermal Property Test

2.2.1 Thermal Gravimetric Analysis (TGA)

Thermo Gravimetric Analysis (TGA) is a method of thermal analysis. In a typical TGA measurement, the sample is loaded on the pan inside a furnace. The amount and rate of weight change is probed, while the temperature is changed over time. Normally, the temperature is increased at constant rate under different atmosphere, mostly ambient air or nitrogen. TGA could provide information about different phenomena, such as phase transition and thermal decomposition. In this work, TGA is mainly used to characterize thermal stability of polymer materials. There will be no mass loss observed if the materials are thermally stable within certain temperature range. Otherwise, the material will start to degrade beyond that temperature and its weight will change. In addition, TGA also helps to detect traces of solvent or moisture, which would strongly affect the conductivity of materials. Evaporation of solvent from the sample will be detected in TGA as additional weight loss in the temperature range where sample should be thermally stable. The TGA curves of pure poly(vinyl alcohol) (PVA) film and poly(vinyl alcohol) borate (PVAPB) gel polymer electrolyte (GPE) are included in Figure 2.3 as an example.¹³¹ Pure PVA film is thermally stable till 230 °C and totally decompose at 650 °C, while PVAPB GPE has about 87% weight loss starting from 100 °C, due to the evaporation of containing KCl aqueous solution within the sample.

2.2.2 Difference Scanning Calorimetric (DSC)

Differential Scanning Calorimetric (DSC) is a thermal analytical technique used to monitor

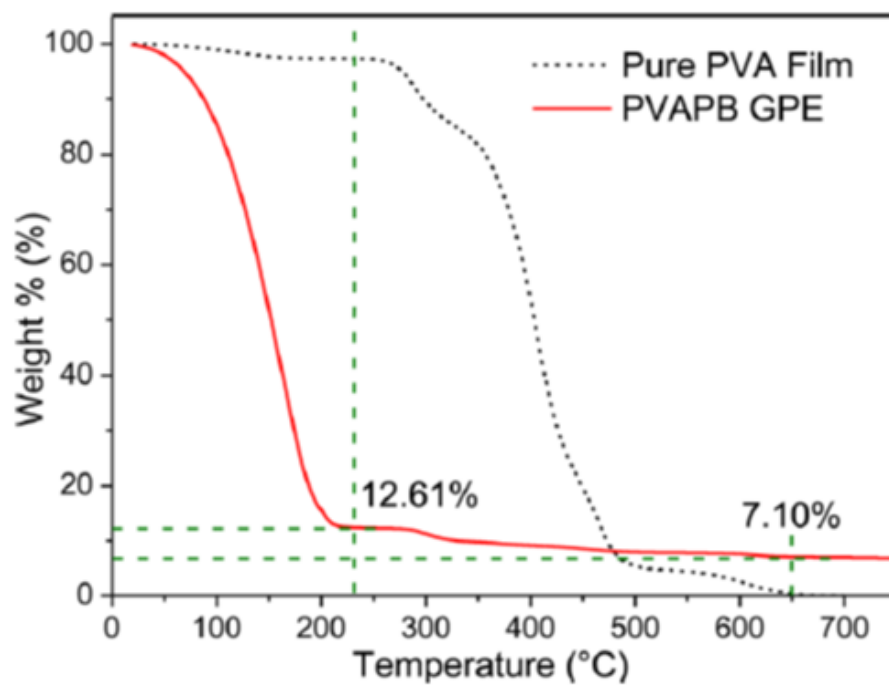


Figure 2.3 Example of TGA curves for pure poly(vinyl alcohol) (PVA) film and poly(vinyl alcohol) borate (PVAPB) gel polymer electrolyte.¹³¹

thermal transition process of materials, such as melting, crystallization and glass transition. In a typical DSC measurement, a pan with sample and an empty pan as reference are both heated or cooled at the same rate. Since the sample would undergo different transition processes upon temperature change, certain amount of heat is needed for sample pan to keep both pans at almost the same temperature through the measurements. Based on the transition process being endothermic or exothermic, the heat of the sample may be larger or smaller than that of the reference.

For some polymers, like PEO, the crystallization and corresponding melting process are shown as exothermic and endothermic peaks in DSC spectra. Another main feature for polymer materials is glass transition, which characterizes the transition of a polymer from a glassy state to a viscous liquid or soft rubbery state with increasing temperature. Different from crystallization, glass transition is not a phase transition but a kinetic transition process. When polymer is at temperature higher than this transition, polymer structure has more freedom and accessible conformations, which results in higher entropy, or heat capacity. Therefore, this transition process shows as a gradually increasing step with increasing temperature in DSC spectra. The glass transition temperature (T_g) is used to describe the temperature range of this transition happens, which is taken as the mid-point of the step.

Temperature modulated DSC (TMDSC) is an advanced technique based on the standard DSC.¹³² Other than the linear heating rate used in standard mode, an additional sinusoidal small amplitude temperature oscillation is also applied in TMDSC, which can improve the sensitivity and resolution of the measurement. In addition, compared to the total flow get from linear heating rate, the heat flow resulted from sinusoidal heating rate is called reversing heat flow,

which contains information about processes such as glass transition and melting. And the non-reversing heat flow is the subtraction of these two values, which includes kinetic process such as crystallization. Due to this feature, these processes are separated from each other in TMDSC, while they may overlap in normal DSC (Figure 2.4). TMDSC were conducted under Ar atmosphere using a TA instrument DSC 2500.

2.3 Mechanical property measurements

2.3.1 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) is mostly used to study the mechanical and viscoelastic property of polymers. In DMA measurement, a sinusoidal stress is applied to a rectangular sample, and the resulting strain is recorded. If the material is elastic solid, the responsive strain is in phase with applied stress, while the out-of-phase strain occur for viscoelastic material. Due to the viscoelastic property of polymers, the responsive strain would have certain phase angle in between above cases. With applied stress $\sigma = \sigma_0 \sin(\omega t)$, the resultant strain would be $r = r_0 \sin(\omega t + \delta)$, in which δ is the angle phase. Therefore, the storage modulus E' and loss modulus E'' are defined as:

$$E' = \frac{\sigma_0}{r_0} \cos \delta \text{ and } E'' = \frac{\sigma_0}{r_0} \sin \delta \quad (2.2)$$

As a major mode in DMA, temperature sweep mode monitors the complex modulus of a sample at a constant frequency upon temperature change. The main purpose of this mode is to verify the T_g of the material. A representative DMA thermogram of polycarbonate is presented in Figure 2.5.¹³³ When the sample transit from glassy behavior to soft rubbery state around T_g ,

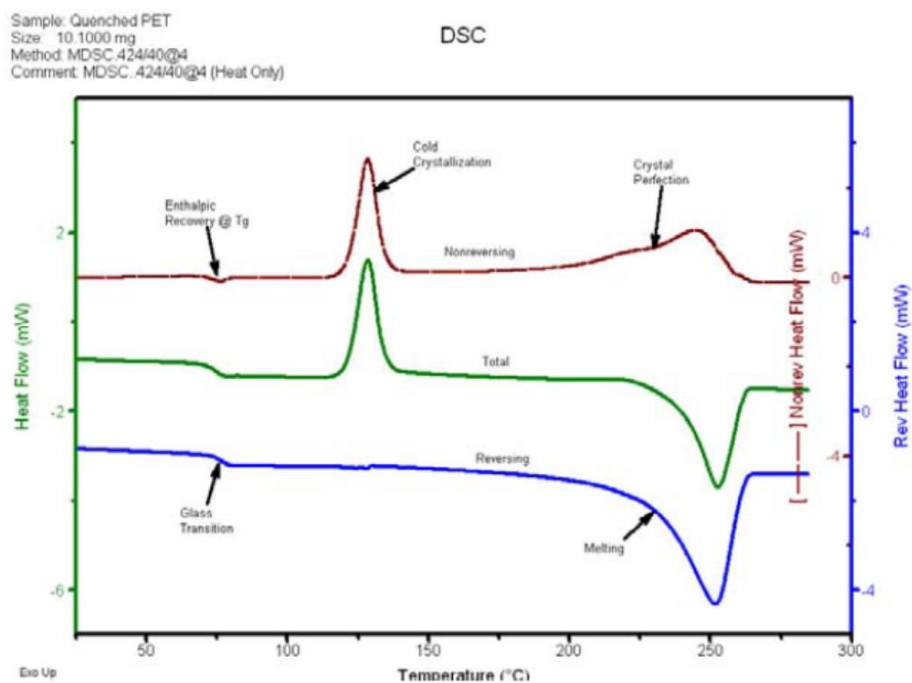


Figure 2.4 Representative curve of TMDSC for PET with total heat flow (green), reversing heat flow (blue, e.g., glass transition and melting) and non-reversing heat flow (brown, e.g., enthalpic recovery and crystallization).¹³²

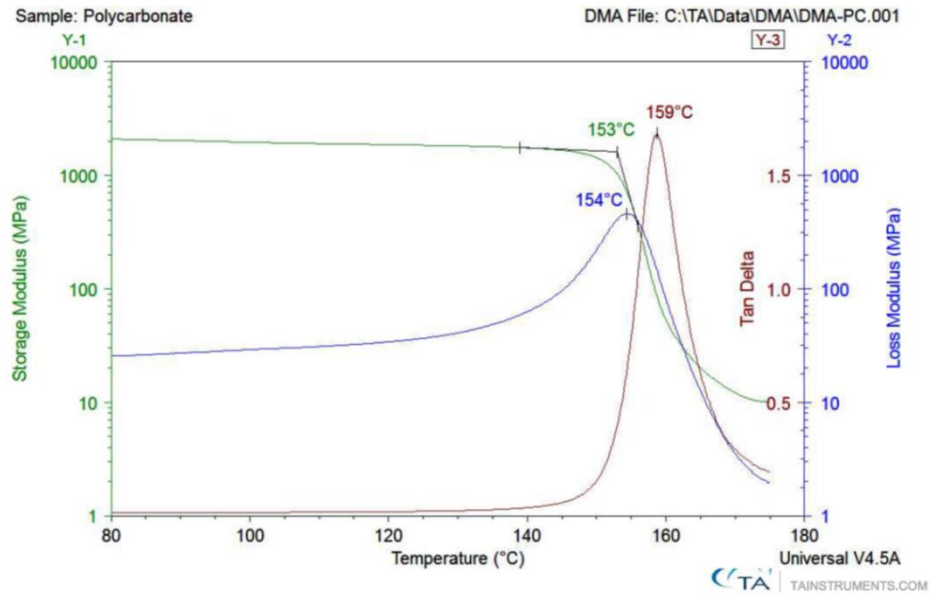


Figure 2.5 Typical DMA thermogram of an amorphous thermoplastic (polycarbonate). Storage Modulus (E') and Loss Modulus (E'') and Loss Factor $\tan(\delta)$ are plotted as function of temperature.¹³³

E' will dramatically decrease, while E'' presents a maximum value. Therefore, the onset of E' drop and the peak value of E'' can be used to estimate T_g . In addition, a peak in $\tan(\delta)$ would be also observed during glass transition, which is also used to estimate T_g . Since the estimation of T_g is also influenced by the frequency of the measurement, it is commonly measured at 1 rad/s, which corresponds to relaxation time ~ 1 s. It is worth noting that the estimated values from these three methods always vary from each other (153 °C for E' onset drop vs. 154 °C for E'' peak vs. 159°C for $\tan(\delta)$ peak).

2.3.2 Rheology

Rheology is another commonly used technique other than DMA to study viscoelastic property of polymer materials. Although DMA and rheometer give similar information of materials, DMA is not suitable for materials with low viscosity, which is opposite to rheometer. In other words, DMA is commonly used for solid-like materials that will not flow on time scale of measurements, while rheometer is more friendly for the easily flowing materials. The small amplitude oscillatory shear measurement is performed on AR2000ex rheometer from TA instrument. Different from DMA where sample is pulled up and down, the sample is sandwiched between two parallel plates in rheological measurement. To have a good contact between sample and plates, the sample is loaded and equilibrated at high temperature before the measurement.

Since the relatively narrow frequency range covered by rheometer, normally from 0.1 to 100 Hz, the time-temperature superposition (TTS) is always applied to overcome this limitation.¹³⁴

With certain temperature taken as reference temperature, the dynamic modulus measured at

other temperatures are shifted horizontally and vertically by the shift factors to build a master curve. Based on this curve, we may predict the behaviors and properties of materials at temperature and frequency beyond the capability of rheometer. It is noteworthy that the TTS is only valid when all relaxation processes in the probed time scale possess same temperature dependence, otherwise it fails at some circumstances. For example, TTS analysis does not work in polystyrene, since chain and segmental relaxation processes are governed by different friction mechanisms.¹³⁵

Among the relaxation processes probed in master curve, two of them are mainly studied in this work (Figure 2.6). The crossover of storage modulus and loss modulus at high frequency range presents segmental relaxation. The relaxation time of this process could be estimated by:

$$\tau_{seg} = 1/(2\pi f(T)) \quad (2.3)$$

Here $f(T)$ is the frequency of the crossover. By plotting the relaxation time over temperature, the data present a non-linear relationship, which can be well fitted by Vogel-Fulcher-Tammann (VFT) equation for T below $T_g + 100^\circ\text{C}$:

$$\tau_{seg} = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \quad (2.4)$$

where τ_0 is the limit of segmental relaxation time at high temperature, B and T_0 are fitting parameters. In addition, the T_g could be also defined as the temperature when $\tau \sim 100\text{-}1000\text{s}$, which should match the value measured by other techniques. After segmental relaxation, the dynamic modulus will gradually transit to Rouse modes (chain relaxation) with the longest mode defining terminal relaxation for PolyILs with low molecular weight. For the entangled

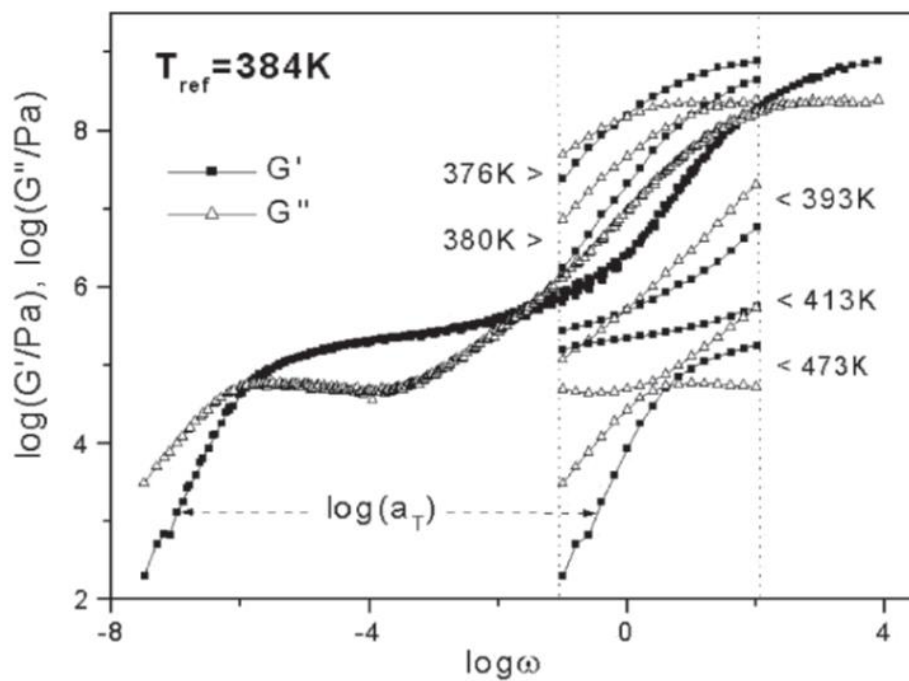


Figure 2.6 Illustration of a construction of a master frequency dependency of G' and G'' for a polystyrene melt ($M_w = 200,000$) taken as an example.¹³⁶

polymer or crosslinking polymers, there's a signature rubbery plateau following Rouse regime.

The plateau value could be used to estimate the entanglement or crosslinking density:¹³⁷

$$M_x = \frac{\rho RT}{G'} \quad (2.5)$$

where M_x is the number-average molecular weight of the polymer segments between crosslinkers or entanglements, G' is the plateau value of storage shear modulus, ρ is density, R is the gas constant, T is the temperature in Kelvin. It is commonly agreed that entanglement is generated by the topological constraints. Therefore, the terminal relaxation would still happen at low frequency regime after the stress is released (Figure 2.6). In a comparison, the chemically crosslinked networks only have infinite long rubbery plateau without terminal relaxation, since the intermolecular constraints will not relax within accessible time range.

2.3.3 Tensile testing

Tensile testing is a fundamental technique used to analyze the mechanical property of sample under controlled tension until fracture.¹³⁸ Compared to DMA, tensile test can measure sample even out of linear viscoelastic range. To be easily gripped, the samples are commonly prepared as dog-bone shaped. The samples will be pulled with certain rate at room temperature during the measurement, while the required force over the elongation of sample is recorded. Through the recorded data, we can directly obtain the properties like maximum elongation and breaking strength (Figure 2.7). Another important parameter can be obtained from the curve is Young's modulus, which characterizes the elasticity of materials. When a sample is pulled with small elongation, the initial deformation is reversible, which exhibits a linear stress-strain relationship. The slope of the stress vs. strain curve in this region is known as Young's modulus.

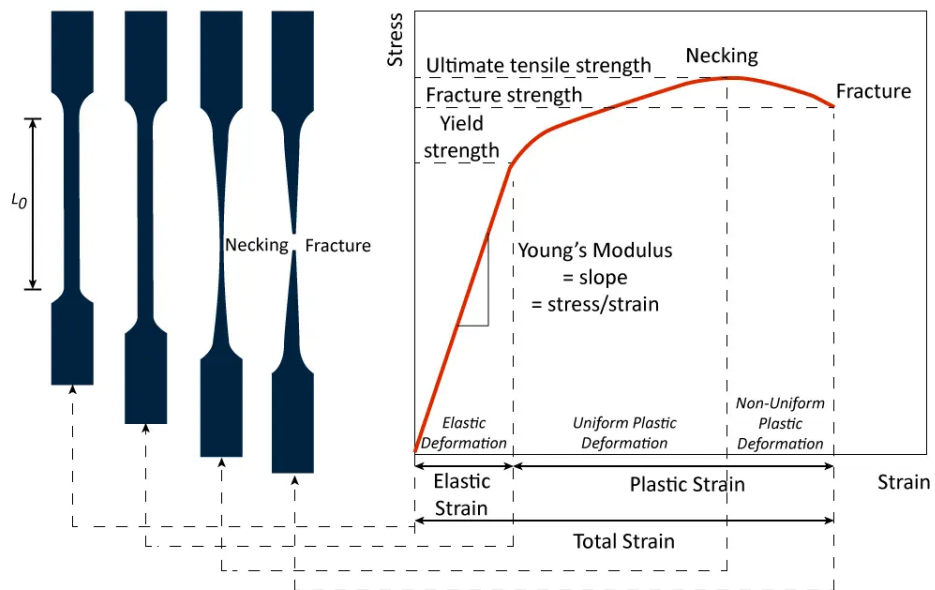


Figure 2.7 Example of a ductile sample changes during tensile testing.¹³⁸

2.4 Broadband Dielectric Spectroscopy (BDS)

2.4.1 Principles of BDS

Broadband Dielectric Spectroscopy (BDS) could monitor the transition of dielectric properties upon temperature and pressure change, which is very useful to probe molecular dynamics within materials. Applied with small perturbation caused by external electric field with strength E , the dipoles within material start to align, which results in dielectric displacement D and gradually relax to a new equilibrium state. The rearrangement of local dipoles after distortion would result in different polarization P in dielectric spectroscopy.

$$D = \epsilon^* \epsilon_0 E \quad (2.6)$$

$$P = D - D_0 = (\epsilon^* - 1) \epsilon_0 E = \chi^* \epsilon_0 E \text{ with } \chi^* = (\epsilon^* - 1) \quad (2.7)$$

where ϵ_0 is the dielectric permittivity of vacuum, ϵ^* is the complex dielectric permittivity, D_0 is the dielectric displacement of vacuum and χ^* is the dielectric susceptibility which describes the difficulty of orientation and relaxation for dipoles under external electric field.

Based on the intrinsic mechanism, different polarizations possess their own characteristic frequency range.¹³⁶ Starting from high frequency, electronic polarization describes the displacement of nuclear and electrons, or electron density, in the atom, which can even occur at optical frequencies. Then the reorientation of atoms, i.e., atomic polarization, could happen around 10^{12} - 10^{14} Hz. At lower frequencies around MHz (GHz for liquids), the permanent and induced dipoles will start to align with external field, which is strongly affected by thermal motion and local viscosity. For the charge containing system, ions also migrate with electric

field, which results in ionic polarization. When the frequency is very low, the transportation of ions is stopped and they start to accumulate at the interfaces between layers with different dielectric constant. In such case, ionic polarization is followed by the interfacial polarization, or Maxwell-Wagner-Sillars polarization.

When electric field is absent, the decreasing of polarization can be characterized by relaxation process, which is commonly described in terms of permittivity. For an ideal system, the change of polarization is simply assumed to be proportional to its actual value. Therefore, the permittivity can be expressed as Debye relaxation:

$$\varepsilon^* = (\varepsilon'(\omega) - i\varepsilon''(\omega)) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+i\omega\tau} \quad (2.8)$$

where τ is relaxation time. However, the spectra for real system always have asymmetric and broader peak compared to Debye relaxation. Therefore, various empirical equations have been proposed for a better fitting, such as Cole-Cole equation:

$$\varepsilon_{CC}^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+(i\omega\tau_{HN})^\beta} \quad (2.9)$$

where β features the symmetric broadening of the peak and Cole-Davidson equation:

$$\varepsilon_{CD}^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1+i\omega\tau_{HN})^\gamma} \quad (2.10)$$

where γ described asymmetric broadening at high frequency range. In addition, the equation combining both features were also proposed by Havriliak and Negami (HN equation):

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1+(i\omega\tau_{HN})^\beta)^\gamma} \quad (2.11)$$

where γ and β are the parameters related to the asymmetry and broadening of the spectra.

The characteristic relaxation time is also related to the position of the loss peak:

$$\tau_{max} = \tau_{HN} \left(\sin \frac{\beta\gamma\pi}{2+2\gamma} \right)^{1/\beta} \left(\sin \frac{\beta\pi}{2+2\gamma} \right)^{-1/\beta} \quad (2.12)$$

Figure 2.8 presents the dielectric spectra with different shape parameters from HN-equation.

2.4.2 Analysis of the dielectric spectra

A major component in the dielectric spectra is α relaxation. Since molecular relaxation leads to a rotation of dipoles, a peak in the imaginary part of permittivity would show up when the frequency of the dipole reorientation is equal to the frequency of applied electric field. Fitted by HN function, the parameters about the relaxation process can be obtained.

For the system containing free ions, another important process is conductivity. The conductive contribution σ^* can be expressed as:

$$\sigma^* = i\omega \varepsilon^* \varepsilon_0 \quad (2.13)$$

in which $\varepsilon_0 (= 8.854 \times 10^{-12} \text{ F/m})$ is the dielectric constant of vacuum. A representative real conductivity spectrum of ionic liquid [OMIM][NTf₂] is presented in Figure 2.9 as functions of frequency at different temperatures.¹³⁹ Three different regimes are observed with decreasing frequency: (1) ac conductivity caused by local motions of ions, (2) dc conductivity plateau reflecting ion diffusion and (3) a sharp decrease due to the electrode polarization. For the regime transit from ac conductivity to dc conductivity, the spectra can be well fitted by the random barrier model (RBM) proposed by Dyre:

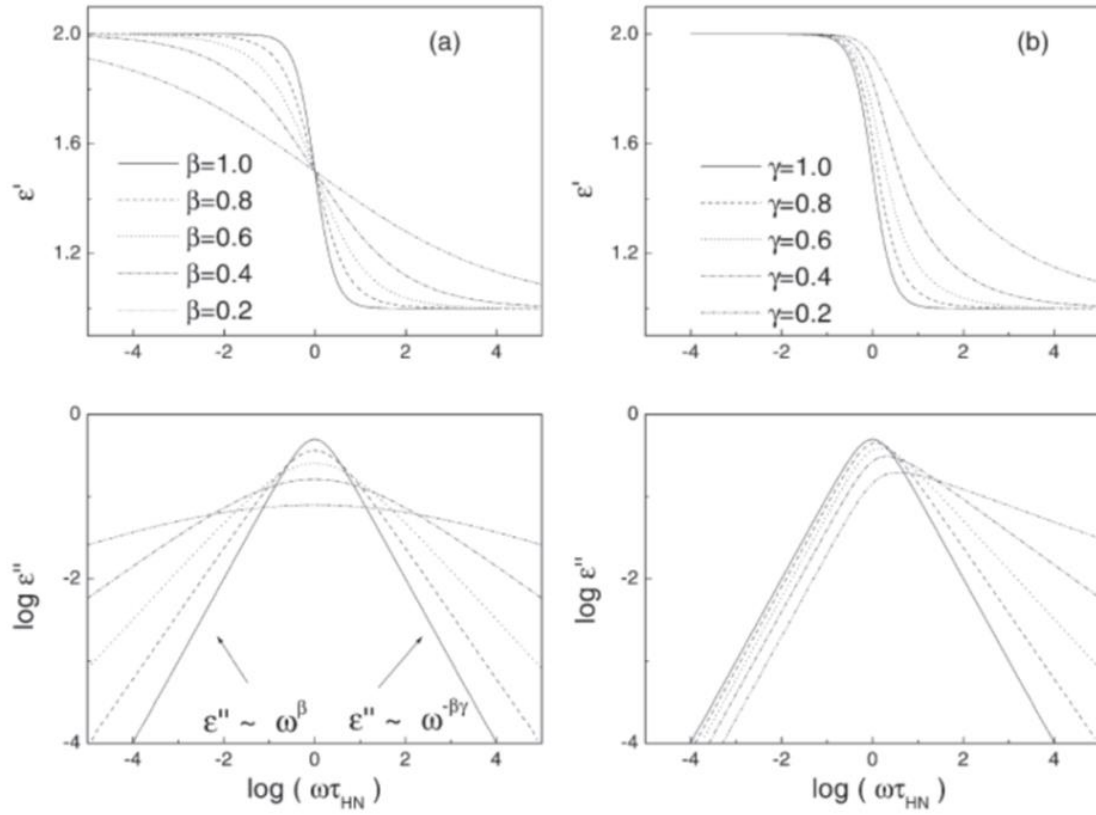


Figure 2.8 Complex dielectric permittivity from the HN-function with fixed: (a) $\gamma=1$; (b) $\beta=1$ (ϵ_∞ , $\Delta\epsilon$ and $\tau_{HN}=1$).¹³⁶

$$\sigma(\omega)=\sigma_0 \left(\frac{i\omega\tau}{\ln(1+i\omega\tau)} \right) \quad (2.14)$$

This model mainly describes the hopping conducting in a spatially randomly varying energy landscape. Therefore, dc conductivity value can be either fitted by RBM model or simply taken as the plateau value (Figure 2.9). When the dc conductivity plotted versus inverse temperature in logarithmic scale, it may present a transition from non-linear relation to a linear relation with decreasing temperature, which can be separately fitted by VFT function and Arrhenius equation. This transition temperature from BDS is always consistent with the T_g measured by DSC.

2.4.3 Measurement set-up

BDS measurements were conducted on Novocontrol Concept 80 system with Alpha-A impedance analyzer, ZGS active sample cell interface and Quatro Cryosystem temperature control unit. The samples were sandwiched between two gold plated electrodes with a Teflon spacer ring (Figure 2.10). This could maintain the thickness of sample when temperature changed during the measurement. The frequency range of measurements were 10^{-1} - 10^6 Hz. A sinusoidal electric field is applied to produce a resulting current, whose phase lag is dependent on the impedance of the circuit (Figure 2.11). The impedance of the sample is measured as $Z^*=U^*/I^*$. As impedance also relies on capacitance of sample, it can be expressed as $C^*=1/(i\omega Z^*)$, in which capacitance is proportional to the surface area of capacitor and inverse sample thickness.

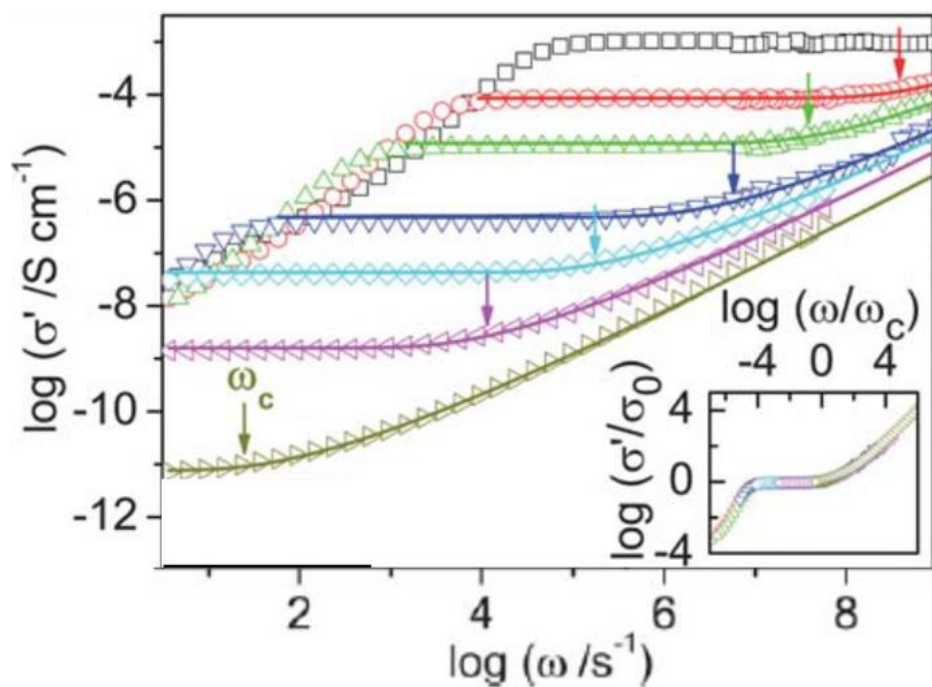


Figure 2.9 Real conductivity of [OMIM][NTf₂] as functions of frequency at different temperatures. The lines denote fits by the random barrier model. Inset: scaling with respect to characteristic radial frequencies, ω_c , and dc conductivity, σ_0 , for the various temperatures.¹³⁹

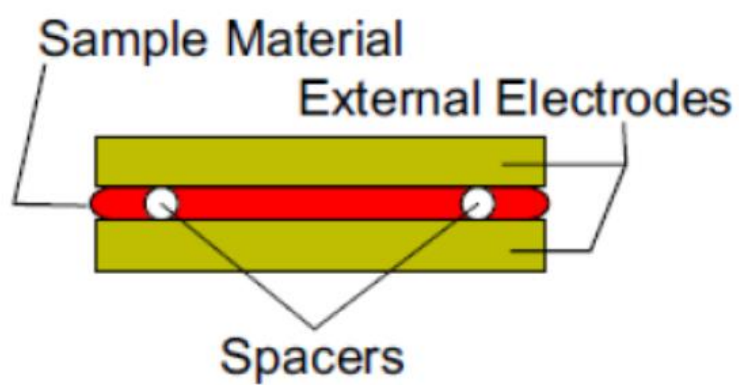


Figure 2.10 Sample cell set up.

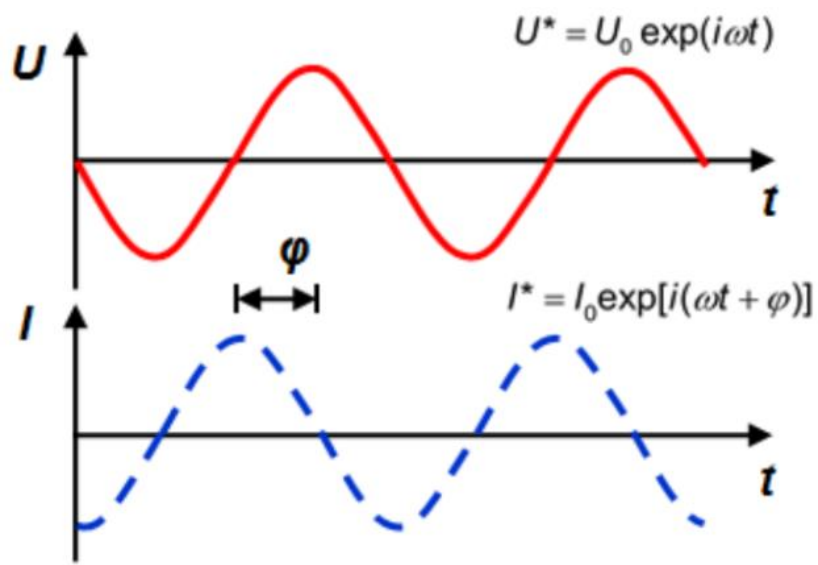


Figure 2.11 Representation of the phase difference between applied voltage and the resultant current in a dielectric spectrometer circuit.

2.5 Battery Test

2.5.1 Coin cell setup

Coin cells have been widely used for the lab-scale measurement of lithium-based batteries due to their small size, ease of cell assembly and need of small amount of materials to conduct test. Commonly, a coin cell is composed of cathode, electrolytes, and anode, which are sealed by the cap and bottom container (Figure 2.12).¹⁴⁰ Different from a cell using liquid electrolyte, a separator is not necessary for the test with polymer electrolyte membrane, since itself may function as separator. However, coin cells with polymer electrolytes can fail due to improper contact with the electrodes. This may happen especially with a thin membrane since the pressure from the wave spring is not sufficient. In this case, a special cell setup providing extra pressure will be helpful, such as stacking spacers or the usage of a thicker spacer. Various electrochemical measurements can be conducted with coin cells to characterize a polymer electrolyte, which will be discussed in detail in the following parts.

2.5.2 Transport number

As an important parameter about electrolyte, ion transference number features the number of moles of ion transferred by migration per Faraday of charge.⁸⁶ However, based on the discussion in Chapter 1, we know that most methods applied in the research actually characterize the transport number rather than transference number. Among them, the potentiostatic polarization method proposed by Bruce and Vincent is most commonly used, which involves a combination of DC polarization test and AC impedanc spectroscopy.¹⁴¹ Typically, a Li/Li symmetric cell sandwiched with electrolyte is polarized with a small step

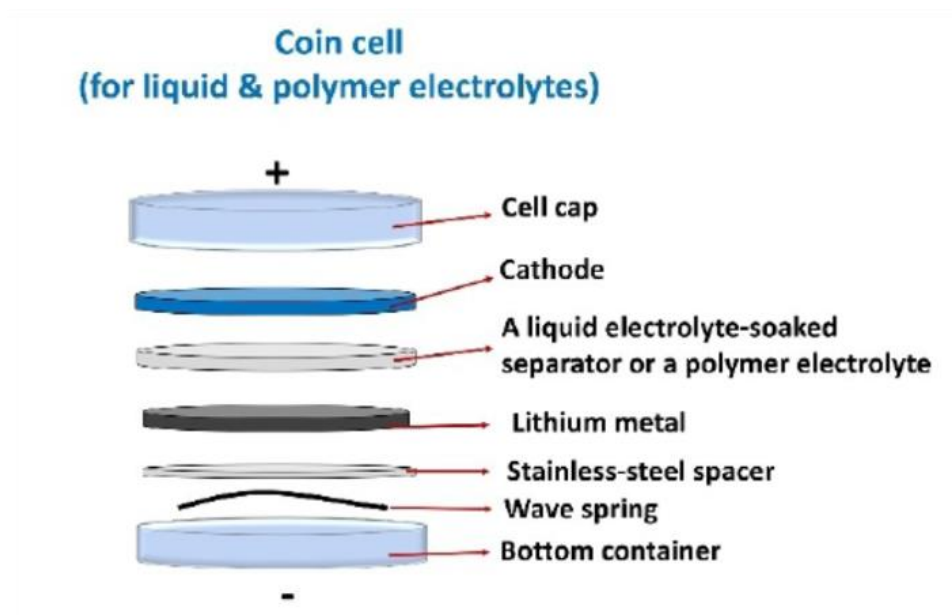


Figure 2.12 Schematic representation of coin cell used for liquid electrolytes and polymer electrolytes.¹⁴⁰

voltage, and the resultant current is monitored as a function of time. Before polarization, the dispersions of anion and lithium-ion can be seen as uniform among the electrolyte layer as shown in Figure 2.13(a).¹⁴⁰ After being applied with a small voltage, the ions start to migrate into opposite direction, which results in a concentration gradient. Finally, a steady state is reached when this concentration gradient will not further change with time (Figure 2.13(b)). Meanwhile, the anions are blocked on the surface of electrode, while lithium-ions can go through the one electrode and come back into the electrolyte from the other electrode. Therefore, the current at steady state I_s is only carried by lithium-ion. Therefore, the lithium-ion transport number is given by the ratio of steady state current (I_{ss}) to the initial current (I_0):

$$t_+ = \frac{I_{ss}}{I_0} \quad (2.15)$$

For real systems, the interfacial impedance has to also be included. In this case, the transport number could be estimated by:

$$t_+ = \frac{I_{ss}(V - I_0 R_0)}{I_0(V - I_{ss} R_{ss})} \quad (2.16)$$

where R_0 and R_{ss} is the interfacial impedance before and after polarization from electrochemical impedance spectroscopy (EIS) and V is the applied voltage.

It is noteworthy that this model is based on the assumption that the interactions among ions are negligible, which is mainly valid for dilute liquid electrolyte (~ 0.01 M). In the concentrated systems, the potential neutral ion pairs will not migrate upon voltage, which results in an overestimation of real transference number. Therefore, the measured t_+ is conceptually defined as “transport” number rather than “transference” number. To distinguish this ambiguity, Hittorf

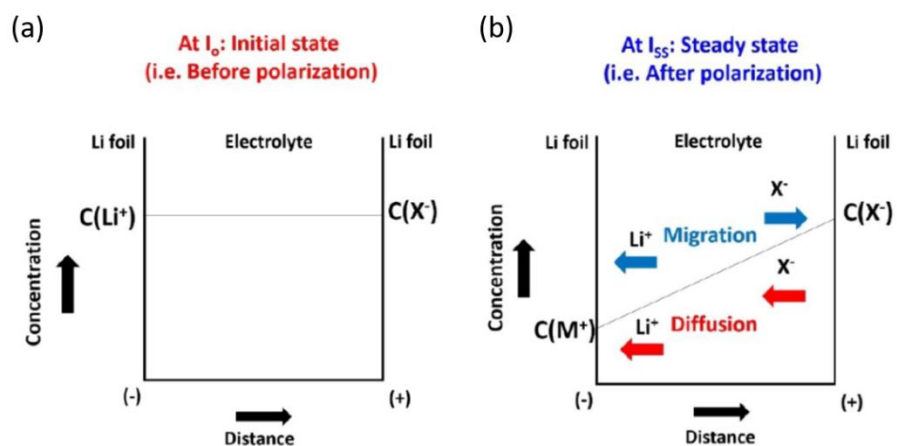


Figure 2.13 Schematic of initial and steady states in DC Polarization. Schematic depicting the concentrations of the ionic species in a symmetric Li/Li cell across the length of the electrolyte with a sample LiX salt (a) at the initial state and (b) after polarization and the steady state is attained. The blue and red arrows indicate the directions of ion movement due to migration and diffusion, respectively.¹⁴⁰

divided the electrolyte into multiple sections to exclude the requirement of electrolyte concentration in model.¹⁴²

Other than Bruce-Vincent method, NMR is another available method to characterize transport number. Rather than solid polymer electrolyte, this method is more accessible for the system having fast ion diffusion, like liquid electrolytes.¹⁴³ Therefore, Bruce-Vincent method is still a very convenient method used by many researchers to measure the transport number. Herein, we also used it to characterize our samples for a better comparison with other works.

2.5.3 Linear Sweep Voltammetry (LSV)

The electrochemical stability window (ESW) of an electrolyte defines the effective working voltage range with respect to working electrodes. Within ESW, the coin cell would be able to work properly without any side reactions or decomposition of electrolyte. Typically, the highest voltage of ESW is determined by conducting Linear Sweep Voltammetry (LSV). A coin cell composed of lithium reference electrode and stainless steel (SS) working electrode is assembled for the measurement. The change of current at SS is recorded upon the voltage linearly swept from open-circuit voltage (OCV) to a high positive voltage.¹⁴⁴ As the molecules on the surface of the working electrode are first reacted, they would move away from the surface, while new molecules are able to come into contact. The flow of electrons during this process would cause the current, which is a direct measure of the exchanging rate through the electrode-electrolyte interface. When this rate becomes higher than the diffusion rate of reacting species from the bulk electrolyte to the surface of electrode, the current signal reaches a plateau or exhibits a peak. Figure 2.14 presents an example of LSV spectra under scanning

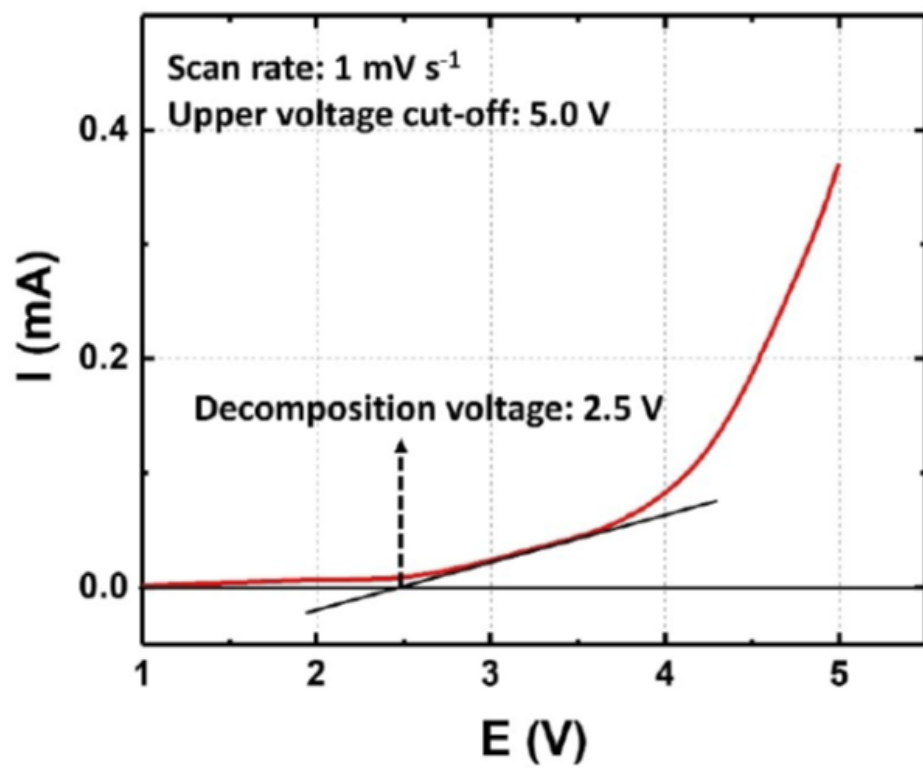


Figure 2.14 Example of Linear Sweep Voltammogram.¹⁴⁰

rate of 1 mV/s.¹⁴⁰ The onset of decomposition happens at 2.5V, which is followed by an exponential increase in current after 4.0V. It is noteworthy that various parameters, such as larger scan rate and higher temperature, may result in overestimation of the onset decomposition voltage.^{145, 146} Therefore, 0.1 V/s or an even slower rate is commonly applied for an accurate estimate.

For polymer electrolytes, different factors could influence their ESW, such as the choice of polymer matrix, lithium salt, solvent and the interfaces between electrolyte and electrode.¹⁴⁶⁻¹⁴⁸ For traditional PEO based electrolytes, the voltage stabilities are mostly below 4.0V vs. Li⁺/Li, which restrict its application with high voltage cathodes and limit the energy density improvement.¹⁴⁹ To extend ESW (typically above 4.2 V), various strategies have been explored, such as the usage of potential additives^{150, 151} and the introduction of neutral units with superior potential stability, e.g., acrylonitrile.¹⁵²

2.5.4 Charging/discharging test

Electrochemically charging and discharging test is a common method used to characterize electrolyte and electrode materials. During the measurement, the coin cell is charged/discharged with a constant current (i.e., galvanostatically), which is expressed as “C-rate”. This term is the expected capacity, C, of working electrode (mA·h) divided by the desired number of hours to fully charge/ discharge it. For example, a battery with a capacity of 100mA·h was discharged at rate of C/4, which means that it would be fully discharged at current 25 mA for four hours.

2.5.4.1 Galvanostatic Cycling (GC)

Galvanostatic Cycling (GC) test is commonly used to verify the reversibility of lithium plating/stripping of electrolytes. The electrolytes are assembled in Li/Li symmetric cell, which are alternatively applied with current and reverse current and the overpotential is recorded as a function of time. GC measurement with symmetric cell is a quick method to evaluate electrolytes. Typically, a test protocol of one hour of stripping and one hour of plating is considered a single cycle in the symmetric cell tests. As a comparison, full cell test takes much longer time, e.g., about twenty hours to obtain a full cycle at rate of C/10.

The shape of voltage is often qualitatively related to electrode stability or failure, which are strongly influenced by various factors, such as current density and electrolyte composition.¹⁵³ In addition, since both electrodes are lithium metal, unreactive lithium, or dead Li, may start to form on both sides. During lithium stripping/plating, it would accumulate, evolve and finally form mossy lithium dendrites. This may result in the destabilization of interfaces between electrolyte and electrodes, which exhibits a gradually increase of overpotential with number of cycles. When the dendrites penetrate through whole electrolytes, the cell would fail due to the short circuit, which results in a dramatically drop in voltage. Figure 2.15 presents the GC measurement results of a Li/Li symmetric cell composed of different concentration of LiTFSi in dimethoxyethane (DME). All cells were cycled at $0.25\text{mA}/\text{cm}^2$ for $0.5\text{mAh}/\text{cm}^2$ per cycle. The author claimed that the less content of solvent molecules for highly concentrated electrolytes results in the formation of thinner solid electrolyte interface (SEI). Therefore, they have weaker ability to terminate the continuous lithium dendrite growth and failed at earlier cycles due to the short circuit.

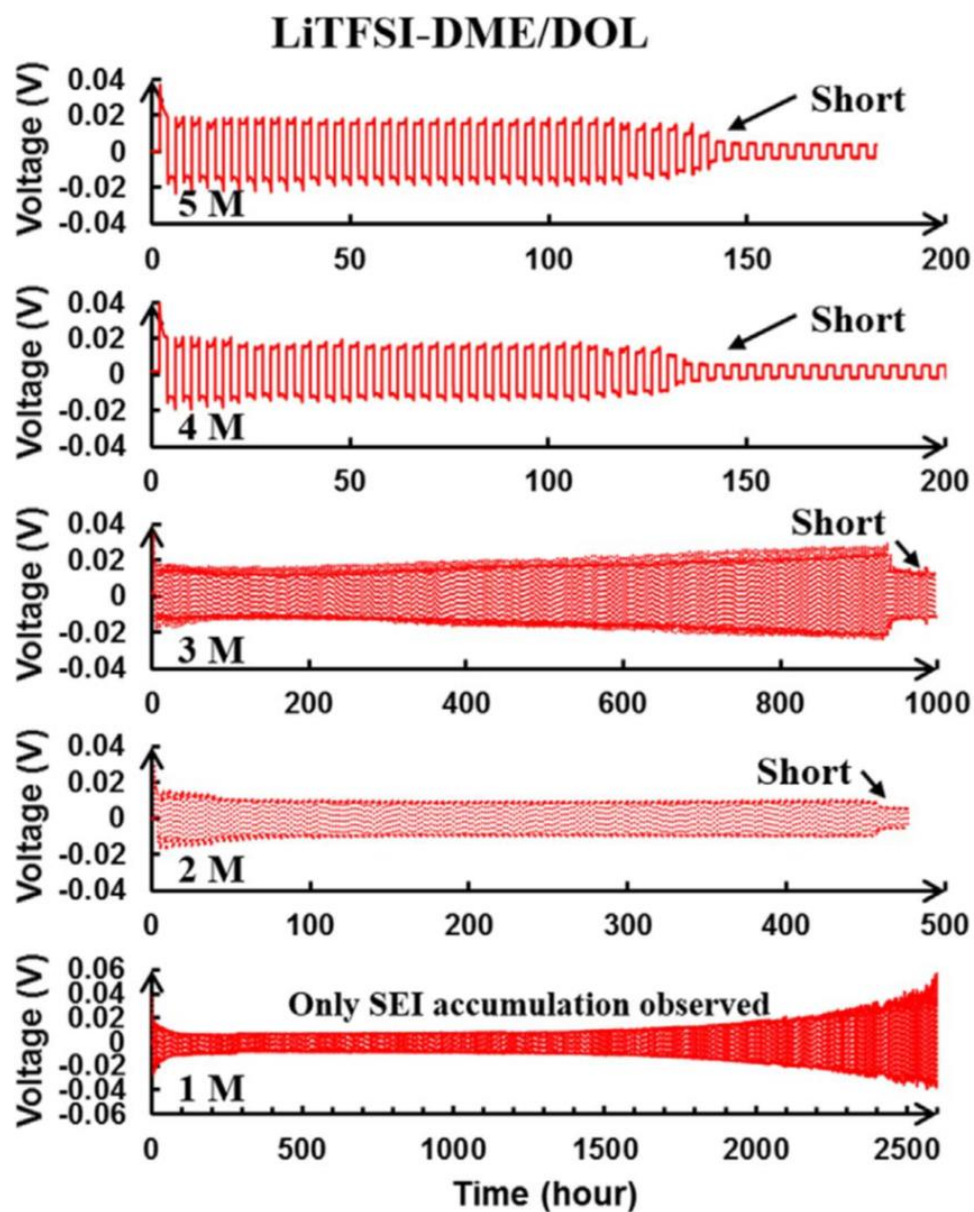


Figure 2.15 Cycling behaviors of Li/Li symmetric cells using glass fiber separator with different concentration of LiTFSI in dimethoxyethane (DME). The cells were charged/discharged with rate of 0.25 mA/cm², or 0.5 mAh/cm² at 25 °C.¹⁵⁴

2.5.4.2 Capacity retention and Coulombic efficiency

Charging/discharging test of full cells can provide detailed information about the change of capacity over electrodes, which can be quantified by the Coulombic Efficiency (CE). It is calculated by the discharge capacity divided by the former charge capacity.^{155, 156} CE can be influenced by various factors, such as C-rate in each cycle and the storage and operation temperature. Ideally, CE would be 100% when no side reactions happened on the electrode, while the flow of Li^+ is also fully reversible. However, the ubiquitous side reactions may consume active materials or produce electrochemically inactive byproducts, which results in real CE being less than 100%, or capacity retention. In other word, a high CE is essential to extend cycle life of battery. Figure 2.16 presents an example of capacity profiles at different C-rate for a full cell composed of Li metal/crosslinked PEO membrane doped with/ LiFePO_4 . In addition, the voltage of selected cycles can also be plotted over specific capacity, which is a measure of the charge or discharge capacity and the state of health for electrode.

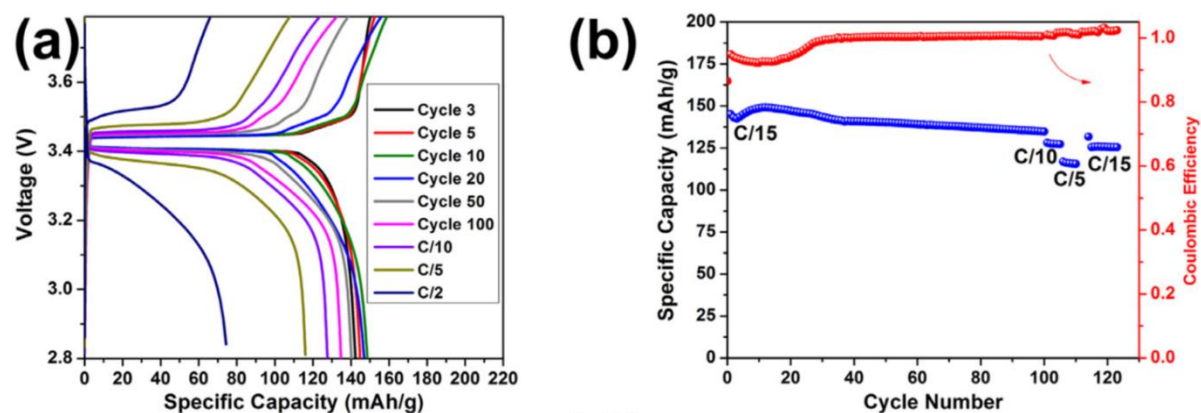


Figure 2.16 (a) Selected charge/discharge profiles of the Li metal | CPE2000 + 10wt%TEGDME | LiFePO₄ cell showing from the first 100 cycles at C/15, and the initial scan at C/10, C/5 and C/2, respectively. (b) The discharge capacity-cycle number plot shows the cell cycling stability at C/15 for 100 scans and the performance at various C-rates.⁶⁹

Chapter III

Effect of Accelerated Segmental Dynamics on the Single-ion Conductivity of Polymer Electrolyte

Reproduced in the part of results and discussion from Sheng Zhao, Yiman Zhang, Hoang Pham, Jan-Michael Y. Carrillo, Bobby G. Sumpter, Jagjit Nanda, Nancy J. Dudney, Tomonori Saito, Alexei P. Sokolov and Peng-Fei Cao “Improved Single-Ion Conductivity of Polymer Electrolyte via Accelerated Segmental Dynamics” *ACS Appl. Energy Mater.* 2020, 3, 12, 12540–12548. American Chemical Society. Sheng Zhao contributed to the materials synthesis and characterization, data analysis and writing. Yiman Zhang contributed to the battery test. Hoang Pham contributed to the monomer synthesis. Jan-Michael Y. Carrillo and Bobby G. Sumpter contributed to the simulation works. Jagit Nanda, Nancy J. Dudney and Tomonori Saito contributed to the writing. Alexei P. Sokolov and Peng-Fei Cao contributed to the idea of project and writing.

3.1 Introduction

As a type of polymer electrolytes, single-ion conducting polymer electrolytes (SICPEs) possess transference number close to unity. The high transference number may suppress the dendrite growth on Li metal electrodes and enable stable battery performance.^{56, 75, 88, 99} However, the low ionic conductivity of SICPEs in comparison to traditional liquid electrolyte remains the bottleneck for their practical applications.

To improved the ionic conductivity of SICPEs, the method to fabricate weakly coordinating anions with highly delocalized negative charge is widely studied. This method mainly relies on

polymers with ionic-liquid like monomers, backbone or side chains, such as sulfonyl(trifluoromethane-sulfonyl)imide structure ($\text{SO}_2\text{-N}^{(-)}\text{-SO}_2\text{-CF}_3$) and its derivative structures.^{74, 105, 106} But these homopolymers have high glass transition temperature (T_g) and still suffer from very low ionic conductivity at ambient temperature.

Accelerating the segmental dynamics by incorporation of low- T_g polymer segments is an efficient way to improve the ionic conductivity of SICPEs.^{74, 79, 157} Aside from physical blending, the current research is mainly focusing on covalently grafting a SICPE block to one or both sides of high molecular weight (M_w) PEO, or on copolymerization with the low M_w PEO ($T_g \sim -60^\circ\text{C}$).^{74, 108, 123} There have been numerous attempts on modifying the side chain, but only a few attempts have been made on tuning the polymer backbones of sulfonyl(trifluoromethane-sulfonyl)imide based SICPEs,^{112, 158} which may significantly influence segmental dynamics.⁷⁹

Herein, we introduce a novel SICPE with both a “soft” polymer backbone and side chain that provides accelerated segmental dynamics. Compared to traditional “rigid” polymer backbones, such as poly(methyl methacrylate) (PMMA), the soft polydimethylsiloxane (PDMS) ($T_g \sim -120^\circ\text{C}$) backbone exhibits much faster segmental dynamics (shorter relaxation time) and hence higher conductivity (6 order improvement). Further co-grafting with PEO side chains results in the SICPEs with further accelerated segmental dynamics that provides significantly improved conductivity in comparison to the state-of-art sulfonyl(trifluoro-methanesulfonyl)imide based SICPE.

3.2 Materials and methods

3.2.1 Materials

(Mercaptopropyl)methylsiloxane homopolymer (PDMS-SH, M_w =4000-7000) was purchased from Gelest. 3-sulfopropyl methacrylate potassium salt, thionyl chloride, trifluoromethanesulfonamide, 4-tertbutylcatechol, lithium hydride (LiH) and sodium hydride (NaH) were purchased from Sigma-Aldrich. LiH and NaH were stored inside glovebox to avoid moisture before usage. Carboxylic acid terminated RAFT agent 2-[(Butylsulfanyl) carbothioyl] sulfanyl propanoic acid (RAFT-CTA) was synthesized according to previous paper.¹

Poly(ethylene glycol) methyl ether methacrylate (PEGMEMA, M_w =500) (Sigma-Aldrich) has been passing through a column with alternative inhibitor remover and aluminum oxide to remove inhibitor. Azobisisobutyronitrile (AIBN) was recrystallized from methanol before used. Dimethylformamide (DMF) and Tetrahydrofuran (THF) were dried and distilled before using.

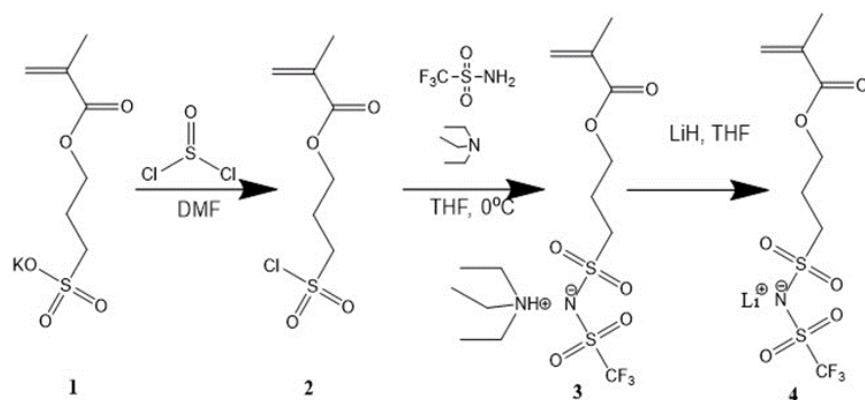
3.2.2 Synthesis of lithium 1-[3-(methacryloyoxy)propyl-sulfonul]-1-1(trifluoromethane-sulfonyl)imide (MPA Li⁺) monomer

MPA Li⁺ was produced via a three-step synthetic procedure based on Shaplov's work with minor change shown in Scheme 3.1.¹⁵⁹ Potassium 3-(methacryloyoxy)propane-1-sulfonate (1) (10.00 g, 40.6 mmol) was suspended in 15 mL of anhydrous DMF in a 250 mL round bottom flask. 4-tertbutylcatechol (0.10 g, 0.6 mmol) was added as an inhibitor to the flask. The reaction was cooled to 0°C and thionyl chloride (25 mL, 128.1 mmol) was added dropwise using a syringe under stirring. The reaction proceeded at 0°C for 1 h, and then at room temperature for 24 h. The resulting suspension was slowly poured into an ice-water (200 mL) beaker under

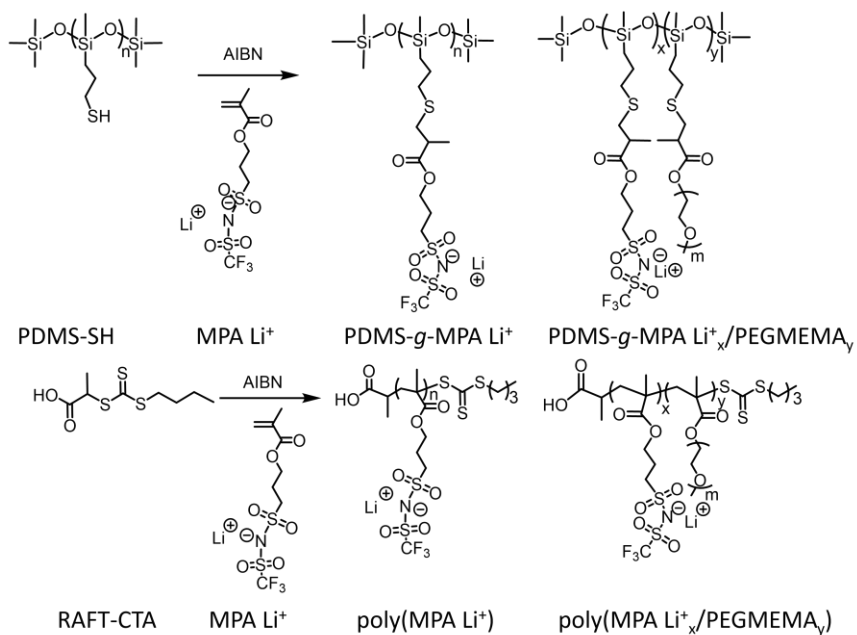
stirring. The content in the beaker was extracted in a 250mL separation funnel with diethyl ether (4x30 mL). The organic layer was dried over anhydrous sodium sulfate. Na₂SO₄ was filtered off and the diethyl ether was gently evaporated using a roto-evaporator to obtain dry 3-(Chlorosulfonyl)propyl methacrylate (2).

Trifluoromethanesulfonamide (5.13 g, 34.4 mmol) was dissolved in 10 mL of anhydrous THF and loaded in a 3-neck round bottom flask. Anhydrous triethylamine (TEA) (14 mL, 100.0mmol) was added under stirring. The solution was diluted with 15 mL more of anhydrous THF and cooled down to 0°C on an ice bath. A solution of 3-(Chlorosulfonyl)propyl methacrylate (13.16 g, 58.1 mmol) in 15 mL of anhydrous THF was added dropwise using a dropping funnel under inert atmosphere to the round bottom flask. The reaction proceeded for 1 h at 0°C then 24 h at room temperature. The resulting mixture was filtered by gravity and the filtrate was roto-evaporated to remove THF solvent. The obtained slightly yellow oil was re-dissolved in 90 mL of dichloromethane and washed with deionized water (4x35 mL). The organic layer was dried over anhydrous sodium sulfate. Na₂SO₄ was filtered off, 4-tertbutylcatechol (1 mg, 0.01mmol) was added and the dichloromethane was thoroughly evaporated to get Triethyl ammonium 1-[3-(methacryloyoxy)propylsulfonul]-1-(trifluoromethane-sulfonyl)imide (3).

A suspension of lithium hydride (0.25 g, 31.7 mmol) in 15 mL of anhydrous THF was added dropwise to a solution of triethyl ammonium 1-[3-(methacryloyoxy)propylsulfonul]-1-(trifluoromethane-sulfonyl)imide (5.78 g, 13.0 mmol) in 20 mL of anhydrous THF at room temperature inside a glove box. The stirring mixture proceeded for 12 h, whereupon the content was filtered by gravity to remove unreacted LiH inside the glove box. The filtrate was roto-evaporated and washed with hexane (3x20 mL) under vigorous stirring. After that, the



Scheme 3.1 Synthesis of lithium 1-[3-(methacryloyloxy)propylsulfonul]-1,1-(trifluoromethanesulfonyl)imide (MPA Li⁺)



Scheme 3.2 Synthesis of a PDMS backboned SICPEs *via* thiol-ene reaction and methyl methacrylate backbones SICPEs *via* reversible addition fragmentation chain-transfer (RAFT) polymerization. (Note: PDMS-g-MPA Li⁺/PEGMEMA refers to both MPA Li⁺ and PEGMEMA were chemically grafted on PDMS backbone).

viscous oil was partially dissolved by dichloromethane (10 mL) and phase separated with hexane (30mL) twice. The viscous oil was thoroughly dried to obtain the desired monomer in powder form. To synthesis MPA Na⁺ monomer, the corresponding amount of sodium hydride was used instead of lithium hydride.

MPA Li⁺: ¹H NMR (400 MHz, DMSO-d₆): δ = 6.04 (s, 1H, CH₂=C(CH₃)–), 5.68 (s, H, CH₂=C(CH₃)–), 4.17 (t, 2H, CO–O–CH₂–, JHH = 6.5 Hz), 3.06 (m, 2H, –CH₂–SO₂–N), 2.01 (m, 2H, O–CH₂–CH₂–), 1.88 (s, 3H, CH₂=C(CH₃)–). ¹⁹F NMR (377 MHz, DMSO-d₆): δ = -77.53 (s, 3F).

3.2.3 Thiol-ene reaction for PDMS-*g*-MPA Li⁺ and PDMS-*g*-MPA Li⁺_x/PEGMEMA_y

Both 487mg (0.09 mmol) PDMS-SH and 1.22g (3.6 mmol) MPA Li⁺ were dried in vacuum before transferring into glovebox. They were then added together with 291mg (1.8 mmol) AIBN into a Schlenk tube equipped with a stirring bar and dissolved by total 10ml dry DMF. The solution was degassed with N₂ and reacted at 65°C overnight. The product was purified by dialysis against DMF and dried in the vacuum oven at 100°C for one day.

The same procedure was applied to synthesize PDMS-*g*-MPA Li⁺_x/PEGMEMA_y. Based on the mole ratio of PEGMEMA over MPA Li⁺, different amount of PEGMEMA was dried together with PDMS-SH and MPA Li⁺ before transferring into glovebox.

3.2.4 RAFT synthesis for poly(MPA Li⁺) and poly(MPA Li⁺₁₃/PEGMEMA₂₇)

34mg (0.14 mmol) RAFT-CTA and 1.96g (5.7 mmol) MPA Li⁺ were dried in vacuum before transferring into glovebox. They were then added together with 5mg (0.03 mmol) AIBN into a Schlenk tube equipped with a stirring bar and dissolved by total 10ml dry THF. The solution was

degassed with N₂ and reacted at 65°C overnight. The product was purified by dialysis against DMF and dried in a vacuum oven at 100°C for one day.

The same procedure was applied to synthesize poly(MPA Li⁺₁₃/PEGMEMA₂₇), which certain amount of PEGMEMA was dried together with PDMS-SH and MPA Li⁺ before transferring into glovebox.

3.2.5 Synthesis of SICPEs with Na⁺

PDMS-g-(MPA Na⁺₁₃/PEGMEMA₂₇) and Poly(MPA Na⁺₁₃/PEGMEMA₂₇) were synthesized with same procedure of Li⁺ SICPEs. The mass of each reactant was adjusted based on the molecular weight of MPA Li⁺ (345g/mol) and MPA Na⁺ (361g/mol) under same mole ratio.

3.2.6 Instrumentation

¹H nuclear magnetic resonance (¹H NMR) and ¹⁹F NMR measurements were done on a Bruker Advance III 400 MHz NMR Spectrometer. The samples were dissolved in d-Chloroform or d-DMSO, depending on the solubility of the samples.

Small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) measurements were performed at the DND-CAT sector 51D-D beamline at the Advanced Photon Source, Argonne National Laboratory. The images have been collected with a Mar CCD detector at a resolution of 1024×1024 pixels with E=9kV. The sample to detector distance was 90cm for SAXS and 2.42cm for WAXS.

Temperature modulated differential scanning calorimetry (TMDSC) measurements were performed under an argon and helium atmosphere using a TA instrument DSC 2500. The

samples were equilibrated at 120 °C for 15mins to remove the thermal history. Two successive cooling-heating scans were conducted at a rate of 20°C/min in the range of -150 °C to 100 °C. The purpose is to make sure no solvent was left inside the samples or no degradation happened by the repeatable lines of these two cycles. The final cooling-heating cycle was conducted with a rate of 3°C/min and modulation speed of $\pm 0.5^\circ\text{C}/\text{min}$, and this heating scan was taken to analyze the T_g of the samples. Because of the high T_g , poly(MPA Li⁺) was measured in the range of 0°C to 200°C with same equilibrated condition and rate. The pan of PC doped PDMS-*g*-(MPA Li⁺₁₀/PEGMEMA₃₀) was assembled in a glovebox to avoid moisture. After being equilibrated at 30°C for 15mins, only one cooling-heating cycle was conducted with a rate of 3°C/min and modulation speed of $\pm 0.5^\circ\text{C}/\text{min}$, and the heating scan was used to analyze its T_g .

The dynamic shear modulus of SICPEs above T_g was measured by small-amplitude oscillatory shear (SAOS) measurements on an AR2000ex rheometer. The experiments were performed between two 4mm parallel steel plates. All the samples were loaded between the plates and equilibrated at the temperature which is at least 60 °C above its own T_g for 30 mins before the measurement to get a homogeneous state. Then several different temperatures were measured with the angular frequency sweep from 15 to 0.015 Hz.

The lithium-ion conductivity of synthesized SICPEs was analyzed by broadband dielectric spectroscopy (BDS) over the frequency range of $10^{-1} \sim 10^6$ Hz on a Novocontrol Concept 80 system. All samples were sandwiched between two gold plated electrodes separated by a Teflon spacer ring and dried under vacuum at 100°C overnight to completely remove the solvent. During the measurements, samples were equilibrated at high temperature for 15 mins, then to lower temperatures (cooling cycle) and finally back to the same high temperature

(heating cycle) under nitrogen atmosphere. The repeatable data at high temperature for both cycles suggests no leftover solvent and absence of degradation. Each temperature was equilibrated for 10 mins before scanning.

The electrochemical measurements were conducted on a Biologic VMP3 potentiostat with the EC-Lab® software at 30°C. The Li/Li symmetric cell composed of 20wt% propylene carbonate (PC) doped PDMS-*g*-(MPA Li⁺₁₀/PEGMEMA₃₀) electrolyte (Li⁺ concentration is 0.1 mol/L) was assembled in the glovebox. The glass fiber separators were wetted with electrolyte solution, sandwiched between two pieces of lithium foils with diameter equal to 1.27 cm (surface area is 1.27 cm²) and sealed in a coin cell. The potentio-static polarization method was used to calculate the lithium-ion “transference” number. The voltage is set as 10 mV for 3600 seconds for the CA test, and EIS was recorded from 1 MHz to 10 mHz with a voltage amplitude of 10 mV. To test the electrochemical stability of the polymer electrolyte, the Li/stainless steel cell composed of dry or PC doped PDMS-*g*-(MPA Li⁺₁₀/PEGMEMA₃₀) was sealed in the glovebox separately and subjected to linear sweep voltammetry (LSV) with a sweep rate of 5 mV/s. To study the lithium stripping/plating process, the galvanostatic cycling tests of the Li/Li symmetric cell with the PC doped PDMS-*g*-(MPA Li⁺₁₀/PEGMEMA₃₀) was performed at room temperature. Each cycle was applied with selected current density for 60 minutes lithium plating/stripping and an intermediate 5 minutes rest step. In addition, the long-term galvanostatic cycling test of PC doped SICPE was also measured with a constant current density 50 μA, i.e., 0.04 mA /cm², up to 1100h.

3.3 Results and discussions

3.3.1 Determination of SICPEs composition

The PDMS based SICPEs, i.e., PDMS-*g*-MPA Li⁺ or PDMS-*g*-MPA Li⁺_x/ PEGMEMA_y, were synthesized by chemical grafting of MPA Li⁺ or co-grafting with varied molar ratio of PEGMEMA on PDMS-SH *via* a thiol-ene reaction (Scheme 3.2 top). Poly(MPA Li⁺) and poly(MPA Li⁺_x/PEGMEMA_y) were synthesized as the control to evaluate the influence of accelerated segmental dynamics on the single-ion conductivity of PDMS-based SICPEs (Scheme 3.2 bottom). The molar ratio of monomers to RAFT-CTA was chosen specifically to have comparable number of functional units per molecule, i.e., degree of polymerization (DP_n), with PDMS-based SICPEs. Their chemical structures were verified by ¹H NMR and FT-IR spectroscopy. The absence of proton signals between 5.5-6.6 ppm corresponding to the alkene group in the ¹H NMR spectra of all SICPEs demonstrated the complete removal of free monomers from the obtained polymers. As illustrated by the IR spectra of PDMS-*g*-MPA Li⁺ and PDMS-*g*-MPA Li⁺_x/PEGMEMA_y, the strong peak at 796 cm⁻¹ corresponding to the deformation mode of Si-O-Si,¹⁶⁰ and the absence of a peak at 2550 cm⁻¹ corresponding to the stretching mode of S-H bond suggested the complete conversion of thiol units (Figure 3.1). This point could also be proven by the equal integrals of the peaks at 0.5-0.7 ppm (-CH₂- connected to silicon) and 4.1-4.3 ppm (-CH₂- adjacent to ester units) in the ¹H NMR spectrum. For PDMS-*g*-MPA Li⁺_x/PEGMEMA_y and poly(MPA Li⁺_x/ PEGMEMA_y), with fixed peak intensity at 1320 cm⁻¹ (S=O rocking mode), the relatively higher intensity of the peak at 2880 cm⁻¹ (C-H stretching mode from PEGMEMA, marked with dash line in Figure 3.1) demonstrated the increased PEGMEMA content in the polymers following the increased feed

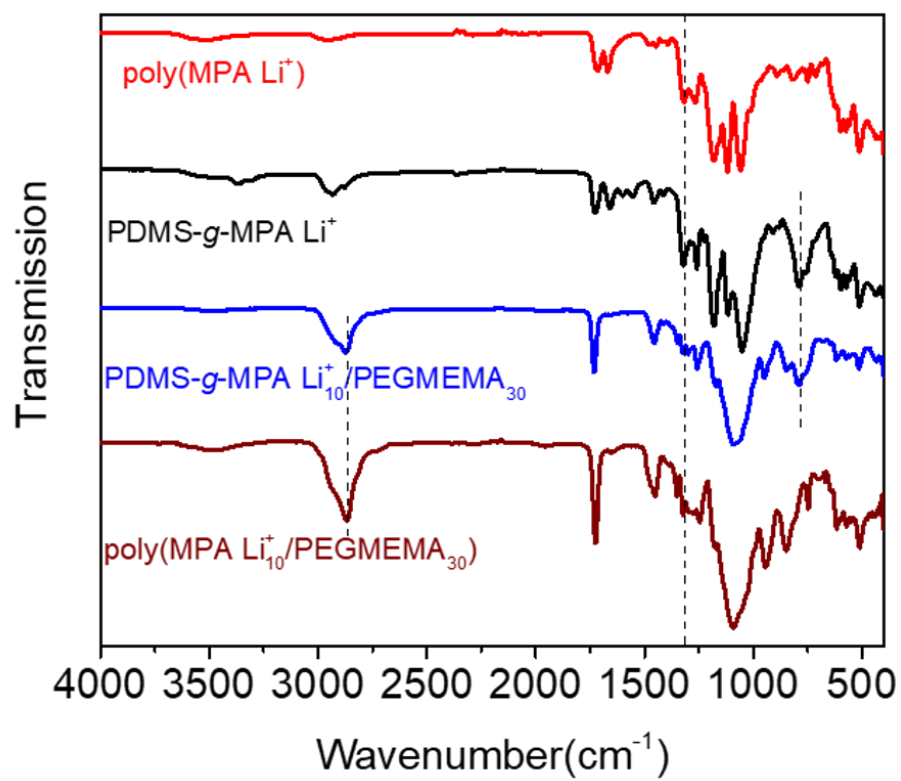


Figure 3.1 FT-IR spectra of poly(MPA Li⁺), PDMS-*g*-MPA Li⁺, PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀ and poly(MPA Li⁺₁₀/PEGMEMA₃₀).

ratio of PEGMEMA to MPA Li⁺. In their ¹H NMR spectra, both MPA Li⁺ and PEGMEMA have a common peak between 4.1-4.3 ppm corresponding to the -CH₂- adjacent to ester units, whereas the -CH₂CH₂- units connected with -SO₂- in the MPA Li⁺ shows two separate peaks between 2.1-2.3 ppm and 3.1-3.3 ppm. The mole ratios of PEGMEMA over MPA Li⁺ can be calculated based on the integration values of these peaks. The ¹H NMR spectra of PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀ and poly(MPA Li⁺₁₀/PEGMEMA₃₀) together with analysis of mole ratio were presented in Figure 3.2 as an example. The calculated mole ratios are slightly higher than their feed ratios which may be explained by the relatively higher reactivity of PEGMEMA than MPA Li⁺ during polymerization process.

3.3.2 The accelerated segmental dynamics by flexible PDMS backbone

As a reference, homopolymer poly(MPA Li⁺) possesses a high *T_g* value of 152°C and hence a very low Li⁺ conductivity, which is out of the measurement range at 30°C (< 10⁻¹⁵ S/cm) and is only 3.9×10⁻¹⁴ S/cm at 100°C (Table 3.1). The first acceleration of segmental dynamics is achieved by changing the “rigid” PMMA backbone to a “soft” PDMS backbone. First, the PDMS-*g*-MPA Li⁺ shows a much better thermal stability in comparison to that obtained for poly(MPA Li⁺) perhaps due to the absence of trithiocarbonate bond in RAFT-CTA.^{36, 161, 162} With the hydrophilic MPA Li⁺ grafted on a hydrophobic PDMS backbone, there are no defined peaks observed in the SAXS and WAXS spectra of PDMS-*g*-MPA Li⁺ (Figure 3.3). Combined with the presence of only one *T_g* in the measured temperature range of differential scanning calorimetry (DSC), it suggests the absence of a micro phase separation between PDMS backbone and grafted sidechains (Figure 3.4). The absence of phase separation is important for efficient acceleration of the segmental dynamics *via* a “soft” backbone effect. The segmental relaxation time for PDMS-*g*-MPA Li⁺ at

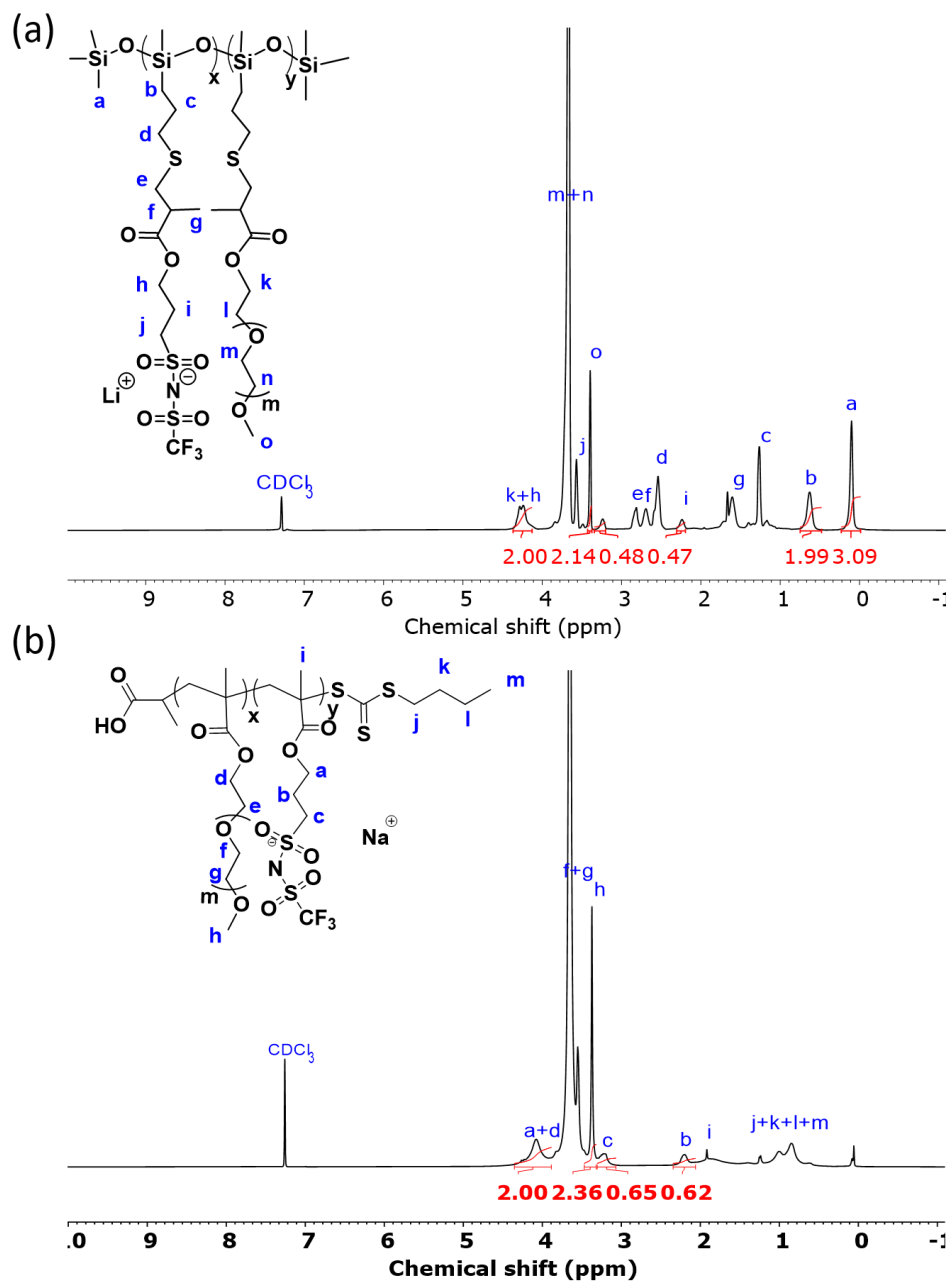


Figure 3.2 ^1H -NMR spectra of (a) PDMS-*g*-MPA Li^+_{10} /PEGMEMA $_{30}$ (MPA $\text{Li}^+=40 \times \frac{(i+j)/4}{\frac{o}{3}+(i+j)/4} = 10$, PEGMEMA=30) and (b) poly(MPA Li^+_{10} /PEGMEMA $_{30}$) (MPA $\text{Li}^+=40 \times \frac{(b+c)/4}{\frac{h}{3}+(b+c)/4} = 10$, PEGMEMA=30) in CDCl_3 .

Table 3.1 Summary of thermal property and conductivity of SICPE.

	T_g (°C)			$T_{d,5\%}$	σ at 30°C
	DSC	Rheology	BDS	(°C) [a]	(S/cm)
Poly(MPA Li ⁺)	152.8	-	150.1	226.9	$< 10^{-15}$
PDMS- <i>g</i> -MPA Li ⁺	31.8	34.8	30.6	271.0	5.9×10^{-15}
PDMS- <i>g</i> -MPA Li ⁺ ₁₅ /PEGMEMA ₂₅	-46.7	-48.5	-51.2	331.7	2.6×10^{-6}
PDMS- <i>g</i> -MPA Li ⁺ ₁₀ /PEGMEMA ₃₀	-55.2	-57.8	-59.2	325.1	4.2×10^{-6}
PDMS- <i>g</i> -MPA Li ⁺ ₇ /PEGMEMA ₃₃	-60.2	-64.4	-62.8	340.3	2.7×10^{-6}
Poly(MPA Li ⁺ ₁₀ /PEGMEMA ₃₀)	-45.5	-44.5	-49.6	326.3	4.6×10^{-7}
PDMS- <i>g</i> -MPA Na ⁺ ₁₁ /PEGMEMA ₂₉	-51.4	-53.4	-52.2	335.4	9.1×10^{-7}
Poly(MPA Na ⁺ ₁₁ /PEGMEMA ₂₉)	-37.7	-34.8	-38.7	328.2	1.61×10^{-7}

[a] This parameter implies the temperature when the weight loss of samples is 5%.

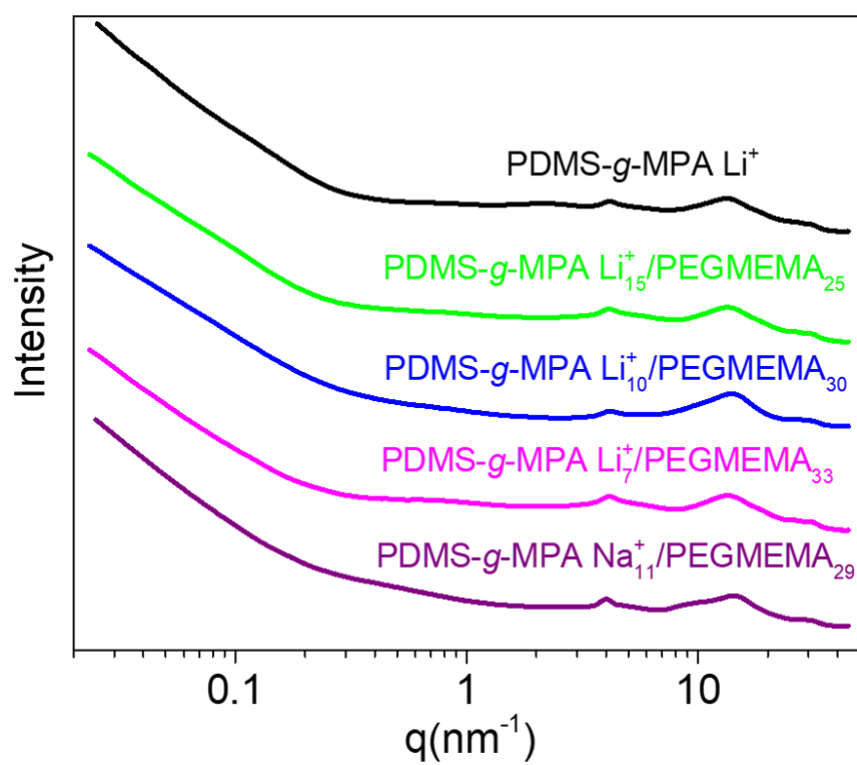


Figure 3.3 SAXS-WAXS profiles of PDMS-*g*-MPA Li⁺, PDMS-*g*-MPA Li_{*x*}⁺/ PEGMEMA_{*y*} and PDMS-*g*-MPA Na₁₀⁺/ PEGMEMA₃₀.

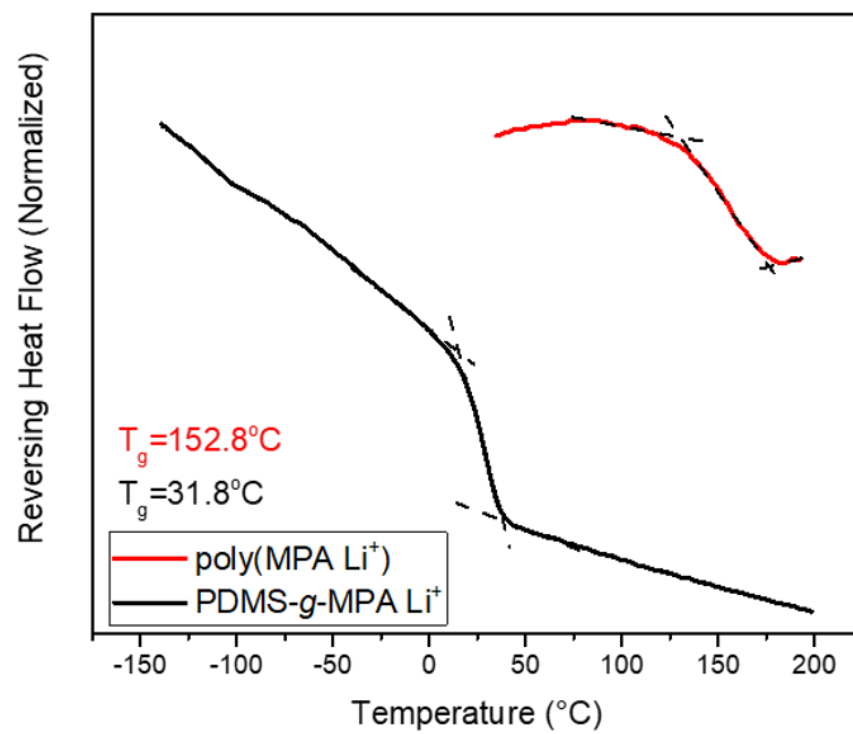


Figure 3.4 Reversible heat flow curve for poly(MPA Li⁺) and PDMS-g-MPA Li⁺.

different temperatures was estimated from master-curve by rheological measurement. The mastercurve of PDMS-*g*-MPA Li⁺ was presented in Figure 3.5 as an example. Unfortunately, no reliable rheological results were obtained for poly(MPA Li⁺) due to its rigid structure, which makes it impossible to directly compare the segmental relaxation time between PDMS-*g*-MPA Li⁺ and poly(MPA Li⁺). However, the significant drop in T_g value (~120°C) suggests faster segmental dynamics at the same temperature (Figure 3.4).

For SICPEs, the conductivity is determined by both concentration and mobility of the free ions. Since lithium-ions have relatively weak electrostatic interaction with bulky TFSI anion, the partially dissociated lithium-ions could still transform through ion-hopping even when the sidechain is frozen. Therefore, the ionic conductivity is decoupled from the segmental relaxation for poly(MPA Li⁺). With no phase separation observed between the polymer backbone and sidechains for PDMS-*g*-MPA Li⁺, the flexible PDMS backbone would cause relatively dense packing of MPA Li⁺ sidechains and accelerate the transportation of lithium-ions efficiently. As the dynamics of lithium-ions are strongly coupled with segmental dynamics for PDMS-*g*-MPA Li⁺ in our system,¹⁶³ the ionic conductivity of PDMS-*g*-MPA Li⁺ is more than six orders of magnitude higher than in poly(MPA Li⁺) (3.9×10^{-14} S/cm vs. 6.9×10^{-8} S/cm at 100°C) as shown in Figure 3.6 and Table 3.2.

3.3.3 The accelerated segmental dynamics by copolymerized with PEO

Though the single-ion conductivity was improved by six orders of magnitude after replacing the PMMA backbone with PDMS one, the ionic conductivity of PDMS-*g*-MPA Li⁺ at ambient temperature is far below that required for practical applications in batteries. Therefore, in

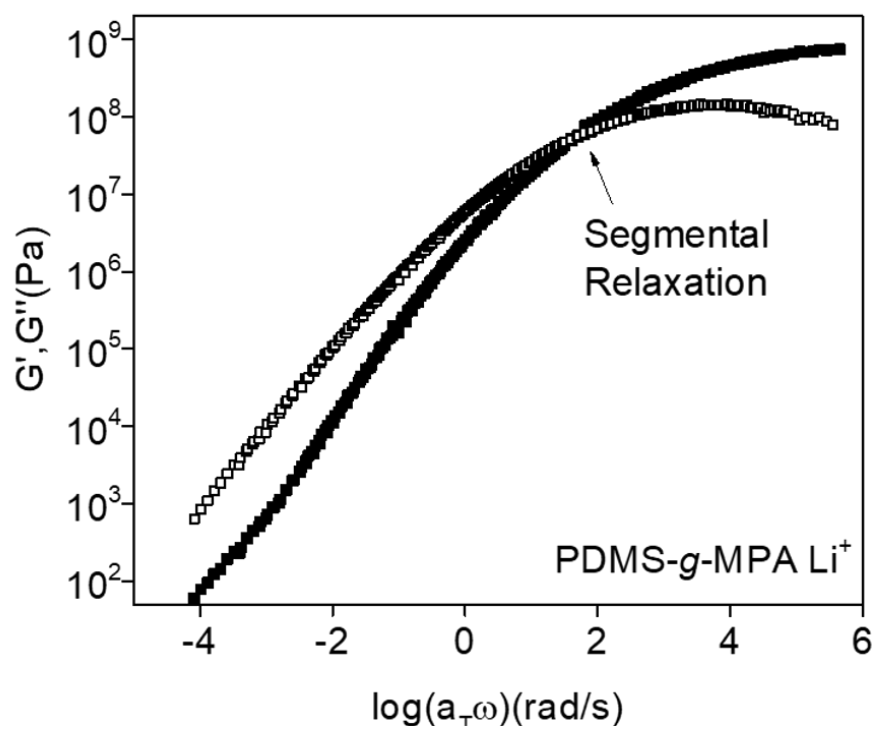


Figure 3.5 Master-curves of storage modulus G' (solid) and loss modulus G'' (empty) for PDMS-*g*-MPA Li^+ at 60°C.

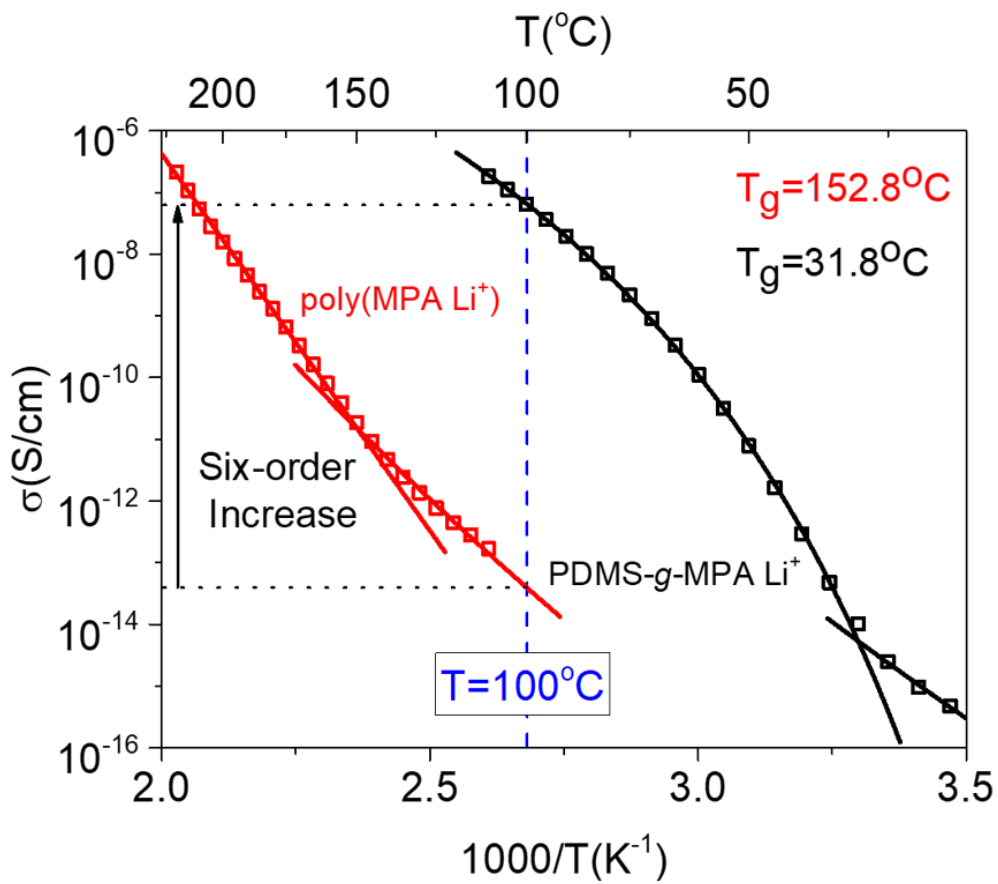


Figure 3.6 Conductivity vs. $1000/T$ of PDMS-*g*-MPA Li⁺ and poly(MPA Li⁺). The data points were fitted by VFT equation above T_g and Arrhenius equation below T_g (solid lines).

Table 3.2 Fitting parameters of VFT equation and Arrhenius equation of SICPEs.

	VFT ($T > T_g$)			Arrhenius ($T < T_g$)	
	B (K)	T_0 (K)	σ_0 (S/cm)	E_a (kJ/mol)	σ_0 (S/cm)
Poly(MPA Li ⁺)	-11094	170.2	1.4×10^8	151.5	8.5×10^6
PDMS- <i>g</i> -MPA Li ⁺	-2111	236.8	0.35	118.3	1.3×10^6
PDMS- <i>g</i> -MPA Li ⁺ ₁₅ /PEGMEMA ₂₅	-1132	183.7	0.034	117.9	2.9×10^{13}
PDMS- <i>g</i> -MPA Li ⁺ ₁₀ /PEGMEMA ₃₀	-1053	178.2	0.018	138.0	2.3×10^{19}
PDMS- <i>g</i> -MPA Li ⁺ ₇ /PEGMEMA ₃₃	-1026	174.6	0.011	105.8	1.3×10^9
Poly(MPA Li ⁺ ₁₀ /PEGMEMA ₃₀)	-1237	181.1	0.011	107.8	9.1×10^9
PDMS- <i>g</i> -MPA Na ⁺ ₁₁ /PEGMEMA ₂₉	-1182	180.2	0.013	109.9	3.1×10^{11}
Poly(MPA Na ⁺ ₁₁ /PEGMEMA ₂₉)	-1516	183.5	0.053	102.2	3.7×10^8

addition to the soft backbone, we also performed sidechain modification *via* co-grafting the PEGMEMA monomer. With flexible PEGMEMA sidechains co-grafted on the PDMS backbone, the PDMS-*g*-MPA Li⁺₁₅/PEGMEMA₂₅ exhibits significantly accelerated segmental dynamics with relaxation time shorter than 10⁻⁶ s at 0°C, which is more than eight orders faster than that of PDMS-*g*-MPA Li⁺ at the same temperature (>100s) in Figure 3.7. The segmental dynamics can be further accelerated with an increasing molar ratio of PEGMEMA to MPA Li⁺. The accelerated segmental dynamic was also confirmed by the significantly reduced T_g value. With equal feed ratio of PEGMEMA to MPA Li⁺ grafted on PDMS backbone, the T_g of PDMS-*g*-MPA Li⁺₁₅/PEGMEMA₂₅ decreased to -45°C. Increasing the feed ratio of PEGMEMA and MPA Li⁺ to two and three, the T_g of PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀ and PDMS-*g*-MPA Li⁺₇/PEGMEMA₃₃ further decreased to -55°C and -60°C, with the latter value being close to the T_g of PEO. The high ratio of PEGMEMA inside the PDMS-*g*-MPA Li⁺₇/PEGMEMA₃₃ even results in a crystalline structure observed only in the heating cycle of the DSC curves. The crystallization was also observed in the rheology measurement, where it causes failure of time-temperature-superposition (TTS) in the construction of master-curve at -40°C.

Comparing with PDMS-*g*-MPA Li⁺, the ionic conductivity of PDMS-*g*-MPA Li⁺_{*x*}/PEGMEMA_{*y*} is increased by nine orders due to the accelerated segmental dynamic *via* co-grafting with PEGMEMA monomers (~10⁻⁶ S/cm vs. 6×10⁻¹⁵ S/cm at 30°C in Figure 3.8. It is noteworthy that although the segmental relaxation time of PDMS-*g*-MPA Li⁺_{*x*}/PEGMEMA_{*y*} decreases significantly with increasing ratio of PEGMEMA, the ionic conductivity is not always improved. This is because the increased ratio of PEGMEMA will not only accelerate segmental dynamics, but also decrease the Li⁺ concentration. Therefore, the conductivity would reach a maximum value only

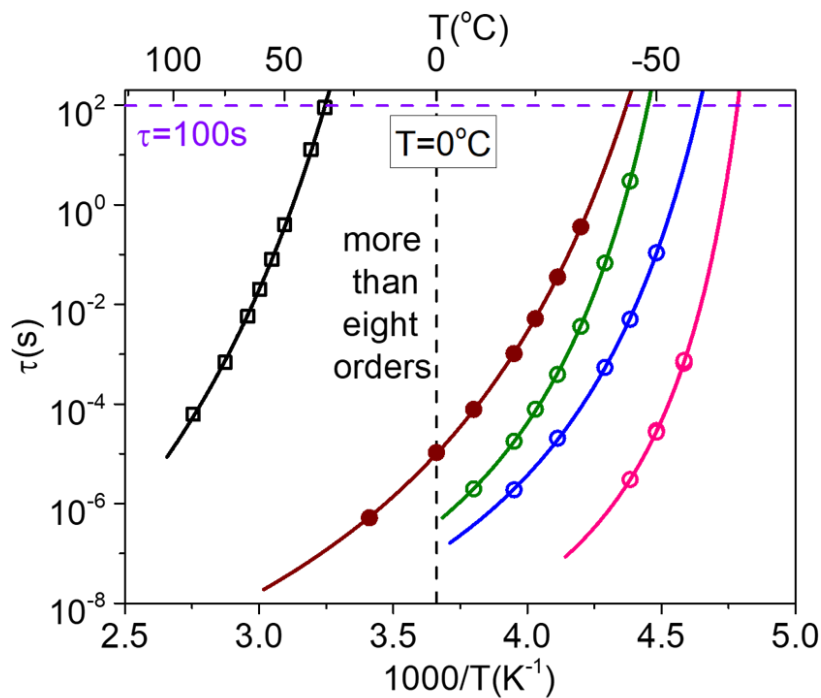


Figure 3.7 The estimation of segmental relaxation times and $1000/T$ for PDMS-*g*-MPA Li^+_x , PDMS-*g*-MPA Li^+_x / PEGMEMA_y and poly(MPA Li^+_{10} /PEGMEMA₃₀). The list of symbols: PDMS-*g*-MPA Li^+ (black empty square), poly(MPA Li^+) (red empty square), PDMS-*g*-MPA Li^+_{15} / PEGMEMA₂₅ (green empty circle), PDMS-*g*-MPA Li^+_{10} / PEGMEMA₃₀ (blue empty circle), PDMS-*g*-MPA Li^+_{7} / PEGMEMA₃₃ (pink empty circle) and poly(MPA Li^+_{10} /PEGMEMA₃₀) (wine solid circle).

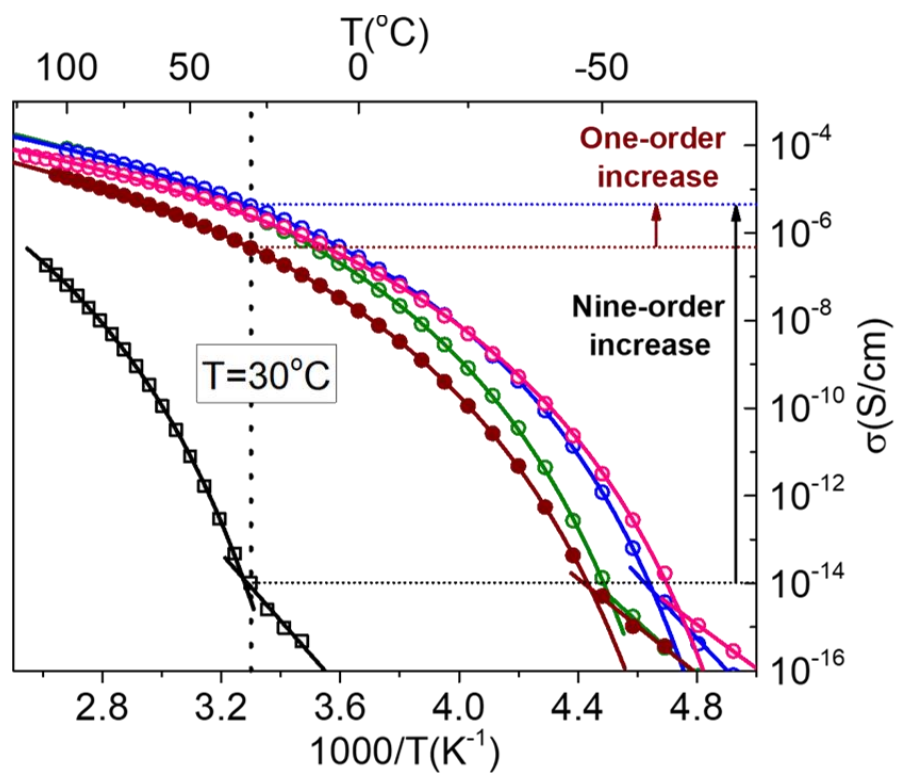


Figure 3.8 Conductivity vs. $1000/T$ for SICPEs.

when the ratio between PEGMEMA and MPA Li⁺, i.e., the ratio of ethylene oxide group (EO) to Li⁺, reaches an optimal value. The relationship between conductivity and ratio of EO/Li⁺ has been widely studied for lithium salt doped PEO, and the optimal ratio may be varied from 9 to 24 depending on the types of lithium salt.^{164, 165} The highest conductivity $\sim 4.3 \times 10^{-6}$ S/cm at 30°C was reached in PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀ with EO/Li⁺ ratio $\sim 27:1$. This single lithium-ion conductivity value is several orders higher than those achieved in structures containing PEO in the backbone,^{74, 123} and half-order higher than the reported sulfonyl(trifluoromethane-sulfonyl)imide based SICPEs with PEO block as sidechains.^{104, 166}

With optimal EO/Li⁺ ratio, the copolymer of MPA Li⁺ and PEGMEMA has been reported as one of the state-of-art SICPEs with highest lithium ionic conductivity.¹⁶⁶ Therefore, poly(MPA Li⁺₁₀/PEGMEMA₃₀) was also synthesized as a control, which has the same ratio of EO/Li⁺ and shows similar thermal stability. Compared with poly(MPA Li⁺₁₀/PEGMEMA₃₀), the soft PDMS backbone enable PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀ have faster segmental dynamic (Figure 3.7), which also corresponds to a 9°C decrease in T_g (-60.2°C vs. -51.4°C in Table 3.1). In addition, as the PEO units would solvate lithium-ions, the transportation of lithium-ions is strongly coupled with the motion of PEO sidechains. Therefore, the faster segmental dynamics of PDMS-*g*-(MPA Li⁺₁₀/PEGMEMA₃₀) would also allow faster lithium-ion transport for coupled systems. As a result, PDMS-*g*-(MPA Li⁺₁₀/PEGMEMA₃₀) has an order higher conductivity at 30°C than poly(MPA Li⁺₁₀/PEGMEMA₃₀) (4.7×10^{-6} S/cm vs. 4.6×10^{-7} S/cm in Figure 3.8).

The accelerated segmental dynamics enabled by softening the backbone was also demonstrated by the Mean Square Displacement (MSD) from coarse-grained molecular dynamics simulations representing for flexible-backbone PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀ and

rigid-backbone poly(MPA Li⁺₁₀/ PEGMEMA₃₀) (Figure 3.9). The simulations were performed in the melt above T_g , and all other pertinent variables such as degrees-of-polymerization are the same for both models to focus only on the effect of backbone rigidity. The computation results show that the dynamics of the backbones and side chains of the coarse-grained model with a soft backbone, representing PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀ are significantly faster than the more rigid model representing poly(MPA Li⁺₁₀/ PEGMEMA₃₀) (Figure 3.9(a) and (b)). As lithium-ions diffusion is coupled with segmental dynamics for both SICPEs, the accelerated polymer dynamics results in a faster lithium-ion diffusion (Figure 3.9(c)), which emphasizes the importance of a soft backbone to accelerate segmental dynamics.

3.3.4 Further study (i.e. application of this method in other single-ion system and battery performance)

To further demonstrate the effect of accelerated segmental dynamics on the conductivity of other SICPEs, single sodium ion conducting polymer electrolytes have also been studied. The PDMS based polymer electrolytes ,i.e., PDMS-*g*-MPA Na⁺₁₁/PEGMEMA₂₉, along with the control poly(MPA Na⁺₁₁/PEGMEMA₂₉) were synthesized and verified with ¹H NMR spectra and FT-IR. Similarly with Li⁺ conducting SICPEs, the soft PDMS backbone leads to a faster segmental dynamic in PDMS-*g*-(MPA Na⁺₁₁/PEGMEMA₂₉) than in poly(MPA Na⁺₁₁/PEGMEMA₂₉) (8×10^{-6} s vs. 6×10^{-2} s at -20°C). This faster segmental dynamic also corresponds to a 13°C lower T_g (-51°C vs. -38°C) and one order of magnitude higher sodium ion conductivity (10^{-6} S/cm vs. 10^{-7} S/cm at 30°C in Figure 3.10). This demonstrates the potential in accelerated segmental dynamics to improve the ionic conductivity of polymer electrolyte with different counter ions, like zinc,¹⁶⁷⁻¹⁶⁹ magnesium¹⁷⁰ and aluminum,¹⁷¹ or charged units, like (fluorosulfonyl)imide.¹¹⁴

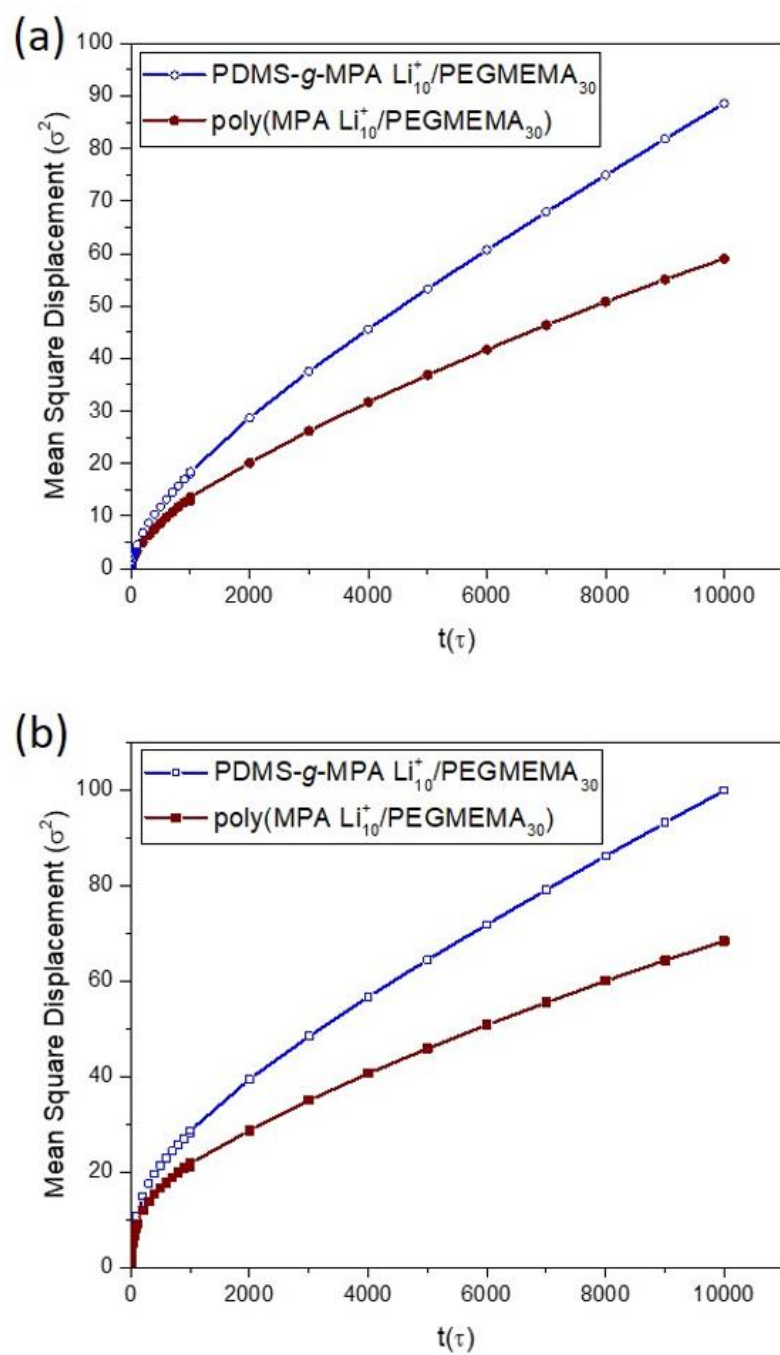


Figure 3.9 Mean square displacement vs. time of (a) backbone (circle), (b) sidechain (square) and (c) counterion (triangle).

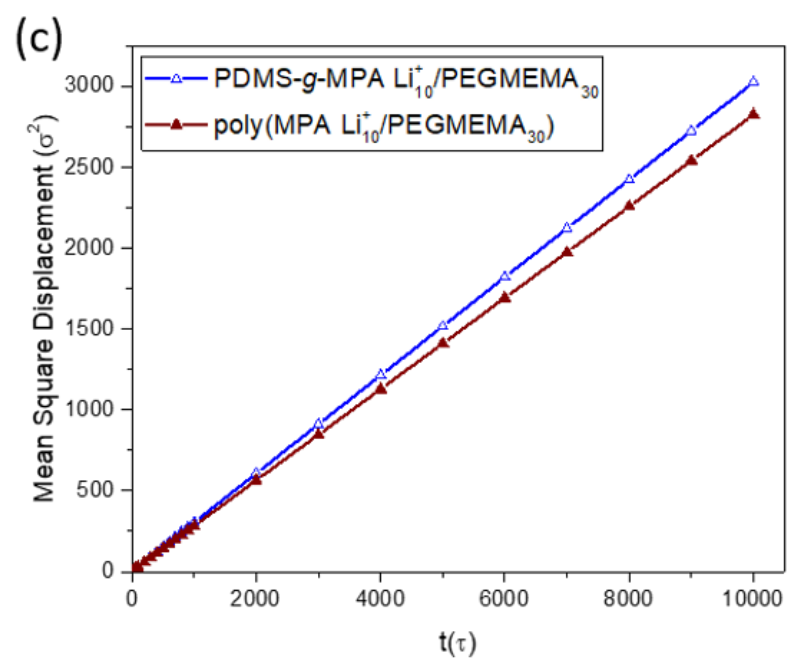


Figure 3.9 continued.

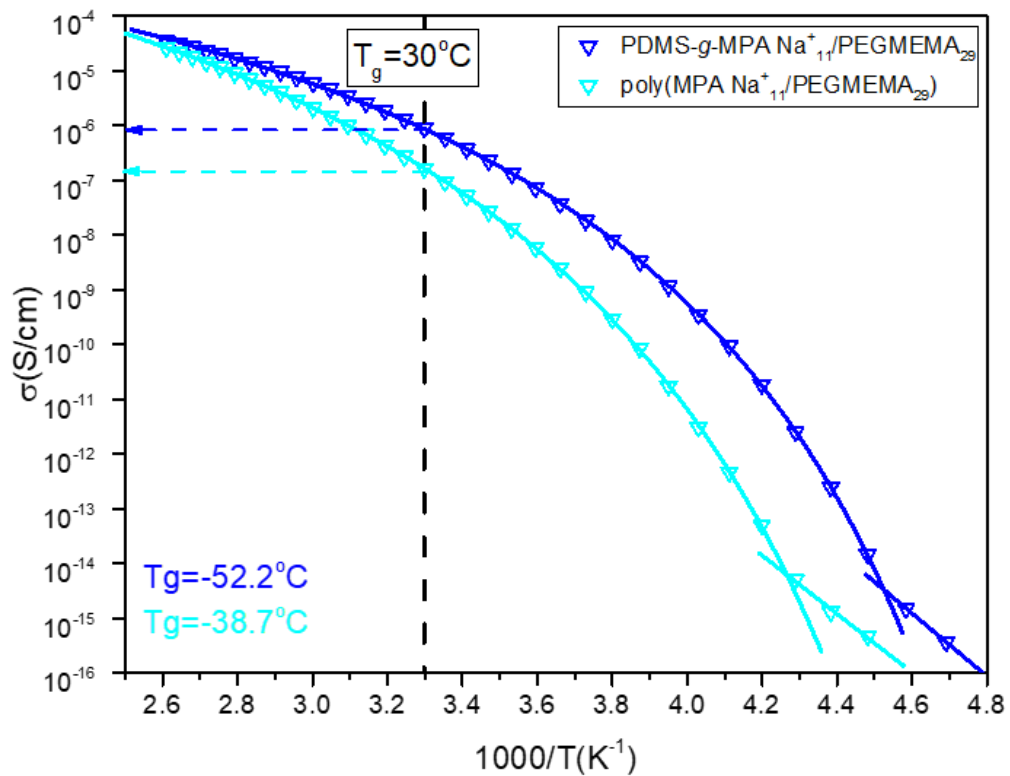


Figure 3.10 The dc conductivity vs. $1000/T$ for Na⁺ SICPEs.

The transport number (t_{Li^+}) was measured *via* potentiostatic polarization method using a Li/Li symmetric cell.¹⁴² With propylene carbonate (PC) as plasticizer, the T_g value of PDMS-*g*-MPA $\text{Li}^+_{10}/\text{PEGMEMEA}_{30}$ was further decreased to -113°C and conductivity at room temperature was improved by 1.5 orders of magnitude ($\sim 1.0 \times 10^{-4} \text{ S/cm}$ at 30°C). The obtained t_{Li^+} was determined to be 0.85 (Figure 3.11(a)), which is comparable with other reported single-ion conducting polymer electrolyte systems,^{107, 112, 116, 123, 172-176} and much higher than a normal dual-ions polymer electrolyte with values of around 0.37.^{57, 177-182} The electrochemical stability of obtained SICPE was tested by linear sweep voltammetry (LSV) using Li/stainless steel cell. There is no obvious anodic current peak till 4V for both dry and PC doped PDMS-*g*-MPA $\text{Li}^+_{10}/\text{PEGMEMEA}_{30}$, indicating their excellent electrochemical stability. To further evaluate the stability of the obtained SICPE against lithium metal electrodes, the Li/Li symmetric cell with the same PC doped PDMS-*g*-MPA $\text{Li}^+_{10}/\text{PEGMEMEA}_{30}$ electrolyte was assembled and tested by performing galvanostatic cycling (GC) test under various current densities. The voltage profile shows a stable response under varied current densities. In addition, the long-term endurance test for more than 1100 hours was also performed (Figure 3.11(b)). The overpotential slightly decreases at initial cycles, followed by a gradual increase and eventually stabilizing after 30h. This slight variation at initial cycles is related to the reorganizing process on the lithium metal surface before final steady state.⁷⁶ No short circuit or other significant change was observed in the long-term voltage profile. In addition, the cells after the galvanostatic cycling test were disassembled in an argon protected glove box, and no significant corrosion was observed on the lithium metal electrode (Figure 3.12). This demonstrates a relatively stable solid electrolyte interface (SEI) layer between the SICPE and lithium metal electrode.¹⁸³

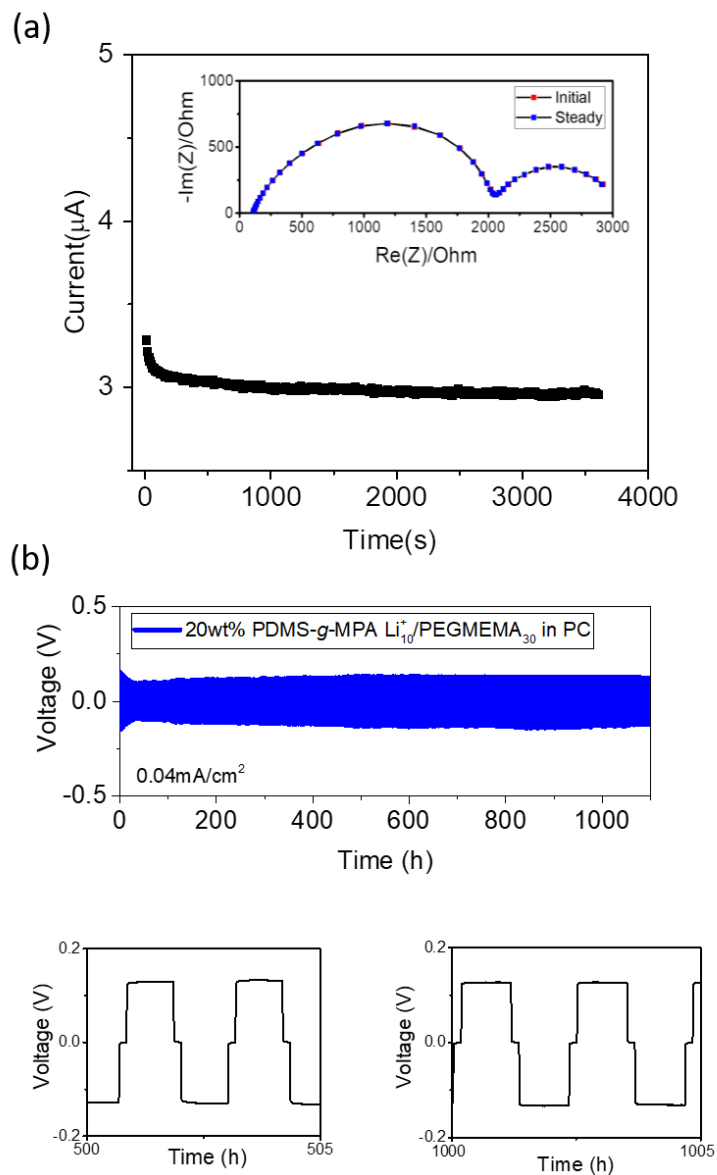


Figure 3.11 Electrochemical performance of PC doped PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀. (a) The chronoamperometry (CA) response of Li/Li symmetric cell under 10mV polarization voltage and electrochemical impedance spectroscopy (EIS) spectra before and after dc polarization (inset). (b) A long-term galvanostatic cycling test of Li/Li symmetric cell at a constant current of 0.04mA/cm² up to 1100h, and selected cycles around 500h and 1000h.



Figure 3.12 Photo images of the lithium metal disassembled from the Li/Li cell with PC doped PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀ after galvanostatic cycling for 1100 hours at 0.04 mA/cm²

3.4 Conclusion

We demonstrated a strategy to significantly improve the Li ionic conductivity of SICPEs based on the concept of accelerated segmental dynamics in polymer design. A series of SICPEs with both “soft” PDMS polymer backbone and PEGMEMA side chains were synthesized by one-spot thiol-ene reaction. In comparison to the SICPE with rigid PMMA backbone, the SICPE with accelerated segmental dynamics, i.e., PDMS-*g*-MPA Li⁺_x/PEGMEMA_y, showed a much faster segmental dynamics and several-orders higher single-ion conductivity, with PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀ achieving the lithium conductivity of 4.7×10^{-6} S/cm at ambient temperature. With a molecular dynamics computation conducted between the flexible-backbone PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀ and the rigid-backbone poly(MPA Li⁺₁₀/ PEGMEMA₃₀), the faster dynamics for all parts of PDMS-*g*-MPA Li⁺₁₀/PEGMEMA₃₀, i.e. mainchain, sidechains and lithium-ions, emphasize the importance of accelerated segmental dynamics enabled by softening the backbone. We demonstrate that the developed concept is also able to improve the conductivity of other SICPEs, e.g., single sodium-ion conducting polymer electrolyte. With “transference” number around 0.85, the assembled Li/Li symmetric cell with PC doped SICPE, i.e., PDMS-*g*-MPA Li⁺₁₀/ PEGMEMA₃₀, also shows excellent electrochemical stability against lithium metal electrodes. The present study demonstrates the clear relationship between the segmental dynamic of SICPEs with their ionic conductivity, and the concept of accelerated segmental dynamics can also be applied to other types of polymer electrolytes, contributing to achieve high-performance solid-state electrolyte.

Chapter IV

Can we find better structure than Polyethylene Oxide for Single-ion Conducting Polymer Electrolytes?

Reproduced in the part of results and discussion from Sheng Zhao, Shenghan Song, Yingqi Wang, Jong Keum, Jiadeng Zhu, Yi He, Alexei P. Sokolov and Peng-Fei Cao “Unraveling the Role of Neutral Units for Single-Ion Conducting Polymer Electrolytes”, *ACS Applied Materials & Interfaces*, 2021, 13, 43, 51525–51534. Sheng Zhao contributed to material synthesis and characterization, including IR, NMR, DSC, SAXS, rheology and BDS, data analysis and writing. Shenghan Song, Yingqi Wang and Yi He contributed to the simulation works. Jong Keum contributed to the SAXS. Jiadeng Zhu contributed to data analysis and writing. Alexei P. Sokolov and Peng-Fei Cao contributed to the idea of project and writing.

4.1 Introduction

In chapter 3, we demonstrated the incorporation of soft PDMS backbone and flexible PEGMEMA sidechains could accelerate segmental dynamics and decrease T_g . As a result, the ionic conductivity is boosted dramatically, though it is still lower than liquid electrolytes. Therefore, we need to explore other potential strategies to further improve their ionic conductivity. From the aspect of chemical structure of SICPE, the utilization of Polyethylene Oxide (PEO) structure dominates most of the recent studies. Other than physically blending with SICPEs,^{115, 116} PEO can be chemically grafted on both sides or one side of SICPE, which presents significant improvement in ionic conductivity at high temperature, especially above

the melting temperature of PEO.^{74, 85, 117-119} However, the ionic conductivity at room temperature is strongly limited, due to the semi-crystalline nature of PEO. Therefore, PEO chains with low molecular weights were copolymerized with single-ion conducting monomers to suppress or even eliminate the crystallinity.^{108, 109, 111} Alternatively, PEO units can also be incorporated as the spacer between different structures,^{120, 121, 124, 125} With numerous research achievements on improving the ionic conductivity of SICPEs *via* incorporation of PEO, the underlying mechanism that makes PEO the benchmark of polymer electrolytes has also been revealed.

PEO is composed of polar ethylene oxide units, where the perfect distance between oxygens could form a well-coordinated structure around small cations (Li^+ or Na^+). These coordination may break and reform with neighboring ethylene oxide units to facilitate the long-range transport of lithium-ions. From this viewpoint, the lithium ionic conductivity of PEO-containing polymer electrolytes is assisted by, or coupled with, the continuous segmental rearrangements of PEO.^{54, 122, 163, 184} Moreover, the unique structure also provides PEO with high chain flexibility and a relatively low T_g . Therefore, the incorporation of PEO usually accelerates the segmental dynamics of SICPEs and promotes ion transport.

To unravel the unique property of PEO, we designed, synthesized and investigated several SICPEs with different types of neutral units that can reduce T_g or increase dielectric constant of the polymer. As the low T_g value and polar group, i.e., fast segmental dynamics and good capability to solvate small ions, are the two dominating features of PEO, the monomers possessing a low T_g value or a polar group have been selected to copolymerize with single-ion conducting monomer STFLi to form a copolymer-type SICPE. The thermal properties and

lithium-ion conductivity are investigated in detail, and the molecular interactions between different units are also studied through theoretical computation. The knowledge gained during the process provides a guidance on design of SICPEs with improved electrochemical performance *via* a systematic functional group selection and rational polymer structure design.

4.2 Materials and methods

4.2.1 Materials

Poly(ethylene glycol) methyl ether methacrylate (PEGMEMA, 500g/mol), 2-ethylhexyl acrylate (EHA), acryloyl chloride, 4-(hydroxymethyl)-1,3-dioxolan-2-one (glycerol carbonate, GC), lithium perchlorate (LiClO_4) and magnesium sulfate anhydrous (MgSO_4) were purchased from Sigma Aldrich. Monomethacryloxy-propyl terminated polydimethylsiloxane, asymmetric (PDMSmMA, 900g/mol) was purchased from Gelest. Carboxylic acid terminated RAFT agent 2-[(butylsulfanyl)carbothioyl] sulfanyl propanoic acid (RAFT-CTA) was synthesized according to the previous paper.^{185, 186} Azobisisobutyronitrile (AIBN) was recrystallized from methanol before use. The monomers, i.e. PEGMEMA, EHA, PDMSmMA and GCA, were passed through a column with alternative inhibitor remover and aluminum oxide to remove inhibitor before polymerization.

4.2.2 Synthesis of lithium (4-styrenesulfonyl)(trifluoro-methanesulfonyl)imide (STFLi)

Due to the high sensitivity of STFLi towards the moisture, the STFK was synthesized instead based on literature with minor change.^{81, 110} The successful synthesis of monomer was verified by ^1H NMR spectrum. STFK monomer was dried under vacuum transferring to the glovebox. The equal mole ratio of LiClO_4 and STFK were dissolved in dry tetrahydrofuran (THF) and stirred

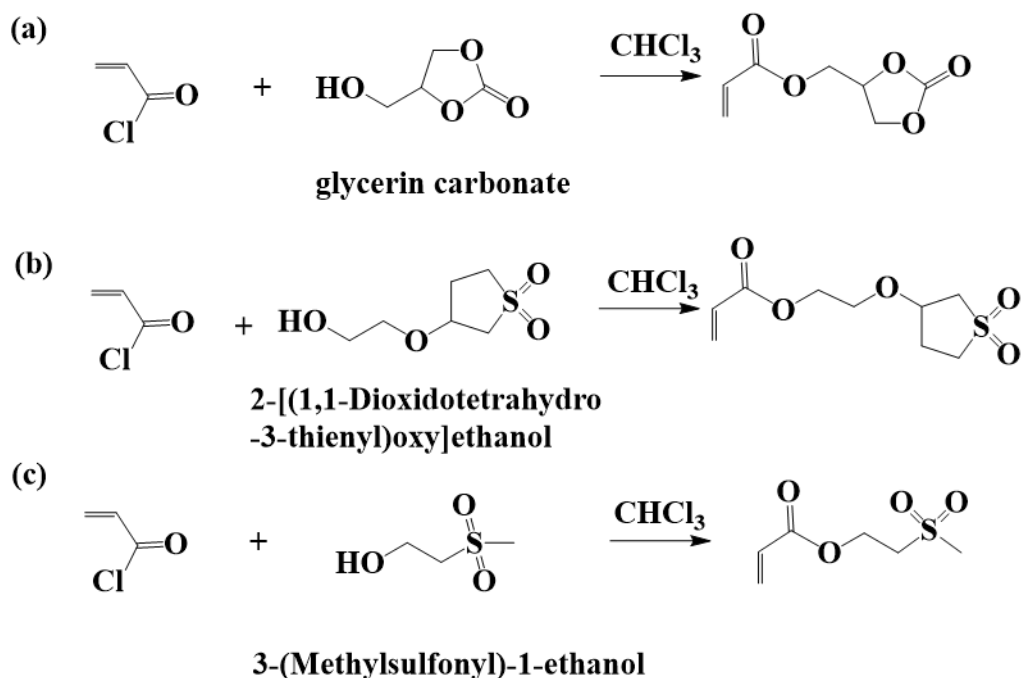
overnight for completing ion exchange. The filtered THF solution of STFLi was used for the following reactions.

STFK ^1H NMR (400 MHz, DMSO- d_6) δ 7.78 – 7.65 (m, 2H), 7.58 (dd, 2H), 6.90 – 6.70 (m, 1H), 5.95 (dd, 1H), 5.38 (dd, 1H).

4.2.3 Synthesis of monomer with polar units

To synthesis (2-Oxo-1,3-dioxolan-4-yl) acrylate or glycerin carbonate acrylate (GCA), 2.5g GC (21.2 mmol) and 2.6 mL acryloyl chloride (31.8 mmol) were separately dissolved in 20 mL and 10 mL anhydrous chloroform, respectively (Scheme 4.1 (a)). The solution with GC was loaded in a two-neck round bottom flask with one of the necks connected with a dropping funnel and the other one sealed. The system has been degassed for 15 min before the addition of acryloyl chloride solution through the dropping funnel by. The reaction was conducted for 6 h under Argon condition at 0°C. The resulted solution was washed with 10 mL of 1M NaHCO₃ aqueous solution to remove extra acryloyl chloride and then extracted by chloroform for three times. The organic layer was dried by the anhydrous MgSO₄, and the monomer was collected after removing chloroform by rotatory evaporation at room temperature. A similar procedure with GCA was applied for 2-[(1,1-Dioxidotetrahydro-3-thienyl)oxy]ethanol acrylate (DTTA) and 3-(Methylsulfonyl)-1-ethanol acrylate (MSEA) in Scheme 4.1(b) and (c). The mass of 2-[(1,1-Dioxidotetrahydro-3-thienyl)oxy]ethanol (DTT, 180.22 g/mol) and 3-(Methylsulfonyl)-1-ethanol (MSE, 124.16 g/mol) was adjusted based on the molecular weight. The successful synthesis of all three monomers was verified by ^1H NMR spectrum.

GCA ^1H NMR (400 MHz, Chloroform- d) δ 6.46 (dd, 1H), 6.15 (dd, 1H), 5.94 (dd, 1H), 5.03 – 4.95



Scheme 4.1 Synthesis of monomer (a) (2-Oxo-1,3-dioxolan-4-yl) acrylate (GCA), (b) 2-[(1,1-Dioxidotetrahydro-3-thienyl)oxy]ethanol acrylate (DTTA), and (c) 3-(Methylsulfonyl)-1-ethanol acrylate (MSEA).

(m, 1H), 4.60 (t, 1H), 4.45 (dd, 1H), 4.38 – 4.32 (m, 2H).

DTTA ^1H NMR (400 MHz, Chloroform-*d*) 6.38 (dd, 1H), 6.23 – 5.98 (m, 1H), 5.83 (d, 1H), 4.45 – 4.05 (m, 3H), 3.67 (t, 2H), 3.27 – 2.95 (m, 4H), 2.34 (t, 2H).

MSEA ^1H NMR (400 MHz, Chloroform-*d*) 6.36 (dd, 1H), 6.05 (ddd, 1H), 5.91 – 5.80 (m, 1H), 4.51 (dt, 2H), 3.32 (q, 2H), 2.94 – 2.84 (m, 3H).

4.2.4 General procedure for synthesizing homopolymers

In a typical synthesis process of poly(PEGMEMA), 11 mg RAFT-CTA (0.05 mmol), 988 mg PEGMEMA (2.0 mmol), 2 mg AIBN (0.05 mmol) were added into a round bottom flask equipped

with a stir bar and dissolved by 7 mL dry THF. After purged with Argon for 1hr at room temperature, the flask was sealed and the reaction was performed at 65°C with magnetic stirring for 24 h. The mixture was purified by dialysis against THF. The sample was dried in a vacuum oven at 110 °C for two days to fully remove solvents before further characterizations. The homopolymers with comparable degree of polymerization (DP_n) for different monomers were synthesized in the similar manner.

Poly(STFLi) ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.47 (s, 2H), 6.51 (s, 2H), 2.50 (d, 1H), 2.11 – 0.49 (m, 2H).

Poly(PEGMEMA) ^1H NMR (400 MHz, Chloroform- d) δ 4.05 (s, 2H), 3.62 (d, 33H), 3.52 (dd, 2H), 3.35 (s, 3H), 1.75 (s, 2H), 1.08 – 0.70 (m, 3H).

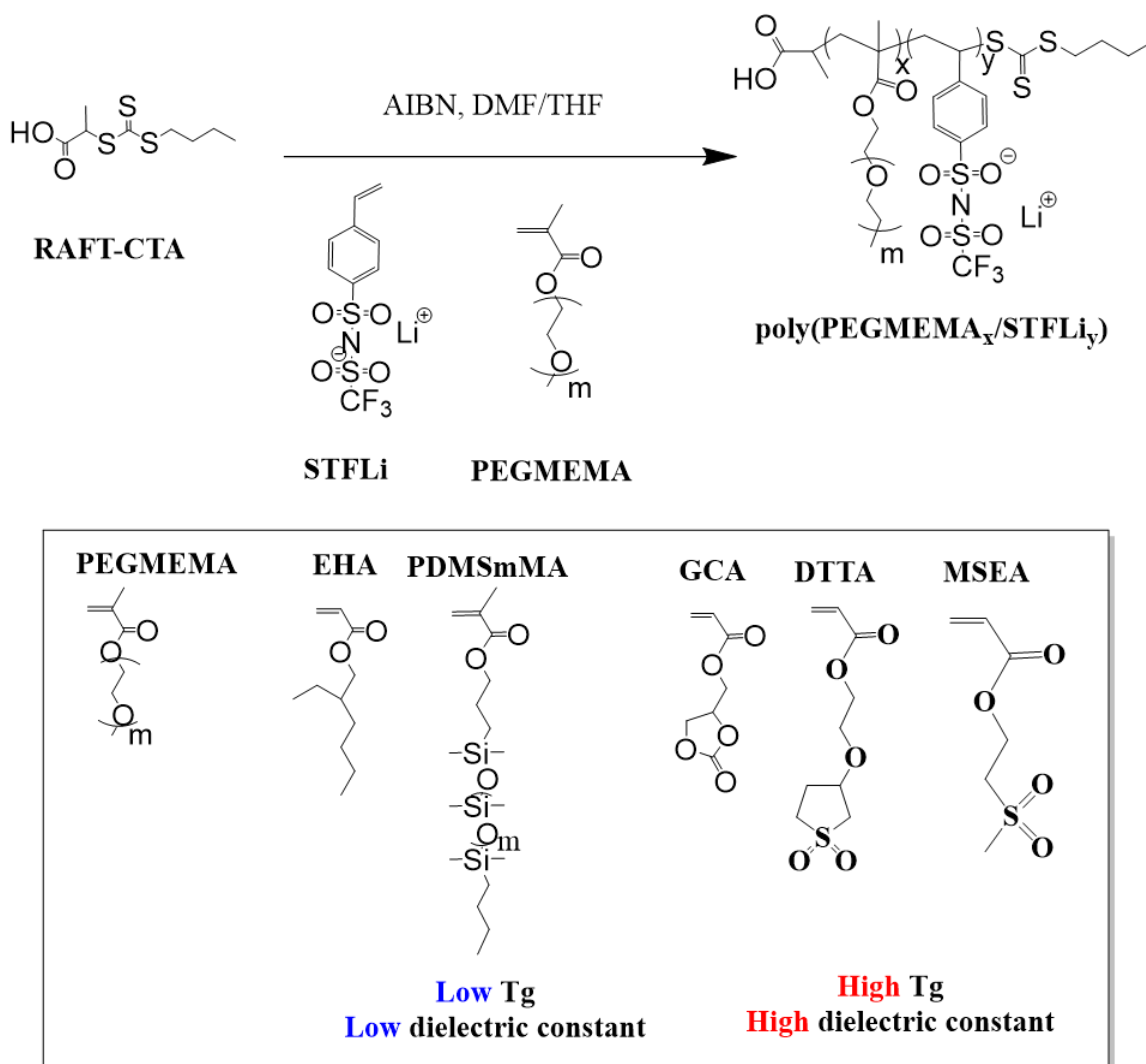
Poly(EHA) ^1H NMR (400 MHz, Chloroform- d) δ 4.16 – 3.76 (m, 2H), 2.50 – 2.18 (m, 1H), 2.01 – 1.73 (m, 1H), 1.75 – 1.51 (m, 2H), 1.47 – 1.16 (m, 8H), 0.88 (q, 6H).

Poly(PDMSmMA) ^1H NMR (400 MHz, Chloroform- d) δ 3.88 (s, 2H), 1.88 (s, 2H), 1.46 – 1.20 (m, 6H), 0.95 – 0.73 (m, 6H), 0.52 (d, 4H), 0.30 – -0.37 (m, 100H).

Poly(GCA) ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 5.02 (s, 1H), 4.59 (t, 1H), 4.43 – 4.02 (m, 3H), 2.33 (s, 1H), 2.02 – 1.39 (m, 2H).

Poly(DTTA) ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 4.35 (s, 1H), 4.13 (s, 2H), 3.62 (s, 2H), 3.35 (s, 1H), 3.12 (s, 3H), 2.27 (s, 3H), 1.62 (s, 2H).

Poly(MSEA) ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 4.37 (s, 2H), 3.49 (s, 2H), 3.04 (s, 3H), 2.32 (s, 1H), 1.64 (s, 2H).



Scheme 4.2 Synthesis of copolymers SICPEs by RAFT polymerization.

4.2.5 General procedure for RAFT synthesizing SICPEs

In a typical one pot synthesis, 26 mg RAFT-CTA (0.11 mmol), 1.2 g PEGMEMA (2.4 mmol) and 3.6 mg AIBN (0.02 mmol) were dried under vacuum before transferring to glovebox (Scheme 4.2). The THF solution containing 772 mg STFLi (2.4 mmol) was added into the round bottom flask containing the above chemicals, followed by addition of another 10mL of dry THF. After purged with Argon for 1 hr at room temperature, the flask was sealed and the reaction was

performed at 65°C with magnetic stirring for 24 h. The product was purified by dialysis against THF, and was dried under vacuum at 110°C for two days before the characterizations.

4.2.6 Instrumentations

¹H Nuclear magnetic resonance (¹H NMR) measurements were performed on a Bruker Advance III 400 MHz NMR Spectrometer with d-Chloroform, d-THF or d-DMSO as solvents. Fourier transform infrared spectroscopy (FT-IR) was measured on a Nicolet iS50 FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The spectra were obtained with 64 scans and averaged with signals.

The thermal stability of samples was measured by thermogravimetric analysis (TGA) on TA instrument TGA Q-50 under N₂ with a heating rate of 20°C/min from room temperature to 800°C. Differential scanning calorimetry (DSC) measurements were performed under Ar atmosphere using a TA instrument DSC 2500. The samples were placed into aluminum hermetic pans, dried in the vacuum oven at 100 °C overnight and sealed before the test. The samples were equilibrated at 120 °C for 30 min to remove the thermal history. The cooling and heating cycles were performed with a rate of 3 °C /min in the range of -90 °C to 250 °C (from -140°C to 200 °C for poly(PDMS-*m*MA₁₇/ STFLi₂₃)). T_g was estimated as the midpoint of the transition process in the final heating cycle.

Small angle X-ray scattering (SAXS) measurements were performed on an Anton Paar SAXSess mc2 at the Center for Nanophase Materials Sciences (CNMS) of the Oak Ridge National Laboratory. The SAXS images were collected with a CCD detector (PI-SCX, Roper) at a pixel

resolution of 2084×2084 and pixel dimensions of $24 \times 24 \mu\text{m}^2$. For the measurements, X-rays were generated at 40 kV/50 mA at a beam wavelength of $\lambda = 1.541 \text{ \AA}$ (Cu K α radiation).

Small-amplitude oscillatory shear (SAOS) measurements were performed on an AR2000ex rheometer. The experiments were performed between two 4 mm parallel steel plates. The temperature was controlled by a system using nitrogen as the gas source. All the samples were loaded between the plates, equilibrated at 60 °C for 30 mins before the measurement, and measured at different temperatures with the angular frequency sweep from 100 to 0.1 rad/s.

Broadband Dielectric Spectroscopy (BDS) was performed in the frequency range of $10^{-1} \sim 10^{-6}$ Hz by using a Novocontrol Concept 80 system. The samples were sandwiched between two gold plated electrodes separated by a Teflon spacer. All the samples were dried in the vacuum oven at 120 °C overnight prior the measurement. During the measurements, samples were equilibrated at 120 °C (170 °C for poly(GCA_x/ STFLi_y), poly(DTTA₂₀/ STFLi₂₀), poly(MSEA₁₉/ STFLi₂₁) and poly(PDMSmMA₁₇/ STFLi₂₃)) for 30 min, then cooled down to -60 °C and went back to the same high temperature under N₂. The repeatable data at high temperature for both cycles suggests the absence of solvent or no degradation happened. Each temperature was equilibrated for 10 min before the measurements.

4.3 Results

4.3.1 Synthesis and physical property of neutral units and SICPEs

With highly delocalized anion center, the lithium 4-styrenesulfonyl(trifluoromethanesulfonyl)imide (STFLi) based polymers are among the mostly studied SICPEs due to the reduced electrostatic interaction and hence improved ionic conductivity.^{74, 110} To evaluate the

influence of neutral units on the physical property of SICPEs, totally six neutral units have been copolymerized with STFLi to form copolymer-type SICPEs *via* one-pot reversible addition-fragmentation chain-transfer (RAFT) polymerization (Scheme 4.2). Including PEO-based monomer, i.e., poly(ethylene glycol) methyl ether methacrylate (PEGMEMA), all of the neutral units were categorized by their structural flexibility and polarity, or the T_g and dielectric constant of their homopolymer.

Due to the low T_g of polyolefin and polydimethylsiloxane, 2-ethylhexyl acrylate (EHA) and monomethacryloxypropyl terminated polydimethylsiloxane (PDMSmMA) were initially introduced to the SICPE system. In the ^1H NMR spectra, the absence of proton signals between 5.5-6.5 ppm related to the alkene group demonstrates the complete removal of monomers in the synthesized SICPEs (Figure 4.1). Different feature peaks were selected to estimate the mole ratios of STFLi over neutral units in the resulting copolymer. The four protons in the benzyl ring of STFLi show peaks between 7.0-8.0 ppm, whereas the $-\text{CH}_3$ at the chain end of PEGMEMA reveals a peak at 3.3 ppm. Due to the high contents of alkyl group in the chemical structure of EHA and PDMSmMA, there are multiple peaks lying between 2.0-0.5 ppm. Attributed to the different reactivity of STFLi over neutral units, the integrated values are slightly different from the feed ratio. In FT-IR spectra, the relatively high contents of alkyl group also results in multiple peaks within $2850\text{-}3000\text{ cm}^{-1}$ from C-H bond stretching for poly($\text{EHA}_x/\text{STFLi}_y$), while the significant peak at 1260 cm^{-1} corresponds to the Si- CH_3 bond in poly($\text{PDMSmMA}_{17}/\text{STFLi}_{23}$) (Figure 4.2(a)).¹⁶⁰

The monomers with high dielectric constant group were synthesized by the reaction between acryloyl chloride and hydroxyl terminated reagents (Scheme 4.1). In ^1H NMR spectra, the

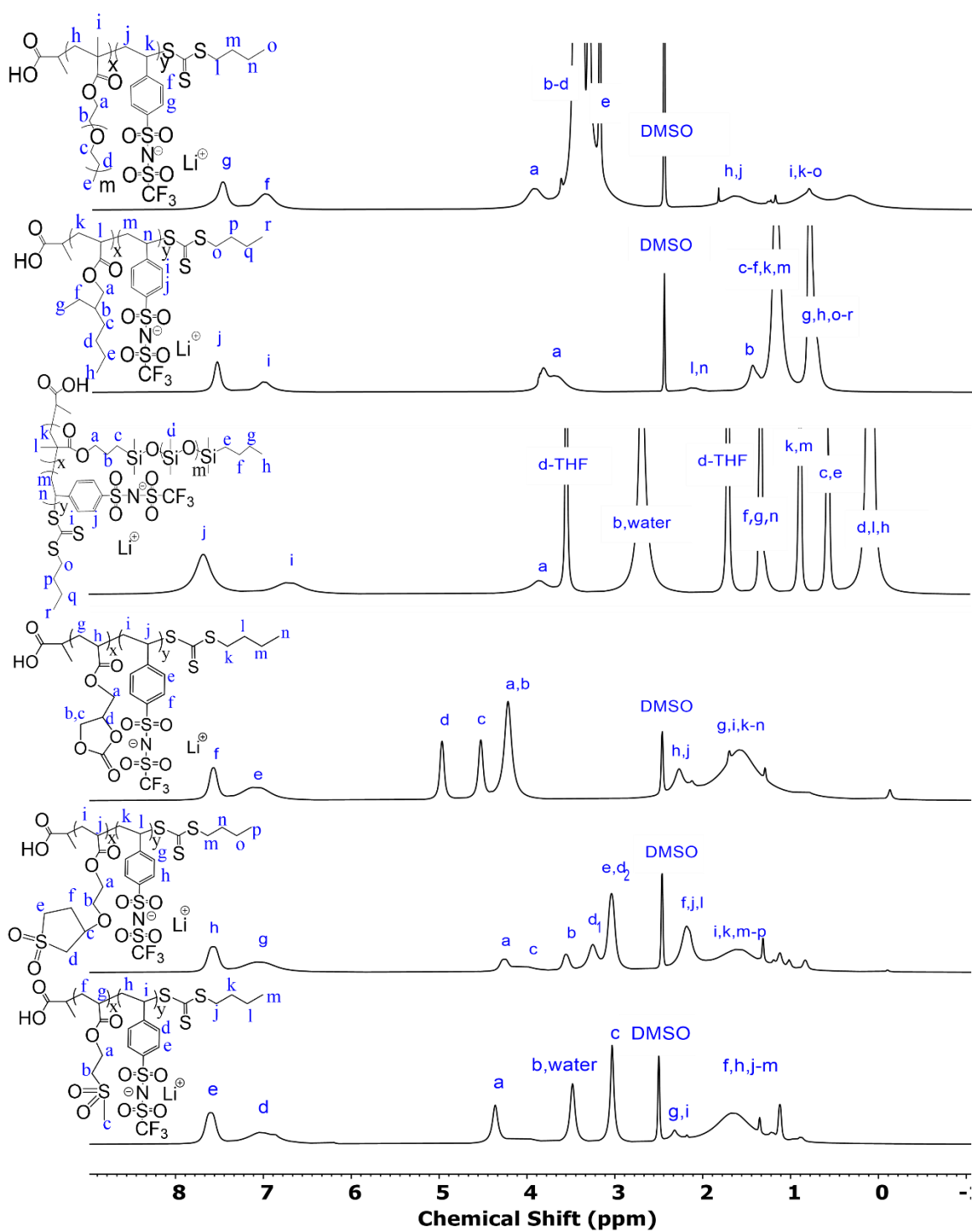


Figure 4.1 ^1H NMR spectra of poly(PEGMEMA₂₀/STFLi₂₀), poly(EHA₂₈/STFLi₁₂), poly(PDMSmMA₁₇/STFLi₂₃), poly(GCA₁₉/STFLi₂₁), poly (DTTA₂₀/STFLi₂₀) and poly(MSEA₂₁/STFLi₁₉).

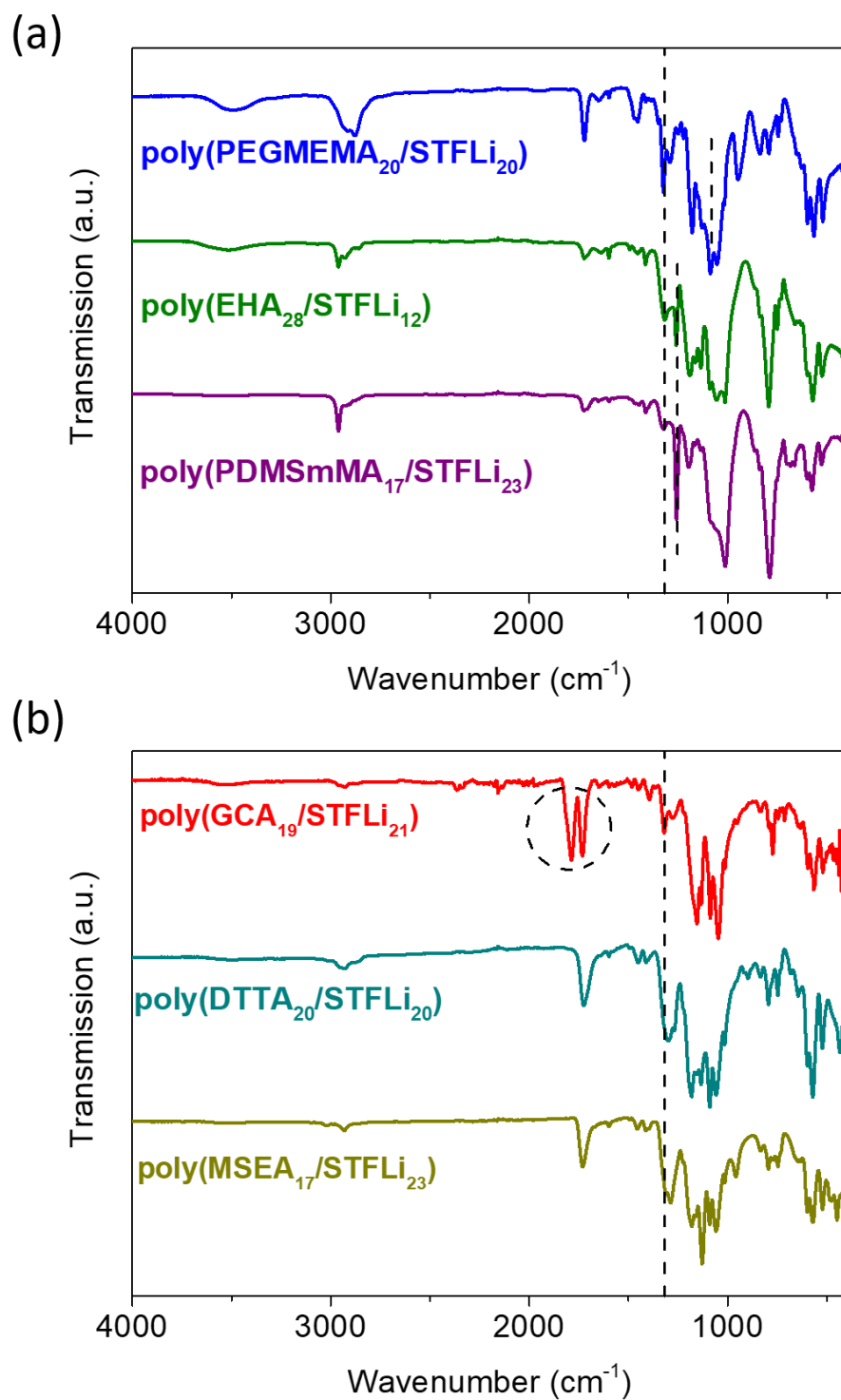


Figure 4.2 FT-IR spectra of selected SICPEs.

integrals of peaks around 4.3 ppm ($-OCH_2-$ from the ester group) being twice as that of peaks at 6.0 ppm ($CH_2=CH-$ connected to the other side of ester group) demonstrates the successful synthesis of glycerin carbonate acrylate (GCA) monomers. The chemical structure of 2-[(1,1-Dioxidotetrahydro-3-thienyl)oxy]ethanol acrylate (DTTA) and 3-(Methylsulfonyl)-1-ethanol acrylate (MSEA) were also verified by the same method, though they show slightly different chemical shift for these characteristic peaks. The integrals of the aforementioned peaks over the featured peaks related to STFLi are also used to estimate the actual ratio of neutral units over STFLi, which fits well with feed mole ratio. In the IR spectra of $\text{poly}(GCA_x/STFLi_y)$, the cyclic carbonate structure shows an extra peak at 1790 cm^{-1} aside from the strong peak around 1730 cm^{-1} from ester structure.^{187, 188} With comparable mole ratio of STFLi, both $\text{poly}(DTTA_{20}/STFLi_{20})$ and $\text{poly}(MSEA_{21}/STFLi_{19})$ exhibit much stronger peak at 1320 cm^{-1} comparing with $\text{poly}(GCA_{10}/STFLi_{21})$ due to the presence of S=O unit in DTTA and MSEA (Figure 4.2(b)).^{189, 190}

4.3.2 Analysis of BDS spectra

The dielectric property for SICPEs and homopolymers, such as permittivity and ionic conductivity, was evaluated by Broadband Dielectric Spectroscopy (BDS). Dc conductivity was simply taken from the plateau value of the spectra.^{191, 192} For polymer electrolytes, the temperature dependence of conductivity will usually cross over from an Arrhenius behavior at temperature below T_g to a VFT-like behavior above T_g . The activation energy for conductivity related to the energy barrier for ion hopping in frozen (glassy) state can be estimated by fitting the conductivity value below the T_g with Arrhenius equation. For many polymers, ionic conductivity is coupled to segmental relaxation. In this case, the conductivity at T_g should be around $\sim 10^{-14} - 10^{-15}\text{ S/cm}$.²¹ On the other hand, a decoupled behavior is also observed in many

systems, where the ionic conductivity is faster than segmental relaxation.^{29, 30} In most of these cases, they have relatively rigid structures with frustrated segments packing and larger free volume for ions diffusion.^{28, 193}

In conductive materials, the static dielectric constant before electrode polarization is obscured because of the overlapped conductivity relaxation. Therefore, to exclude the influence of ionic conductivity on spectra analysis, the real part of permittivity spectra for all homopolymers were independently fitted by the Havriliak–Negami (HN) function:

$$\varepsilon^* = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{[1+(i\omega\tau_{HN})^{\alpha}]^{\beta}} \quad (4.1)$$

where $\Delta\varepsilon$ is the amplitude of the dielectric relaxation process, τ_{HN} is the characteristic relaxation time, α and β are the shape parameters. The static dielectric constant ε_s is estimated from the low frequency plateau before electrode polarization.

4.4 Discussion

4.4.1 Influence of flexible structure, or low T_g , in accelerating segmental dynamics

With relatively rigid structure and decent lithium-ion concentration, the homopolymer poly(STFLi) exhibits a very high T_g value (~ 168 °C) and low ionic conductivity at ambient temperature ($< 10^{-14}$ S/cm) in Table 4.1 and 4.2. One major strategy to improve the ionic conductivity of single-ion conducting polymer electrolytes (SICPEs) is forming the copolymer with neutral units, in which PEO structure is the benchmark. Therefore, poly(PEGMEMA_x/STFLi_y) was synthesized as a reference. With the incorporation of PEGMEMA, poly(PEGMEMA_x/STFLi_y) has a dramatically decreased T_g depending on the mole ratio of PEGMEMA over STFLi. For

Table 4.1 Summary of the physical properties for SICPEs, including glass transition temperature T_g estimated from three different techniques, decomposition temperature T_d , conductivity σ at $T=30^\circ\text{C}$ and T_g , and activation energy for conductivity below T_g , i.e., E_σ .

	T_g ($^\circ\text{C}$)			$T_{d,5wt\%}$ ($^\circ\text{C}$) ^a	σ (S/cm)		E_σ (kJ/mol) ^b
	DSC	Rheology	BDS		30 $^\circ\text{C}$	T_g	
poly(STFLi)	168.2	-	163.1		$<10^{-14}$	1×10^{-10}	155.0
poly (PEGMEMA ₂₀ / STFLi ₂₀)	-5.6	-8.0	-11.6	345.2	4.7×10^{-9}	1.6×10^{-14}	128.5
poly (PEGMEMA ₂₅ / STFLi ₁₅)	-23.5	-29.6	-31.7	347.2	1.2×10^{-7}	1.1×10^{-14}	111.6
poly (EHA ₂₈ / STFLi ₁₂)	57.3	63.5	55.9	329.7	$<10^{-14}$	1.7×10^{-14}	122.3
poly (EHA ₃₄ / STFLi ₆)	7.2	10.1	3.9	314.9	1.6×10^{-12}	1.2×10^{-14}	116.4
poly (PDMSmMA ₁₇ / STFLi ₂₃)	-125.7/ 131.3	-	140.8	259.6	$<10^{-14}$	3.5×10^{-12}	85.1
poly (GCA ₁₉ / STFLi ₂₁)	137.7	-	134.6	283.8	$<10^{-14}$	1.0×10^{-11}	146.2

Table 4.1 continued.

	T _g (°C)			T _{d,5wt%} (°C) ^a	σ (S/cm)		E _σ (kJ/mol) ^b
	DSC	Rheology	BDS		30 °C	T _g	
poly (GCA ₂₅ / STFLi ₁₅)	106.4	-	103.7	274.8	<10 ⁻¹⁴	1.0×10 ⁻¹²	152.3
poly (GCA ₃₀ / STFLi ₁₀)	79.4	-	84.0	279.6	<10 ⁻¹⁴	1.2×10 ⁻¹²	151.5
poly(DTTA ₂₀ /STFLi ₂₀)	113.7	-	110.0	291.7	<10 ⁻¹⁴	1.0×10 ⁻¹¹	138.3
poly(MSEA ₂₁ /STFLi ₁₉)	90.3	-	85.3	280	<10 ⁻¹⁴	1.5×10 ⁻¹¹	142.3

a. The temperature when the weight loss of samples is 5%.

b. The activation energy of conductivity for coupled systems, poly (PEGMEMA_x/ STFLi_y) and poly (EHA_x/ STFLi_y), is calculated from the extrapolated conductivity value by time-temperature-superposition (TTS)

Table 4.2 Fitting parameters of VFT equation and Arrhenius equation of SICPEs

	VFT ($T > T_g$)			Arrhenius ($T < T_g$)	
	B (K)	T_0 (K)	σ_0 (S/cm)	E_a (kJ/mol)	σ_0 (S/cm)
poly(STFLi)	-3153	266.9	0.012	155.0	3.5×10^7
poly (PEGMEMA ₂₀ / STFLi ₂₀)	-1560	207.0	0.063	128.5	7.0×10^{11}
poly (PEGMEMA ₂₅ / STFLi ₁₅)	-1358	194.0	0.029	111.6	1.5×10^{10}
poly (EHA ₂₈ / STFLi ₁₂)	-5670	165.8	16	122.3	8.4×10^8
poly (EHA ₃₄ / STFLi ₆)	-3550	154.2	0.037	116.4	8.0×10^8
poly (PDMSmMA ₁₇ / STFLi ₂₃)	-2600	260.3	1.2×10^{-4}	85.1	60
poly (GCA ₁₉ / STFLi ₂₁)	-13633	135.8	5.4×10^{10}	146.2	1.3×10^8
poly (GCA ₂₅ / STFLi ₁₅)	-3501	262.6	26	152.3	4.7×10^{10}
poly (GCA ₃₀ / STFLi ₁₀)	-1746	287.8	0.093	151.5	2.2×10^{10}
poly(DTTA ₂₀ /STFLi ₂₀)	-8575	160.8	5.1×10^5	138.3	1.7×10^8
poly(MSEA ₂₁ /STFLi ₁₉)	-2351	255.8	0.11	142.3	6.6×10^9

example, the T_g of poly(PEGMEMA₂₀/STFLi₂₀) is 170 °C lower than that of homopolymer poly(STFLi) (-5.6 °C vs. 168 °C), while the T_g of poly(PEGMEMA₂₅/STFLi₁₅) was further decreased to -37 °C as shown in Table 4.1. Lower T_g always corresponds to faster segmental dynamics at ambient temperature. Since the motion of lithium-ions can be strongly coupled to the segmental dynamics of poly(PEGMEMA_x/STFLi_y), its ionic conductivity improves significantly in comparison with homopolymer poly(STFLi). The conductivity of poly(PEGMEMA₂₀/STFLi₂₀) has more than five-order of magnitude improvement at 30 °C (4.7×10^{-9} S/cm), while the conductivity of poly(PEGMEMA₂₅/STFLi₁₅) was increased by another order of magnitude at the same temperature (1.2×10^{-7} S/cm). To surpass the limitation of PEO-based SICPEs and explore other potential neutral units, we need to provide an insight on the unique role of PEO units, in which flexible structure or low T_g is an important parameter. Based on the above results, we may assume that copolymerization with monomers having even lower- T_g than PEO may further accelerate segmental dynamics and improve ionic conductivity of SICPEs.

Similar to PEGMEMA, EHA and PDMSmMA also have flexible chemical structure and even lower T_g for their homopolymers (-66.7 °C for poly(PEGMEMA) vs. -72.5 °C for poly(EHA) and -121.7 °C for poly(PDMSmMA). Therefore, a decrease in T_g was expected for their respective copolymers with STFLi. However, both poly(EHA_x/STFLi_y) and poly(PDMSmMA₁₇/STFLi₂₃) show much higher T_g values compared to poly(PEGMEMA_x/STFLi_y). For example, the T_g of poly(EHA₂₈/STFLi₁₂) is 50 °C higher than that of poly(PEGMEMA₂₀/STFLi₂₀) (14 °C vs. -37 °C, see Figure 4.3(b)), even though they have comparable weight ratio of charged units to neutral units (STFLi to PEGMEMA or EHA). For poly(PDMSmMA₁₇/STFLi₂₃), there are even two T_g s along with a broad transition process observed from the DSC curve, i.e., one is related to the PDMSmMA segment (~ -127 °C)

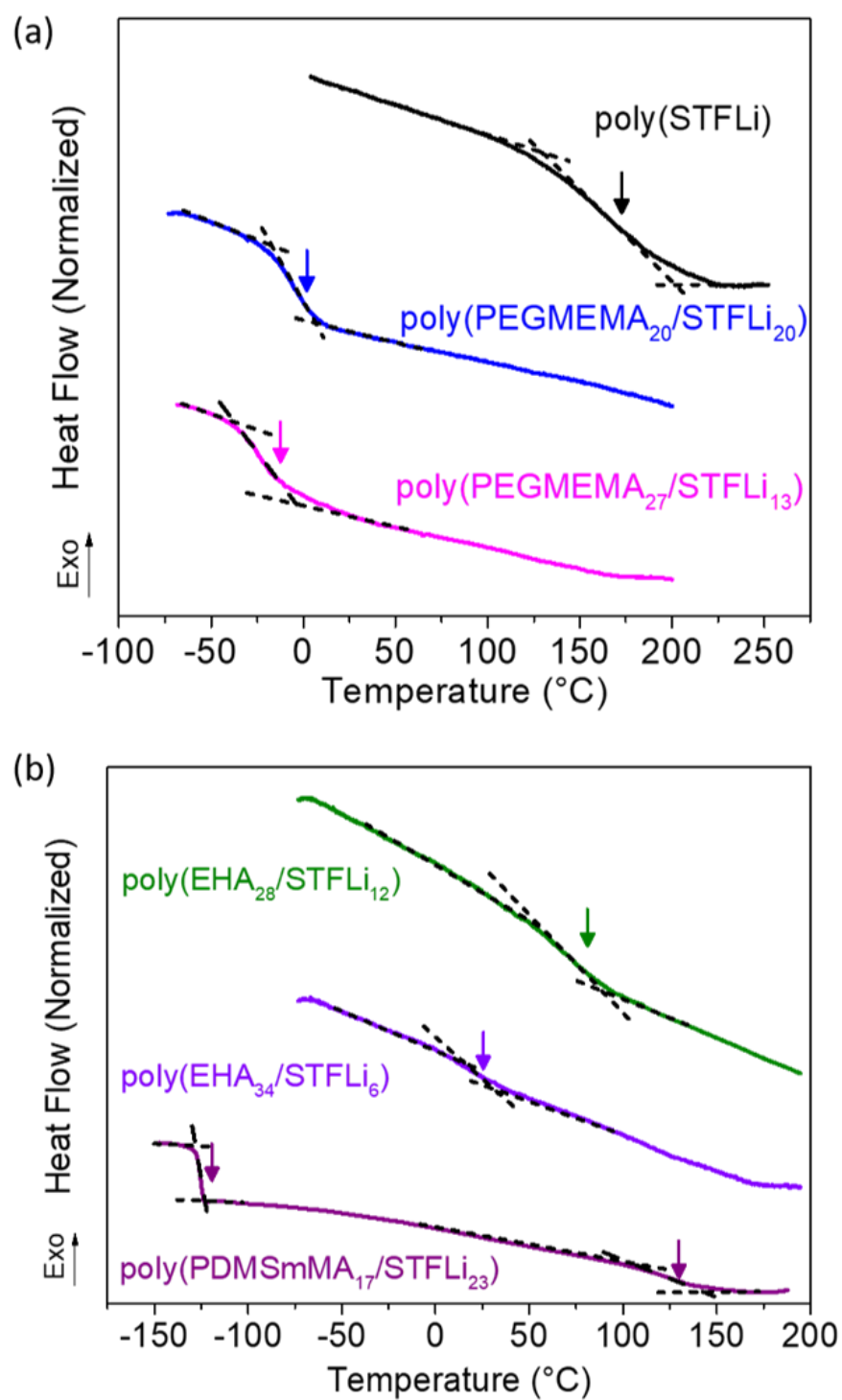


Figure 4.3 DSC spectra of (a) poly(STFLi) and poly(PEGMEMA_x/STFLi_y), (b) poly(EHA_x/STFLi_y) and poly(PDMSmMA₁₇/STFLi₂₃).

Table 4.3 Binding Energy of complex between Li^+ , STF^- and each neutral units.

	$E_{\text{PEGMEMA}+\text{STF}+\text{Li}}$	$E_{\text{GCA}+\text{STF}+\text{Li}}$	$E_{\text{EHA}+\text{STF}+\text{Li}}$	$E_{\text{PDMS}+\text{STF}+\text{Li}}$
Binding Energy	-0.47063 ev	-0.27012 ev	-0.22373 ev	3.038214 ev

and the other one is 131 °C, perhaps from the partially mixed phase with PDMSmMA and STFLi. This deviation can be explained by different polarities of neutral units that results in different miscibility with charged units.^{79, 194-196}

Compared with PEGMEMA, the more hydrophobic nature of EHA reduces its affinity with STFLi. This was also confirmed by the computational results with density functional theory (DFT) method, which indicates that EHA+STFLi has less negative binding energy value ($E_{\text{binding}} = -0.47$ eV for PEGMEMA+STFLi vs. $E_{\text{binding}} = -0.22$ eV for EHA+STFLi in Table 4.3). As a result, EHA has lower miscibility with STFLi, and will be less efficient in decreasing the T_g .¹⁹⁷ Moreover, while poly(PEGMEMA_x/STFLi_y) has no obvious peaks in the small angle X-ray scattering (SAXS) data, there is a clear peak in SAXS spectra of poly(EHA₃₄/STFLi₆) in Figure 4.4. It corresponds to a microphase separation with characteristic length about 5nm. When the weight ratio of EHA is high, the presence of potential second phase confirms the poor miscibility between EHA and STFLi as well. For PDMSmMA segments, they are even more hydrophobic than EHA. The calculated binding energy between STFLi and PDMSmMA even shows a positive value, i.e., $E_{\text{binding}} = 3.03$ eV. This means that the PDMSmMA possess repulsive force with hydrophilic STFLi and phase separates. This significant micro-phase separation is demonstrated by the SAXS data with a broad peak at 0.18 nm^{-1} , which corresponds to a characteristic length $\sim 35\text{nm}$ (Figure 4.4).

The poor miscibility between EHA and STFLi also caused sluggish segmental dynamics and lower ionic conductivity at ambient temperature (Figure 4.5 and 4.6). For example, with comparable weight ratio of neutral units over STFLi, the conductivity of poly(EHA₃₄/STFLi₆) at room temperature is five-order of magnitude lower than that of poly(PEGMEMA₂₅/STFLi₁₅) (1.6×10^{-12}

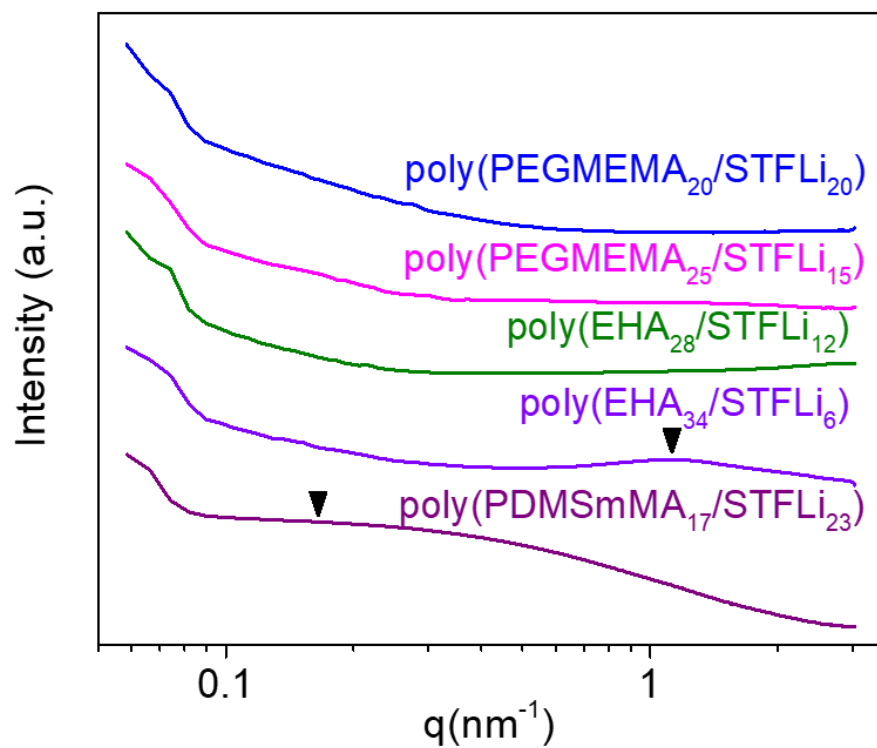


Figure 4.4 SAXS profiles of SICPEs.

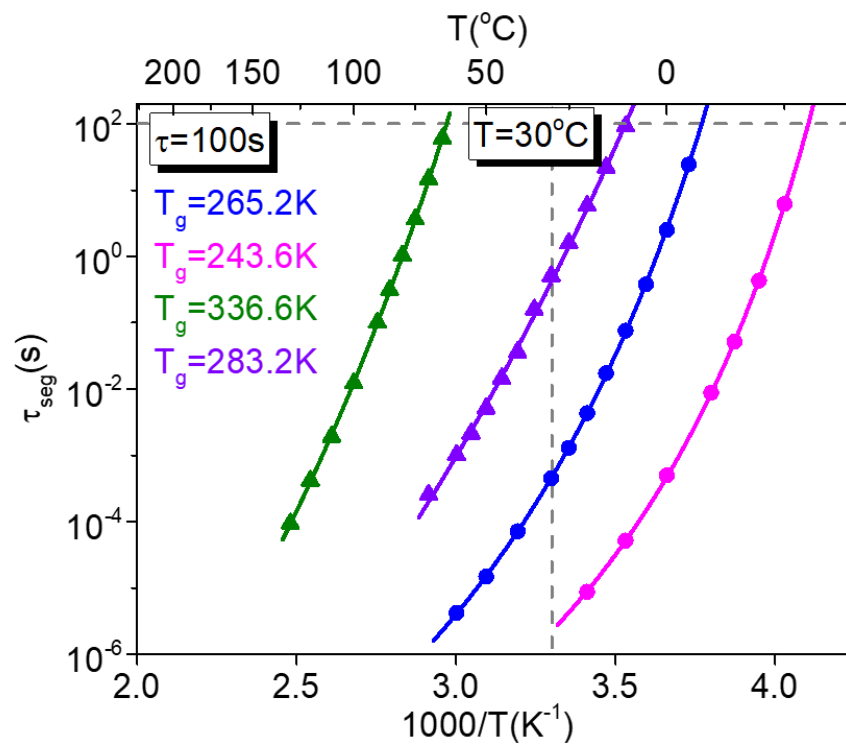


Figure 4.5 Segmental relaxation time (τ_{seg}) and the estimated T_g . The data points of τ_{seg} were fitted by VFT equation above T_g (solid lines).

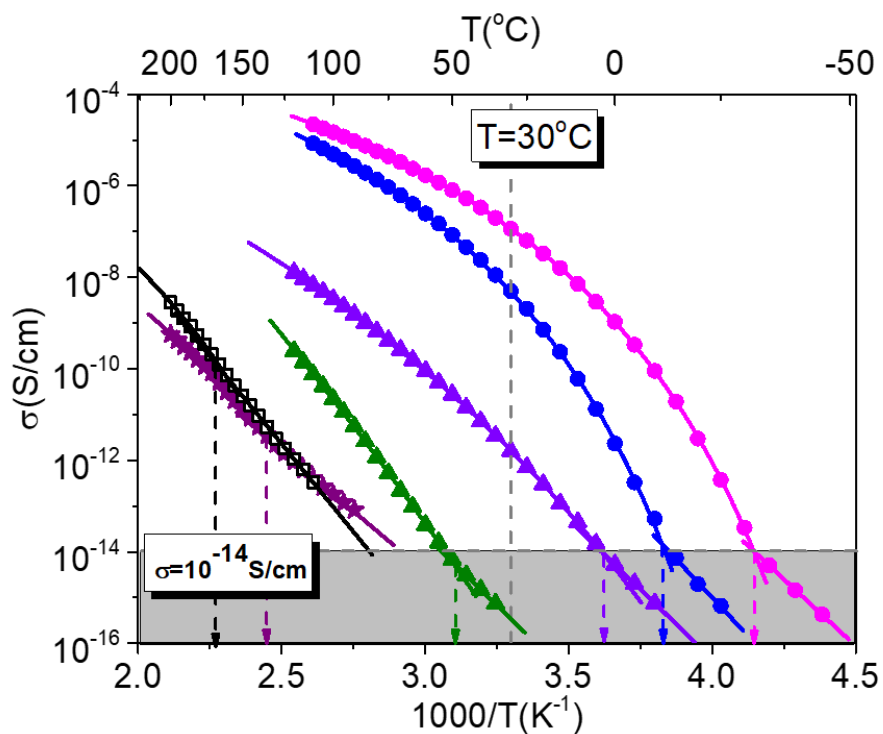


Figure 4.6 The dc conductivity vs. $1000/T$ graphs. The conductivity were fitted by VFT equation above T_g and Arrhenius equation below T_g (solid lines). The data points at room temperature are marked with dashed lines. The list of symbols: poly(STFLi) (black empty square), poly(PEGMEMA₂₀/STFLi₂₀), (blue solid circle), poly(PEGMEMA₂₅/STFLi₁₅), (magenta solid circle), poly(EHA₂₈/STFLi₁₂) (olive solid triangle), poly(EHA₃₄/STFLi₆) (violet solid triangle) and poly(PDMSmMA₁₇/STFLi₂₃). (purple solid star).

S/cm vs. 1.2×10^{-7} S/cm as shown in Figure 4.6). For poly(PDMSmMA₁₇/STFLi₂₃), no reliable rheology data was obtained as it is not at a homogeneous state. In addition, it is worth noticing that the conductivity of poly(PDMSmMA₁₇/STFLi₂₃) is even lower than that of the homopolymer poly(STFLi), while it still presents a weak decoupling effect (3.5×10^{-12} S/cm at the T_g corresponding to STFLi phase 131 °C). Earlier studies reported the improved conductivity of SICPEs having PDMS backbone.^{112, 198, 199} Apparently, using PDMS as a side chain leads to the phase separation, decrease fraction of conducting polymer and results in no improvement in conductivity. Since PDMSmMA has poor solvation of lithium-ion, the ion transport is mainly confined within STFLi domain. More specifically, different from PDMS backbone that can efficiently accelerate segmental dynamics of ionic conducting units, the PDMS sidechains would just phase separate from ionic conducting domains, leading to more tortured channels for lithium-ion transport.²⁰⁰⁻²⁰² The presented results clearly demonstrate that the neutral units with flexible structure but weak capability to solvate lithium-ions could not efficiently improve the polymer dynamics in ionic conducting domains and hence render low ionic conductivity.

4.4.2 Effect of polar structure for lithium-ion dissociation

To improve Li⁺ dissociations of the SICPEs, the neutral units with polar structure, i.e., high constant, the small molecules containing cyclic carbonate or sulfonyl groups have been widely used as plasticizers in lithium-based batteries. Their dielectric constants are much higher than PEO structure (~ 7) at ambient temperature, e.g., $\epsilon_s=112$ for glycerin carbonate, $\epsilon_s=44$ for sulfolane and $\epsilon_s=95$ for ethylmethyl sulfone.^{151, 203-207} In addition, the improved ionic conductivity of SICPEs with PDMS as backbone versus reduced conductivity for those with PDMS as sidechains also suggests the important role of location of functional units in the

dynamic.¹⁹⁸ Therefore, the monomer bearing high dielectric constant group at the side chain end were synthesized and copolymerized with STFLi to verify the assumption.

To exclude the influence of conductivity, the dielectric constant of homopolymer poly(GCA), poly(DTTA) and poly(MSEA) were estimated from the permittivity spectra in the accessible temperature range. The real part of permittivity spectrum for poly(PEGMEMA) is presented in Figure 4.7(a) as an example. All these homopolymers have ϵ_s above 10, significantly higher than those of PEGMEMA ($\epsilon_s \sim 5$), nonpolar EHA and PDMSmMA ($\epsilon_s < 3$ for both of them) in Figure 4.7(b).^{124, 208, 209} As the macroscopic dielectric constant is indeed higher for neutral units with polar groups, they were further randomly copolymerized with STFLi to form SICPEs. The T_g of all these SICPEs are above room temperature, which suggests their relatively rigid structure. In addition to a single high T_g in the DSC (Figure 4.8), the absence of characteristic peaks in the SAXS spectra confirms good miscibility between these polar units and ionic conducting unit STFLi (Figure 4.9). With high dielectric constant and good miscibility, it is expected to improve lithium-ions dissociation and the ionic conductivity of SICPEs after inserting GCA, DTTA and MSEA groups into the polymer structure.

However, the conductivities of the SICPEs with comparable mole ratio of polar units to STFLi, i.e., poly(GCA₁₉/STFLi₂₁), poly(DTTA₂₀/STFLi₂₀) and poly(MSEA₂₁/STFLi₁₉), appear below the measurable range at ambient temperature, while they present similar ionic conductivity ($\sim 10^{-11}$ S/cm) at their respective T_g (Figure 4.10(a) and 4.11(b)). Actually, the ionic conductivity of the SICPEs with polar group is still suppressed by their high T_g . For example, increasing the ratio of GCA to STFLi units by three times, the T_g of poly(GCA_x/STFLi_y) is decreased by about 60°C and the ionic conductivity at 100 °C is increased by almost three orders of magnitudes (1.2×10^{-10}

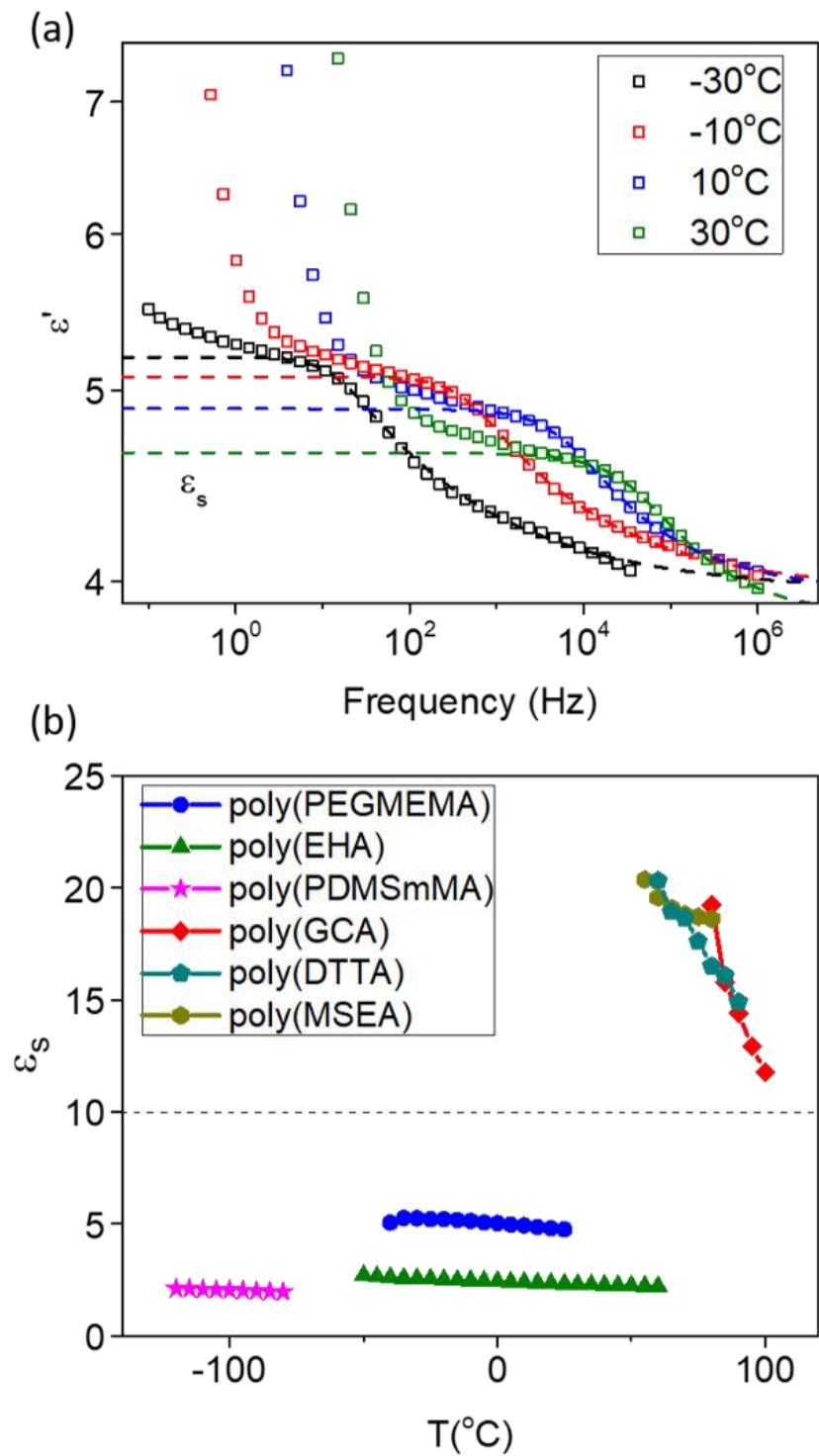


Figure 4.7 (a) Real part of permittivity spectrum for poly(PEGMEMA). The permittivity spectra are fitted by HN function (dashed-line). (b) The static dielectric constant for all homopolymers.

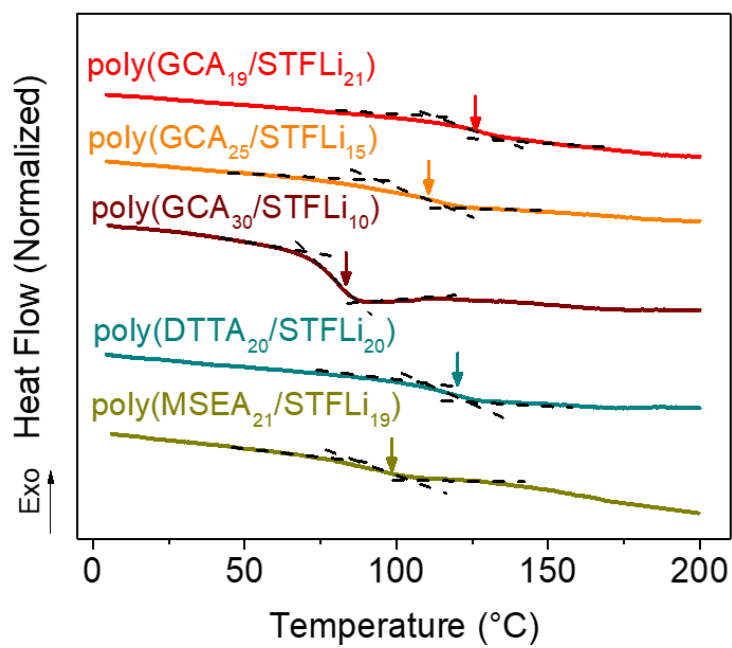


Figure 4.8 DSC spectra of poly(GCA_x/STFLi_y), poly(DTTA₂₀/STFLi₂₀) and poly(MSEA₂₁/STFLi₁₉).

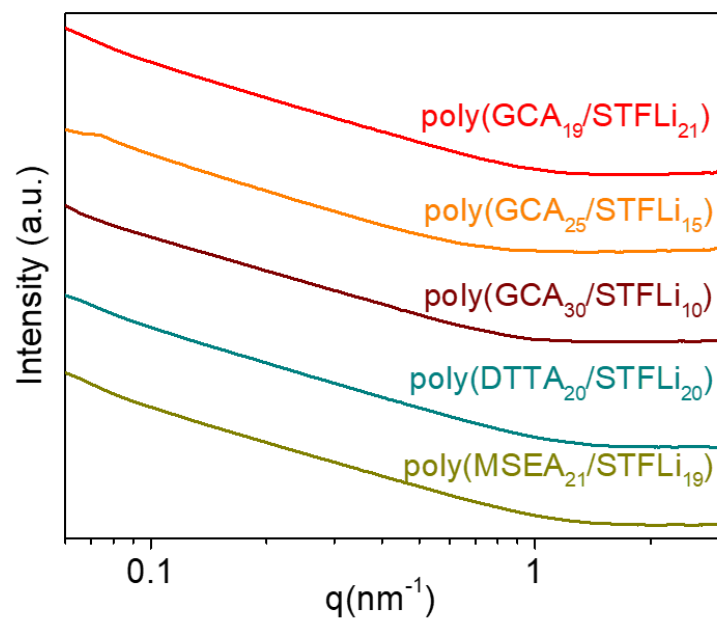


Figure 4.9 SAXS spectra of SICPEs with polar units.

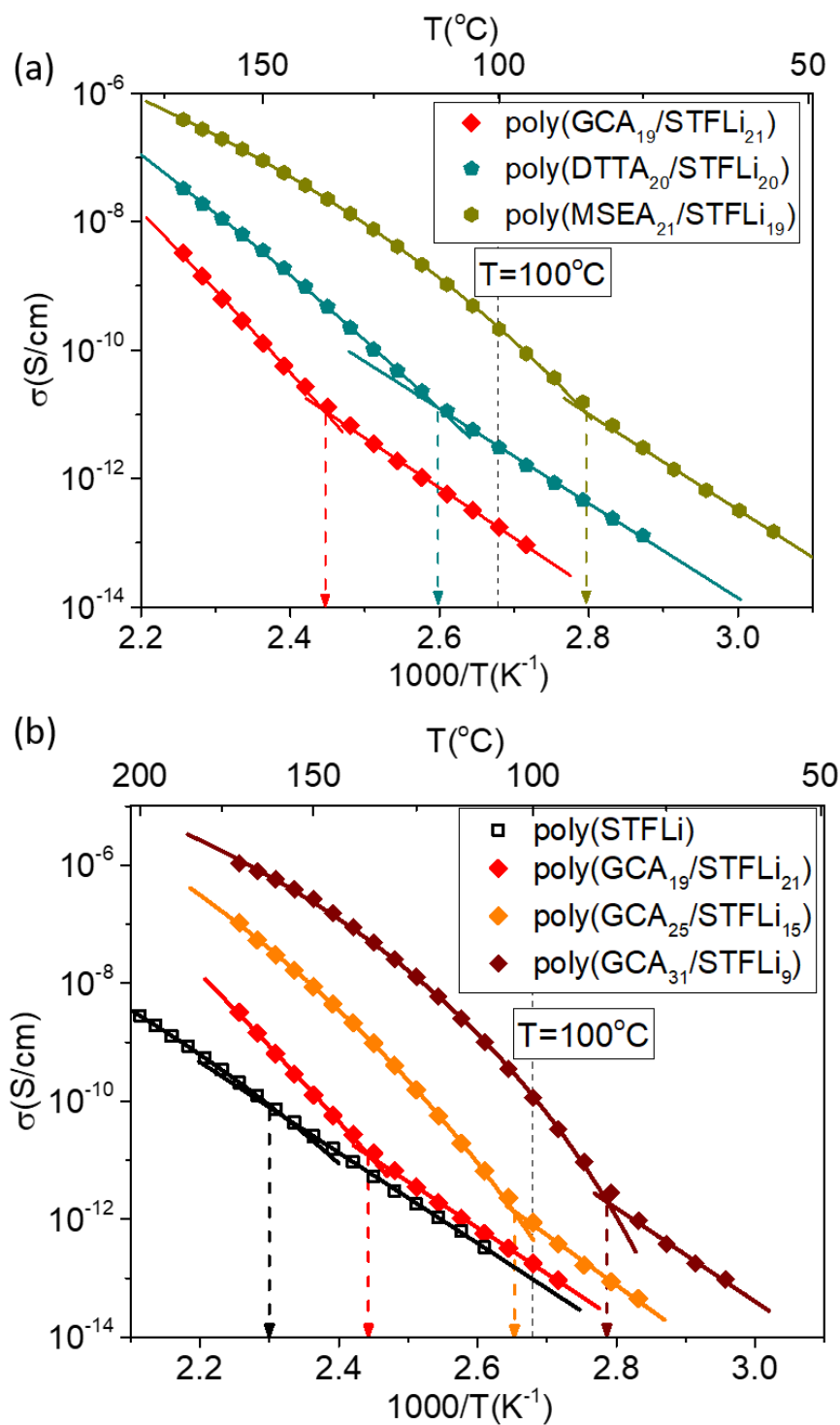


Figure 4.10 The dc conductivity vs. $1000/T$ for (a) $\text{poly}(\text{DTTA}_{20}/\text{STFLi}_{20})$ and $\text{poly}(\text{MSEA}_{21}/\text{STFLi}_{19})$, (b) $\text{poly}(\text{STFLi})$ and $\text{poly}(\text{GCA}_x/\text{STFLi}_y)$.

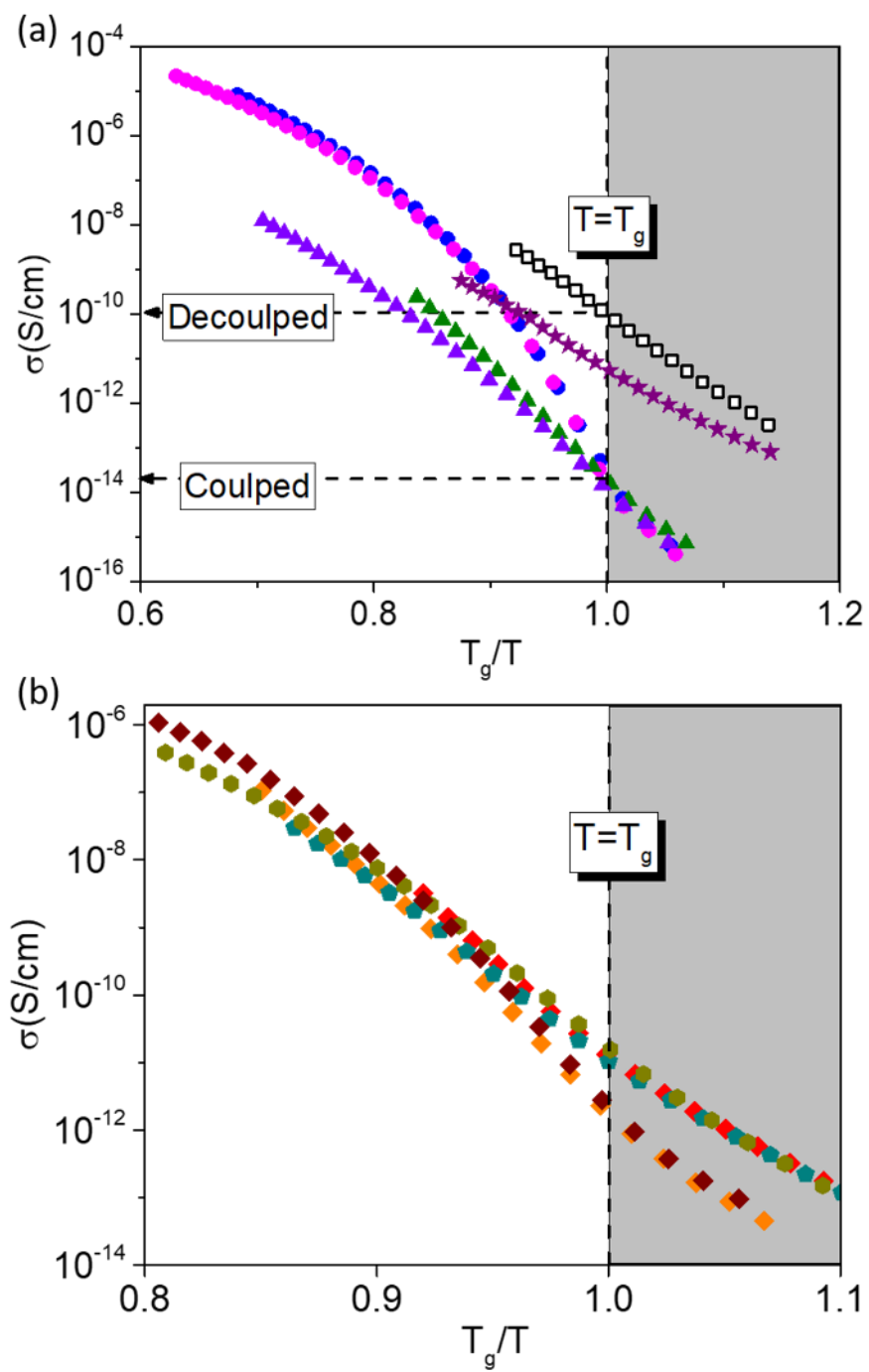


Figure 4.11 Conductivity vs. T_g/T for all SICPEs.

S/cm for poly(GCA₃₀/STFLi₁₀) vs. 1.7×10^{-13} S/cm for poly(GCA₁₉/STFLi₂₁) in Figure 4.10(b)). While PEGMEMA has continuous coordination sites along the sidechains, these polar units mainly coordinate with lithium-ions at a single site, i.e., carboxyl group in GCA and sulfonyl group in DTTA and MSEA.²¹⁰⁻²¹³ This may result in reduced ion solvation in comparison to poly(PEGMEMAx/STFLiy), which is also supported by the theoretical computation results. For example, the binding energy of GCA monomer with STFLi is only about half of the value compared to the binding energy between PEGMEMA and STFLi (-0.27eV for GCA+STFLi vs. -0.47eV for PEGMEMA in Table 4.3), which suggests lower miscibility of GCA with ionic phase. In conventional liquid electrolyte, ion-dipole interaction between solvent molecules and lithium ion far outweighs that between solvent molecules and anion. As a result, lithium-ion is commonly coordinated with several carbonate solvent molecules and form stable “solvated shell structure”. This leads to screening of anion-cation interactions and efficient lithium-ion transport with vehicular mechanism.²¹⁴ In contrast, the lithium-ion motions within polymer electrolytes are mainly contributed by the intra-chain diffusion and codiffusion with polymer segments.^{21, 215} Although the polar units within GCA, DTTA and MSEA are localized at the end of side chain, the chemical attachment strongly restricts their mobility, and they cannot form a solvation shell. As a result, the attached polar groups cannot reduce cation-anion interactions as evidenced by still high T_g and high activation energy for conductivity below T_g (Figure 4.8 and Table 4.1). Subsequently, the polar units attached to the polymer chain could not easily insert between the anion and cation to efficiently reduce Coulombic interactions, while the flexible PEO side chains could easily wrap around small cations and provide efficient solvation. Therefore, simply increasing the macroscopic dielectric constant of a polymer does not help to

improve the ionic conductivity of SICPEs at ambient temperature. This conclusion is consistent with the recent results reported by Segalman and co-workers,²¹⁶ where similar ionic conductivity (when normalized by T_g) was observed for imidazole based polymer electrolytes with different backbone polarities. The polarity of backbone mainly contributes to the shift of T_g and has little influence on ion aggregation/solvation. These results reveal that the polarity of backbones or sidechains may not provide significant improvement of conductivity in SICPEs.

4.4.3 Analysis of activation energy

An interesting observation is that the activation energy below T_g is almost the same ($E_\sigma \sim 120$ -150 kJ/mol) for all the studied here SICPEs (Table 4.1), except poly(PDMSmMA₁₇/STFLi₂₃). The obtained value is comparable with E_a estimated for other known poly-anions with TFSI-Li structure, regardless whether TFSI was attached to styrene or methacrylate unit.^{28, 198} The activation energy for conductivity below T_g is related to the energy barrier for ion hopping in frozen (glassy) structure, and for small ions, e.g., Li^+ and Na^+ , depends mostly on the Coulombic interaction with polymerized counterion.^{21, 28} As a reference, the activation energy for homopolymer poly(STFLi) is ~ 155 kJ/mol, and copolymerization with units having different polarities provide minimal effect on E_σ . Thus, all these copolymers do not reduce significantly the strength of Coulombic interactions between TFSI-based polyanion and Li^+ , even including the copolymers with PEO, and this strongly limits ionic conductivity. As a result, as long as segmental dynamics is sluggish, the obtained ionic conductivity of SICPEs at ambient temperature will remain low. Only poly(PDMSmMA₁₇/STFLi₂₃) shows significantly reduced activation energy ($E_\sigma \sim 85$ kJ/mol). As PDMSmMA domain barely solvate lithium-ion, the T_g related to STFLi-rich domain (131°C) is used to estimate activation energy for

poly(PDMSmMA₁₇STFLi₂₃). This can be explained that the phase separated PDMS-based domain with much faster segmental dynamics maybe helpful to reduce the energy barrier, although they barely solvate ions. Apparently, this poor solvation of ions is the reason for lower conductivity of poly(PDMSmMA₁₇/STFLi₂₃) in comparison to the homopolymer.

Earlier estimates show that to reach required conductivity $\sim 10^{-3}$ S/cm at ambient temperature, the activation energy for conductivity should be ~ 20 -30kJ/mol.²¹ Our results reveal that attaching polar groups to SICPE structure does not reduce significantly the Coulombic interaction of Li⁺ with polymerized TFSI anion. Therefore, a promising direction might be designing polyanion with more delocalized charge, which can strongly reduce the Coulombic energy barrier for Li⁺ transport. This idea is supported by the recent report,¹¹⁴ where SICPE with a different polyanion, (fluorosulfonyl)imide (N⁽⁻⁾-SO₂-F, AFSI⁻) showed conductivity about 5×10^{-4} S/cm at ambient temperature with apparent activation energy ~ 21 kJ/mol for conductivity above T_g. Although conductivity below T_g was not included in the work, the relatively high conductivity at room temperature for the material with T_g = -30 °C and T_m=93°C highly suggests that ion transport is decoupled from the segmental dynamics. Therefore, the improved ionic conductivity demonstrated the favorable Li⁺ dissociation with AFSI anion structure.

4.5 Conclusion

To explore the potential structures that may surpass the ionic conductivity of PEO-based SICPEs, copolymers with different neutral units have been synthesized and comprehensively studied. The PEO-based monomer, PEGMEMA, can sufficiently solvate the Li⁺, lower the T_g, accelerate segmental dynamics and hence improve the ionic conductivity of copolymer-typed

SICPE. Utilization of other neutral units possessing flexible structure, with T_g even lower than PEO, still cannot efficiently decrease the T_g of copolymer-typed SICPEs, due to their limited miscibility with ionic groups. More specifically, compared to PEGMEMA, the poor miscibility of EHA and PDMSmMA with the ionic conducting unit STFLi renders weak capability to solvate lithium-ions, resulting in slow segmental dynamics and limited Li^+ transport. Moreover, copolymerizing STFLi with high dielectric constant moieties also results in low ionic conductivity at ambient temperature due to the high T_g and slow segmental dynamics of SICPEs. Together with previous reports by Segalman and coworkers,²¹⁶ these results suggest that designing SICPEs with high dielectric constant unit incorporated to the polymer most probably will not result in significantly improved ionic conductivity at ambient temperature.

An interesting discovery of our studies is that the activation energy for ionic conductivity below T_g is not strongly affected by various neutral units copolymerized with STFLi. Apparently, the Coulombic interactions between polymerized TFSI and Li^+ are not significantly affected by different neutral units in the copolymers, including PEO. Aside from focusing on exploring different sidechain or backbones that may reduce T_g , we should also devote efforts to other strategies, such as a design of polyanions with more delocalized charge structure, which can strongly reduce the activation energy of small cation dissociation and transport.

Chapter V

Effect of transport number on lithium battery performance

Sheng Zhao, Jiadeng Zhu, Nitin Muralidharan, Harry M Meyer III, Alexei P. Sokolov, and Peng-Fei Cao “Unravel the electrochemical performance of single-ion polymer electrolyte on Li surface”, in preparation. Sheng Zhao contributed to material synthesis and characterization, including DSC, DMA, SAXS, WAXS, BDS and battery test, data analysis and writing. Jiadeng Zhu contributed to the battery test. Nitin Muralidharan contributed to the SEM. Harry M Meyer III contributed to XPS. Alexei P. Sokolov and Peng-Fei Cao contributed to the idea conception and writing.

5.1 Introduction

As we discussed in Chapter 1, many theoretical models have been proposed to investigate the effect of lithium-ion transport number (t_{Li^+}) on the electrochemical performance of lithium-based batteries. For example, both works from Chazalviel *et al.*⁹⁴ and Tikekar *et al.*⁹⁵ have pointed out that the immobilization of anions is favorable for homogeneous lithium deposition, which may slow down the lithium dendrite growth. At the same time, the system with a high t_{Li^+} also has limited tendency to form concentration gradient, which can avoid the problems like increased internal impedance and slow charge/discharge process. On the other hand, it was demonstrated that high t_{Li^+} can lead to uniform reaction of active materials, which enables battery to obtain high energy density without losing active materials, especially during fast charging.

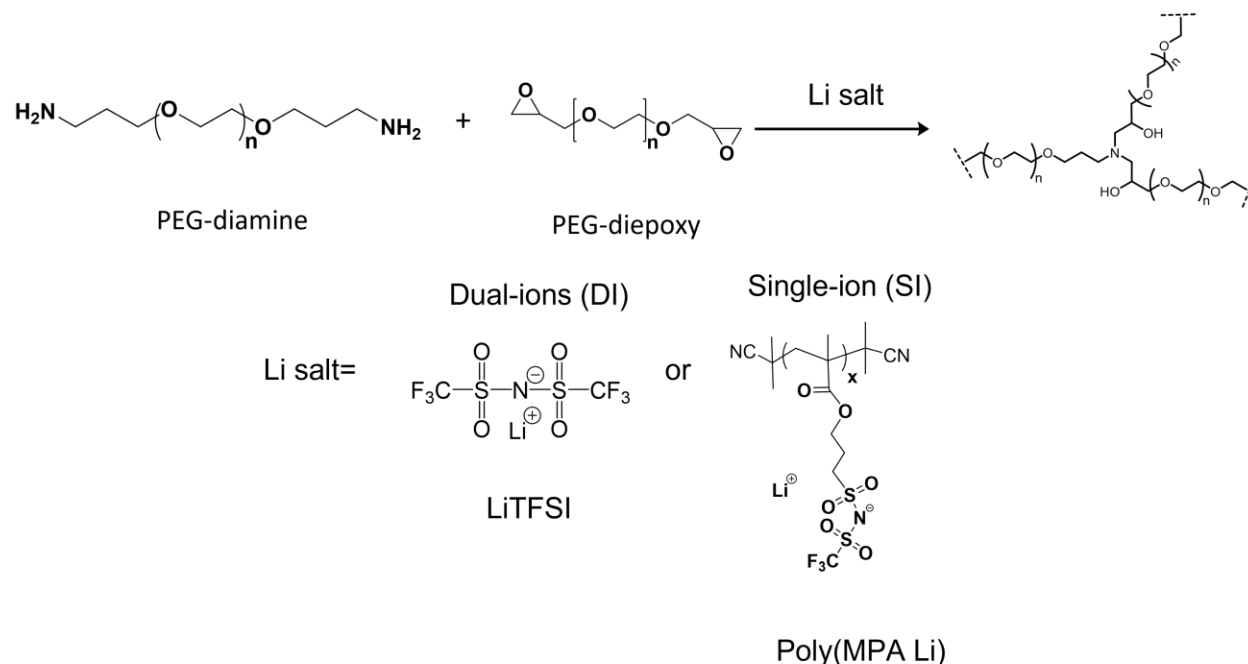
However, moving from the ideal computation scenario, it becomes more challenging to investigate the effect of t_{Li}^+ under the actual experimental condition, since the battery performance is also highly depending on the other parameters, such as chemical composition, mechanical robustness, and ionic conductivity. The influence of these parameters was not carefully considered for most previous works, in which the high t_{Li}^+ was simply given the credit for improved battery performance. For example, a single-ion conducting gel electrolyte with poly(vinylidene fluoride-co-hexafluoropropylene) (HFP-PVDF) matrix has been synthesized by Li and coworkers and characterized in Li/Li symmetric cell by galvanostatic cycling measurement.⁷⁵ They also prepared commercial dual-ions electrolyte, i.e., lithium hexafluorophosphate (LiPF_6) in the same carbonate solvent mixtures, blended in polypropylene film for the comparison of battery performance. Other than a stable voltage profile for more than 1600 hours, the cell of SICPE after cycling also presented smoother lithium metal surface, which suggests that the high t_{Li}^+ can suppress lithium dendrite growth. However, different polymer matrices correspond with different mechanical strength and chemical composition, which would also influence the lithium dendrite growth process. The similar case also occurs in the research work from Gao and his coworkers, in which a lithiated nafion polymer electrolyte plasticized with propylene carbonate (PC) has been synthesized and compared with dry PEO membrane blended with lithium perchlorate (LiClO_4).²¹⁷ Additionally, it also has been demonstrated that the system with high ionic conductivity may promote a uniform potential distribution near the interface and alter the stability of lithium dendrite.²¹⁸ Since most of synthesized SICPE has relatively lower conductivity than dual-ions conductors, the difference of ionic conductivity would also render different electrochemical behaviors.

Herein, we delicately build up a system that can experimentally demonstrate the sole effect of transport number on battery performance by fixing other parameters. To obtain the same chemical composition and comparable mechanical strength, a PEO-based crosslinked polymer matrix blended with different lithium salts has been synthesized. Two types of lithium salts (commercial dual-ions lithium salt, i.e., LiTFSI vs. synthetic SICPE, i.e., poly(MPALi)) were selected to provide polymer films with different t_{Li^+} , while the same polymer matrix is utilized for similar chemical composition and mechanical strength. To have comparable ionic conductivity with SICPE, the dual-ions conducting polymer electrolyte (DICPE) with different concentrations of LiTFSI were prepared together with the application of PC as plasticizer. The electrochemical performance of Li/Li symmetric cells with different polymer electrolytes was monitored at 60°C, and the lithium metal electrodes after cycling were also characterized by SEM and XPS. The results experimentally demonstrate that the polymer electrolyte with high t_{Li^+} itself will benefit the uniform lithium deposition, suppress lithium dendrite growth, and form a stable solid electrolyte interphase (SEI) layer. The knowledge gained will help us further understand the mechanism behind battery performance.

5.2 Materials and Experimental details

5.2.1 Materials

Poly(ethylene glycol) bis(3-aminopropyl) terminated (PEG-diamine, $M_n=1500$ g/mol), Lithium Bis(trifluoromethane)sulfonimide (LiTFSI), anhydrous tetrahydrofuran (THF, inhibitor free) and anhydrous propylene carbonate (PC) were purchased from Sigma Aldrich. Poly(ethylene glycol) diglycidyl ether (PEG-diepoxy, $M_n=1000$ g/mol) was purchased from Polysciences.



Scheme 5.1 Membrane fabrication.

Azobisisobutyronitrile (AIBN) was recrystallized from methanol before use.

5.2.2 Membrane preparation

Monomer lithium sulfonyl(trifluoromethane sulfonyl)imide methacrylate (MPALi) was synthesized based on the method from our previous work.¹⁹⁸ Single-ion conducting polymer electrolyte (SICPE), i.e., poly(MPALi) was synthesized *via* the free radical polymerization. 2.0 g (6.9 mmol) MPALi was dried in vacuum before transferring into glovebox. It was added together with 25mg (0.15 mmol) AIBN into a Schlenk tube equipped with a stirring bar and dissolved in 10ml dry THF. The solution was degassed with N₂ and reacted at 65 °C overnight. The product was purified by dialysis against THF and dried in a vacuum oven at 100°C for one day.

Poly(ethylene glycol) bis(3-aminopropyl) terminated (PEG-diamine) and Poly(ethylene glycol) diglycidyl ether (PEG-diepoxy) were dissolved in 3.0ml of anhydrous THF and stirred at 50 °C for

1hr. Both SICPE and LiTFSI were separately dissolved by 1.0ml of anhydrous THF, added to the PEG solution and stirred for 30 mins. The solution was poured into Teflon dish and left in the hood for 2hr to evaporate most solvent, which was then transferred to the glovebox and reacted at 100 °C for 3hr. The membrane was dried in a vacuum oven at 100 °C overnight. The plasticized membranes were all doped with 20wt% propylene carbonate (PC) inside glovebox overnight before characterization measurement.

5.2.3 Instrumentation

Fourier transform infrared spectroscopy (FT-IR) was measured on a Nicolet iS50 FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The spectra were obtained with 64 scans and averaged with signals.

The thermal stability of samples was measured by thermogravimetric analysis (TGA) on TA instrument TGA Q-50 under N₂ with a heating rate of 10°C/min from room temperature to 800°C. Differential Scanning Calorimetry (DSC) was conducted on TA instrument DSC Q2500. The blended membranes were dried in the oven before sealed in the aluminum hermetic pan. The samples were equilibrated at 120 °C for 15mins to remove the thermal history. A cooling-heating scans was conducted at a rate of 3°C/min in the range of -90 °C to 120 °C. For plasticized membranes, they were loaded into aluminum hermetic pan inside glovebox. After equilibration at 25 °C for 20min, the same procedure of cooling-heating scans was applied to plasticized membranes.

Storage and loss modulus of membranes were measured by dynamic mechanical analysis (DMA) on TA instrument DMA Q800 at an operatin frequency of 1 Hz. The samples were heated from -90 °C to 100 °C at 5 °C/min under nitrogen.

The conductivity of prepared membranes were characterized by broadband dielectric spectroscopy (BDS). The samples were sandwiched with two gold plated electrodes. For dry membranes, they were dried in the vacuum oven at 110 °C overnight prior the measurement. During the measurements, samples were equilibrated at 120 °C for 30 min, then proceeded to -30 °C and went back to the same high temperature under N₂. The plasticized membranes were equilibrated at 20 °C for 20 mins, and then the samples were measured from 10 °C to 80 °C.

The electrochemical measurements were conducted on a Biologic VMP3 potentiostat with the EC-Lab® software at 60°C. In the glovebox, the plasticized membranes were sandwiched between two pieces of lithium foils with diameter equal to 1.0 cm (surface area is 0.78 cm²) and sealed in a coin cell. The potentio-static polarization method was used to calculate the lithium-ion transport number. The voltage is set as 10 mV for 3600 seconds for the CA test, and EIS was recorded from 1 MHz to 10 mHz with a voltage amplitude of 10 mV.

To test the electrochemical stability, the Li/stainless steel cell composed of plasticized membranes was sealed in the glovebox and subjected to linear sweep voltammetry (LSV) with a sweep rate of 5 mV/s.

To study the lithium stripping/plating process, the galvanostatic cycling tests of the Li/Li symmetric cell with plasticized membranes was performed at 60 °C. Each cycle was applied

with a constant current density 0.1 mA, i.e., 0.127 mA /cm², for 60 minutes lithium plating/stripping and an intermediate 5 minutes rest step.

For full cell test, a coin cell configuration composed of lithium iron phosphate (LiFePO₄, LFP) composite cathode, plasticized membranes, and a lithium metal was used. All coin cells were prepared and assembled in an argon-filled glovebox. The LFP cathode was fabricated on a carbon-coated Al foil current collector followed the procedure from previous work.⁶⁹ The cathode had an LFP loading of 1.2 mg/cm².

Scanning electron microscope (SEM) micrographs were obtained by a cold-cathode field emission (FE) SEM system (Hitachi TM3030Plus Tabletop Microscope) at 15 kV accelerating voltage. The energy dispersive X-ray spectrometer (EDX) were used to obtain the elemental composition distribution of the Li anode surface (15 kV). The sample transferring time to the vacuum chamber of the SEM was less than 30 s.

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific (Waltham, MA, USA) Model K-Alpha XPS instrument. The instrument utilizes monochromated, micro-focused, Al K_α X-rays (1486.6 eV) with a variable spot size (i.e., 30-400 μm). Analyses of the sample was performed with the 400 μm X-ray spot size for maximum signal and to obtain an average surface composition over the largest possible area. The instrument has a hemispherical electron energy analyzer equipped with a 128-channel detector system. Base pressure in the analysis chamber is typically 2 x 10⁻⁹ mbar or lower. The samples were loaded into a vacuum transfer module (VTM) inside an Ar-ion glovebox. The VTM was sealed under vacuum inside the vacuum load-lock of the glovebox. THE VTM was transported to the XPS

instrument and loaded into its vacuum load-lock. The VTM is released in the XPS load-lock during pump down. After transferring the samples into the analysis chamber, survey spectra (pass energy = 200 eV) were acquired for each sample. Next, high-resolution core level spectra (pass energy = 50 eV) were acquired for detailed chemical state analysis. All spectra were acquired with the charge neutralization flood gun turned on to maintain a stable analysis condition. The flood gun uses a combination of low energy electrons and argon ions for optimum charge compensation. The typical pressure in the analysis chamber with the flood gun operating is 2×10^{-7} mbar. Data were collected and processed using the Thermo Scientific Advantage XPS software package (v.5.96).

5.3 Results

5.3.1 Structure analysis and property evaluation

To evaluate the effect of lithium-ion transport number (t_{Li^+}) on the battery performance, a polyethylene oxide (PEO) based crosslinked membranes with different concentrations of lithium salts were synthesized. By using the same polymer matrix synthesized under the same condition, we could obtain samples with almost the same chemical composition and mechanical strength. To differentiate t_{Li^+} , two types of lithium salts have been selected: commercial dual-ions lithium salt, i.e., LiTFSI and synthetic homopolymer SICPE, i.e., poly(MPALi). The polymer electrolyte membranes were named by the type of lithium salts, i.e., SI and DI, and the lithium-ion concentration. The latter one was defined by the ratio of overall ethylene oxide units (EO) over the lithium-ions. For example, DI-20 represents crosslinked PEO membranes blended with LiTFSI by ratio of EO:Li⁺=20. Using ionic conductivity of SI-20 as a reference, the

concentration of LiTFSI was varied from DI-20 to DI-200 to achieve the ionic conductivity of SI-20. The successful synthesis of crosslinked PEO membranes is indicated by the absence of peaks around 3500-3700 cm^{-1} in the FT-IR spectra, which related to the amine bond from PEO-diamine (Figure 5.1). The common peak at 1350 cm^{-1} (S=O in LiTFSI and poly(MPALi)) demonstrates the existence of lithium salts, while polymer membrane with poly(MPALi) also shows an additional peak at 1730 cm^{-1} corresponding to C=O bonds.

For DI-x, only one T_g with comparable value was observed, suggesting that the T_g of membranes is mainly determined by the chemical composition of membranes rather than lithium-ion concentration (Figure 5.3(a)). In contrast, the concentration has a bigger impact on the crystallization of PEO structure. For example, when the lithium-ion concentration was increased by ten times (DI-200 vs. DI-20), the melting temperature (T_m) was decreased from 40 $^{\circ}\text{C}$ to 23 $^{\circ}\text{C}$ (Table 5.1). Additionally, the smaller area of peak related to crystallization also suggests decreased degree of crystallinity with increasing lithium-ion concentrations. Compared to DI-20, both higher T_g and T_m of SI-20 can be explained by the relatively slower dynamics of poly(MPALi).

The morphology of synthesized membranes were characterized by the small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) in Figure 5.2(a). In the SAXS range, a common peak with q ranging from 10 to 20 nm was observed for all membranes. Since a peak with similar q was also observed from PEG-diamine (Figure 5.2(b)), this ordered structure may be related to the distance between crosslinks in polymer network. It is also noteworthy that the amplitude of this peak decreased with the ratio of LiTFSI. A possible explanation is that lithium-ions would coordinate with ethylene oxide group and disturb the ordered packing of PEG-

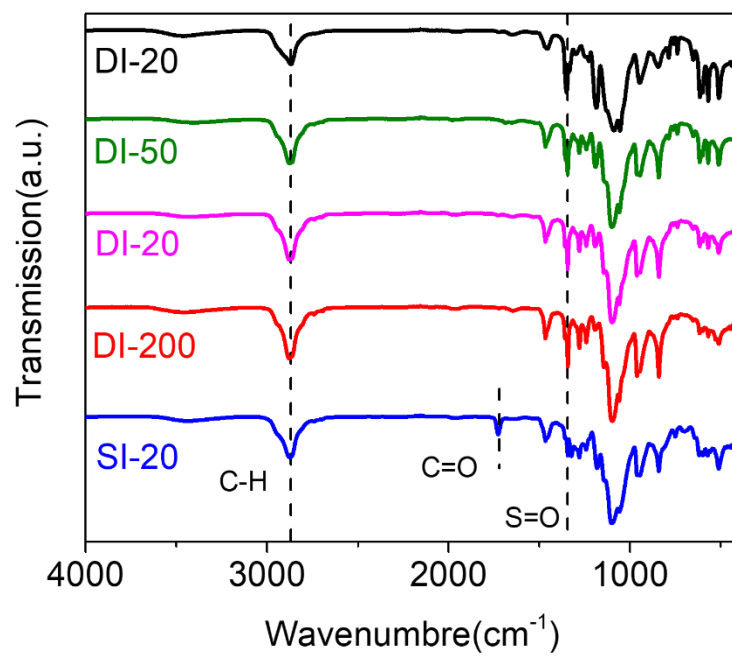


Figure 5.1 FT-IR spectra of dry membranes.

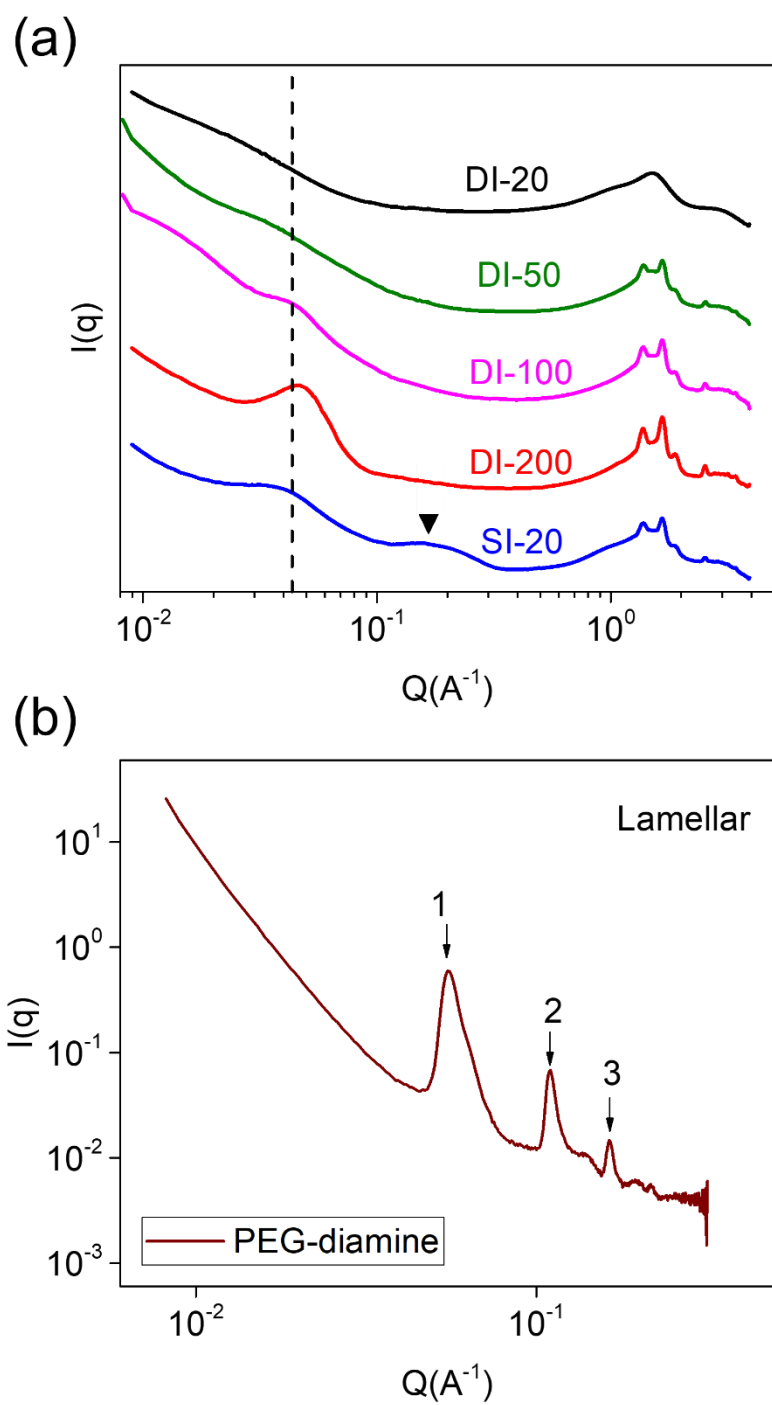


Figure 5.2 (a) SAXS-WAXS spectra of dry membranes and (b) SAXS spectrum for PEG-diamine.

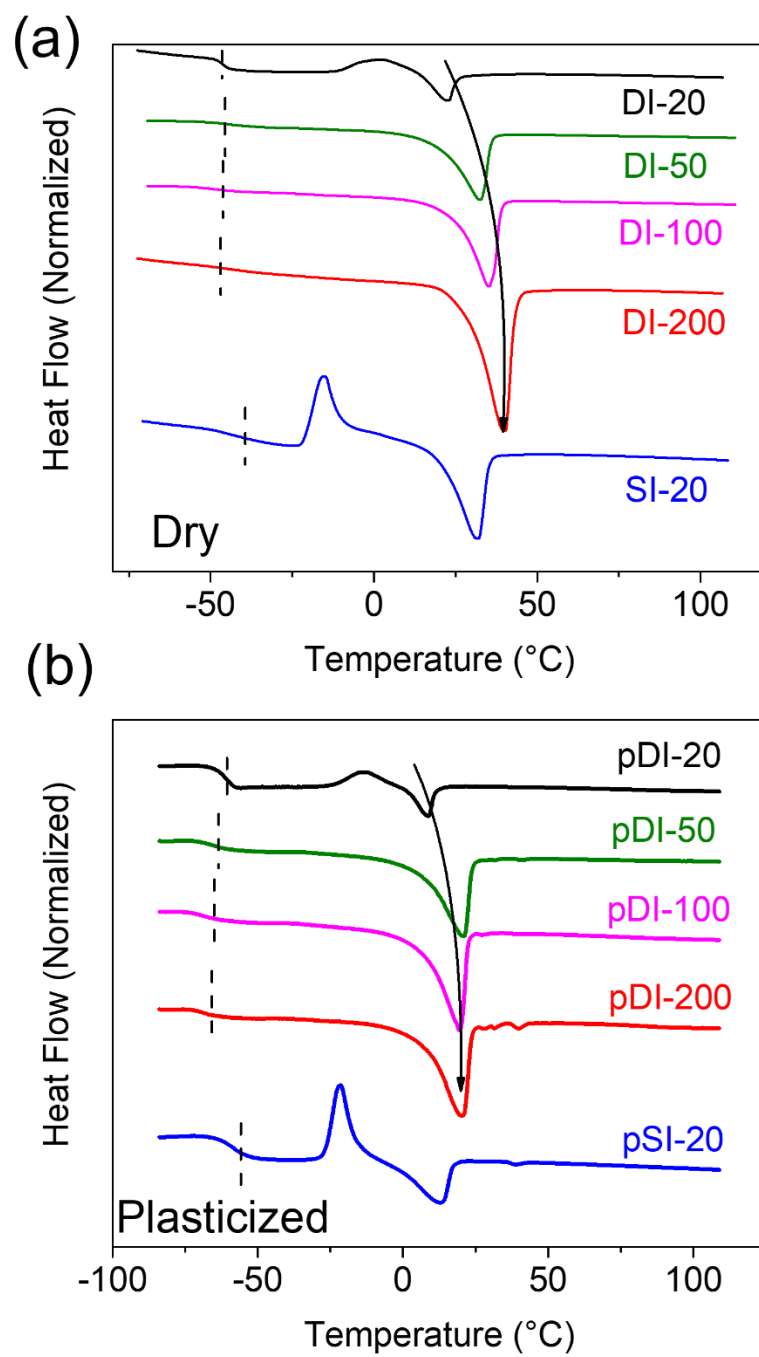


Figure 5.3 DSC spectra of (a) dry membranes and (b) plasticized membranes with 20wt% of PC.

Table 5.1 Thermal properties, storage modulus and conductivity of dry membranes.

		Thermal properties		E' at 60 °C (MPa)	σ at 60 °C (S/cm)
		T _g (°C)	T _m (°C)		
Dual-ions	DI-20	-47	23	0.64	2.0×10^{-4}
	DI-50	-44	33	1.2	1.2×10^{-4}
	DI-100	-45	35	1.3	7.0×10^{-5}
	DI-200	-43	40	1.0	3.9×10^{-5}
SI-20		-41	32	1.1	5.1×10^{-6}

diamine.²¹⁹ The amplitude of peaks at WAXS range also decreased with increased concentration of lithium-ions. This suggests the reduced degree of crystallinity with increasing ratio of LiTFSI, which is consistent with our DSC results (Figure 5.3(a)). For SI-20, an additional peak with characteristic length of 5nm was observed. Since the presence of only one T_g in DSC spectra suggests the absence of phase separation, this ordered structure is probably due to the nanoclusters formed by poly(MPALi) itself.

5.3.2 Mechanical property

To exclude the effect of mechanical property on the following electrochemical test, it would be essential to have comparable storage modulus for all samples. The storage modulus of crosslinked membranes (E') were characterized by dynamic mechanical analysis (DMA) with temperature sweep mode at 1 Hz (Figure 5.4(a)). With different crystallinities, the storage modulus at room temperature was varied from 100 MPa to 10 MPa, which was also influenced by the heating rate of measurement. Therefore, the storage modulus above melting temperature, i.e., at 60 °C, was selected, which possess comparable values for all studied membranes (~ 1 MPa). Additionally, as the crosslinking density is proportional to E' , we may also conclude that all the membranes possess comparable crosslinking density, due to the same chemical network (Table 5.1).

5.3.3 Conductivity

The conductivity of polymer electrolyte membranes was measured by Broadband Dielectric Spectroscopy (BDS) as illustrated in Figure 5.5. Since the conductivity exhibited a sharp decrease for all membranes around 30 °C, the ionic conductivity at 60 °C would be our focus for

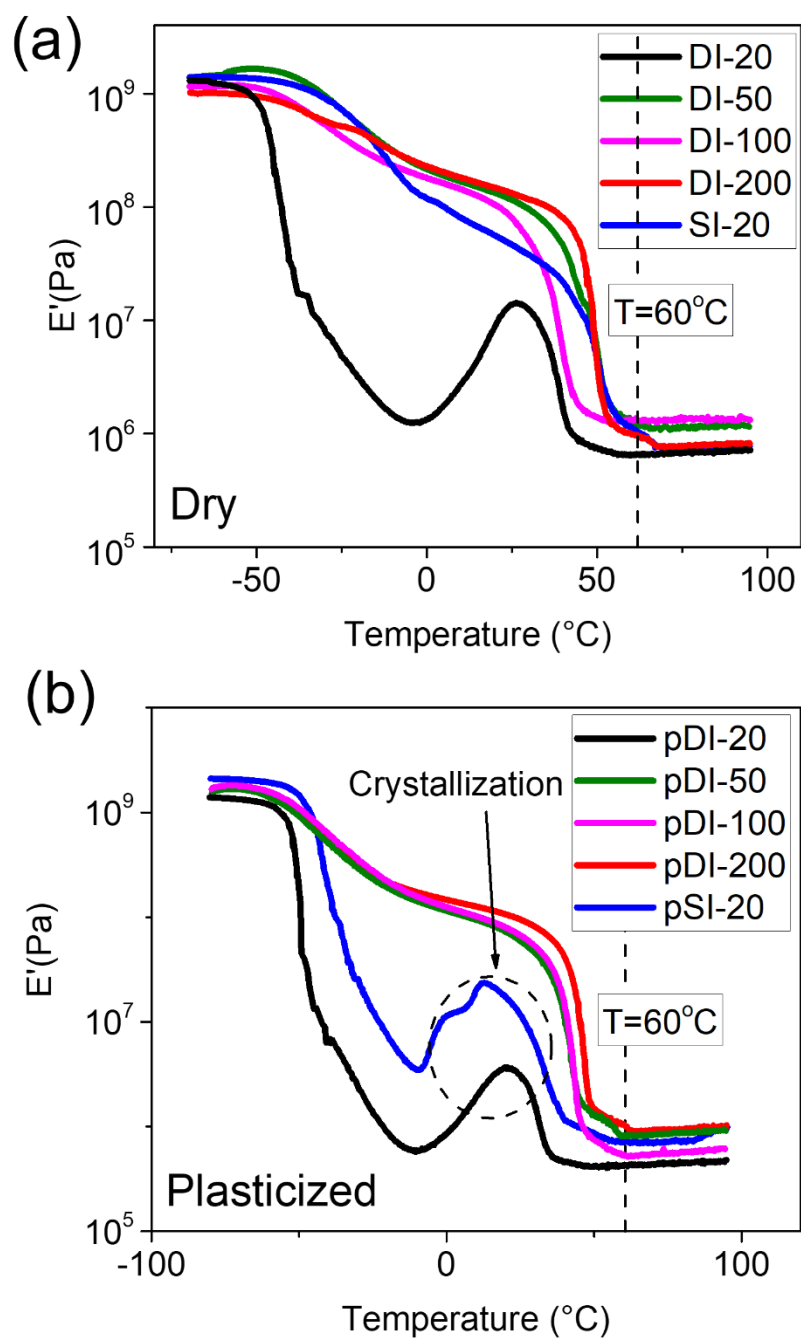


Figure 5.4 DMA curve of (a) dry and (b) plasticized membranes.

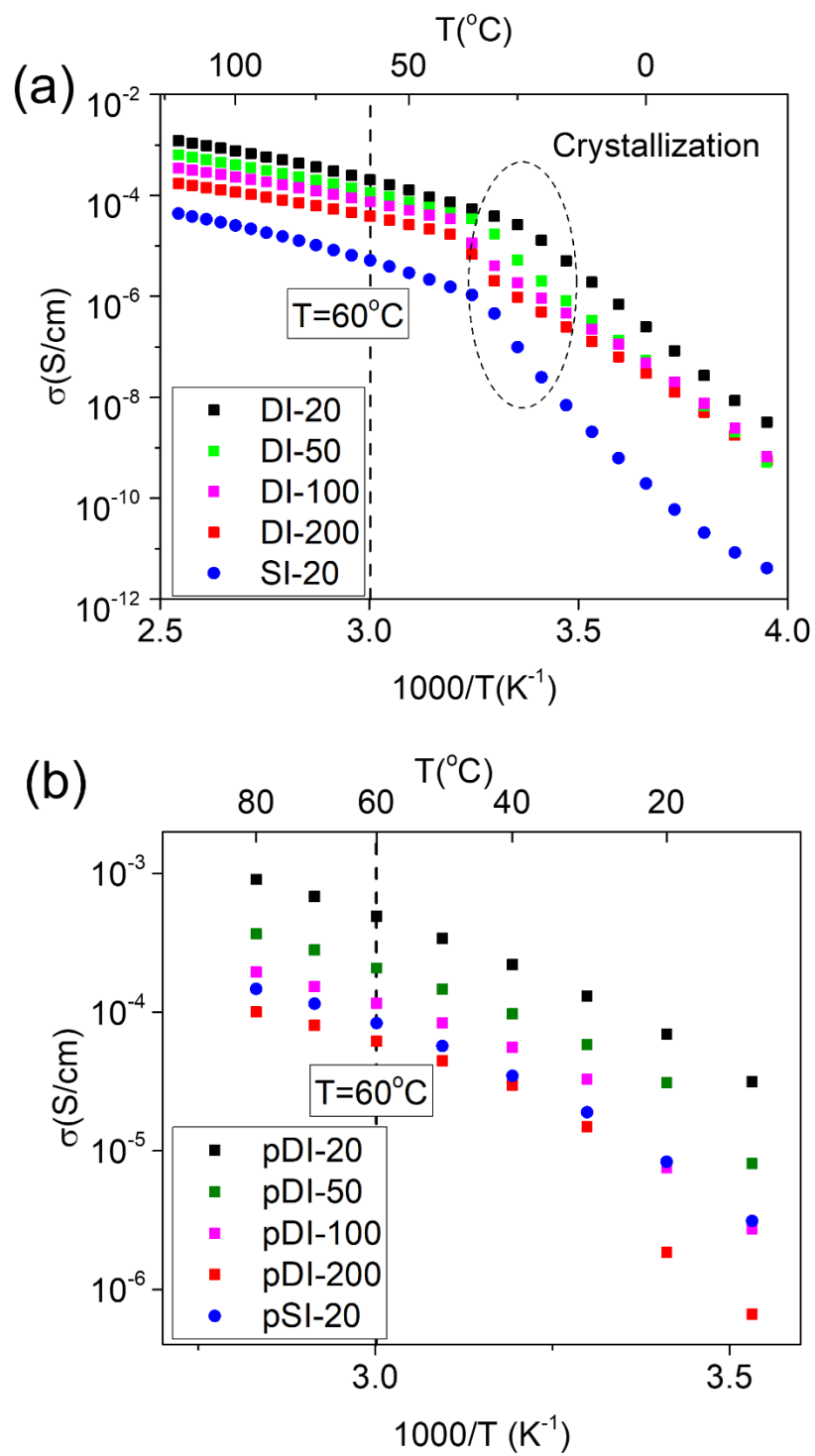


Figure 5.5 Conductivity of (a) dry and (b) plasticized membranes.

the following characterizations. Without participation of anion transport, SI-20 had the lowest conductivity compared to all DI-x. For example, with comparable content of lithium-ions, DI-20 exhibits almost 40 times higher ionic conductivity than SI-20 (2.0×10^{-4} S/cm for DI-20 vs. 5.1×10^{-6} S/cm for SI-20 at 60 °C). Even for DI-200 with just 10% of lithium-ion concentration, its ionic conductivity, i.e., 3.9×10^{-5} S/cm at 60 °C, was still one order of magnitude higher than that of SI-20.

To increase the ionic conductivity for battery test and minimize the difference of ionic conductivity among samples, the polymer membranes were doped with 20wt% of plasticizer propylene carbonate (PC), which are labeled as pDI and pSI. Both T_g and T_m of plasticized membranes were lower than the original dry membranes due to the accelerated dynamics and suppressed crystallinity (Figure 5.3(b)). Similar to dry membranes, T_m of plasticized membranes decreased with increased ratio of lithium-ions, while their T_g barely changed. Additionally, the storage modulus at 60 °C were still comparable (~ 0.5 MPa) and slightly lower than the dry membranes (Figure 5.4(b)). With plasticizer, the ionic conductivity of pSI-20 was improved by more than an order of magnitude to 8.3×10^{-5} S/cm at 60 °C, while pDI-x were only boosted by around two times. In this case, the ionic conductivity of pDI-200, i.e., 6.2×10^{-5} S/cm, was comparable with pSI-20 (Figure 5.5(b)).

5.4 Discussion

5.4.1 pSI vs. pDI with the same lithium-ion concentration

Other than the same chemical composition and comparable storage modulus, pSI-20 and pDI-20 also have the same lithium-ion concentration. With reduced interaction with ethylene oxide

Table 5.2 Thermal properties, storage modulus, conductivity and electrochemical properties of plasticized membranes.

		Thermal properties		E' at 60 °C (MPa)	σ at 60 °C (S/cm)	t_{Li}	Cycle Life ^a
		T _g (°C)	T _m (°C)				
Dual-ions	pDI-20	-62	9	0.44	5.0×10^{-4}	0.28	~1900 h
	pDI-50	-64	18	0.81	2.0×10^{-4}	0.27	~1000 h
	pDI-100	-66	21	0.53	1.3×10^{-4}	0.26	~30 h
	pDI-200	-67	21	1.0	6.2×10^{-5}	0.22	N/A
pSI-20		-58	14	0.72	8.3×10^{-5}	0.87	>2200 h

a. time before the failure of Li/Li symmetric cell with plasticized membranes at 60 °C under 0.1 mA, i.e., 0.127 mA/cm².

units and being barely solvated by solvent molecules, anion commonly has a higher mobility than lithium-ion.^{54, 220} Therefore, with the participation of anion transport, the ionic conductivity of pDI-20 is six times higher than pSI-20 at 60 °C (5.0×10^{-4} S/cm for pDI-20 vs. 8.3×10^{-5} S/cm for pSI-20 in Table 5.2), although they have the same lithium-ion contents. The lithium-ion transport number (t_{Li^+}) was characterized by Bruce-Vincent method with Li/Li symmetric cell at 60 °C. The t_{Li^+} of pDI-20 is 0.28, which is common for the conventional PEO-based polymer electrolytes,¹⁷⁷⁻¹⁸² whereas the t_{Li^+} of pSI-20 is 0.87, indicating that the ionic conductivity is mainly contributed by lithium-ions.

To investigate the influence of t_{Li^+} on the electrochemical stability of polymer electrolytes over lithium metal electrode, the lithium stripping/plating measurement has been conducted with a Li/Li symmetric cell configuration. As shown in Figure 5.6(a), with a current density of 0.1 mA at 60 °C, the voltage of pDI-20 was much lower (~ 0.05 V) at initial cycles compared to that of pSI-20 due to the significantly higher ionic conductivity. However, the voltage gradually increased to 0.23 V before the cell failed after 2000 hours of cycling, indicating the accumulation of “dead” lithium. On the other hand, even with six times lower ionic conductivity, pSI-20 still presented a very stable voltage ~ 0.25 V for more than 2200 hours (~ 3 months) of cycling (Figure 5.6(a)). Additionally, there’s no significant increase of impedance for pSI-20 even after the cycling test, which demonstrates the good electrochemical stability of pSI-20 over the lithium metal electrode (Figure 5.6(e)).

The improved electrochemical stability for pSI-20 can be explained through the following aspects. The high t_{Li^+} of pSI-20 would benefit homogenous lithium deposition and suppress the growth of lithium dendrite.^{94, 95} Scanning electron microscope (SEM) was applied to

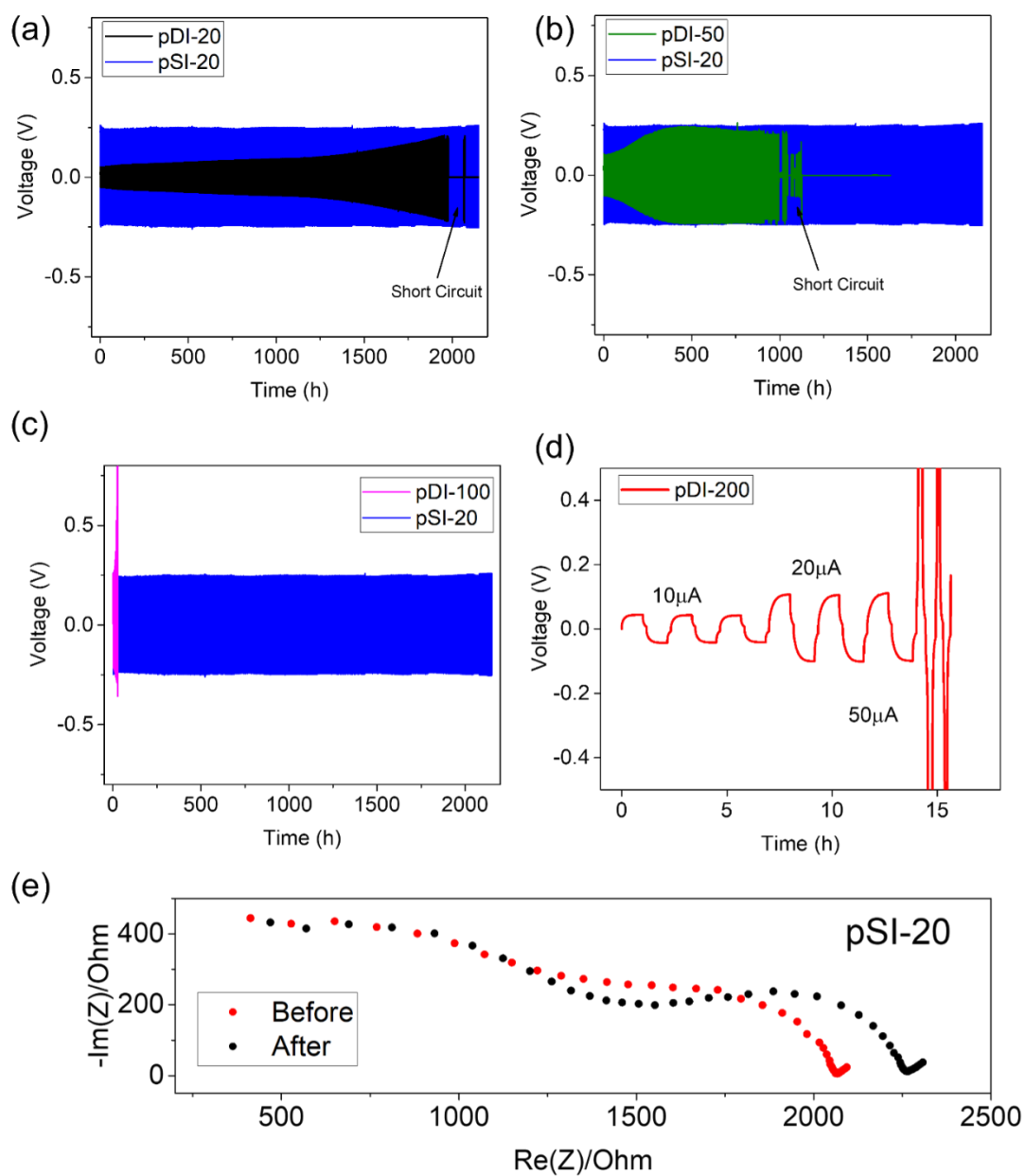


Figure 5.6 (a)-(d) A long-term galvanostatic cycling test of Li/Li symmetric cell composed of plsaticized membranes at 60 °C with a constant current of 0.1mA, i.e, 0.127 mA /cm. (e) The impedance of pSI-20 before and after 2200 hrs of stripping /plating.

characterize the surface morphologies of lithium metal electrodes. For pSI-20, a relatively uniform surface with only tiny roughness was observed (Figure 5.7(e)), while the lithium metal electrodes of pDI-20 exhibited more ramified structure (Figure 5.7(f)). Even with a lower ionic conductivity, pSI-20 has a uniform lithium deposition on the lithium metal surface, which guarantee the good contact between polymer electrolyte membrane and lithium metal electrodes. In a comparison, the low t_{Li}^+ would lead to the rapid anion depletion in PEO-based electrolyte, which accelerates the nucleation of dendrite structure.²²¹ The accumulation of “dead” lithium was also observed from the photographs of lithium metal surface for pDI-20 (Figure 5.7 (c)), which presented much darker surface than that of pSI-20 (Figure 5.7(a)).¹⁵³

Secondly, the high t_{Li}^+ of pSI-20 may also alter the formation of solid electrolyte interface (SEI) layer for improved electrochemical stability. The chemical composition of SEI layer on lithium metal surface after stripping/plating measurement was characterized by X-ray Photoelectron Spectroscopy (XPS) in Figure 5.8. The SEI layer is commonly composed of Li_2CO_3 , LiF and Li_2O , which all of them were detected in both samples.²²²⁻²²⁴ There’s only one single peak related to LiF observed at 686.5V in F 1s spectra, which is generated from the reduction of TFSI-like structure in both LiTFSI and poly(MPALi) (Figure 5.8(a) and (d)).²²⁵ In O 1s spectra, the significant peak at 533 eV was assigned to the existence of Li_2CO_3 , which was accompanied with two small peaks at 530 and 535 eV corresponding to Li_2O and C-O bond from plasticizer PC (Figure 5.8(b) and (e)).^{226, 227} The brittle Li_2CO_3 also exhibits a peak with binding energy ~ 57 eV in Li 1s spectra, while the additional peak at ~ 55.5 eV corresponds to the metallic lithium (Li^0) (Figure 5.8(c) and (f)). Different from F 1s spectra and O 1s spectra, the peaks in Li 1s spectra have significantly different ratio of amplitude between pSI-20 and pDI-20. Particularly, the

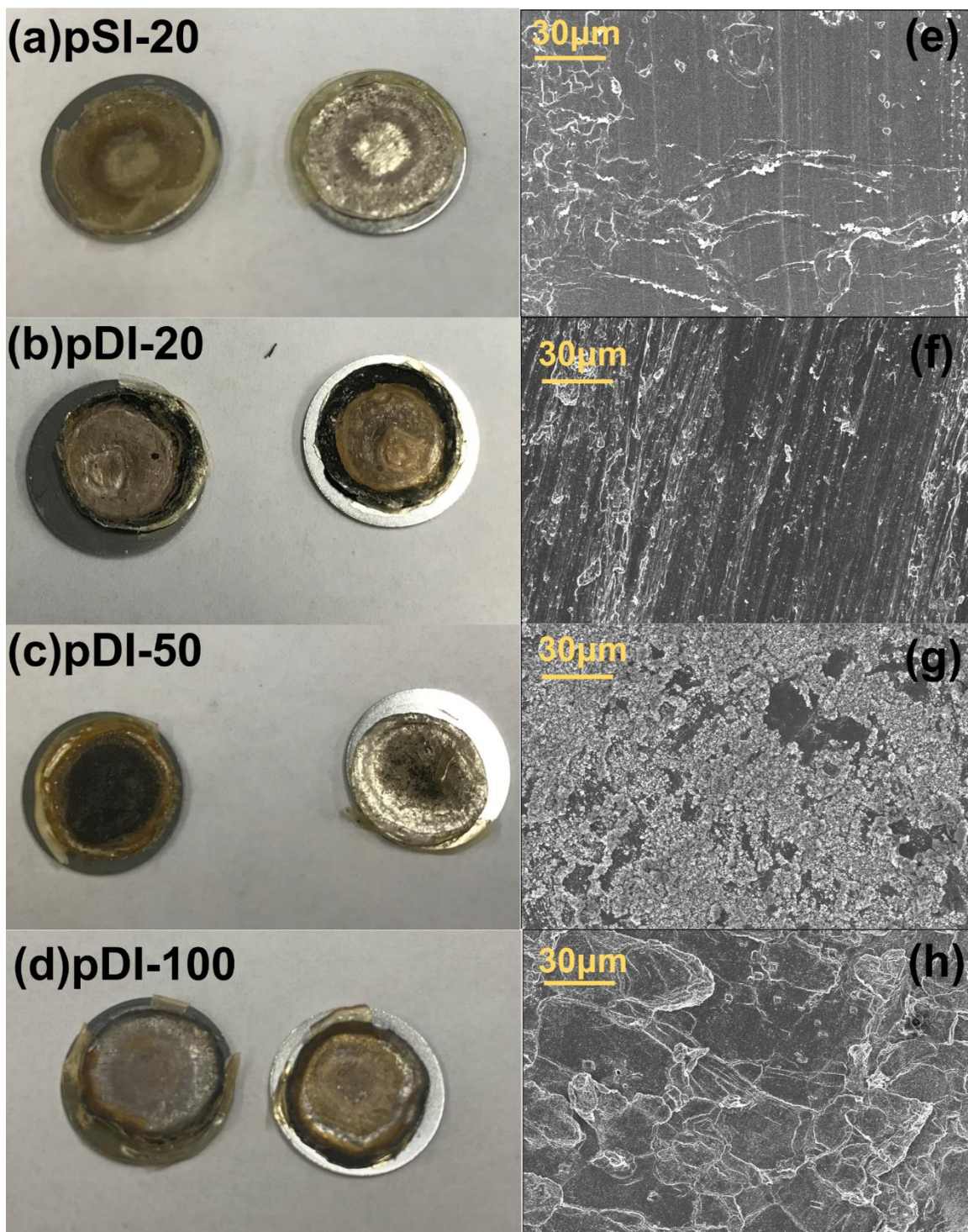


Figure 5.7 Photos and SEM micrographs showing the surface morphology of the cycled Li electrodes for (a) pSI-20, (b) pDI-20, (c) pDI-50 and (d) pDI-100.

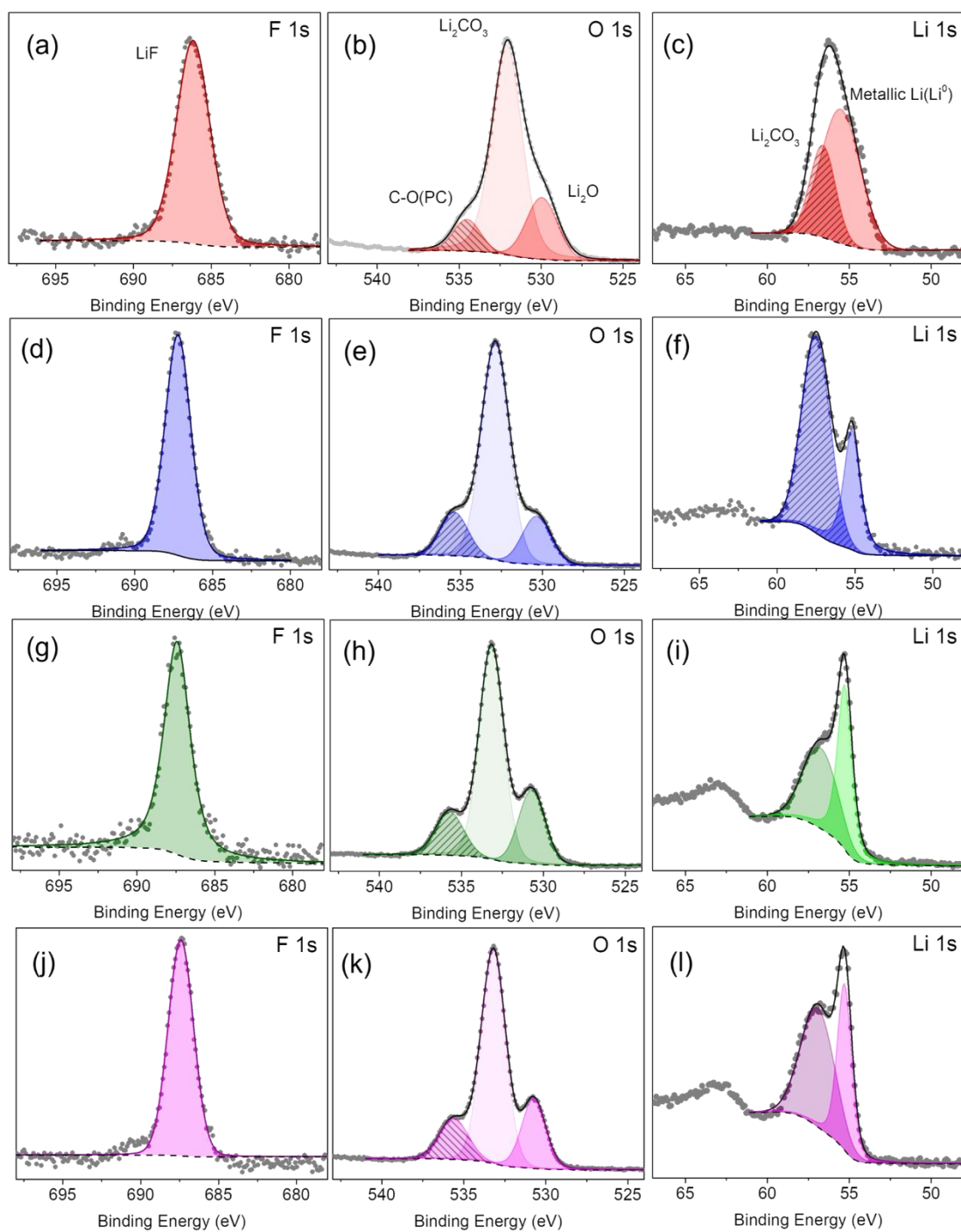


Figure 5.8 The F 1s, O 1s and Li 1s spectra of SEI formed on lithium metal electrode surface after stripping/plating measurement for Li/Li symmetric cells with (a)-(c) pSI-20, (d)-(f) pDI-20, (g)-(i) pDI-50 and (j)-(l) pDI-100.

much lower percentage of Li^0 in pDI-20 suggests more side reactions consuming lithium metal electrode to “dead” Li (Figure 5.8(f)).²²⁷ In comparison, the large presence of active metallic lithium observed in pSI-20 manifests the reduced lithium dendrite on the surface of lithium metal (Figure 5.8(c)). These results reveal that even with lower ionic conductivity than pDI-20, the high t_{Li^+} of pSI-20 would afford a more stable SEI layer with less side reaction.

5.4.2 pSI vs. pDI with comparable ionic conductivity

Other than pDI-20, the pDI-x with different concentrations of LiTFSI were also prepared to provide DICPEs with ionic conductivity comparable to SICPEs. These DICPEs have both comparable mechanical property (~ 0.5 MPa) and t_{Li^+} with pDI-20, i.e., ~ 0.25 as shown in Table 5.2. The ionic conductivity of pDI membranes gradually decreased with the reduced lithium-ion concentration (pDI-50 to pDI-200). The latter exhibited ionic conductivity comparable to pSI-20. The electrochemical stability of pDI-50, pDI-100 and pDI-200 over lithium metal electrode were also characterized by lithium stripping/plating measurement with Li/Li symmetric cell configuration. With slightly higher ionic conductivity, the initial voltage of pDI-50 is 0.1 V, which is lower than that of pSI-20 (~ 0.25 V). Then, the voltage increased and stabilized at 0.25 V, before the cell finally failed after 1000 hours of cycling (Figure 5.6(b)). The unstable voltage profile were also observed for the other pDI membranes with reduced lithium-ion concentration. For example, the voltage of pDI-100 evolved over 4 V after only 40 hours cycling, while the cell with pDI-200 did not even work under the same current density (Figure 5.6(c) and (d)). This rapid increase in voltage is attributed to the lack of mobile lithium-ions. Although both pDI-100 and pDI-200 have comparable ionic conductivity with pSI-20, their conductivity is mainly from anion

transport. If we assume that the lithium-ion conductivity (σ_{Li^+}) can be estimated as the measured conductivity multiplied by the lithium-ion transport number for simplicity, then the σ_{Li^+} of pSI-20 would be much higher than in these two pDI membranes, i.e., 7.2×10^{-5} S/cm for pSI-20 vs. 3.4×10^{-5} S/cm for pDI-100 and 1.4×10^{-5} S/cm for pDI-200. Therefore, rather than overall conductivity, the high conductivity of lithium-ion plays a more important role in battery performance, and this is directly related to t_{Li^+} .

With comparable ionic conductivity, the electrochemical stability of polymer electrolytes over lithium metal electrode is strongly influenced by t_{Li^+} and lithium-ion concentration. It has been demonstrated that the liquid electrolyte with high concentration can realize cycling at a high current density without significant lithium dendrite growth for hundreds of cycles.^{228, 229}

Although both pDI-50 and pDI-100 have comparable ionic conductivity, their lithium metal electrode surfaces are much rougher compared to those of pSI-20. Especially for pDI-50, the probed surface is almost fully covered by the “cauliflower”-like ramified structure as illustrated in Figure 5.7(f), while the relatively better surface morphology of pDI-100 is due to the much shorter times of cycling before the cell failure (Figure 5.7(h)). Additionally, both pDI-50 and pDI-100 have more side reactions happened near the surface of lithium metal before the cell failure, which is supported by the relatively lower percentage of metallic lithium than pSI-20 in Li 1s spectra (Figure 5.8(i) and (l)). Therefore, pSI-20 still has the most stable SEI layer compared to both pDI-50 and pDI-100, which emphasizes the important role of both t_{Li^+} and lithium-ion concentration on the electrochemical stability of polymer electrolytes.

5.5 Full battery test

To further evaluate the influence of t_{Li}^+ on electrochemical performance, the galvanostatic cycling test was conducted with full cell configuration having lithium metal as anode and $LiFePO_4$ (LFP) composite cathode. Based on the linear scanning voltammetry (LSV) result measured by Li/stainless steel (SS) cell, the electrochemical stability window (ESW) for all plasticized membranes is above 4.0 V (Figure 5.9). Therefore, the full cell test was performed at 60 °C with potential range set to 2.8 V -3.8 V. The cycling stability was indicated by the discharge capacity at C/10 (assuming a theoretical capacity of 170 mAh/g for LFP) and Coulombic Efficiency in Figure 5.10. With comparable ionic conductivity, the capacity retention of pSI-20 is quite stable (~150 mAh/g) after 100 cycles, while the Coulombic Efficiency maintained above 99%. This is in dramatic contrast to the pDI-100 and pDI-50. Particularly, the full cell of pDI-50 had a comparable specific capacity at the beginning (~ 150mAh/g) and functioned for 50 cycles, before it rapidly faded below 25 mAh/g at 65 cycles. The cell with pDI-100 even only started from 125mAh/g and soon faded below 25 mAh/g after 10 cycles (Figure 5.10(a)). Although with comparable ionic conductivity, the significantly extended cycling life of pSI-20 is ascribed to the improved interface stability for polymer electrolytes having high t_{Li}^+ . Additionally, with same lithium ion concentration, the specific capacity of pDI-20 presented a slight decrease from 155 mAh/g to 133 mAh/g till now, while the Coulombic Efficiency is still above 98.5%. The longer term battery test, even with a higher C-rate, is necessary for both pSI-20 and pDI-20 to finally evaluate the effect of t_{Li}^+ on capacity retention.

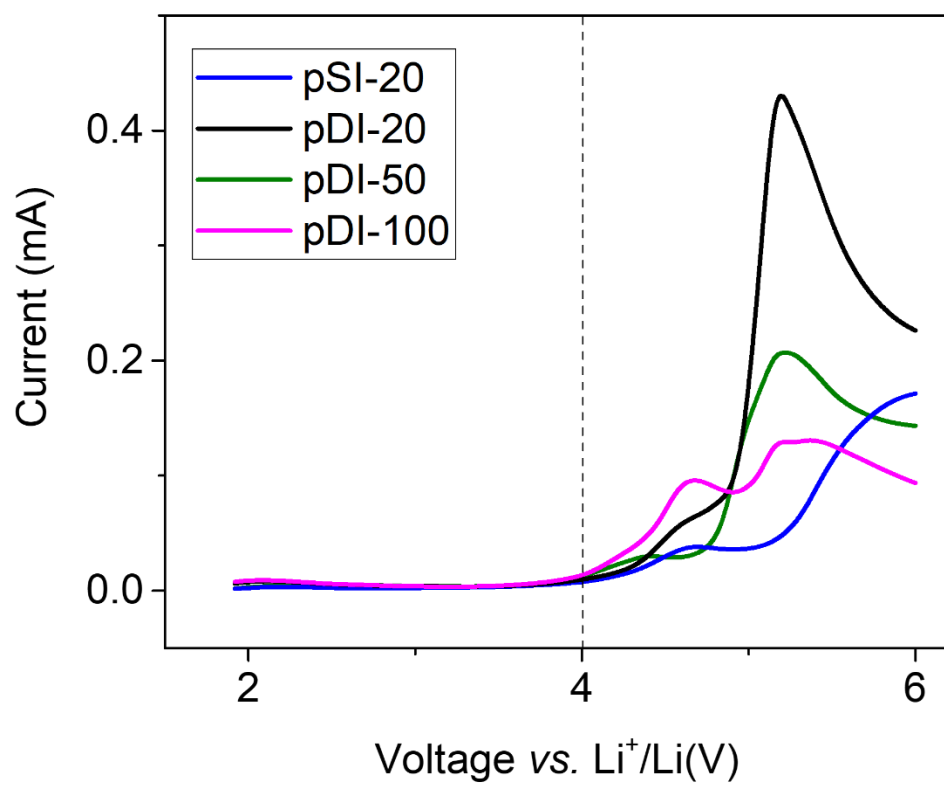


Figure 5.9 Linear sweep voltammetry (LSV) of Li/SS cell composed of plasticized membranes.

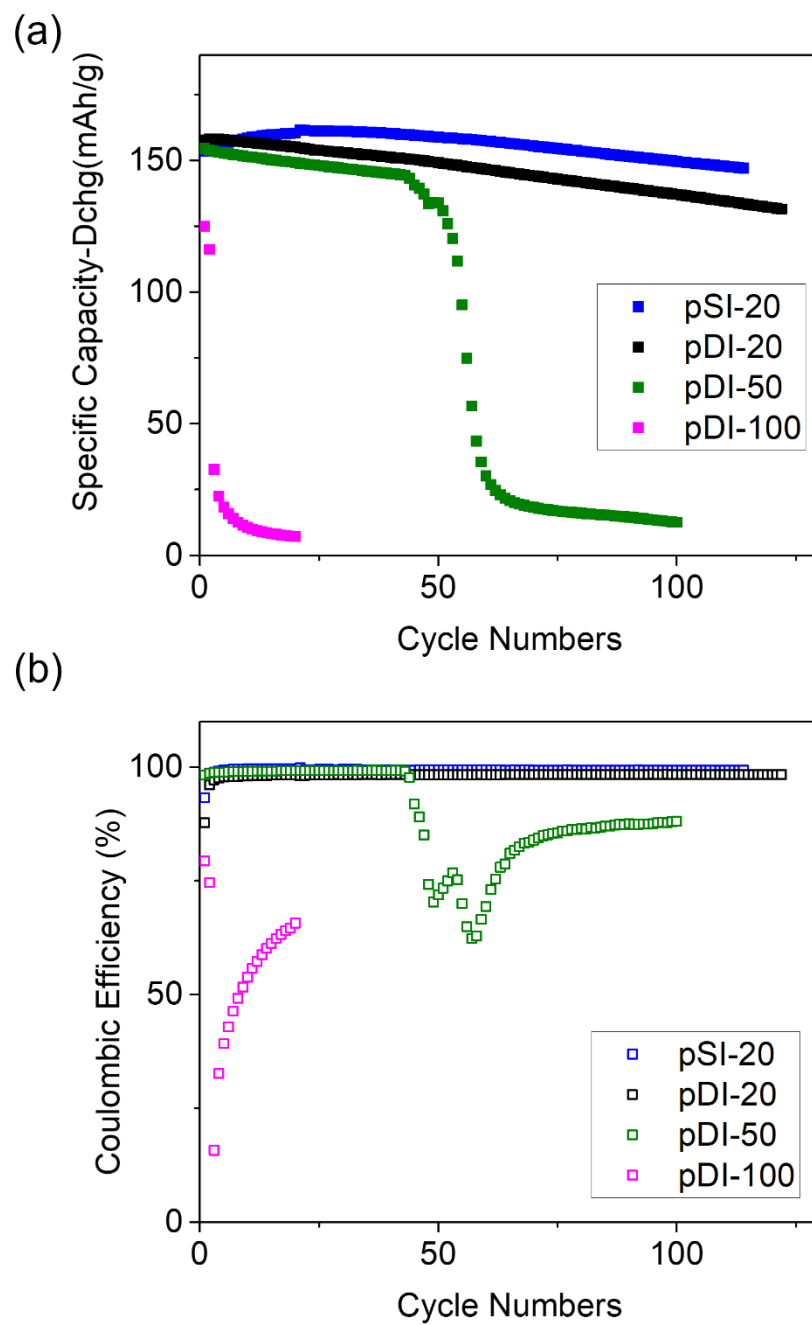


Figure 5.10 (a) The discharge capacity and (b) Coulombic Efficiency vs. cycle numbers plot of LFP/plasticized membranes/Li cell at C/10 under 60 °C.

5.6 Conclusions

In this work, we performed a point-to-point study focusing on the effect of lithium-ion transport number (t_{Li^+}) on lithium battery performance by fixing other parameters, such as mechanical property and chemical composition. The plasticized crosslinked PEO membranes with SICPE or different ratio of typical dual-ions lithium salts, i.e., pSI and pDI, have been prepared for the battery measurement. Even with same lithium-ion concentration and lower ionic conductivity, the Li/Li cell of pSI-20 still presented a stable voltage profile over 2200 hours, while the cell of pDI-20 failed after around 2000 hours cycling under same condition. For the pDI-x having comparable ionic conductivity with pSI-20, the cells either failed at much earlier cycles (~1000 hours for pDI-50 and ~30 hours for pDI-100) or did not work under the same current density (pDI-200). The better electrochemical performance of pSI-20 was ascribed to the uniform lithium electrodeposition process and the suppressed growth of lithium dendrite, which guarantees the good contact between electrodes and membranes during cycling. Additionally, the XPS results also clearly demonstrate that pSI-20 has much fewer side reactions happened near to the surface of lithium metal electrodes, which leads to the formation of more stable SEI layer. The full cell test with a configuration of LiFePO_4 (LFP)/plasticized membranes/Li were also prepared to further evaluate the effect of t_{Li^+} on electrochemical performance. Both pDI-50 and pDI-100 presented rapid capacity fading, while the pDI-20 and pSI-20 could maintain specific capacity with slight decrease till current measured cycles, which suggests that the long-term cycling or a higher C-rate is needed.

CONCLUSIONS AND FUTURE WORK

Solid polymer electrolytes (SPEs) have been studied as a potential candidate to realize next generation batteries with enhanced safety and breakthrough in energy density. As a special type of SPEs, single-ion conducting polymer electrolytes (SICPEs) have been widely studied due to the feature of almost unity lithium-ion transport number, which is favorable to suppress lithium dendrite growth and extend battery cycle life. However, the relatively low ionic conductivity, especially compared to traditional liquid electrolytes, limit their practical application in batteries. In this study, we explore various strategies that can improve ambient temperature ionic conductivity of SICPEs and the sole effect of lithium-ion transport number on battery performance. The main experimental techniques used were Broadband Dielectric Spectroscopy, rheology, Differential Scanning Calorimetry, and coin cell measurements.

First, a polydimethylsiloxane (PDMS) based SICPE was designed to improve ionic conductivity through the incorporation of soft “PDMS” backbone and flexible polyethylene oxide (PEO) side chains. In comparison to the SICPE with a rigid PMMA backbone, PDMS-*g*-MPA Li_x⁺/PEGMEMA_y showed much faster segmental dynamics and several orders of magnitude higher single-ion conductivity, with PDMS-*g*-MPA Li₁₀⁺/PEGMEMA₃₀ achieving the lithium conductivity of 4.7×10^{-6} S/cm at ambient temperature. The assembled Li/Li symmetric cell of PDMS-*g*-MPA Li₁₀⁺/PEGMEMA₃₀ doped with PC possessed a t_{Li} around 0.85 and showed excellent electrochemical stability against lithium metal electrodes. The present study clearly demonstrates the relationship between the accelerated segmental dynamic and boosted ionic conductivity, which can be applied to achieve high-performance solid state electrolyte.

Employing PEO-like structures is one of the main strategies to improve the ionic conductivity of polymer electrolytes, since they can sufficiently solvate the Li^+ , lower T_g , and accelerate segmental dynamics. Therefore, to explore the potential structures that may surpass the ionic conductivity of PEO-based SICPEs, SICPEs copolymerized with different neutral units have been synthesized and comprehensively studied. Due to the limited miscibility with ionic groups, the neutral units possessing T_g even lower than PEO result in poor solvation of lithium-ions, slow segmental dynamics and limited lithium-ion transport. Moreover, SICPEs with high dielectric constant moieties also have low ionic conductivity at ambient temperature due to the high T_g and slow segmental dynamics. Actually, the similar activation energy for ionic conductivity below T_g indicates the limited influence of copolymerized neutral units on the Coulombic interactions between polymerized TFSI and lithium-ion. In other word, the design of polyanions with a more delocalized charge structure to strongly reduce the activation energy would be another promising method to improve lithium ionic conductivity at ambient temperature.

Although many theoretical models investigate the effect of lithium-ion transport number (t_{Li^+}) on battery performance, the practical case is also strongly influenced by other parameters, such as mechanical property, chemical composition, and ionic conductivity. Herein, a point-to-point study focusing on the sole effect of t_{Li^+} on the battery performance is conducted with plasticized crosslinked PEO membranes having different concentrations and types of lithium salts, i.e., pSI or pDI. Even with relatively lower ionic conductivity, the Li/Li symmetric cell of pSI-20 presented a stable voltage profile over 2200 hours, while the cells of pDI-x either failed after much shorter time of cycling or did not work under the same current density. The SEM spectra clearly demonstrate that the high t_{Li^+} benefits uniform lithium deposition and suppresses

lithium dendrite growth. This guarantees a good contact between the lithium metal electrodes and membrane. Additionally, according to XPS results, the high t_{Li}^+ also reduces the possibility of side reactions consuming the lithium metal electrode, which leads to the formation of a more stable SEI layer. For this reason, the full cell of pSI-20 with a configuration of LiFePO₄ (LFP)/Li could maintain a stable specific capacity till current cycles, while the cells pDI-50 and pDI-100 presented rapid capacity fading, though they all have comparable ionic conductivity. As pDI-20 did not reveal any significant difference in specific capacity with pSI-20, further investigation, possibly with a higher C-rate, is needed.

As mentioned in Chapter 1.4, electrolytes with strong mechanical property possess high resistance over lithium dendrite growth. Due to the crystallization of PEO, some of the PEO-based polymer electrolytes only work at high temperatures, which may results in the loss of mechanical property. Therefore various strategies have been proposed to improve the mechanical property of SPEs, like the construction of block copolymers⁶³⁻⁶⁵ or crosslinking of the membrane.⁶⁶ Use of composite materials is another main method that has been widely studied.^{67, 68, 230} Depending on the conductive property of composite materials, they could be simply categorized as lithium-ion insulative/inert or lithium-ion conducting ceramics. The latter may enhance both mechanical property and ionic conductivity at the same time.⁷⁰ Therefore, we may explore a composite SICPE with both high t_{Li}^+ and mechanical property. However, composite materials may also introduce extra interfaces, voids or defects, where the dead lithium may deposit, accumulate and then sprout out during battery cycling. Therefore, there is still a lot of questions to be addressed in this area.

The self-healing materials have drawn huge attention due to their ability to recover from the mechanical damage and restore the original properties, which have potential application in electronic and energy storage devices. Besides adding extrinsic self-healing agent, self-healing property can be also realized by having non-covalent physical interaction, such as hydrogen bonding and metal-ligand complexation,²³¹⁻²³³ or dynamic covalent bond, like Diels-Alder reaction, disulfide exchange, and boronic ester.²³⁴ Therefore, introducing the above interactions within SICPE structure may endow the ability to recycle and reprocess even after crack or deformation, which may extend the lifetime and improve the cycling stability. Certainly, the healing efficiency of material is a concern for their application in batteries, which needs further investigation.

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