



공학박사 학위논문

# Enhanced electrochemical stability and long-term durability of next-generation LIBs through solid electrolytes

고체 전해질을 이용한 차세대 리튬이온배터리의 전기화학적 안정성 및 수명 특성 향상

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# Enhanced electrochemical stability and long-term durability of next-generation LIBs through solid electrolytes

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Department of Materials Science and Engineering Graduate School Seoul National University Enhanced electrochemical stability and long-term durability of next-generation LIBs through solid electrolytes

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## Abstract

Today, the application field of lithium-ion batteries (LIBs) is not confined to small portable devices and has expanded to medium and large scales like electric vehicles and energy storage systems. However, liquid electrolytes in current LIBs are exposed to the danger of evaporation and ignition because of their low thermal stabstability. Therefore, LIBs as well have the risk of fire and explosion caused by liquid electrolytes. Meanwhile, harsher operation conditions also have put LIBs in jeopardy. As higher energy density and capacity demands increased, LIBs have been required to work until a higher potential range and contain labile materials like lithium metal. LIBs consequently generated more operation heat and were exposed to more side reactions. Eventually, the current volatile safety of LIBs gradually raised concerns for long-term stability and usability. Due to the possibility of huge-scaled accidents, safety is especially regarded as a crucial requirement in LIBs for medium and large devices. Therefore, liquid electrolytes should be replaced with thermally stable electrolytes for safe LIBs. For this reason, there are massive studies on solid electrolytes having thermal stability. This dissertation dealt with these solid electrolytes overall and discussed three studies aimed at the electrochemically stable operation of LIB systems with these solid electrolytes.

We dealt with solid-state polymer electrolytes (SPEs) first. SPEs have a chronic problem with low ionic conductivity at low temperatures. In this study, poly(ethylene oxide)(PEO)-based polymeric structure having poly (propylene oxide)(PPO) units was designed. SPEs having the designed polymeric structure showed

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better ionic conductivity at low temperatures and electrochemical stability. We next discussed the combination of SPEs having better electrochemical performance. Conclusionally, we verified that poly(propylene oxide) is helpful to enhance the electrochemical performance of poly(ethylene oxide)-based SPEs.

In a second study, we combined ionic liquid and solid-state polymer electrolyte (SPE) and then attempted to secure high thermal stability and ionic conductivity together. Typically SPEs had significantly low ionic conductivity below 0.1 mS cm<sup>-1</sup>. Thus, gel polymer electrolytes (GPEs) can be a compromise between SPEs and liquid electrolytes. A crosslinker having an ionic liquid-based structure was synthesized in this study, and a GPE was fabricated using this crosslinker. As a result, the GPE showed better electrochemical and thermal stability than a liquid electrolyte and GPEs having a PEO-based polymer network.

Additives for sulfide-based inorganic solid electrolytes (ISEs) were thirdly explored. Two type materials of polymer electrolytes and carbon conductive additives were chosen and introduced to a cathode of a sulfide-based cell. Polymer-based additives are aimed at protecting cathodic materials from harmful reactions and supplement ion transport loss caused by voids in the cathode. On the other hand, another additive in this study, electronic conductive carbons are necessary materials to raise energy density by thickening a cathode. Through this study, electrochemically stable additives with sulfide-based ISEs were found. The excellent effectiveness of polymer additives as a buffer layer was then

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confirmed. In addition, a carbon material that is less reactive to sulfide-based ISEs could be selected.

In summary, this dissertation suggested a method to secure better electrochemical stability and the long-term lifespan of solid electrolyte LIBs. While supplementing the shortcomings of each solid electrolyte, better electrochemical performance was achieved by introducing various methods and strategies. Even though solid electrolytes have shortcomings given a pause to a real application, the introduction of a solid electrolyte is unavoidable to secure the safety of LIBs. Thus, this dissertation will be helpful to enhance the performance and advance the commercialization of solid electrolytes. Furthermore, it is anticipated that the safety of LIBs will be greatly improved by applying solid electrolytes through methods and strategies dealt with in this dissertation.

**Keywords** : Solid electrolyte, Polymer electrolyte, Sulfide-based Inorganic electrolyte, Solid-state battery, Next generation lithium ion battery

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## **Chapter 1. Introduction**

### 4.1. Background

Now batteries are recognized as an essential power supply for wireless devices like portable appliances, electric vehicles, and energy storage systems. Technological advances have led to higher performance and longer operation times for devices. Along with this trend, batteries have also progressed to provide higher power to the device for longer times. Many industrial fields have utilized various types of batteries based on lead acid or NiMH. However, the everincreasing requirements for batteries with higher energy density were connected to the demand for lithium-ion batteries (LIBs). Therefore, since Sony's commercialization in 1991, LIBs have gradually expanded their application scope from small appliances to electric storage systems (ESS). [1–3]



**Figure 1-1** Estimated second-life EV battery supply by region and utility-scale demand change between 2020 and 2030 by McKinsey and Company. <u>Figures gained from reference</u> [3]

#### Battery energy

State-of-the-art specific energy of Li-ion cells in academic research



**Figure 1-2** As of February 2021, the best example of a high-energy Liion cell has been reported by the Battery500 Consortium. It is a pouch cell with commercially relevant capacity (2.0 Ah) and cycle life (~350 cycles, tested at C/10 charge and C/3 discharge). The cell has a specific energy of 350 Wh/kg and is based on Li-metal a node and NMC (or NCM) cathode chemistry. <u>Figures gained from reference</u> [4] The downsizing and densification of components are improving the portability and spatial efficiency of the wireless device. Besides, LIBs in the device are being advanced to provide maximum performance at a minimal volume, as with other parts. [4,5] Multiple materials have been used for a higher energy density of LIBs. Cathodic materials are designed to accommodate more energy and work at a broader potential range. Active materials of layered crystal structures like LiNiCoMnO<sub>2</sub> or LiNiCoAlO<sub>2</sub> are representative.[6–8] On the other hand, high reversible capacity and low redox potential are requisite for anodic materials. Graphite[9–11] or silicon–based[12–14] anodic active materials are being studied most actively. However, the utilization of lithium metal in the anode is also an ongoing research topic for increasing the energy density of LIBs.[15–17]

As an ionic connector between both electrodes, electrolytes should fulfill several requirements to enhance the energy density of LIBs. First, electrochemically stable electrolytes allow for the operation of LIBs in broader potential ranges.[18–20] Active materials with a layered-crystal structure serve more capacity as higher as operating potentials. Therefore, the electrochemical stability window of electrolytes has to cover the cut-off potential of LIB to ensure stable operation. Meanwhile, to increase the volumetric energy density, the unit cell of LIBs are arranged densely. Thus, heat generated during LIB operation might be released insufficiently due to too-densified cell arranges. Operation heat accelerates the side-reaction of components in LIBs, as well as electrolytes. Besides, the side reaction might produce electrolyte vapors or flammable gases.[21– 23] This problem hugely threatens the safety of electric automobiles, which are exposed to impact and fire. Hence, applying thermally

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stable electrolytes is suitable to secure the safety of LIBs while improving energy density. However, current liquid electrolytes consist of organic solvents having low flammable points and high vapor pressures (Table 1-1). These organic solvents are improper for the safe operation of LIBs, as the reasons mentioned above. Thus, it is important to use electrolytes that satisfy electrochemical- and thermal stability at the same time. [23–26]



**Figure 1–3** A scheme of the roadmap for Li battery technology. <u>Figures</u> gained from reference [18]

	substance	Acronym	Flash point ℃	SET s g <sup>-1</sup>	Vapor pressure (25 ℃), kPa	Boiling point ℃
	Dimethyl carbonate	DMC	16 ±1	122 ±4	8.0	90.5
	Ethyl acetate	EA	0.5 ±1	98 ±4	14.3	77.1
	Ethyl methyl carbonate	EMC	23.5 ±1	143 ±11	3.9	107
Solvent	Diethyl carbonate	DEC	33 ±1	158 ±17	2.4	126
	Vinylene carbonate	VC	73 ±1	159 ±8		162
	N,N-Dimethylformamide	DMF	58 ±1	161 ±13		153
	Ethylene carbonate	EC	145.5 ±4	-		248
	EC:DMC (1:1 wt)	EC:DMC	25 ±1	44 ±2	4.8	
	EC:EMC (1:1 wt)	EC:EMC	32 ±1	48 ±3	2.9	
	EC:DEC (1:1 wt)	EC:DEC	39 ±1	55 ±7	1.9	
Mixture	1M LiPF <sub>6</sub> / EC:DMC (1:1 wt)	LP/EC:DMC	25.5 ±1	42 ±3	4.4	
(Electrolyte)	1M LiTFSI/ EC:DMC (1:1 wt)	LT/EC:DMC	26 ±1	38 ±5	4.9	
	1M LiPF <sub>6</sub> / EC:EMC (3:7 wt)	LP/3EC:7EMC	28 ±1	59 ±2	3.3	
	1M LiPF <sub>6</sub> / EC:EMC (1:1 wt)	LP/EC:EMC	31 ±1	46 ±5	2.6	
	1M LiPF <sub>6</sub> / EC:DEC (1:1 wt)	LP/EC:DEC	38 ±1	59 ±4	1.7	

Table 1-1 Flashpoints, self-extinguishing times, vapor pressures (at 25 ℃), and boiling points of various solvents, solvent mixtures, and electrolytes. The information reorganized from [25]

#### 4.2. Needs for Solid-state Electrolytes (SSEs)

Solid-state electrolytes (SSEs) have been studied to replace the liquid electrolyte and stably operate LIBs at higher temperatures. SSEs consist mainly of solid-state polymers or inorganic materials that are thermally stable and resistant to fire.[27–29] These materials for SSEs also have high ionic conductivity above ~ 0.01 mS cm<sup>-1</sup> and less electric conductivity.[30,31] Furthermore, SSEs have excellent mechanical strength sufficient to suppress lithium dendrite growth.[32] Therefore, in SSE-LIB systems, the lithium metal anode can be operated with keeping uniform surface morphology for a long time.[33] For these reasons, SSEs introduction might be a way to the safety and better performance of next-generation LIBs.

Meanwhile, most liquid electrolytes are less-viscous, thus readily permeating electrodes inside and forming sufficient interfaces with electrode materials. [34] Contrastively, SSEs have difficulty in interface formation with other components due to their firmness. Thus, SSEs have been applied by various strategies to maximize interfaces. Inorganic solid electrolytes (ISEs) are pressurized to contact as possible with other components.[35,36] Meanwhile, polymer electrolytes (PEs) can be applied in a state of the liquid precursor in the cell assembly process.[37,38] Aside from these, many studies are being suggested various methods to make enough interfaces of SSEs.[39,40]

Even if SSEs need a further process to form sufficient interfaces with other materials, the benefits obtained by SSEs introduction are considerable. First, SSEs with high ionic conductivity [41–43], such as sulfide-based ISEs, allow faster charging and discharge rates. [44]

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As the demand for electric vehicles increases, shortening charging time becomes a weighty requirement of LIBs to substitute the internal combustion engine. Meanwhile, chemically- and electrochemically stable SSEs, like oxide-based ISEs, have sufficient compatibility with various types of materials. [45,46] These SSEs can combine with various materials, and supplement their shortcomings while gaining additional functions. Finally, flexible PEs are suitable for utilization in portable and wearable devices. [47] PEs are relatively lighter than other types of SSEs and easy to fabricate free-form LIBs.

#### **4.3.** Gel Polymer Electrolytes (GPEs)

Gel polymer electrolytes (GPEs) might be an alternative that enhances the safety of LIBs and mediates liquid electrolytes to SSEs. GPEs are typically soft but seldom flowable, like puddings. GPEs compose of a liquid-state ionic conductor and a porous membrane. The membrane confines the liquid-state ionic conductor and impedes the flowing off them. [48] Besides, as the membrane suppresses the vaporization of the ionic conductor, GPEs can be thermally stable. Thus, the membranes should consist of thermally stable materials such as PVdF[48] and PAN[49] or PEO[50]-based materials. On the other hand, current liquid electrolytes are also available as ionic conductors in GPE. Liquid electrolytes have guaranteed their excellent ionic conductivity for a long time. Ionic liquids with good thermal and electrochemical stability can also be applied to GPEs. [51,52] Ionic liquids are suitable materials for enhancing the thermal stability of GPEs. Through various combinations of membranes and liquid ionic conductors, GPEs can be optimized to enhance the performance and properties of LIBs. [53]

Meanwhile, there are some requirements, GPEs should satisfy. Above all, thermal- and electrochemical stability are necessary factors.[50] However, depending on the application of GPE, other properties are additionally asked. In the ex-situ GPEs, the mechanical strength is highlighted because ex-situ GPEs are usually prepared in the shape of a free-standing membrane as a prefabricated state. Besides, ex-situ GPEs should not be torn or shattered during the cell assembly process.[54,55] How much liquid ionic conductors can be held is also important for ex-situ GPEs.[48]

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On the other hand, in-situ GPEs are prepared in a precursor of liquid mixtures. [37] The precursor of in-situ GPEs is injected during the cell assembly process like liquid electrolytes. In the fabrication of in-situ GPEs, a separator is also necessary for cell assembly. Thus, the liquid-state precursor of in-situ GPEs should be soaked well into a separator and electrodes. [56,57] Consequently, after additional processes such as heating [58] or UV [59], finished in-situ GPEs have to form sufficient interfaces with electrode components. Which GPE fabrication method is applied can be determined according to each characteristic of GPEs mentioned above. The ex-situ GPE allows continuous fabrication with a relatively easy process of stacking them with other cell components. However, the completed ex-situ membrane has some hardness, thus it is difficult to penetrate through electrodes. [37] Hence, it is necessary to use electrodes of low loading density or include ionic conductive materials in electrodes. Meanwhile, in-situ GPEs can secure sufficient interfaces with electrodes of high loading density as liquid-state precursor applying.[60]

#### 4.4. Solid-state Polymer Electrolytes (SPEs)

Solid-state polymer electrolytes (SPEs) are a candidate to solve the safety issue in current LIBs. SPEs consist of high molecular polymers, which play the role of ionic conductors [61,62] or membranes [50,63], and lithium salts. [64] Therefore, compared with liquid electrolytes. SPEs are thermally more stable and safe at high temperatures. [65,66] Furthermore, SPEs are harder than GPEs but more flexible than inorganic solid electrolytes. [67] That is, SPEs have excellent applicability for various industrial fields. The paramount advantage of SPEs is the designable polymer structure according to desired physical- and electrochemical properties.[68] Since polymeric chains in SPEs transport ions by their segmental movement and interaction with lithium ions. SPEs can have different electrochemical performances depending on the type of ionic conducting polymer.[69] For instance, poly(ethylene oxide) (PEO), which is the most representative SPE material, has high ionic conductivity but low electrochemical oxidation potential. However, poly (propylene oxide) and poly (ethylene carbonate) have relatively low ionic conductivity but better electrochemical stability at high potentials than PEOs. [70] Meanwhile, various polymers for the membrane in SPEs can be applied. Not only non-conductive polymers like PVdF[71,72] and PAN[73] but ionic-conductive polymers [74] can be applied as membrane material. Membrane fabrication of SPEs proceeds in ex-situ or in-situ fabrication, similar way to GPEs, but SPEs fabricated have different characteristics from GPEs. First, SPEs do not come out of the liquid component by external pressure and have enough mechanical strength to be molded

with a knife or scissors. [67] Second, the main agents of ionic transfer are polymeric chains. Hence, characteristics of ionic conductive polymer chains are the decisive factor for the performance of SPEs and cells. [75] Third, SPEs might have the crystallinity by physical properties of polymer ionic conductors, unlike GPEs. The higher the molecular weight of ionic conductors, the easier SPEs tend to crystallize at room temperatures. When SPEs are crystallized and solidified, polymer chains are fixed with each other and have difficulty transferring lithium ions. [69] Finally, the physical properties of SPEs can be designed by controlling polymeric structure and combining various polymers. [76–78]. Since SPEs can have elasticity and flexibility together, these properties of SPEs are suitable for LIBs in portable devices, such as health care and wearable appliances. [79]

#### 1.1.1 Poly(Ethylene Oxide)-based SPEs

Poly (ethylene oxide) (PEO) - based polymers have been currently utilized in many studies as ionic conductors. Furthermore, due to good solubility in lithium salts, PEO-based SPEs have also been studied for a long time. [80] The base chemical structure of PEO is  $H-(O-CH_2-CH_2)_n-OH$ , but terminal groups of -H and -OH might occur in side reactions with other components of the cell, such as lithium metal.[81] Hence, some literature replaces terminal groups of PEO with methyl groups or others. Meanwhile, PEOs with higher molecular weight have increased toughness and lowed elasticity. [82,83] Hence, PEO alone can be sufficiently fabricated to freestanding SPEs by controlling polymer structures. However, as the higher the molecular weight of PEOs, the ionic conductivity is conversely decreased due to the slower motion and the crystallization of polymeric chains. [84,85] The crystallization at room temperatures, where we mainly use devices and LIBs, is the biggest problem with the practical application of PEO-based SPEs. Crystallized PEO-based SPEs typically show ionic conductivity below 1/1000 of the liquid electrolytes. [69] For enhancing the ionic conductivity of PEO-based SPEs, strategies to decrease the crystallinity of PEO are required.

There seem to be mainly two ways to lower the PEO crystallinity: additive introduction and polymeric structure designing. [86] Both methods aim to increase the amorphous phases in PEO by reducing the interaction between PEO chains. Additives at SPEs refer to other types of polymers and inorganic materials. Lithium salts also can be recognized as a kind of additive that affects the crystallinity of PEObased SPEs. [87] However, PEO-based SPEs have optimal ionic conductivity at particular lithium salt concentrations. [88] Thus, there is some restriction on applying lithium salts to decrease PEO's crystallinity. On the other hand, polymeric structure design means synthesizing the PEO of multi-arm or attaching different types of polymer units to PEO-based polymers.[77] However, it has to be noted that excessive application of both methods might decrease the ionic conductivity more than PEO alone and increase the cost and preparation times.[89,90]

#### 1.1.2 Additive for PEO-based SPEs

Various kinds of additives have been applied to PEO-based SPEs for performance enhancement. Additives affect the electrochemical performances of SPEs and the interfacial resistance and surficial properties of electrodes.[91,92] In particular, additives might help suppress the dendritic growth of lithium metal, which is one of the anodes in next-generation LIBs.[93] In addition, easy process is the most significant advantage of additive introduction to PEO-based SPEs. By the simple preparation of mixing with PEOs, additives introduction can easily control the properties and performance of PEO-based SPEs.[90,94] In this light, ceramics and polymers have been mainly addressed in many studies as suitable additives that bring good electrochemical and physical properties for PEO-based SPEs.

The advantages of ceramics and inorganic-based additives are based on their excellent mechanical strength.[64], [95,96] Among them, representative materials of inorganic-based additives are Al<sub>2</sub>O<sub>3</sub>[96], ZnO<sub>2</sub>[97], and CuO[98] of nano-scaled. Ionic conductive ceramics such as LLZO are also appropriate materials for an additive of PEO-based SPEs.[99] Inorganic additives' mechanical strength physically suppresses the dendrite growth on the lithium metal anode. [93] As a result, by preventing uneven surfaces and detachment of lithium metal, the cell consisting of lithium metal anode and PEObased SPEs can prolong its lifespan.[99] However, it is difficult to
uniformly disperse inorganic additives into PEO because inorganic powders of nano-size aggregate easily.[100]

Polymer additives mixing well within PEO can efficiently suppress the crystallization of PEO. It is possible by creating uniform amorphous phases that interact differently between polymeric components.[86] The polymer additives such as cellulose[101], PVdF[102], and PFPE[103] enhance mechanical strength and thermal stability. Meanwhile, PEOs have relatively low electrochemical oxidation stability compared to other polymers. [64,70] Thus, PEO-based SPEs should be enhanced in electrochemical stability. Besides, this electrochemical enhancement is accorded with the current tendency to increase the operating voltage of LIBs for energy density. For electrochemical improvement, higher poly (ethylene carbonate) (PEC) [104] and poly (propylene oxide) (PPO) [105] are suitable additives to enhance the electrochemical stability of PEO-based SPEs. In addition, the electrochemical- and physical properties of the PEO-based SPEs can be controlled as the type or combinations of lithium salts. [106] Organic materials like ethylene carbonate [84], propylene carbonate [107], and ionic liquids[108] can also increase the ionic conductivity of highmolecule PEO-based SPEs.

#### **1.1.3 SPEs with the complex structure**

Below crystallization temperatures, the linear PEO easily becomes less active and solidifies by interacting with other PEO chains. [109] Aggregated ionic conducting chains within a crystalline phase have limits in the segmental movement to transfer lithium ions. As a result, it is necessary to find a means to create free volume and prevent PEO aggregation; adding different kinds of materials is one such method, as mentioned above. As another approach, the polymeric structure design of PEO is also an effective strategy for weakening the cohesion between PEO chains. [110,111] It is possible to prevent PEO crystallization by designing PEOs without additional dispersing or mixing techniques to create a homogeneous phase. Thus, in order to obtain even quality and performance of SPEs, without worrying about phase separation, the PEO structure design is a useful tool. The PEO structure design primarily uses two techniques to improve the performance of PEO-based SPEs: connecting other types of polymer with PEO[78] and synthesizing a multi-arm structure of PEO[112].

First, other types of polymer units can be grafted into the PEO structure. Polymer units in the PEO structure can be configured like AB, ABC, alternating, or random. [86] Introduced polymer units form partially different interactions in an ionic conductive chain. Due to these partial interaction differences, ionic conductive chains are hard to be entangled each other. [113] As a result, heterogeneous polymer chains in the PEO can transfer lithium ions easier, and hence the ionic

conductivity and electrochemical performances can be improved. [114,115]

On the other hand, designing the PEO structure to multiple arms is also a helpful method for preventing the crystallization of PEO-based SPEs.[112] Due to structural characteristics, PEO with three or more branches densify less at low temperatures and thus have lower crystallization temperatures than linear PEOs.[116,117] Besides, as more branches in PEO-based SPEs, easier to generate amorphous phases with decreased density between PEO chains. Consequently, PEO-based SPEs having a complex structure have higher ionic conductivity and a softer phase at room temperature than linear PEO of the same molecular weight.[118] By attaching other types of polymers to PEO arms, multi-arms PEO can be a more effective way to improve the electrochemical and physical properties of PEObased SPEs.[86]

# 4.5. Inorganic solid-state electrolytes (ISEs)

Achieving high ionic conductivity of electrolytes is an essential objective to maximize the performance of LIBs. Liquid electrolytes have satisfied this requirement and be applied to current LIBs.[119] However, LIBs had steady demands to secure more capacity and high operating voltage ranges for raising energy density. Furthermore, fast charging times as well have been required in automobile fields. [19] As these requirements put LIBs into harsher operating conditions, LIBs are easily exposed to side reactions. In the meantime, the problems of liquid electrolytes such as low flash points and vaporization by side reaction were raised.[22,120] Although SPEs have attempts and studies to replace liquid electrolytes, their low ionic conductivity still delays the practical application.[121] these backgrounds nowadays have motivated the development of inorganic-based electrolytes (ISEs).

ISEs consist of inorganic superionic conductors.[122] There are various types of inorganic superionic conductors like nitrides[123], hydroxides[124], oxides[125], and sulfides[35]. Among them, oxide- or sulfide-based materials have been mainly studied for LIBs. [126,127] By ISE introduction, LIBs can be entirely configured in hard solid phases, called all solid-state batteries (ASSBs). ASSBs have better structural- and thermal stabilities, thus appropriate to enhance the safety of LIBs.[128,129] Firstly, ISEs can exclude a non-conductive separator, which causes the incomplete performance of electrolytes. High mechanical strength of ISEs is enough to suppress the dendritic growth of lithium and prevent a physical short circuit of electrodes.[130] Furthermore, ISEs rarely evaporate at high temperatures. Hence, ISEs might dispel worries about the volume expansion and explosion of the LIB package.[126] That is, ISEs have distinct advantages to replace the liquid electrolyte. For instance, oxide-based ISEs have wide electrochemical stability windows.[131] Sulfide-based ISEs have high ionic conductivity close to that of liquid electrolytes.[132] Consequently, ISEs might be a component indispensable to developing next-generation LIBs.

#### 1.1.4 The problems of ISEs

Unlike liquid electrolytes or the precursor of SPEs, the void between SEs and active materials might be unfilled gaps due to the nonfluidity of ISEs.[133,134] Because ions cannot move across voids, the gap between constituent powders decreases ionic conductivity and increase the whole resistance in the cell. Therefore, in order to minimize the remaining voids, pressing all of the cell components with great pressure is necessary.[135] In particular, hard oxide-based ISEs should be undergone an annealing process to remove stress and defects in the ISE powder generated during the pressing.[136] The need for pressing is a big difference in the manufacturing process of other types of electrolytes. Since the pressing process increases costs and difficulty in manufacturing, it requires studies on methods to maximize interfaces of ISEs with minimized pressure and time.

Furthermore, the volume changes occur repeatedly in the ISEs powder during the charge and discharge period, like the electrode materials.[137] These repeated volume changes of ISEs and electrode materials cause the pulverization of interfaces and powder themselves.[138-140] Continuous pulverization generates the voids and the gap in interfaces and incurs the performance degradation of the cell due to decreased ion transport path.[140] Therefore, buffer layers between electrode materials and electrolyte powders might release the damage by pulverization. In addition, the interface pulverization might be minimized through the controlled morphology of electrode and electrolyte powders.[86,141]

On the other hand, the ductility of sulfide-based ISEs makes it possible to fabricate the cell without an annealing process after the pressurization. [142,143] However, due to the low electrochemical oxidation stability of sulfide-based ISEs, usable materials and fabrication methods in sulfide-based ASSB are limited.[134] In particular, the reactivity with lithium metal anode for enhancing the cell's energy density is one of the problems. [144] In order to apply lithium metal into sulfide-based ASSBs, the surface of lithium metal should be modified and protected through alloying and passivation layers using other metals (In[145], Sn[146], Al[147]) and Furthermore, the polymers[148,149]. local concentration distribution of ions at interfaces might accelerate side-reactions of sulfide-based ISEs, and followed side-reaction at the interface increases the inner-impedance of the cell.[149] Therefore, the study on both side-reaction prevention and suppression at interfaces is necessary to realize sulfide-based ASSBs.

## 1.1.5 Sulfide-based ISEs

Even though sulfide-based ISEs are electrochemically unstable and vulnerable to moisture and atmosphere, their high ionic conductivity closed to liquid electrolytes is an attractive advantage to replacing liquid electrolytes. [150] Many studies have reported sulfide-based ISEs having super-high ionic conductivity such as  $Li_{10}GeP_2S_{12}$  [151], Li<sub>9.54</sub>Si<sub>1.74</sub>P<sub>1.44</sub>S<sub>11.7</sub>Cl<sub>0.3</sub>[152], and Li<sub>5.5</sub>PS<sub>4.5</sub>Cl<sub>1.5</sub>[153]. These ISEs exhibited ionic conductivity above 10 mS cm<sup>-1</sup>, and which were superior performance to the ionic conductivity of liquid electrolytes. Therefore, sulfide-based ISEs attract interest and expectations for ASSBs introducing sulfide-based ISEs. The crystal structural factor of sulfide-based ISEs for high ionic conductivity has also been analyzed. [154,155] According to the literature, the movement of lithium ions between tetragonal sites in the sulfide-based ISEs has lower activation energy and faster diffusion of lithium ions than in other directions. This tendency was verified using DFT and shows a somewhat consistent trend in actual sulfide-based ISEs.

## 1.1.6 The Cathode of sulfide-based ASSBs

The problems in sulfide-based ASSBs mainly occur at the cathode. [156] Cathodes in sulfide-based ASSBs consist of various materials of active material, a conductive additive, and sulfide-based ISEs. These constituents differ in shape and physical and electrochemical characteristics.[157] Therefore, physical and electrochemical interfacial problems are more pronounced in sulfide-based ISEs than in other electrolytes. As a physical approach, to removing voids in the cathode, pressing pressure and time can be controlled in cell fabrication. [158] However, over-pressurization and long pressing times can shatter cathodic components including active material, and bring inefficient fabrication process.[159] Meanwhile, repeated volume changes in cathodic materials might break the interfaces between cathodic materials and make spatial gaps that interrupt mass transfer.[137] Therefore, it is needed to explore appropriate materials for improved fabrication processes and physical protection of interfaces in the cathode.

Additionally, the side reaction between cathodic materials also increases the inner resistance of the cell and then lowers the performance of sulfide-based ASSBs.[133] Many studies have reported on the electrochemical reaction between oxide-based active materials in particular. Transition metal ions in NCA or NCMbased active materials can be eluted into the sulfide-based ISEs.[160] The crystal structure of active materials is consequently distorted during repeated charging/discharging processes.[161] Furthermore, the chemical reaction between conductive additives and sulfide-based ISEs has also been reported.[162,163] Conclusionally,

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these chemical- and electrochemical phenomena in sulfide-based cathodes impede the stable operation of sulfide-based ASSBs. Therefore, searching for proper compositions of cathodic materials is required for the long-term working of sulfide-based ASSBs.

# 4.6. Research objectives

This dissertation mainly handled the way to secure performance enhancement and electrochemical stability of the cell based on solid electrolytes, which are studied to replace commercialized liquid electrolytes. As substitutes for liquid electrolytes, solid electrolytes should be thermally and electrochemically stable. However, their shortcomings, such as interfacial problems and low ionic conductivity, postpone the practical application of solid electrolytes. Therefore, this dissertation aimed to complement these weaknesses of solid electrolytes while securing the long-term cycle stability of cells containing them.

First, chapter 2 introduced PEO/PPO copolymer-based SPEs. In this chapter, poly (propylene oxide) (PPO) was applied to a polymeric structure of PEO for electrochemical improvement of PEO-based SPEs. We confirmed the effectiveness of PEO/PPO copolymers in the aspect of the improvement of crystallinity suppression and ionic conductivity in low temperatures. In addition, the electrochemical stability of PEO/PPO-copolymer SPEs was also evaluated. After then, by mixing PEO/PPO plasticizer and PEO plasticizer, we tried to optimize the performance of SPEs. Finally, Using NCM622 cells, we tried to confirm the electrochemical properties of optimized SPEs by practical application.

The next chapter 3 dealt with the GPE prepared by in-situ thermal crosslinking of the ionic liquid-based crosslinker. In this study, we synthesized the ionic liquid having an EO unit and cross-linkable end group. The synthesized ionic liquid(IL2) was used as a crosslinker for GPE fabrication. We verified whether IL2 keeps its good thermal

stability and electrochemical stability even if it is crosslinked state. Furthermore, to maximize the performance of IL2–GPE, we fabricated HIL2–GPE, which has a higher ratio of a liquid ionic conductor, by introducing an additional crosslinker. The electrochemical performance of HIL2–GPE was tested to check the effect of the amount of an ionic conductor.

The final chapter 4 is on additives in the sulfide-based cathode. We introduced two types of additives for the cathode. As the first additives, ionic-conductive polymers were considered. We attempted to find suitable polymer materials as a buffer material or a protection layer for cathodic materials. To this end, various ionic-conductive polymers were evaluated the electrochemical stability and performance. Meanwhile, as another additive, various electronic-conductive carbon materials with different shapes were evaluated. After the physical and chemical states were analyzed, we confirmed whether their intrinsic characteristics affect electrochemical performance.

# Chapter 2. Stable cycling of lithium polymer battery enabled by in-situ cross-linked ethylene oxide/propylene oxide copolymer electrolytes with controlled molecular structures

# **2.1. Introduction**

Solid-state polymer electrolytes (SPEs) with flame-resistivity and mechanical strength are considered promising alternatives to overcoming the inherent safety problem of the liquid electrolyte.[164,165] In addition, its softness and flexibility allow SPE to be compatible with the roll-to-roll fabrication process, which is a significant advantage over solid inorganic electrolytes from a manufacturing point of view. For the realization of SPE-based batteries, however, several issues such as ionic conductivity, interfacial resistance, and electrochemical stability should be addressed.[166,167]

Herein, we report a 4 V class lithium polymer battery showing stable long-term cycling by incorporating in situ crosslinked ethylene oxide (EO)/propylene oxide (PO) copolymer electrolytes. The SPEs were prepared by thermal crosslinking of a mixture of crosslinkers and plasticizers to form a polymer network structure and the plasticizers transport lithium ions within the networks. The crystallization behavior and ionic conductivity of the SPEs were optimized by controlling the molecular weight and structural morphology of the plasticizers and introducing EO/PO groups into the SPEs. Electrochemical stability was also enhanced by using the EO/PO copolymer SPEs, making the SPEs compatible with the high-Ni NCM cathode. The in situ crosslinking method, in which a liquid precursor first wetted the electrode and was then solidified by consecutive thermal crosslinking, allowed the SPEs to penetrate the 60  $\mu$ m-thick electrode and minimize interfacial resistance with the electrode. The resulting 4 V class lithium polymer battery performs stable cycling with a marginal fading in capacity for as long as 100 cycles

# 2.2. Experimental

## 2.2.1 Preparation of plasticizers and crosslinkers

EOPL-1000, which is poly (ethylene glycol) dimethyl ether with an average molecular weight of 1014 g mol<sup>-1</sup> and a PDI of 1.22, was purchased from Sigma-Aldrich Korea. EOPL-500, EOPLM-1000, and EOCL were provided by Hannong Chemicals Inc. The EO/PO block plasticizers (POPL-1000 and POPLM-500) and cross-linker (POCL) were synthesized by the following procedure.

#### 2.2.2 Synthesis of POPL-1000

Methanol (32.0 g, 1.0 mol) and potassium hydroxide (1.0 g, 17.8 mmol) were added into an autoclave under a nitrogen atmosphere. The autoclave was heated to 140 °C with the internal pressure regulated at 2–4 kgf cm<sup>-2</sup>. EO (638 g, 14.5 mol) was continuously added into the reactor for 5 h, and then, PO (366 g, 6.3 mol) was subsequently added for another 5 h. After further reaction for 3 h, an intermediate product was obtained. The intermediate (517.5 g, 0.5 mol) and sodium hydroxide (9.6 g, 0.24 mol) were mixed into a 1 L flask and then dehydrated under vacuum at 80 °C for 1 h. Under a nitrogen atmosphere, dimethyl sulfate (75.5 g, 0.6 mol) was added dropwise into the flask at 50 °C. After the reaction was completed, the mixture was neutralized by adding sulfuric acid and then dried under vacuum at 100 °C. After filtration to remove the solid byproduct, POPL-1000 was obtained as a colorless liquid (495 g).

The average molecular weight and PDI of POPL-1000 were 1050 g mol<sup>-1</sup> and 1.06, determined using GPC (Waters 2690), respectively. FTIR (cm<sup>-1</sup>): 2860 (s, C-H), 1100 (vs, C-O). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 3.32-3.04 (m), 0.82 (m, CH-CH<sub>3</sub>).

## 2.2.3 Synthesis of POPLM-500

Trimethylol propane (134.17 g, 1.0 mol) and potassium hydroxide (1.0 g, 17.8 mmol) were added into an autoclave under a nitrogen atmosphere. The autoclave was heated to 140 °C with the internal pressure controlled at 2-4 kgf cm<sup>-2</sup>. EO (317 g, 7.20 mol) was continuously added for 5 h, and then, PO (82 g, 1.41 mol) was added for 2 h. After another 3 h of reaction, an intermediate product was obtained. The intermediate (500 g, 0.94 mol) and sodium hydroxide (54 g, 1.35 mol) were added to a 1 L flask and then dehydrated under vacuum at 80 °C for 1 h. Under a nitrogen atmosphere, dimethyl sulfate (426 g, 3.38 mol) was added dropwise into the flask at 50  $\,^\circ\,$  C. After the reaction was completed, the mixture was neutralized by adding sulfuric acid and then dehydrated under vacuum at 100  $^{\circ}$  C. After filtration to remove the solid byproduct, POPLM-500 was obtained as a colorless liquid (496 g). The average molecular weight and PDI of POPLM-500 were measured to be 570 g mol<sup>-1</sup> and 1.05 using GPC, respectively. FTIR (cm<sup>-1</sup>): 2860 (s, C-H), 1100 (vs, C-O). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 3.34–2.93 (m), 1.06 (q, CH<sub>2</sub>–  $CH_3$ ), 0.83 (m, CH-CH<sub>3</sub>), 0.55 (t, CH<sub>2</sub>-CH<sub>3</sub>).

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## 2.2.4 Synthesis of POCL

The intermediate (400 g, 0.75 mol), which was prepared for the synthesis of POPLM-500, and acrylic acid (180 g, 2.50 mol) were dissolved in toluene (360 g). Methansulfonic acid (10 g, 0.10 mol) and hydroquinone (0.7 g, 6.36 mmol) were added to the solution. The mixture was refluxed for 12 h. After the reaction was completed, the solvent and water were removed by vacuum. After filtration, multiarm EO/PO cross-linker POCL was obtained as a colorless liquid (493 g). The average molecular weight and PDI of POCL were measured to be 690 g mol<sup>-1</sup> and 1.06 using GPC, respectively. FTIR (cm<sup>-1</sup>); 2868 (s, C-H), 1720 (vs, C—O), 1636 & 1617 (m, C—C), 1100 (vs, C–O). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 6.18 and 5.63 (m, CH—CH<sub>2</sub>), 5.93 (m, CH—CH<sub>2</sub>), 4.09–3.10 (m), 1.25 (m, CH<sub>2</sub>-CH<sub>3</sub>), 1.06 and 0.93 (m, CH—CH<sub>3</sub>), 0.66 (t, CH<sub>2</sub>-CH<sub>3</sub>).

#### **2.2.5 Preparation of polymer electrolytes**

A homogeneous liquid-state precursor was prepared by mixing the cross-linkers, plasticizers, lithium bis(trifluoromethanesulfonyl) imide (Sigma-Aldrich), and a thermal initiator t-butyl peroxypivalate (Seki Arkema Co., Japan). The precursor was then solidified by thermal cross-linking at 90 °C for 30 min, resulting in SPEs. The cross-linker and plasticizer were mixed at a weight ratio of 2:8. The thermal radical initiator was added at 2 wt % with respect to the cross-linker. The lithium salt was dissolved in the SPE at a molar ratio of [Li<sup>+</sup>] to [EO] of 1:15. All the processes for preparing

the polymer electrolytes were performed in an Ar-filled glovebox or drying room.

## 2.2.6 Preparation of lithium polymer cells

Ni-rich LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> (LG Chem, Korea) or LFP (Hanwha Chemical, Korea) was used as the positive electrode. Lithium metal (Honjo Metal Co., Japan) was used as the negative electrode. An electrospun membrane with 70% porosity and a thickness of 30  $\mu$  m was obtained from Amogreentech Co. (model: Nano Membrane). It was used as a supporting separator membrane of the polymer electrolyte. The membrane was wetted with the liquid-state precursor and then placed between the positive and negative electrodes during the cell assembly. After a sufficient time for the precursor to be soaked into the electrodes elapsed, it was solidified via in situ cross-linking by placing the cell in the oven at 90  $^{\circ}$ C. The cross-linking reaction was confirmed using an FT-IR spectrometer (Nicolet 6700, Thermo Fisher Scientific Inc.). For a cross-sectional image, the electrodes were cut using a sharp knife, and then, the cross section was observed by FESEM (XL30S FEG, Philips). In this study, we used a coin cell of the 2032 type and a pouch cell with 3  $\times$  4 cm in size. The charge/discharge cycling test was performed on a multichannel battery tester (WBCS Battery Cycler, Wonatech Co.) at 60 °C. It should be noted that the separator-supported SPE shows approximately 50% of the ionic conductivity of the SPE itself. For example, the separator-supported POSPE-2 exhibits  $1.41 \times 10^{-4}$  S cm<sup>-1</sup> at 25 °C, whereas POSPE-2 shows 2.82  $\times$  10<sup>-4</sup> S cm<sup>-1</sup> at the same temperature, as shown in Figure 2-1

# 2.2.7 Characterization

DSC (Q1000, TA Instrument) analysis was used to observe the thermal transition behavior of the polymer electrolytes in the temperature range from -85 to 100 °C at a scanning rate of 10 °C min<sup>-1</sup> under nitrogen flow. The ionic conductivity and electrochemical stability of the polymer electrolytes were measured via electrochemical impedance analysis and LSV, as described in these papers. (42–44) An electrochemical floating test was performed to investigate the oxidative stability of the polymer electrolyte in contact with the cathode materials. A 2032 coin cell was prepared by placing the polymer electrolyte between the lithium metal anode and the NCM cathode. The cell was initially charged to 4.2 V, and the cell current was monitored for 10 h with the potential being maintained constant. The potential was then increased by 0.1 V stepwise with the cell current being observed for each 10 h.



**Figure 2-1** Temperature-dependent ionic conductivity plots comparing POSPE-2 and electrospun separator membrane-supported POSPE-2

# 2.3. Results

## 2.3.1 Preparation of SPEs by thermal crosslinking

We prepared SPEs by the thermal crosslinking of a mixture of crosslinkers and plasticizers for lithium polymer batteries, as described in Figure 2–2. Crosslinkers provide mechanical integrity by building a three-dimensionally interconnected network through a crosslinking reaction, whereas plasticizers are trapped within the crosslinked network and transport lithium ions via segmental movement inside a local pocket (see the schematics shown in Figure 2-2(b). To optimize the ionic conductivity and electrochemical stability, we investigated the effect of the molecular structure of the polymer electrolytes on their properties by using various plasticizers and crosslinkers with different molecular weights, structural morphologies (linear or multi-arm), and functional groups (with or without the propylene oxide group), the effect of the molecular structure of the polymer electrolytes was investigated how their properties and summarized in Table 2-1. EOPL-1000 and EOPL-500 are linear plasticizers with ethylene oxide (EO) groups, and EOPLM-1000 is a multi-arm plasticizer with EO units. POPL-1000 is a linear plasticizer with EO and propylene oxide (PO) blocks, and POPLM-500 is a multi-arm plasticizer with EO-PO groups. EOCL is a crosslinker with the EO group, whereas POCL is a crosslinker with EO and PO groups.



**Figure 2-2** (a) Synthetic procedures of the plasticizers and crosslinkers with EO/PO blocks, (b) schematic and photograph of the SPEs, which were prepared by the thermal cross-linking of the mixture of the cross-linker, plasticizers, lithium salt, and thermal initiator, and (c) schematic of fabrication of the lithium polymer cells by the method of precursor wetting and then in situ cross-linking and the photograph of pouch-type lithium polymer cells.

**Table 2-1** Cross-Linkers, Plasticizers, and SPEs, which were Prepared and Studied in this Work. The numbers in parenthesis are the average molecular weight and polydispersity index (PDI) of each molecule, measured using gel permeation chromatography (GPC) analysis. For example, 680 and 1.06 are the average molecular weight and PDI of EOCL, respectively.



#### 2.3.2 Synthesis of plasticizers and crosslinkers

A linear chain EO/PO di-block plasticizer (POPL-1000) was synthesized through the continuous oxyanionic polymerization of ethylene oxide and propylene oxide, as shown in Figure 2-2(a). [168] Methanol was activated by adding a potassium hydroxide catalyst in a pressurized autoclave reactor at a high temperature. Initially, ethylene oxide was continuously added to make EO blocks by oxyanionic polymerization, and then propylene oxide was fed into the reactor to form PO blocks. Finally, dimethyl sulfate was used to convert the hydroxyl terminal to the methoxy group. The average molecular weight of POPL-1000 was measured to be 1050 g mol<sup>-1</sup> by gel permeation chromatography (GPC) analysis. The methyl proton in PO blocks was distinctively recognized at 0.8 ppm in the <sup>1</sup>H-NMR spectrum, whereas other protons are mixed in the region of 3.32-3.04 ppm, as depicted in Figure 2-3(a). By comparing the integration of the methyl proton in PO with one of the other protons, the ratio of EO and PO blocks could be calculated. The estimated ratio of EO and PO blocks by <sup>1</sup>H-NMR spectroscopy is very close to the feed ratio, as described in the inset table in Figure 2-3(a), which confirms that the oxyanionic polymerization was properly controlled for the synthesis of the EO-PO block plasticizer. The FT-IR spectrum shows the characteristic peaks due to C-H and C-O functional groups, verifying the synthesis of POPL-1000.



**Figure 2–3** <sup>1</sup>H–NMR spectrum and FT–IR spectrum of (a) POPL–1000, (b) POPLM–500, and (c) POCL. The inset table shows the feed ratio between EO blocks and PO blocks, as well as the measured ratio from the <sup>1</sup>H–NMR spectrum.

4 0

The synthetic procedure for the multi-arm EO-PO plasticizer POPLM-500 is almost identical to POPL-1000, except for using trimethylol-propane as a starting material instead of methanol. EO blocks and then, in succession, PO groups were added to the activated trimethylol propane, followed by the formation of a methoxy terminal by reacting with dimethyl sulfate, as described in Figure 2-2(a). GPC shows that POPLM-500 has an average molecular weight of 570. In the <sup>1</sup>H-NMR spectrum of POPLM-500 (Figure 2-3(b)), another distinct peak due to ethyl protons of trimethylol-propane appeared at 1.06 and 0.55 ppm, together with other peaks comparable to those of POPL-1000. Similar to POPL-1000, the ratio of EO and PO blocks in the POPLM-500 plasticizer estimated by <sup>1</sup>H-NMR spectroscopy is not much different from the feed ratio.

The cross-linker POCL has the same structure as POPLM-500, except for the terminal acrylate of POCL instead of the methoxy group of POPLM-500, as shown in Table 3-1. Terminal acrylate was introduced by the esterification reaction of acrylic acid with the intermediate, which was prepared by the addition of EO and PO to trimethylol-propane. <sup>1</sup>H NMR and FTIR spectroscopy confirmed the successful synthesis of POCL, as shown in Figure 2-3(c). The proton peaks were observed at 6.18, 5.93, and 5.63 ppm in the <sup>1</sup>H NMR spectrum due to acrylate. In addition, the absorption bands due to C—O and C—C stretching vibration in the acrylate group appeared at 1720 and 1636 and 1617 cm<sup>-1</sup> in the FT–IR spectrum, respectively.

#### 2.3.3 The effect of PO groups introduction

To investigate the effect of introducing PO groups, EOSPE-1 and POSPE-1 were prepared and compared in terms of crystallization behavior, ionic conductivity, and electrochemical stability as shown in Figure 2-4. EOSPE-1 was fabricated using the EO crosslinker EOCL and the EO plasticizer EOPL-1000, whereas POSPE-1 was prepared by mixing the EO-PO crosslinker POCL and the EO-PO plasticizer POPL-1000, as shown in Table 3-1. For a correct comparison, the molecular weight and structural morphology between EOSPE-1 and POSPE-1 are closely matched. For example, the molecular weight of EOPL-1000 is similar to that of POPL-1000 (1014 for EOPL-1000 and 1050 for POPL-1000), and both plasticizers have a linear chain structure. The cross-linker EOCL has a molecular weight similar to that of POCL (680 for EOCL and 690 for POCL), and both cross-linkers have the same multiarm structure. In the first heating scan of differential scanning calorimetry (DSC) analysis for EOSPE-1, there is a distinct exothermic peak at -29 °C due to crystallization and an endothermic one at 20  $^{\circ}$  C due to melting transition (Figure 2-4(a)), indicating that EOSPE-1 has a crystalline domain. A certain amount of the EOPL-1000 plasticizer is thought to crystallize inside a local pocket of the cross-linked polymer network. In contrast, there is no noticeable peak in the first heating scan for POSPE-1, as shown in Figure 2-4(b), which suggests that POSPE-1 is amorphous. The trend is also reproduced in the second heating scan for both SPEs. Such a difference in the thermal phase transition behavior can be explained by the bulky methyl groups in the PO unit. Methyl in the PO unit is much bulkier than the proton in the EO unit. Methyl disrupts intimate interactions

between neighboring molecular chains and, hence, suppresses crystallization. [169,170]

Figure 2-4(c) compares the ionic conductivities of EOSPE-1 and POSPE-1 in the temperature range from −10 to 100 °C. EOSPE-1 exhibits a similar ionic conductivity with or a slightly higher value than POSPE-1 at temperatures from 25 to 100  $^{\circ}$ C. However, the lithium-ion transport in EOSPE-1 is poorer than that in POSPE-1 below 25  $^{\circ}$ C, and the situation worsens as the temperature decreases. Such transition behavior in the ionic conductivity curve for EOSPE-1 is closely associated with the thermal transition of the polymer electrolyte. The apparent crystalline domain below 25  $\,^{\circ}$ C is believed to disturb the transport of lithium ions, resulting in a decrease in the ionic conductivity in EOSPE-1 and a deflection point in the ionic conductivity curve at approximately 25 °C. Subsequently, the ionic conductivity of SPEs influences cell performance, as shown in Figure 2-5. Coin cells were prepared using a lithium metal anode, LFP cathode with a loading density of 1.4 mg  $cm^{-2}$ , and EOSPE-1 or POSPE-1 as the electrolyte. The cells were then operated at Crates of 0.2, 0.5, 1.0, and 2.0 C at 10 ℃. The cell using POSPE-1 exhibited a discharge capacity of 50 mAh g<sup>-1</sup> at 0.2 C, 22 mAh g<sup>-1</sup> at 0.5 C, and 10 mAh  $g^{-1}$  at 1.0 C. However, the cell based on EOSPE-1 fails to run a proper charge/discharge cycle even at 0.2 C. Such poor cell performance is mainly due to the low ionic conductivity of EOSPE-1, which is only a third of the ionic conductivity of POSPE-1 at 10  $\,^\circ\!\! C$  (1.2  $\,\times\,$  10^{-5} S cm^{-1} for EOSPE-1 and 3.5  $\,\times\,$  10^{-5} S cm^{-1} <sup>1</sup> for POSPE-1).

Electrochemical stability is another important requirement of the electrolyte for proper cell performance. PEO-based polymer electrolytes are known for their low oxidative stability, which restricts their utilization to 3 V class cathode materials such as LFP. We demonstrate that the introduction of PO groups enhances the oxidative stability of SPE; hence, the SPE can be utilized at 4 V class cathode materials. For the linear sweep voltammetry (LSV) test, coin cells were assembled by placing an SPE membrane between the lithium metal and stainless steel (SUS) electrode. The potential increased from the open-circuit voltage (OCV) to 5.5 V at a scan rate of 0.05 mV s<sup> $^{-1}$ </sup> at 60 °C, and the current change was monitored. The LSV result in Figure 2-4 (d) indicates that POSPE-1 with PO groups showed a much enhanced oxidative stability than EOSPE-1. POSPE-1 exhibited an oxidative current higher than 1  $\mu$ A cm<sup>-2</sup> from 4.75 V, which was 0.5 V higher than EOSPE-1. The EOSPE-1 showed an oxidative current 4 times larger at 4.75 V than POSPE-1. Although the LSV test is a simple and reliable technique to observe the oxidative stability of the SPE, the test is based on an inert electrode such as SUS. To evaluate the electrochemical stability of the SPE in contact with the cathode active materials, an electrochemical floating test was performed at 60  $\,^{\circ}$ C as described in a recent paper. [171] For the test, 2032 coin cells were prepared by placing the polymer electrolyte between the lithium metal anode and the NCM cathode. Figure 2-4(e) shows that the current in the cell based on EOSPE-1 was stabilized immediately after a spike until 4.5 V but changed at 4.6 V. The current increased instead of stabilization, indicating that a certain amount of electrochemical oxidation occurred in the cell. On the contrary, the cell with POSPE-1 displayed stabilizing behavior in the current after an increment in the potential up to 4.8 V in Figure 2-4(f), which suggests that POSPE-1 is electrochemically more stable in contact with the NCM cathode at such high potential.



**Figure 2-4** DSC thermographs of (a) EOSPE-1 and (b) POSPE-1. (c) Temperature-dependent ionic conductivity plots of EOSPE-1 and POSPE-1 in the temperature range from -10 to 100 °C. (d) LSV results of EOSPE-1 and POSPE-1 from OCV to 5.5 V with a scan speed of 0.05 mV s<sup>-1</sup> at 60 °C. Inset is an enlarged graph from 4.0 V to 5.0 V. Electrochemical floating test results of (e) EOSPE-1 and (f) POSPE-1 with a 0.1 V increment in potential and a 10 h stabilization time at 60 °C.



**Figure 2-5** C-rate test results comparing the cells with POSPE-1 and EOSPE-1 at 0.2, 0.5, 1.0, and 2.0 C at 10  $^{\circ}$ C.

#### **2.3.4** The effect of polymeric properties on SPEs

We will now discuss the effect of the molecular weight of plasticizers on the properties of the polymer electrolytes. POSPE-2was prepared using the crosslinker POCL and the plasticizer EOPL-500 with a molecular weight of 460. Then it was compared with EOSPE-1, based on the crosslinker EOCL and the plasticizer EOPL-1000 with a molecular weight of 1014. Both plasticizers have the same linear EO chain structure, except for a different number of EO groups. When the DSC thermograph of POSPE-2 in Figure 2-6(a)was compared with that of EOSPE-1 in Figure 2-4(a), it could be noticed that the melting transition temperature for POSPE-2 decreased by 20 °C. Figure 2-6 (b) demonstrates that the shift in the melting transition temperature lowered the deflection point in the temperature-dependent ionic conductivity curve for POSPE-2 by approximately 20  $^\circ$ C and enhanced the ionic conductivity at a temperature below 25 ℃. For example, POSPE-2 exhibits 1 order higher ionic conductivity at 0  $\,^\circ C$  than EOSPE-1 (7.8  $\,\times 10^{-5} \; S \; cm^{-1}$ for POSPE-2 and 2.7  $\times$  10<sup>-6</sup> S cm<sup>-1</sup> for EOSPE-1). In addition, even in temperatures over 25 °C, POSPE-2 shows 2-3 times higher ionic conductivity than EOSPE-1. This higher ionic conductivity is because EOPL-500 with a lower molecular weight has more freedom in segmental motion inside a local network pocket because of the decreased van der Waals interaction between the neighboring molecules and decreased formation of the crystalline domain than EOPL-1000, resulting in a facilitated transport of lithium ions. It should be noted that our preliminary results suggested that the ionic conductivity of the crosslinked polymer electrolytes was not much affected by the type of crosslinker as shown in Figure 2-7. The SPE-1 based on the crosslinker EOCL shows a similar ionic conductivity with the SPE-2 based on the crosslinker POCL. Both SPEs are based on the same plasticizer POPL-1000.

The structural morphology of plasticizers is another key factor affecting the ionic conductivity of the polymer electrolyte, as shown in Figure 2-6(c) and (d). EOSPE-2 with a multi-arm plasticizer EOPLM-1000 was prepared and compared with EOSPE-1 based on a linear EO plasticizer EOPL-1000. Both plasticizers have similar molecular weights (1070 for EOPLM-1000 and 1000 for EOPL-1014) but different morphology. EOSPE-2 does not exhibit any peaks due to crystallization, as depicted in Figure 2-6(c), which corresponds to an amorphous state. As expected from the morphology, multi-arm plasticizers have great difficulty aligning. As such, the molecular chains interact with neighboring chains for crystallization. Therefore, the ionic conductivity curve for EOSPE-2shows an Arrhenius plot without any sharp deflection point (Figure 2-6(d)), resulting in higher ionic conduction than EOSPE-1 at temperatures lower than 25  $\,^{\circ}$ C, where a crystalline domain is formed in EOSPE-1. It should be noted that EOSPE-1 with a linear plasticizer shows a slightly higher ionic conductivity than EOSPE-2in the temperature range over 25 °C. This result suggests that lithium ions transport more effectively through a linear plasticizer than a multi-arm one given both plasticizers have the same molecular weight.



**Figure 2-6** DSC thermographs of (a) POSPE-2 and (c) EOSPE-2. Temperature-dependent ionic conductivity plots comparing (b) between EOSPE-1 and POSPE-2, and (d) between EOSPE-1 and EOSPE-2. The green dashed lines in (b) represent a deflection point in the ionic conductivity curves and the arrow indicates that POSPE-2 has a deflection point at a lower temperature than one of EOSPE-1.



**Figure 2–7** Temperature-dependent ionic conductivity plots comparing between SPEs based on a different crosslinker. SPE1 and SPE2 were prepared using EOCL and POCL as a crosslinker, respectively. Both SPEs are based on the same plasticizer POPL-1000.

## 2.3.5 Optimization of PEO/PEO-PPO composite SPEs

Using the above results, we will demonstrate that the ionic conductivity and electrochemical stability of the SPEs can be optimized by a proper combination of plasticizers with a controlled molecular weight, morphology, and PO functional groups. POPLM-500 was designed and synthesized to have a multi-arm structure with EO-PO groups with a molecular weight of about 500. When POPLM-500 was mixed with the linear EO plasticizer EOPL-500 in the crosslinked network from the EO-PO crosslinker POCL, several synergistic effects could be anticipated. First, the multi-arm plasticizer could suppress the close packing and crystallization of the plasticizer, enhancing the ionic conductivity linear EO at temperatures below 0 °C. Figure 2-8(a) shows that 20 wt.% of the multi-arm plasticizer is not enough for flattening the deflected ionic conductivity curve. When POPLM-500 was mixed with a concentration of 40 wt.%, the endothermic and exothermic peaks due to crystalline domains of the linear EO plasticizer EOPL-500 were highly suppressed as shown in Figure 2-8(b), when compared with the DSC curve for POSPE-2 with only EOPL-500 in Figure 2-6(a). The SPE ionic conductivity curve shows the Arrhenius plot without any sharp deflection point (Figure 2-8(a)). As the concentration of POPLM-500 was increased to 60 wt.%, the SPE exhibited a lower ionic conductivity than the SPE with 40 wt.%, suggesting that 40 wt.%
was optimal. Figure 2–9 shows the Vogel-Tamman-Fülcher (VTF) plot of POSPE-4, which follows the VTF equation,

$$\sigma = AT^{-0.5} exp(-E_a/(R(T-T_0)))$$

where A is related to the number of charge carriers,  $E_a$  is the activation energy for the conductivity, R is the gas constant, and  $T_0$ is the equilibrium glass transition temperature ( $T_0 = T_g - 50$ ). [172,173] The glass transition temperature for POSPE-4 was measured -72 °C by DSC as shown in Figure 2-8(b). From the linearity in the VTF plot, the activation energy of POSPE-4 could be calculated at 9.1 kJ mol<sup>-1</sup>. Second, the multi-arm plasticizer could provide a three-dimensionally free volume inside the network for a more segmental motion of the linear EO chains, facilitating lithiumion transport via the linear EO chains. In the solid polymer electrolyte, lithium ions are coordinated with the oxygen atoms in the EO units. Lithium ions are transported by intrachain or interchain hopping with a consecutive forming and breaking of the lithium-oxygen coordinate bonds, aided by the segmental motion of the EO chains. [174] With the addition of the multi-arm plasticizer, a greater free volume could be provided around the linear EO chains, resulting in more segmental motion of the molecules and higher lithium-ion conduction. Third, the addition of the linear EO plasticizer compensates for the low ionic conductivity of the multi-arm EO-PO plasticizers. As shown in Figure 2-8(a) and (c), POSPE-3 with only POPLM-500 shows much lower ionic conductivity than POSPE-2 with only EOPL-500 in the temperature range above 0 °C. However, the addition of EOPL-500 positively enhanced the ionic conductivity of the SPE. For example, POSPE-3 has an ionic conductivity of 1.5  $\, imes\,$  10<sup>-4</sup> S cm<sup>-1</sup> at 25 ℃, which is only a third of POSPE-2. By adding 60 wt.% EOPL-500 into POSPE-3, the SPE undergoes a jump in the ionic

conductivity to  $3.5 \times 10^{-4}$  S cm<sup>-1</sup>. As a result, mixed plasticizers can compensate for the ionic conductivity drawbacks of linear plasticizers or multi-arm plasticizers. Finally, the PO groups in the multi-arm EO-PO plasticizer and the EO-PO crosslinker POCL could enhance the electrochemical stability of the SPE, as discussed in Figure 2-4.



**Figure 2-8** (a) Temperature-dependent ionic conductivity plots of the SPEs with a different weight ratio of POPLM-500. (b) DSC thermographs of POSPE-4 with 40 wt.% of POPLM-500. (c) Table showing the ionic conductivity of the SPEs with a different weight ratio of POPLM-500 at several temperatures.



Figure 2-9 Vogel-Tamman-Fülcher (VTF) plot of POSPE-4.

#### 2.3.6 Electrochemical performance of POSPE-4

The optimized polymer electrolyte POSPE-4 was used to assemble lithium polymer cells with lithium as the anode and  $Ni_{0.6}Co_{0.2}Mn_{0.2}$  $O_2(NCM)$  as the cathode. A liquid-state precursor was prepared by mixing the plasticizers EOPL-500 and POPLM-500, crosslinker POCL, lithium salt, and thermal initiator without any solvent, before being solidified by thermal crosslinking. The complete crosslinking reaction was confirmed by FT-IR spectroscopy, as shown in Figure 2-10, in which the absorption bands due to C-C stretching vibration in the acrylate group at 1636 and 1617 cm<sup>-1</sup> disappeared, whereas other peaks were intact. Thermal crosslinking transformed the liquid precursor into a free-standing solid film with softness and flexibility, as shown in Figure 2-2(b). When the free-standing SPE was applied to the cell assembly, it was difficult for the solid film to penetrate the thick electrode, as schematically depicted in Figure 2-11(b). In this study, a typical NCM cathode was approximately 60  $\mu$  m thick with a high loading density of more than 8 mg cm<sup>-2</sup>. Hence, only the top surface of the electrode could be contacted or wetted by the SPE, resulting in the blocking of lithium-ion transport between the SPE and cathode materials. Transport blocking is common with a conventional free-standing SPE film. To address this problem, we utilized an in situ crosslinking method. The electrode was first wetted with the liquid precursor, followed by in situ crosslinking to form a solid polymer electrolyte in contact with the cathode materials. The cross-sectional images of the electrodes observed by scanning electron microscopy (SEM) revealed that the polymer electrolytes penetrated the thick cathode to the bottom of the electrode. All of the cathode materials were well-soaked or covered with the SPE [Figure 2-11(a)]. Most of the voids between the NCM particles in the pristine electrode were filled with polymer electrolytes through which lithium ions could be transported.



Figure 2-10 FT-IR spectra comparing the liquid precursor and the crosslinked SPE. The dashed lines indicate the absorption bands due to C=C group of the acrylate in the crosslinker.





**Figure 2-11** (a) Cross-sectional SEM images of (top) the pristine NCM cathode and (bottom) the NCM cathode with in situ crosslinked SPE. (b) Schematic illustrations representing (left) a block in lithium-ion transport between the free-standing SPE and the cathode, and (right) a facile transport of lithium ions from the in situ crosslinked SPE to the cathode materials in the thick electrode.

We evaluated the cycling performance of the lithium polymer cells by galvanostatic charge and discharge tests at 60 °C. The charge process was carried out at a 0.3 C-rate with a cutoff potential of 4.2 V in a constant current/constant voltage (CC/CV) mode of 0.1 C/4.2 V. The discharge process followed at 0.5 C-rate with a cutoff potential of 3.0 V. Figure 2-12(a) and (c) display the charge/discharge potential curves and the capacity retention with cycle numbers during 100 cycles for the lithium/NCM polymer cells, respectively. The cell exhibited a specific capacity of 156 mAh  $\mathrm{g}^{-1}$ in the first cycle and retained highly stable potential profiles for long-term cycling with only a marginal fading in the capacity. The cell maintained almost the initial capacity during 50 cycles with over 99% capacity retention and had a specific capacity of 143 mAh  $g^{-1}$ even after 100 cycles, suggesting that the capacity retention exceeded 92% after 100 cycles. The lithium polymer cell with the LFP cathode showed more stable performance in the cycling test, as displayed in Figure 2-13(a) and (c). The cell exhibited almost constant profiles during the discharge and charge processes for 100 cycles without any noticeable deterioration in capacity and polarization. Even after 100 cycles, the initial capacity was almost maintained with over 99% capacity retention.



**Figure 2–12** (a) Potential profiles in the discharge and charge processes of the lithium polymer cells for 100 cycles at 60 ° C with NCM, (b) Potential profiles of the lithium polymer cells at different C-rates and different operation temperatures with NCM. For lithium/NCM cells, the charging process was carried out at a 0.3 C-rate with a cutoff potential of 4.2 V in CC/CV mode of 0.1 C/4.2 V, and then the discharge process followed at a 0.5 C-rate with a cutoff potential of 3.0 V. (c) Capacity retention with cycle numbers of the lithium polymer cells during 100 cycles at 60 ° C with NCM





Such superior cell performance is believed to be attributed to the enhanced properties of the SPE and the stabilized interface between the SPE and electrode. We introduced EO/PO copolymer electrolytes to overcome the drawbacks of the conventional PEO-based polymer electrolyte in terms of electrochemical stability. We also used mixed plasticizers with a controlled molecular weight, structural morphology, and EO/PO groups for optimizing the ionic conductivity. The precursor-wetting and consecutive in situ crosslinking method is another key factor for minimizing the interfacial resistance between the SPE and the electrode. Such intimate contact between the SPE and NCM electrode seemed to be maintained even after 100 cycles, as shown in Figure 2-13 (d). There is no noticeable degradation in the well-mixed state between the SPE and the electrode particles in the cell cross-sectional SEM image after 100 cycles. The SPEs are well distributed from the membrane to the cathode, and even the boundary between the membrane and cathode is not distinguishable. This indicates that SPE has long-term stability when in contact with the NCM cathode during the charging process up to 4.2 V, a highly promising result for application in 4 V class batteries. We believe that the optimized SPE and in situ crosslinking method combine to provide a lithium polymer cell with facile lithiumion transport and a stable electrochemical reaction for long-term cycling.

It should be noted that the cycling test was carried out at an elevated temperature of 60 °C for the following reasons. First, the lithium polymer cells with a high electrode loading of more than 8 mg cm<sup>-2</sup> showed poor electrochemical performance at high current densities such as 1.0 C-rate at room temperature. At 25 °C, the discharge capacity decreased by 90% to 14 mAh g<sup>-1</sup>, and the cell polarization

highly increased at a 1.0 C-rate, compared with those at a 0.2 Crate, as shown in Figure 2-12 (b Second, the strong dependence of ionic conductivity on the temperature in the SPEs could lead to a much higher enhancement in electrochemical performance in the lithium polymer cells with a small increase in the operation temperature. When the cells were cycled at 60  $^{\circ}$ C, they showed a jump in the discharge capacity from 14 to 130 mAh g<sup>-1</sup> and much lower polarization at a 1.0 C rate, than those at 25 °C, as shown in Figure 2-12 (b). The enhancement of the rate capability at elevated temperatures was also observed in the lithium/LFP polymer cells, as shown in Figure 2-13(c). Such enhancement in rate capability at elevated temperatures could be explained by the strong dependence of the ionic conductivity of the SPE upon temperature. The polymer electrolyte POSPE-4 exhibited 3 times higher ionic conductivity as a result of increasing temperature from 25 to 60 °C, which reached  $1.3 \times 10^{-3}$  S cm<sup>-1</sup> (Figure 2-8). As a result, the rise in the operation temperature from 25 to 60 °C enabled 3 times higher ionic conductivity in SPEs and 10 times larger capacity at a 1.0 C rate in the cells. Third, considering that the first commercialized lithium polymer cells have been adopted for Bolloré Bluecar at the operating temperature of 80 °C, [175,176] the lithium polymer battery operable at 60 °C would be a highly plausible scenario for commercial EVs. More and more cells have been packed into EVs to extend mileage-per-charge, resulting in more difficulty dissipating the heat generated by the cell operation. Hence, it is not unusual for EV batteries to be self-heated by the cell operation to over 60  $^{\circ}$ C. Current LIBs based on volatile liquid carbonate electrolytes are susceptible to heat and require a sophisticated cooling system to avoid an accumulation of the electrolyte vapor and catastrophic explosion of the cell. The SPEs studied in this work consisted of virtually nonvolatile and thermally stable components. They possessed sufficient electrochemical stability at 60 °C, verified by LSV and electrochemical floating test, as shown in Figure 2–4. In addition, the lithium polymer cells based on the SPEs were tested to have long-term cycling stability at 60 °C, as displayed in Figure 2–12 and 13. Based on the above results, we believe that the lithium polymer cells are suitable for EV batteries operable at such elevated temperatures as 60 °C, which is advantageous in reducing the cost of the cooling system.

# 2.3.7 Safety tests of lithium polymer cells

Finally, we tested the stability of the SPEs and the lithium polymer cells under harsh operating conditions such as flame, bending, and cutting. Figure 2-14 compares the stability of the polymer electrolyte POSPE-4 and the liquid electrolyte ethylene carbonate/diethyl carbonate (EC/DEC) in a flame by torch. The liquid electrolyte was caught in the flame after it was torched for only 10 s. The SPE showed no event and maintained its initial state even after the film was torched for 90 s, highlighting the superior flameresistivity of the SPE. Pouch-type lithium polymer cells were prepared and then severely bent or cut several times with the LED lighting or the cell potential monitoring. Figure 2-15 demonstrates that the cells work well by emitting the same intensity of LED light and maintaining the cell voltage even under harsh operating conditions such as severe bending and being cut twice.



Figure 2–14 Flammability test of (a) POSPE–4 and (b)  $LiPF_6$  in EC/DEC electrolytes by torch flame.



Figure 2-15 (a) Bending and (b) cutting test of the pouch-type lithium polymer cells.

# 2.4. Summary

This work has demonstrated stable long-term cycling in a 4 V class lithium polymer battery using in situ crosslinked EO/PO copolymerbased SPEs. The properties of the SPEs such as ionic conductivity and electrochemical stability were optimized under easy modification in the molecular structure of the SPEs. The introduction of EO-PO groups was found to be effective in suppressing crystallization and enhancing ionic conductivity. In addition, the introduction of PO groups also enhanced electrochemical oxidative stability in the PEObased SPEs, which was verified by LSV and electrochemical floating tests. Tuning the molecular weight in the plasticizers from 1000 to about 500 resulted in 2-3 times higher ionic conductivity, mainly due to reduced van der Waals interactions between the neighboring chain molecules and increased segmental motion in the chains. Multi-arm structure plasticizers had much more difficulty in crystallization and provided an amorphous nature to the SPEs, leading to enhanced ionic conductivity at low temperatures. When using both the multi-arm EO-PO plasticizer and the linear EO plasticizer with a tuned molecular weight of approximately 500 with the EO-PO crosslinker, the resulting crosslinked SPEs showed a synergic effect on ion transport and electrochemical stability. The SPEs exhibited ionic conductivities as high as 3.5  $\,\times10^{-4}~{\rm S~cm^{-1}}$  at 25  $\,^\circ{\rm C}$  and 1.3  $\,\times10^{-3}$ S cm<sup>-1</sup> at 60 °C. The SPEs also guaranteed sufficient electrochemical stability for compatibility with the high-Ni NCM cathode. In situ crosslinking is a simple but effective method for SPEs to mimic the conformal contact between the liquid electrolyte and the electrode. Cross-sectional SEM images visualized the SPEs to penetrate the 60  $\mu$ m-thick electrodes with a high loading density of more than 8 mg cm<sup>-2</sup>. By combining all these strategies, we successfully utilized the SPEs into a 4 V class NCM battery, which retained stable cycling with a marginal fading in capacity even after 100 cycles at 60 °C. We believe that our strategy for optimizing SPE and in situ crosslinking is highly useful and readily adaptable for lithium polymer cells stable enough for EV batteries.

# Chapter 3. Gel polymer electrolyte based on crosslinked networks by the introduction of an ionic liquid crosslinker with ethylene oxide arms

# **3.1. Introduction**

Solid-state electrolytes (SSEs) such as solid polymer electrolytes are potential alternatives to liquid electrolytes in LIBs for enhancing their safety. Thermally stable SSEs allow LIBs to operate stably at high temperatures.[177] However, low ionic conductivity and high interfacial resistance between the electrolyte and electrodes result in the poor performance of batteries based on solid polymer electrolytes.[177] Gel polymer electrolytes (GPEs), which are composed of a polymer containing a large volume of a liquid ionic conductor, can be a compromise between liquid and solid electrolytes. [178,179] GPEs have high ionic conductivity and good interfacial contact, comparable with that of liquid electrolytes while exhibiting higher thermal stability than these electrolytes. In addition to the conventional liquid electrolytes, [180,181] ionic liquids are also employed as liquid ionic conductors owing to their high thermal stability and nonvolatility. [180,182] Several polymers such as poly (vinylidene fluoride) and poly (acrylonitrile) have been employed as ex-situ polymers to hold the liquid ionic conductor in GPE; [166,181] However, externally formed polymers have difficulty in enough contact with the uneven surface of electrodes, and then it causes higher interfacial resistance. On the other hand, an in-situ polymer network, which is prepared by thermal crosslinking of a liquid-state precursor in a contact state with the electrode can minimize the interfacial resistance. Thus, crosslinked networks derived from crosslinkers, with terminal curable groups such as acrylate and vinyl, have been intensively studied as in-situ polymers in GPE.

Herein, we report gel polymer electrolytes based on a newly designed ionic liquid crosslinker, which has a pyrrolidiniumbis(trifluoromethyl sulfonyl)amide (Py-TFSI) structure and an acrylate terminal group with an ethylene oxide (EO) spacer connecting them.

# 3.2. Experimental

## 3.2.1 Materials

Pyrrolidine, 2-(2-chloroethoxy) ethanol, triethylamine, acetonitrile, and LiTFSI were purchased from Tokyo Chemical Industry (TCI). Methacryloyl chloride, anhydrous MC, and silica gel (40–60  $\mu$  m, 230–400 mesh) were purchased from Merck. Reactions were monitored by thin-layer chromatography (0.25 mm Merck silica gel plates, 60F–254) using UV light as the visualizing agent. ARM2, poly (ethylene glycol) dimethacrylate (average Mn 550 g mol<sup>-1</sup>), was obtained from Merck. ARM3 (average Mn 680 g mol<sup>-1</sup>) and ARM4 (average Mn 528) were provided by Hannong Chemicals Inc.

# 3.2.2 Synthesis of IL2

After refluxing pyrrolidine (1.0 equiv), 2-(2-chloroethoxy)ethanol (2.0 equiv), and triethylamine (2.0 equiv) in acetonitrile for 15 h, 1,1-bis(2-(2-hydroxyethoxy))ethyl)pyrrolidine-1-ium chloride (EG2P-Cl) was obtained by the removal of solvents and unreacted reactants upon evaporation at 90 °C.

LiTFSI solution of 30% concentration was added to EG2P-Cl and stirred for 1 h. After removing the water layer, 1,1-bis(2-(2hydroxyethoxy)ethyl)pyrrolidine-1-ium bis((trifluoromethyl)sulfonyl) amide (<u>EG2P-TFSI</u>) was obtained using column chromatography. EG2P-TFSI (1.0 equiv), methacryloyl chloride (2.2 equiv), and triethylamine (2.0 equiv) were refluxed in anhydrous MC for 15 h. After removing solvents by evaporation at 30 °C and washing 3 times, 1,1-bis(2-(2-(methacryloyloxy)ethoxy)ethyl)pyrrolidin-1-ium bis((trifluoromethyl)sulfonyl)amide (<u>IL2</u>) was obtained and purified using column chromatography (methanol/MC = 1:20). FT-IR (cm<sup>-1</sup>); 2980-2880 (m, C-H), 1720 (vs, C=O), 1637 (w, C=C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm);  $\delta$  6.10 (s, C=CH<sub>2</sub>), 5.63 (s, C=CH<sub>2</sub>), 4.35-4.25 (m, -O-CH<sub>2</sub>-), 3.95-3.83 (m), 3.76-3.70 (m), 3.68-3.62 (m), 3.62-3.57 (m), 2.23-2.16 (m), 1.93 (s, -CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm);  $\delta$  167.6 (C=O), 135.9 (C=CH<sub>2</sub>), 126.0 (C=CH<sub>2</sub>), 119.8 (q, J = 319 Hz, -CF<sub>3</sub>), 69.4, 64.9, 64.4, 63.0, 59.7, 21.1, 18.2 (-CH<sub>3</sub>).

#### **3.2.3 Preparation of GPE**

A liquid-state precursor was prepared by homogeneously mixing a crosslinker, a liquid electrolyte, and a thermal initiator. The liquid electrolyte, which was prepared by dissolving 1.0 M LiPF<sub>6</sub> in a 1:1 mixture of EC and DEC, was purchased from Soulbrain (Korea). The thermal initiator, t-butyl peroxypivalate, was obtained from Seki Arkema Co. (Japan). The precursor was gelled by thermal crosslinking at 90 °C for 30 min. The condition for thermal crosslinking was determined by monitoring the change in the stretching vibration absorption band due to C—C of methacrylate at 1637 cm<sup>-1</sup> using FT-IR spectroscopy (Nicolet 6700, Thermo Fisher Scientific Inc.). The thermal stability of the precursor was assessed using a TGA instrument (Thermo plus EVO II TG8120 series). TGA

was performed in an  $N_2$  environment, wherein the temperature was raised from room temperature to 600 °C at a rate of 10 °C min<sup>-1</sup>.

# 3.2.4 Measurement of electrochemical properties of GPE

A 2032-type coin cell was assembled for ionic conductivity measurements. The coin cell consisted of two disc-type SUS electrodes and a ring-shaped polyimide film with an inner diameter of 11 mm and a thickness of 130  $\mu$  m sandwiched between them. GPE was placed inside the polyimide ring film. The ionic conductivity of the GPE was measured by EIS at room temperature using an electrochemical workstation (IM6, ZAHNER). Its electrochemical stability was determined by LSV at room temperature using a potentiostat (VMP3, Biologic). The measured range was from OCV to 5.5 V at a scan rate of 1.0 mV s<sup>-1</sup>. For the LSV test, A 2032-type coin-cell was prepared with a 50  $\mu$  m lithium foil and SUS disc as electrodes.

## **3.2.5 Preparation of Cells**

The (LFP cathode consisted of active materials or LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> (NCM622)), Super P, and PVdF binder in a weight ratio of 75:19:6. The slurry of the cathode materials in NMP (Nmethyl-2-pyrrolidinone) was coated on an aluminum foil of 20  $\mu$ m thickness and dried at 120 °C overnight. The electrode was punched in a diameter of  $\phi$  14 mm and then vacuum-dried at 120 °C before the cell assembly. The cell was assembled in an Ar-filled glovebox. 2032-type coin cells were made with the cathode (LFP or NCM622), a separator wetted by a GPE precursor, and a lithium foil of 50  $\mu$ m. The assembled coin cells were placed in a convection oven for crosslinking of the precursor.

#### 3.2.6 Electrochemical measurement

The charge-discharge cycling performance was investigated using LiFePO<sub>4</sub> or NCM622|GPE|Li coin cells. The cell was charged to 4.1 (LFP)/4.3(NCM622) V and discharged to 2.5(LFP)/3.0(NCM622) V using an electrochemical potentiostat (VMP3, Biologic/WBCS3000, WonATech). The rate capability of the cells was tested at different C-rates: 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 C. The capacity stability in cells using NCM622 cathode was also evaluated at a 1.0C rate.

# 3.3. Results

#### 3.3.1 Design of IL2-GPE

IL2 is designed to have a pyrrolidinium cation and TFSI anion as its core unit and polymerizable methacrylate as its terminal, with an EO spacer connecting them (Figure 3-1(a)). The cation structure of the ionic liquid affects its physical and electrochemical properties. [183,184] An increase in the cation ring size increases the electrochemical stability and viscosity of the ionic liquid. [175,185] The cation's type also influences the ionic conductivity and thermal stability of the ionic liquid. [186] In this study, pyrrolidinium cation is chosen to ensure better thermal and electrochemical properties. The anion is another crucial factor that determines the characteristics of the ionic liquid. [175,187,188] TFSI anions are known to exhibit higher thermal stability than that of halide anions. [178,189,190] It was reported that a GPE with a TFSI anion showed the best thermal stability amongst GPEs prepared with different anions. [191] The length of the arm also affects the electrochemical performance of ionic liquids. [192-194] Increasing arm length increases the viscosity of ionic liquids, thereby decreasing their ionic conductivity. In addition, the introduction of an EO group in the ionic potentially contributes to the liauid enhancement of its electrochemical properties, [192] as longer EO chains in the arm may decrease the liquid's ionic conductivity. Therefore, one EO chain

was introduced herein as a spacer between the pyrrolidinium cation and the methacrylate end group.

IL2 was synthesized by reacting 2-(2-chloroethoxy) ethanol with pyrrolidine, followed by an attachment reaction of methacrylate in the terminal as shown in Figure 3-1 (b). The molecular structure of IL2 was examined by <sup>1</sup>H and <sup>13</sup>C NMR, mass, and FT-IR spectroscopy. characteristic peaks corresponding to the protons in Two methacrylate —  $CH_2$  were identified at 6.1 and 5.6 ppm in <sup>1</sup>H NMR, as shown in Figure 3-1(c). Methyl protons  $(-CH_3)$  were observed at 1.9 ppm. In <sup>13</sup>C NMR (Figure 3-2(a)), the carbon in the carbonyl group, C-O, was identified at 167.6 ppm. The two carbons in methacrylate  $-C-CH_2$  were observed at 135.9 and 126.0 ppm. The carbon in the trifluoromethyl group, -CF<sub>3</sub>, of TFSI was evidenced by the characteristic quartet peaks due to heteroatom couplings between C and F, centered at 119.8 ppm, with a large coupling constant of 319 Hz. The molecular weight of IL2 measured by mass spectroscopy was identical to its calculated counterpart, as shown in Figure 3-2(b). The FT-IR spectrum of IL2 (Figure 3-3) showed a strong absorption band at 1720 cm<sup>-1</sup> due to the carbonyl group and a weak peak at 1637 cm<sup>-1</sup> due to C-C in methacrylate. Hence, it can be confirmed that the desired crosslinker was successfully synthesized.

IL2, which is a complex of pyrrolidinium cation and TFSI anion, is a colorless viscous liquid. It is virtually nonvolatile at ambient temperature and highly stable thermally. The TGA of IL2 shows that there is no observable weight loss until 330 °C, as shown in Figure 3-1 (d). This is highly remarkable when compared with that of other crosslinkers. For example, poly(ethylene glycol)dimethacrylate (ARM2, its structure is shown in Figure 3-8) is a crosslinker with two methacrylates and EO spacers, commonly used in preparing

GPEs. The TGA of ARM2 shows that it starts losing weight at 200 °C. The difference in the thermal stabilities of either crosslinker does not result from the influence of their arm lengths. Referring to literature comparing PEO-based polymers with different EO lengths, there is no significant effect of the length of arms or EO groups on the thermal stability of PEO-based polymers. [195] By contrast, the structural characteristics of the ionic liquids such as the cation-arm combination [192] and the anion choice [196,197] affect their thermal stability. Thus, rather than the arm length, the characteristic of IL2' s intrinsic structure seems to be an influential factor in giving it better thermal stability than that of ARM2.

(a) Design of IL2 crosslinker



**Figure 3–1** (a) Chemical structure, (b) synthetic procedure, (c) <sup>1</sup>H NMR spectrum, and (d) TGA analysis of IL2. In the <sup>1</sup>H NMR spectrum,  $CDCl_3$  is an NMR solvent, and MC (methylene chloride) is a residual solvent. In TGA, a common crosslinker, poly(ethylene glycol)dimethacrylate (ARM2), was compared with IL2.



Figure 3-2 (a) <sup>13</sup>C NMR spectrum of IL2, (b) Mass spectrum of IL2.



**Figure 3-3** FT-IR spectra of IL2, t-butyl peroxy pivalate, and liquid electrolyte (mixture of EC and DEC with LiPF<sub>6</sub>). A peak at near 1640 cm<sup>-1</sup> corresponding C=C stretching occurred at only ionic liquid crosslinker IL2.

#### **3.3.2 Preparation of IL2-GPE**

We prepared a gel polymer electrolyte (GPE) named IL2-GPE by introducing IL2 as a crosslinker (Figure 3-4(a)). The IL2-GPE consisted of a three-dimensional polymer network derived from thermally crosslinked IL2 and a large volume of liquid electrolyte within the network. A mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with 1.0 M LiPF<sub>6</sub> was used as the liquid electrolyte. It is known that LiPF<sub>6</sub> can improve the electrochemical stability of the cell by interacting with lithium bis((trifluoromethyl)sulfonyl) amide (LiTFSI), a lithium salt. [198] IL2-GPE was fabricated by allowing the thermal crosslinking reaction of the liquid-state precursor, which consisted of IL2 and a liquid electrolyte in a ratio of 15/85 (w/w). After the thermal crosslinking reaction, the liquid precursor turned into a transparent gel, which retained its morphology at the bottom of the overturned vial, as shown in Figure 3-4(a).

Thermal crosslinking reaction for the preparation of IL2–GPE was monitored by observing the change in the stretching vibration absorption band due to C=C of methacrylate, using FT–IR spectroscopy (Figure 3–4(b)). Figure 3–3 shows the IR spectra of IL2, the liquid electrolyte, and the initiator. In the IR spectrum of IL2, a peak corresponding to the C—C stretching vibration of methacrylate was observed at 1637 cm<sup>-1</sup>. Figure 3–4(b) shows the change in the absorption spectrum of IL2–GPE at a different crosslinking reaction time at 90 °C. The precursor before the crosslinking reaction showed a prominent peak at 1637 cm<sup>-1</sup>. As the crosslinking proceeded, the peak intensity due to C=C decreased and was hardly noticeable after 20 minutes. Except for the peak at  $1637 \text{ cm}^{-1}$ , other functional groups such as C=O and C-H were intact throughout the reaction. Based on the FT-IR data, we confirmed the complete crosslinking of the precursor, resulting in IL2-GPE



**Figure 3–4** Schematic illustration of (a) IL2–GPE fabrication and (b) thermal crosslinking reaction for the preparation of IL2–GPE, monitored by FT–IR spectroscopy.

#### 3.3.3 Thermal/Electrochemical stability of IL2-GPE

The thermal stability of IL2-GPE was evaluated by TGA analysis, as shown in Figure 3-5(a). For comparison, the liquid electrolyte (a mixture of EC and DEC with LiPF<sub>6</sub>) and ARM2-GPE were also tested. ARM2-GPE was prepared by crosslinking the mixture of ARM2 and liquid electrolyte in the same ratio as that of IL2–GPE (crosslinker / liquid electrolyte =15 / 85, w/w). The liquid electrolyte rapidly lost weight at room temperature owing to its volatile character and remained in negligible amounts at 240 °C. By contrast, IL2-GPE and ARM2−GPE retained most of their original weight until 100 °C. Both GPEs lost their weight at a rate of 0.5 %  $^{\circ}C^{-1}$  in the range of 140  $^{\circ}C$ to 200 °C, reaching 44 % of their original weight at 200 °C. The weight loss in the 100-200 °C range was probably due to the vaporization of the liquid electrolyte from the GPEs. Interestingly, in the subsequent temperature range above 200 °C, IL2-GPE showed a different tendency in its weight loss compared to that of ARM2-GPE. ARM2-GPE lost its weight at the rate of 0.4 %  $^{\circ}$ C<sup>-1</sup> until 250  $^{\circ}$ C, whereas IL2-GPE's weight loss slowed down to 0.2 %  $^{\circ}C^{-1}$  in the same temperature range. At 250 °C, the weight of IL2-GPE remained at 34.1%, 9.3% higher than the 24.8 % of ARM2-GPE. According to the literature, the crosslinked network showed better thermal stability when longer arms or a large number of units were applied. [199-201] Considering that IL2-GPE, with arms shorter than that of ARM2, showed better thermal stability until 250  $^{\circ}$ C, it can be

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assumed that the intrinsic structural characteristics of IL2 enhanced the thermal stability of IL2–GPE.

The conductivity of IL2-GPE was obtained ionic from electrochemical impedance spectroscopy (EIS) analysis at room temperature, as shown in Figure 3-5(b). The ionic conductivity of IL2-GPE was measured to be  $5.37 \text{ mS cm}^{-1}$ . Compared to those of other gel polymer electrolytes in literature, [180,202-205] the ionic conductivity of IL2-GPE is relatively high. For example, the GPE based on a crosslinker, polyethylene glycol diacrylate) (PEGDA, average Mn 400), a liquid electrolyte, and a mixture of EC and DEC with 1.0 M LiPF<sub>6</sub>, according to a recent report by Liu et al., exhibited 2.9 mS cm<sup>-1</sup> at room temperature. [206] The high ionic conductivity of IL2–GPE may have resulted from the incorporation of EO groups and the structural backbone of the ionic liquid in the polymer network, which is favorable for ion transport. Figure 3–6 shows that IL2–GPE is electrochemically more stable than the liquid electrolyte (the mixture of EC and DEC with 1.0 M LiPF<sub>6</sub>). For comparing the electrochemical stability, linear sweep voltammetry (LSV) was performed in the range of open-circuit voltage (OCV) to 5.5 V at room temperature. IL2-GPE showed electrochemical oxidation stability higher than that of the liquid electrolyte. Better electrochemical stability may be related to the operation of LIBs at a higher potential. The TGA and LSV results verified that IL2-GPE can be used in LIBs for stable operation at high voltages and temperatures.



**Figure 3-5** (a) TGA scans of IL2-GPE, ARM2-GPE, and liquid electrolyte and (b) Nyquist plot of IL2-GPE obtained by EIS analysis. The resistance of IL2-GPE was measured to be 2.51  $\Omega$  and calculated to the ionic conductivity of 5.37 mS cm<sup>-1</sup>.



**Figure 3–6** Comparison of electrochemical stability of IL2–GPE with that of a liquid electrolyte through LSV analysis. IL2–GPE showed the slope change of current at a higher voltage (potential) than the case of a liquid electrolyte. Hence, IL2–GPE was considered to have better electrochemical stability than the liquid electrolyte.

# 3.3.4 Electrochemical performance of IL2-GPE

The discharge and charge cycle tests and the rate capability test were carried out using coin cells for evaluating the electrochemical performance of IL2-GPE. As shown in Figure 3-7, the LiFePO<sub>4</sub>|IL2-GPE|Li cell showed a capacity of 160 mAh g<sup>-1</sup> at 0.1 C under cut-off voltages of 2.5-4.1 V (vs Li/Li<sup>+</sup>) at room temperature. At higher C-rates, the cell showed slightly lower capacities of 157 and 143 mAh g<sup>-1</sup> at 0.2 and 1.0 C, respectively. Each discharge capacity corresponded to 98% at 0.2 C and 89% at 1.0 C when compared with the capacity at 0.1 C. These results confirmed the high rate capability of the IL2-GPE cells.


**Figure 3-7** (a) First cycle at 0.1 C and (b) rate capability test from 0.1 to 1.0 C of the LiFePO<sub>4</sub>|IL2-GPE|Li coin cell. The electrochemical performance was assessed under cut-off voltages of 2.5-4.1 V at room temperature. The loading density of LiFePO4 (LFP) was 1.2 mg cm<sup>-2</sup>.

## **3.3.5 Preparation of HIL2-GPE**

For a higher ionic conductivity, the precursor should be gelled as little as possible using the crosslinker; the resultant GPE should thus contain as much liquid electrolyte content as possible. Three crosslinkers were prepared with similar structures and molecular weights but different numbers of arms. Based on the number of arms, the crosslinkers were named ARM2, ARM3, and ARM4. The molecular structure of the crosslinkers and the gelation status in the GPEs at a different concentration of each crosslinker are shown in Figure 3-8. The liquid electrolyte was mixed with each crosslinker in a different ratio; then, the minimum amount of the crosslinker to fabricate GPE was examined. Subsequently, it was confirmed that the minimum amount of ARM2 for the complete gelation by crosslinking was 10 wt%. Meanwhile, the concentrations of ARM3 and ARM4 required for gelation were 5 and 3 wt%, respectively. This result shows that the crosslinker with more arms maximized the content of liquid electrolytes in the GPE.

Based on the aforementioned experiment, ARM4 was used with IL2 for the preparation of GPE to increase the concentration of the liquid electrolyte. When IL2, ARM4, and the liquid electrolyte were mixed in a weight ratio of 1:3:96, a gelled GPE (HIL2-GPE) was successfully prepared after thermal crosslinking, as shown in Figure 3-9(a). The HIL2-GPE contains 96 wt% of the liquid electrolyte, more than that of 85 wt% in IL2-GPE. The thermal stability of HIL2-GPE was evaluated by TGA, as shown in Figure 3-9(b). With an increase in the content of the liquid electrolyte, its vaporization in HIL2-GPE occurred more rapidly than that in IL2-GPE; the

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electrolyte lost 7.8% (92.2% remaining) of its original weight at 100 °C. However, at 200 °C, the remaining liquid electrolyte content in HIL2-GPE was approximately 42%, similar to that in IL2-GPE (44%). At subsequent temperatures, the weight loss for HIL2-GPE continued, with approximately 12% of the original weight remaining at 300 °C. Although HIL2-GPE showed a rapid weight loss compared to IL2-GPE, it also showed that even 4 wt % of the crosslinker (IL2 and ARM4) could interfere with the vaporization of the liquid electrolyte upon sufficient interactions in HIL2-GPE. Additionally, in the 160-200 °C temperature range, HIL2-GPE lost weight at a rate similar to that of IL2-GPE.

The ionic conductivity of HIL2-GPE was assessed using the EIS method. As shown in Figure 3-9(c), HIL2-GPE had a resistance of 2.089 Q. The ionic conductivity was calculated by applying the area and thickness of HIL2-GPE to the resistance value. The calculated ionic conductivity of HIL2-GPE was 6.45 mS cm<sup>-1</sup>, approximately 20 % higher than that of IL2-GPE. Meanwhile, in Figure 3-9(d), HIL2-GPE showed good electrochemical oxidation stability in the LSV test. HIL2-GPE had an oxidation potential 0.3-0.4 V higher than that of the liquid electrolyte. Summarizing these electrochemical evaluations, we believe that the crosslinked polymer network in HIL2-GPE exhibited better electrochemical stability and ionic conductivity than that in IL2-GPE.



**Figure 3–8** Molecular structure of three crosslinkers with different arms and gelation statuses of the GPEs corresponding to different concentrations of each crosslinker observed in overturned vials after thermal crosslinking. The picture shows that at least 10 wt% of ARM2, 5 wt% of ARM3, and 3 wt% of ARM4 were required for complete gelation.



**Figure 3-9** (a) Photo image of HIL2-GPE at the bottom of the overturned vial after thermal crosslinking, (b) comparison of the thermal stabilities of HIL2-GPE, IL2-GPE, and the liquid electrolyte by TGA, (c) ionic conductivity of HIL2-GPE measured by EIS, and (d) comparison of the electrochemical stabilities of HIL2-GPE, IL2-GPE, IL2-GPE, and the liquid electrolyte.

#### **3.3.6 Electrochemical performance of HIL2-GPE**

How HIL2-GPE with improved ionic conductivity affected the actual electrochemical performance was examined by assembling a LiFePO<sub>4</sub>|HIL2-GPE|Li coin cell and performing cycle tests. Charged and discharged in the 2.5-4.1 V cut-off range at room temperature, the rate capability of the coin cell with HIL2-GPE was assessed at 0.1, 0.2, 1.0, and 0.1 C in order. As shown in Figure 3-1 (a), the coin cell with HIL2-GPE at 0.1 C exhibited a capacity of 165 mAh g<sup>-1</sup>, higher than that of IL2-GPE. Furthermore, the HIL2-GPE coin cell exhibited capacities of 162 and 146 mAh g<sup>-1</sup> at 0.2 and 1.0 C, respectively, performing better than the cell with IL2-GPE. The capacity at each C-rate corresponded to 98% (0.2 C) and 88% (1.0 C) compared with that at 0.1 C.

When the potential profiles for the HIL2-GPE cell shown in Figure 3-10 were compared with those for the IL2-GPE cell shown in Figure 3-7, the HIL2-GPE cell showed a much lower polarization than that of the IL2-GPE cell during charge and discharge. Figure 3-11 shows a comparison of the charge and discharge potential profiles for the HIL2-GPE cell with those for the IL2-GPE cell at 1.0 C. Table 3-1 summarizes the potentials measured at 50% of the state of charge (SOC) (during charge) or 50% of the depth of discharge (DOD) (during discharge) of the cells. The HIL2-GPE cell showed 3.54 V at 50% SOC at 1.0 C, 0.1 V lower than that of the IL2-GPE cell. Similarly, the potential it showed at 50% of SOC was lower than that of the IL2-GPE cell at other C-rates, as shown in Table 2-1. Such lower polarization in the HIL2-GPE cell may be due

to the ionic conductivity of HIL2-GPE being higher than that of IL2-GPE.



**Figure 3-10** (a) First charge and discharge cycle at 0.1 C and (b) rate capability tests of the LiFePO<sub>4</sub>|HIL2-GPE|Li cell from 0.1 to 1.0 C. The loading density of LFP was 1.2 mg cm<sup>-2</sup>.



**Figure 3-11** Charge and discharge potential profiles for the cells using IL2-GPE and HIL2-GPE at 1.0 C. The circle and square marks in the charge and discharge potential lines correspond to the points at 50% SOC and 50% DOD, respectively.

**Table 3-1** Potentials measured at 50% state of charge (SOC) (during charge) or 50% depth of discharge (DOD) (during discharge) of the  $LiFePO_4|GPE|Li$  cells at different C-rates using IL2-GPE or HIL2-GPE. The gaps indicate the difference between the potentials at 50% SOC and 50% DOC in the cell at each C-rate. For example, the cell based on IL2-GPE showed a gap of 0.47 V at 1.0 C, which was the difference between 3.64 V at 50% SOC and 3.17 V at 50% DOD

		Potential at SOC/DOD 50% (V)		
		0.1C	0.2C	1.0C
IL2-GPE	Charge (SOC)	3.49	3.49	3.64
	Discharge (DOD)	3.38	3.35	3.17
	gap	0.11	0.14	0.47
HIL2-GPE	Charge (SOC)	3.46	3.47	3.54
	Discharge (DOD)	3.38	3.37	3.30
	gap	0.08	0.10	0.24

In addition, a cell was also prepared using a high-voltage cathode  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  (NCM622). Li metal was used as an anode and HIL2-GPE was used as an electrolyte. The loading density of NCM622 was 4.4 mg cm<sup>-2</sup>. The rate capability of the cell was evaluated by discharging and charging at different C-rates from 0.1 to 5.0 C as shown in Figure 3-12(a-b). The cut-off voltages were 3.0 V and 4.3 V. The cell showed 164 mAh g<sup>-1</sup> at 0.1 C, 155 mAh g<sup>-1</sup> at 0.5 C, 144 mAh g<sup>-1</sup> at 1.0 C, 118 mAh g<sup>-1</sup> at 2.0 C, and 58.0 mAh g<sup>-1</sup> at 5.0 C. This result indicated the superior rate capability of the GPE cell up to 5.0 C. Figure 3-12(c-d) shows the cycle stability for 100 cycles at a 1.0 C rate. The cell showed a capacity retention of 90.1% for 100 cycles. This result suggested that the cell based on the GPEs maintained superior long-term stability even with high-voltage cathode materials over 100 cycles.



**Figure 3–12** (a) Potential profiles and (b) change of the capacity in the rate capability test of the NCM622|HIL2-GPE|Li cell with a current rate from 0.1 to 5.0 C. (c) Potential profiles and (d) change of the capacity in the cycle stability test of the NCM622|HIL2-GPE|Li cell at a 1.0 C rate for 100 cycles. The loading density of the NCM622 active material was 4.4 mg cm<sup>-2</sup>. The test was performed under cut-off voltages of 3.0-4.3 V at room temperature.

#### 3.3.7 Flammability and stability tests

Figure 3–13 shows a comparison of the flammability test results between HIL2–GPE and the liquid electrolyte (mixture of EC and DEC at a volume ratio of 1/1 with 1 M LiPF<sub>6</sub>) in a flame by torch. The liquid electrolyte was caught in the flame after it was torched for only 10 s. HIL2–GPE showed no event and maintained its initial state even after the GPE was torched for 30 s, highlighting the superior safety of the HIL2–GPE.

Figure 3-14 shows a comparison of the cycle stability test results between HIL2-GPE and the liquid electrolyte at 60 °C with a current rate of 2.0 °C. We prepared Li/NCM622 cells by using HIL2-GPE and the liquid electrolyte, respectively. The loading density of NCM622 was 4.9 mg cm<sup>-2</sup>. The cells were discharged and charged at an elevated temperature of 60 °C to evaluate the thermal stability of the electrolytes. The cell with HIL2-GPE showed a stable cycle performance over 15 cycles, whereas the cell with the liquid electrolyte exhibited a fast capacity fading. This demonstrates that HIL2-GPE possessed superior thermal stability and safety than the conventional liquid electrolyte.



**Figure 3–13** Flammability test of (a) liquid electrolyte (mixture of ethylene carbonate and diethyl carbonate at a volume ratio of 1/1 with 1 M LiPF<sub>6</sub>) and (b) HIL2-GPE by torch flame.



Figure 3-14 Potential profiles of (a) NCM622|HIL2-GPE|Li cell and (b) NCM622|Liquid electrolyte|Li cell at 60  $^{\circ}$ C with a current rate of 2.0 C during 15 cycles. (c) The change of capacity of NCM622|HIL2-GPE|Li cell and NCM622|Liquid electrolyte|Li cell at 60  $^{\circ}$ C with a current rate of 2.0 C during 15 cycles. The loading density of NCM622 was 4.9 mg cm<sup>-2</sup>.

# 3.4. Summary

In this study, we designed a novel ionic liquid crosslinker and developed a GPE by in-situ polymerization of the crosslinker. The GPE showed high thermal stability, ionic conductivity, and electrochemical stability. The ionic liquid crosslinker (IL2) had a pyrrolidinium cation and bis(trifluoromethyl sulfonyl)amide (TFSI) anion, and terminal methacrylate with EO arm. Its successful synthesis was confirmed by several techniques such as  $^1\mathrm{H}$  and  $^{13}\mathrm{C}$ NMR and mass and FT-IR spectroscopy. TGA scan verified that the crosslinker was virtually nonvolatile at ambient temperature and remained intact until 330 °C due to its ionic liquid nature. Another GPE was prepared by in-situ thermal curing of the precursor containing IL2 and liquid electrolyte. Its complete gelation was confirmed by FT-IR spectroscopy monitoring the disappearance of the C=C stretching vibration peak due to methacrylate. The enhanced thermal stability of the resultant IL2-GPE was verified by TGA measurement upon comparison with that of the liquid electrolyte and the GPE derived from a common crosslinker. IL2-GPE exhibited a high ionic conductivity of 5.37 mS cm<sup>-1</sup> in impedance measurement and good electrochemical stability in the LSV test. The discharge and charge cycle test was performed on the cell with IL2-GPE sandwiched between the LiFePO4 cathode and Li anode. The cell showed a capacity of 160 mAh g<sup>-1</sup> at 0.1 C at room temperature. It also exhibited a capacity of 143 mAh  $g^{-1}$  at 1.0 C, which was 89% of that at 0.1 C, indicating high rate capability. By introducing a crosslinker with four acrylate terminals to the IL2 crosslinker, we obtained HIL2-GPE, which contained a large volume of liquid electrolyte in its gel state. The resultant HIL2-GPE possessed 20% higher ionic conductivity than that of IL2-GPE. The HIL2-GPE cell showed a capacity of 165 mAh g<sup>-1</sup> at 0.1 C, higher than that of IL2-GPE. Furthermore, the HIL2-GPE cell exhibited a capacity of 162 mAh g<sup>-1</sup> and 146 mAh g<sup>-1</sup> at 0.2 C and 1.0 C, respectively, thereby demonstrating better performance than the IL2-GPE cell. The HIL2-GPE results have motivated us to expand our study to ionic liquid crosslinkers with more arms (such as three or four acrylate terminals). The project is ongoing and the results will be covered elsewhere.

# Chapter 4. Additives for electrochemical stability of the composite cathode in argyrodite-based all-solidstate batteries.

# 4.1. Introduction

All-solid-state batteries (ASSBs) have been studied to improve performances for energy density, safety, and operating temperatures than current LIBs. Next-generation LIBs have been expected to work more stably and safely in harsher conditions by replacing flammable liquid electrolytes with solid-state electrolytes. [207] As an electrolyte in next-generation LIBS, sulfide-based inorganic solid electrolytes (ISEs) especially have drawn interest due to their high ionic conductivity above 1 mS  $cm^{-1}$  and relatively simple synthesis procedure. [208,209] Furthermore, the ductility of sulfidebased ISEs makes it possible to fabricate high-density pellets at pressure.[42] However. chemicalrelatively low and electrochemical instability have disturbed the practical use of sulfide-based ISEs. [210] The physical interfacial problems of ISEs are also chronically latent in sulfide-based ISEs. Unlike liquid electrolytes, non-fluidizable sulfide-based ISEs might have pores or voids inside even when pressurized. [158] In addition, in the charging/discharging process, the repeated volume change of sulfide-based ISEs causes the pulverization of the powder surface and the interfacial short with other materials. [139]

Herein, we dealt with two kinds of additives to alleviate the instability and the chronic physical problems between the cathodic materials and sulfide-based ISEs. As the first type of additive in the

cathode, we chose two types of ionic conductive polymer: poly(ethylene oxide) - based and poly(ethylene carbonate) - based polymers. We tried to introduce ionic conductive polymers as a binder and a buffer layer material. Ionic conductive polymers are expected to bind cathodic materials as well as sustain the ionic transfer path by replenishing the void and crack in the cathode. On the other hand, as the second additive type to be discussed, we selected three carbon materials having electronic conductivity: carbon black, carbon nanofiber, and carbon nanotube. Most cathodes in LIBs contain a conductive additive to smooth the electron transfer. However, as it has been reported that the conductive additive might cause critical degradation of sulfide-based cathodes, some studies have attempted cathode fabrication excluding conductive additives. Nonetheless, for increasing the energy density of sulfide-based ASSBs, the cathode should have a higher loading density. Therefore, in common with other LIBs, conductive additives are an essential component of the cathode in sulfide-based ASSBs.



**Figure 4-1** A schematic diagram of methods introduced in this study for securing the electrochemical stability of sulfide-based cathodes and LIBs

# 4.2. Experimental

#### 4.2.1 Cathodic materials

Active material, LiNiCoAlO<sub>2</sub> (NCA) was provided by ECOPRO BM. Argyrodites (Li<sub>6</sub>PS<sub>5</sub>Cl) with different diameters (3 um and 5 um) were purchased from POSCO JK Solid Solution Co,. Ltd. Each argyrodite powder of 3 um and 5 um was used for electrode and electrolyte fabrication. Carbon black(Super P, Alfa Aesar) carbon nanofiber(CNF, Sigma-Aldrich), and carbon nanotube(CNT, Korea nanomaterials) were prepared as conductive additives. Excluding argyrodite powders, all the cathodic materials were dried by heating in a vacuum oven for one day.

#### 4.2.2 Preparation of ionic conductive polymer additives

As PEO-based ionic-conductive polymer additives, poly (ethylene glycol) dimethyl ether (PEGDME) with different molecular weights of about 500 and 1000 g mol<sup>-1</sup> (PEGDME 500 and 1000) were prepared. PEGDME500 was provided by Hannong Chemicals Inc. PEGDME1000 was purchased from Sigma-Aldrich Korea. Meanwhile, PEC-based ionic conductive polymer additives, poly (propylene carbonate) (PPC, Mw 50000) and poly (trimethylene carbonate) (PTMC) were prepared. PPC was purchased from Sigma-Aldrich Korea. PTMC was synthesized by referring to the literature.[211] In addition, 1.0M LiPF6 in EC: DEC (1:1 v:v) liquid electrolyte was also purchased from

SoulBrain Korea to verify the chemical stability of carbonate-based materials.

## 4.2.3 Preparation of cathode materials

Before the cell fabrication of a sulfide-based all-solid-state cell, cathodic materials were mechanically mixed using mortar in a glove box filled with Argon gas. The ratio of the cathode was 70:27:3 of active material, argyrodite, and conductive additive. In ordering this ratio, the active material and the conductive additive were first mixed for 10 minutes. In the experiment using ionic conductive additives, polymers were injected at this step and mixed together. Sulfide-based ISE, argyrodite was then added and mechanically mixed for 10 minutes again.

## 4.2.4 Cell fabrication

Cell fabrication proceeded in a glove box filled with Ar gas. The sulfide-based all-solid-state cell was assembled by stacking up lithium/indium foil, argyrodite powder for electrolyte, and cathode powders in order, as shown in Figure 4-2. Before the assembly, cell parts such as lithium, indium, and stainless steel foils were punched to have a diameter of 13 mm. First, after  $\Phi$ 13 mm of lithium and indium foils were stacked within the mold, argyrodite powder for the electrolyte was then poured on stacked Li/In foil. Afterward, a slight pressure was applied to densify an argyrodite electrolyte layer. Prepared the mixture for cathode fabrication was added on stacked

layers, and then pressurized again under 300 Mpa pressure for one minute. Lastly, SUS current collector and an upper SUS cylinder were stacked and pressurized by tightening a lid screw using a torque wrench.



Figure 4-2 Schematic structure of the sulfide-based cell.

## 4.2.5 Characterization

The chemical structure and molecular weight of PTMC were characterized using gel permeation chromatography (GPC, Waters 2690) and nuclear magnetic resonance (NMR, 500 MHz, CDCl<sub>3</sub>, ppm). The chemical state of each conductive additive and cathodes were estimated through Raman spectroscopy (Bruker FRA 106/S), X-ray diffraction analysis (XRD, Rigaku D/Max 2200V), and X-ray photoelectron spectroscopy (XPS, ThermoFisher Scientific K-Alpha+ and ULVAC PHI 5000 Versaprobe).

#### 4.2.6 Electrochemical Measurement

The electrochemical stability of composite cathodes applied to each type of additives was evaluated by linear sweep voltammetry (LSV) and cyclic voltammetry (CV) using VMP3, Biologic and WBCS3000, WonATech. The measurement range of LSV was set up from OCV to 5.0 V in a scan rate of 0.1 mV s<sup>-1</sup>. CV measurement proceeded in a range from 2.0 to 3.7 V (vs. Li–In/Li<sup>+</sup>) (2.6–4.3 V vs. Li/Li<sup>+</sup>) in a scan rate of 1.0 mV s<sup>-1</sup>.

The electrochemical performance of the sulfide-based all-solidstate cell was assessed using VMP3 and WBCS3000. Electrochemical impedance spectroscopy (EIS) was done in a frequency range from 1.0 MHz to 100 mHz at the amplitude of 5.0 mV. The long-term stability and rate capability of the cell were tested in the voltage range from 2.0 to 3.7 V (vs. Li-In/Li<sup>+</sup>) [2.6-4.3 V (vs. Li/Li<sup>+</sup>)]. The long-term stability proceeded in the charging and discharging rate of 0.1C, 0.5C, or 1.0C. The rate capability of cells was tested at different rates of 0.1, 0.2, 0.5, and 1.0C in order.

# 4.3. Ionic-conductive polymer(ICP) additives

In this section, we introduced polymer-based additives with ionic conductivity. As with cathodes in other LIBs, we tried to wrap cathodic materials in polymer material and protect them from harmful reactions that degrade the performance of LIBs. To this end, we explored ionic-conductive polymers which have low reactivity with sulfide-based ISEs and proper processability.

#### 4.3.1 PEO-based ICPs

We first prepared poly (ethylene glycol) dimethyl ether (PEGDME) with a different molecular weight of about 500 g mol<sup>-1</sup> (PEGDME500) and 1000 g mol<sup>-1</sup> (PEGDME1000), as a PEO-based ionic-conductive polymer additive (ICP additive). PEO-based ICPs have been broadly applied due to their high ionic conductivity. However, some literature reported that the terminal -OH and -H in PEO react with sulfide-based ISEs. Therefore, we chose PEGDMEs which are capped terminal groups by methylation. Before evaluating the properties of PEGDME ICPs, we verified characteristics in bare cathode and argyrodite without ICPs. To check the chemical stability by LSV, the cell was fabricated by stacking Li/In foil, argyrodite electrolyte, and bare argyrodite for the electrode in order. Figure 4-3(a) shows that bare argyrodite does not react in a testing potential range of 2.5-5.6 V (vs. Li/Li<sup>+</sup>). Furthermore, a bare cell without ICPs showed the 1st capacity of 180 mAh g<sup>-1</sup> at 0.1C. As proceeded cycles until the 10th,

the capacity of the bare cell was slightly decreased and became 160 mAh g<sup>-1</sup>.

As the next step, we compared the electrochemical stability of PEGDME ICPs with argyrodite electrolytes. To prepare the electrochemical verification, each PEGDME was mixed in a ratio of 5 wt% with argyrodite powder. After then, the mixture was applied to the cell in the same procedure in bare state tests. We performed the electrochemical stability test first according to the presence of a lithium salt in PEGDME500. As the result, as seen in Figure 4-3(c), PEGDME500 with a LiTFSI showed more good electrochemical stability than that without LiTFSI. This result indicates the suppression effect of lithium salts on the reactivity of PEGDMEs. Lithium salts inhibit the contact between PEGDME polymer chains and then prevent the electrochemical degradation of PEGDMEs. At a magnified LSV result in Figure 4-3(d), in contrast to PEGDME500 alone, we can confirm that PEGDME500+LiTFSI sustained its electrochemical stability until 4.5 V. Therefore, lithium salts can be regarded as a necessary component to improve the electrochemical stability of ICPs. Figure 4-3(d) also shows the chemical stability according to the molecular weight of PEGDMEs. As seen earlier, PEGDME500+LiTFSI underwent the current increase at 4.5 V as potentials increased. Meanwhile, PEGDME1000+LiTFSI had a lesser current change than PEGDME500+LiTFSI. The result means that the higher molecular weight of PEGDME ICPs has better electrochemical stability. It seems that the activity of high molecular weight PEGDME is lowered as the long polymer chains are entangled, and the electrochemical reactivity is eventually decreased due to less contact between PEGDME molecules. [55] Hence, the higher molecular weight of ICPs can improve electrochemical stability. On the other

hand, for ICPs to be located stably in the gap within the cathode, the high molecular weight of ICPs is needed to secure their viscosity and mechanical properties. Since Polymers with lower molecular weight are easier to flow, large flowable ICPs are improper to fill the void between cathodic materials. Thus, the ICPs of higher molecular weight are advantageous to adhere and wrap on the surface of cathodic materials and thus secure good sustainability and structural stability as the protective layer.

In order to verify the electrochemical performance of PEGDMEs, composite cathodes were fabricated by mixing each 5 wt% PEGDME ICP with cathodic materials, as explained in an experimental section. Unfortunately, as shown in Figure 4-3(e) and (f), composite cathodes with each PEGDME ICP could not be operated with insufficient capacity and stability. The reason for the abnormal working of composite cathodes seems to be due to the reactivity of PEGDME ICPs. PEGDME ICPs undoubtedly reacted with the argyrodite in LSV analyses. The reactivity of PEGDME ICPs might become greater in the cathode, which is a more electrochemically harsh environment than in the LSV. The cell for PEGDME500 ICP showed a capacity of 110 mAh  $g^{-1}$ , which is larger than that for PEGDME1000. The lower capacity in the PEGDME1000 composite cathode is because of its lower ionic conductivity than PEGDME500. However, as examinations proceeded until the 10th cycle, the capacity of the cell for PEGDME500 was rapidly degraded. Meanwhile, although the cell for PEGDME1000 had a lower capacity in the 1st cycle, the capacity degradation was slightly slower than PEGDME500. This result demonstrates that the relatively higher electrochemical stability of PEGDME1000 resulted in better life performance of sulfide-based cells. In conclusion, we verified that

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PEGDMEs as PEO-based ICPs are inappropriate for sulfide-based cathodes due to their electrochemical instability with the sulfidebased ISEs in the cathode. Literature has reported that PEO-based polymers are unstable with sulfide-based ISEs and their instability comes from hydroxyl end groups in PEO. [149,212] However, this study introduced PEGDME which is converted terminal group by methylation. Therefore, interfaces between PEGDME and argyrodite might undergo less chemical reaction than that of PEO. However, most studies on the reactivity between PEOs and sulfide-based ISEs introduced PEO as electrodes, like a PEO|sulfide-ISEs|PEO configuration. Referring to some studies, when the mixture of PEO and sulfide-based ISEs is applied as the electrolyte, the cell with a PEO-sulfide ISE electrolyte layer showed good electrochemical stability and performance. [213,214] Hence, It can be assumed that the instability of PEGDME ICPs originated in electrochemical side reactions at the high potential in a cathode. Furthermore, due to the high lithium salt solubility of PEGDME, irreversible lithium ion transfer at the PEGDME/argyrodite interfaces might be induced and cause the degradation of argyrodite and performance deterioration.



**Figure 4-3** (a) LSV result on bare argyrodite. (b) The charging and discharge profile of NCA|bare argyrodite|Li/In cell. (c) Electrochemical stability test of PEGDME500 5 wt% +argyrodite according to adding a lithium salt. (d) Electrochemical stability comparison of PEGDME500 and PEGDME1000 mixed with argyrodite. (e-f) The cycle stability of composite NCA cathodes with PEGDME500 or PEGDME1000 for 10 cycles. The cycle stability of each composite cathode was evaluated under potential ranges of 2.0-3.7 V (vs. Li-In/Li<sup>+</sup>) and a scan rate of 1.0 mV s<sup>-1</sup>. The potential range in figures was converted to Li/Li<sup>+</sup> reference.

#### 4.3.2 Characteristic prediction of PEC-based ICPs

We explored PEC-based ICPs next, which are well-known other ICPs. PEC-based ICPs have a higher electrochemical oxidation potential than PEO-based ones. [70] Hence, PEC-based ICPs can be expected to be more electrochemically stable for the sulfide-based cathode. Since active materials for the cathode, like NCM and NCA, do redox reactions even above 4.0 V (vs. Li/Li<sup>+</sup>), the higher electrochemical oxidation potential might be an important key to improving the stability of ICPs for cathodic materials. Before the exploration of proper PEC-based ICPs, we predicted the electrochemical stability of PEC-based ICPs using a carbonate-based liquid electrolyte, 1.0 M LiPF<sub>6</sub> in ethylene carbonate/diethylene carbonate solvent (EC/DEC, 1/1 v/v). Since organic materials in the liquid electrolyte consist of various carbonate groups, the liquid electrolyte might be proper to anticipate the characteristics of PEC-based ICPs.

First of all, we evaluated the electrochemical stability of the liquid electrolyte for the argyrodite sulfide electrolyte. As shown in Figure 4-4(a), the liquid electrolyte exhibited significantly good electrochemical stability. In contrast to PEGDME500, the liquid electrolyte had no changes in the current value in an LSV result. Therefore, referring to the LSV result, we can expect that carbonate functional groups in PEC-based ICPs would be stable for sulfide-based ISEs. The cell performance of the composite cathode was examined by introducing a liquid electrolyte of 5 wt% into the cathode fabrication. We first tested the rate capability in different charging/discharging rates, and the long-term stability test then followed at 0.5C [Figure 4-4(c-d)]. In an earlier 0.1C step, the

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composite cathode showed a capacity of 180 mAh  $g^{-1}$  at the 1st cycle and 150 mAh g<sup>-1</sup> at the 10th cycle. This result is considerably in contrast to the results for PEGDME ICPs. At the following capability tests at different rates in Figure 4-4(e), the composite cathode also stably worked without rapid capacity changes. Meanwhile, the composite cathode in a long-term cycle test retained 62.4% of the initial capacity until the 200th cycle. In sum, there were no sharp capacity changes during the performance verification. The capacity of the composite cathode declined linearly. Furthermore, as shown by the capacity change in an initial 0.1C step, this composite cathode had a similar capacity and the tendency in degradation pattern with the bare cell. The degradation tendency of liquid electrolyte composite cathode indicates that the liquid electrolyte does not strongly react with argyrodite. In addition, the rate capability test indicates that the liquid electrolyte is electrochemically stable for sulfide-based cathodes in even high voltage and currents. In conclusion, we could conclude that the carbonate groups are stable enough for the argyrodite sulfide electrolytes.



**Figure 4-4** (a) Electrochemical stability comparison of a carbonatebased liquid electrolyte(1.0 M LiPF<sub>6</sub> in EC/DEC v/v) and PEGDME500. (b) The rate capability and cycle stability of NCA composite cathode with the liquid electrolyte. (c) Charging/discharging profiles and (d) the transition of discharge capacity in NCA composite cathode with a liquid electrolyte in a charging/discharging rate from 0.1 to 1.0C. (e) The capacity retention rate of the composite NCA cathode with a liquid electrolyte at a 0.5C rate for 200 cycles. The cell consisted of composite NCA|argyrodite|Li/In, and the composite cathode contained a liquid electrolyte of 5 wt%. The cut-off voltage was set up from 2.0 to 3.7 V (vs. Li-In/Li<sup>+</sup>) (2.6-4.3 V vs. Li/Li<sup>+</sup>).

# 4.3.3 Introduction of PPC-ICP

Based on previous results on PEGDMEs and a carbonate-based liquid electrolyte, we applied poly (propylene carbonate) (PPC) with a high molecular weight of  $50000 \text{ g mol}^{-1}$  as a PEC-based ICP. As seen in a small picture of Figure 4-5(a), PPC had a bead shape and was rarely stretched or torn at room temperature like elastomers. Therefore, we expected that PPC would serve as a protective layer of cathodic materials having good mechanical strength and durability. However, these excellent mechanical properties of PPC are disadvantageous to mechanically mixing with cathodic materials, unlike previous experiments about PEGDMEs and a liquid electrolyte. Hence, we decided to apply PPC on the surface of active material by heating or dissolving.

The electrochemical stability of PPC with argyrodite was evaluated by LSV. For this, a 3 wt% PPC and argyrodite were mixed in a mortar while heating at 120 °C. After mixing PPC and argyrodite well, the cell was fabricated and applied to LSV analysis. The cell was organized in the structure of the mixture argyrodite Li-In foil. In Figure 4-5(a), PPC showed considerable electrochemical stability even without lithium salts, like the liquid electrolyte. This result can be explained by the effects of the high molecular weight and the carbonate introduction mentioned above. Meanwhile, as shown in Figure 4-5(c), we also measured the ionic conductivity of the mixture of argyrodite and 3 wt% PPC. Compared to a bare argyrodite, the mixture showed about half the ionic conductivity of argyrodite alone. Since PPC has quite a low ionic conductivity as seen in Figure 4-5(b), this high ionic conductivity of the mixture mostly originated from the interfaces between argyrodite powders. Therefore, PPC might be regarded to wrap argyrodite very thinly and be located well in the void between the powders. As a result, a PPC-ICP additive slightly lowers the performance of the argyrodite due to inherently low ionic conductivity. Nonetheless, the mixture in this study exhibit ionic conductivity above 0.6 mS cm<sup>-1</sup>, thus it is expected that PPC-ICPs become useful materials through the optimization of application methods and conditions.

In order to apply PPC as a buffer or protective material, it needs the proper way how thinly coat cathodic materials with PPC as possible while minimizing the ionic conductivity loss. Hence, we tried to thin coat of NCA active material with a PPC solution. The coating solution was prepared by solvating PPC into N-methylpyrrodione(NMP) solvent. After then, NCA powders were added and dispersed to the PPC solution using a sonicator. Well-dispersed NCA-PPC solution was finally filtrated and dried in a vacuum atmosphere. To check the coating amount of PPC on the NCA surface, we performed a TGA analysis as shown in Figure 4-5(d). As PPC is sharply pyrolyzed from a temperature of about 250  $^{\circ}$ C, we could estimate the PPC amount on the active material surface to 0.25 wt%. The electrochemical effect on thin PPC coating was verified by fabricating the cell with a PPC-coated NCA (PPC-NCA) composite cathode. In Figure 4-5(e), the PPC-NCA composite cathode exhibited a slightly lower initial capacity of 170.0 mAh  $g^{-1}$  compared to the bare cell. Besides, the polarization at a PPC-NCA composite cathode was larger than the bare cell. The degradation in electrochemical performance is due to the low ionic conductivity of PPC. As PPC wraps the NCA, the ionic transfer between NCA particles might be lowered. Furthermore, the electron slightly transport for electrochemical reactions also can be delayed because PPC has hardly electric conductivity. However, in the aspect of cycle stability, PPC-NCA composite cathode showed better performance than the bare cell and the liquid electrolyte composite cathode. Even though the liquid electrolyte did not react with sulfide-based electrolytes, the capacity was degraded at the same rate as the bare cell. This degradation pattern in the capacity means that the liquid electrolyte rarely roles of protection layer due to their high fluidity and less adhesion. On the other hand, the PPC-NCA composite cathode showed enhanced cycle stability than the bare cell. As seen in Figure 4-6 (b) and (c), both results for cycle stability for 100 cycles showed a capacity retention rate near 85% at the 100th cycle. These capacity retention rates in a PPC-NCA cathode are about 10% higher than that of the liquid electrolyte. Thus, we can confirm that PPC effectively protects an NCA active material and the role of a buffer layer for long-term cycles. In conclusion, PPC was effective to protect NCA and other cathodic materials from side reactions, which deteriorate the chemical condition and electrochemical performance of sulfide-based cathodes. Besides, the solution coating method in this study is proper for the mass production of ICP-active materials and thus might contribute to the commercialization of sulfide-based ASSBs. If further studies proceed on the coating process or conditions, PPC will be useful as a buffer material or protective layer for sulfide-based cathodes.



**Figure 4-5** (a) A electrochemical stability of the mixture of 3 wt% PPC and argyrodite. (b) A Nyquist plot of PPC alone. (c) Nyquist plots of bare argyrodite and argyridte+3 wt% PPC. (d) A TGA result on PPC-NCA. (e) Rate capability test and (f) followed cycle stability test in 0.5C rate of PPC-NCA|argyrodite|Li-In cell. Cut-off voltage was set up from 2.0 to 3.7 V (vs. Li-In/Li<sup>+</sup>) (2.6-4.3 V vs. Li/Li<sup>+</sup>).



**Figure 4-6** The capacity changes of PPC-NCA composite cathode in (a) the capability test (b) the followed cycle stability test at 0.5C, and (c) the cycle stability test at 0.1C

# 4.3.4 Introduction of PTMC-ICP

Although PPC with Mw 50000 g mol<sup>-1</sup> showed excellent performance as a protective layer in the sulfide-based cathode, high elasticity and mechanical strength made it difficult for the physical mixing process. Furthermore, the solution coating method in a previous experiment using PPC was suitable for the active material coating. However, it is improper to sulfide-based ISEs due to the difficulty in selecting chemically stable solvents for sulfide-based materials. In other words, to improve the utilization of PEC-based ICPs, the processability of ICPs should be considered, as well as the chemical and electrochemical stability. Meanwhile, For PEC-based ICPs to serve as a buffer layer while improving ionic conductivity, the molecular weight compromise of viscosity and high ionic conductivity together should be explored. For this reason, we synthesized poly (trimethylene carbonate) (PTMC) with 1000-2000 g mol<sup>-1</sup> molecular weight, as another PEC-based ICP additive. The synthesized PTMC had enough viscosity to adhere without flowing.

The electrochemical stability of PTMC was first evaluated, prior to the performance verification. A sample was fabricated by mixing 5 wt% PTMC and argyrodite and applied to LSV analysis. As shown in Figure 4–7(a), the PTMC showed good electrochemical stability for argyrodite sulfide-based ISE, as same with a PPC and a carbonatebased liquid electrolyte. Furthermore, the ionic conductivity of PTMC alone was measured as  $1.4 \times 10^{-3} \text{ mS cm}^{-1}$  as seen in Figure 4–7 (b), which is 30 times higher than PPC. Because the molecular weight of PTMC is 1/30 of PPC, PTMC can be flowable but quite highly viscous.
Due to these characteristics, PTMC would be suitable to wrap cathodic materials and play as a protective layer well.

To confirm the performance in the sulfide-based cathode, a PTMC-ICP of 5 wt% was added to the cathode. As shown in Figure 4-7 (cf), the PTMC composite cathode showed a relatively low capacity of about 155 mAh g<sup>-1</sup> at the 1st cycle. During followed 10 cycles, the capacity of the PTMC composite cathode was steadily reduced and reached 75 % of the 1st capacity. It is determined that various factors affected the deterioration of initial electrochemical performance until the 10th cycle. The first factor is the low ionic conductivity of PTMC. When PTMC-ICP wrap on the surface of cathodic materials, interfaces between cathodic materials might undergo the resistance of ion transport due to PTMC layers. In addition, PTMC was applied into the cathode in a 20 times amount higher than PPC coating on active material. As a result, although PTMC-ICP has higher ionic conductivity, the PTMC composite cathode showed worse electrochemical performance than the PPC-NCA composite cathode. Additionally, a terminal hydroxyl group and ethylene oxide units in PTMC seem to react with an argyrodite in the composite cathode. The high reactivity of the hydroxyl group causes the oxidation of sulfide-based ISEs and the passivation layer formed on the surface of active materials. In addition, ethylene oxide units as well deteriorate the performance of sulfide-based cathodes, as discussed above section on PEGDME. However, despite these side reactions which are harmful to the cathode, the excellent capacity retention rate after the 10th cycle indicates that PTMC-ICP continuously protects cathodic materials from these side reactions. The large input amount of PTMC caused the resistance increase in interfaces of the cathode but served a clear effect on keeping the capacity for the long term. In summary, in this experiment, the molecular weight of PTMC-ICP was adjusted to have glue-like viscosity. It is also confirmed that PTMC as a protective layer can enough protect cathodic materials from side reactions. If disadvantageous factors in a PTMC-ICP are corrected, PTMC-ICPs will be more appropriate materials as a protective layer for sulfide-based cathodes.



**Figure 4–7** (a) LSV result of the mixture of argyrodite and 5wt% PTMC. (b) Nyquist plot of PTMC containing LiTFSI of 100 mol%. (c) Charging/discharging profile and (d) capacity transition in the rate capability test from 0.1 to 1.0 C. (e) Charging/discharge profile and (f) the capacity change in cycle stability test at 0.5C. The electrochemical performance of the composite cathode with PTMC was tested in a potential range of 2.0-3.7 V (vs. Li–In/Li<sup>+</sup>) (2.6-4.3 V vs. Li/Li<sup>+</sup>).

### 4.4. Electronic-conductive carbon(ECC) additives

We compared three carbon materials as an electronic-conductive additive (ECC). The physical- and chemical conditions of carbon materials were first investigated. After that, we examined the effect of each conductive additive on the electrochemical performance in a sulfide-based all-solid-state cell. In this way, we aimed to select an electronic conductive material that has better performance in sulfide-based ISE systems.

#### 4.4.1 Crystallinity of ECCs

We identified the chemical state of prepared ECC additives. First, the carbon bonding state in each ECC was verified using Raman spectroscopy. As shown in Figure 4-8(a-c), each ECC showed a different ratio in intensities of the D and G band peaks (I<sub>D</sub>/I<sub>G</sub>). D and G bands demonstrate the degree of the defect and graphitic bonding, respectively. Therefore, a high I<sub>D</sub>/I<sub>G</sub> value indicates that the carbon material has good carbon crystallinity and low defect concentration. CNF exhibited the highest I<sub>D</sub>/I<sub>G</sub> ratio, while carbon black had the lowest value among ECCs. That is, Raman spectra of ECCs implied that CNF has fewer defects than carbon black. In Figure 4-8 (d), XRD patterns of each ECCs provided a supporting explanation of the result in Raman spectroscopy. While CNF and CNT showed an obvious peak at about 28° indicating the carbon crystal structure, carbon black seems to have an amorphous phase. Thus, we can reason that CNF

and CNT have well-developed carbon bonding and low defect concentration compared with carbon black.



**Figure 4–8** Raman spectrum of (a) CNF, (b) CNT, and (c) Carbon black. And (d) XRD patterns of ECCs.

### 4.4.2 The chemical state of ECCs

For detailed verification of chemical bonding in ECCs, we performed XPS analyses. To understand atomic distribution inside CNF and carbon black, an XPS depth profiling proceeded. We checked the chemical state of the total of 5 depth points including the surface. As a result, few atoms were detected except carbon and oxygen, and the XPS depth profiles shown in Figure 4-9 were obtained. In this result, CNF showed a higher carbon concentration than carbon black [Figure 4-9(a)]. However, as the etching proceeded, the atomic concentration of carbon in both ECCs gradually became similar. Meanwhile, carbon black exhibited 3 times higher oxygen atom concentration on the surface than CNF, as seen in Figure 4-9 (b). From these XPS depth profiles, it can be inferred that surface defects in carbon black might bond with oxygen atoms. Therefore, the electronic conductivity of the carbon black surface might be reduced due to the binding with oxygen. However, oxygen did not permeate the carbon black inside, thus electron transport inside the carbon black would not be significantly degraded.

We then compared the XPS patterns on carbon 1s (C 1s) and oxygen 1s (O 1s) of ECCs, as shown in Figure 4–10. In the XPS pattern on C 1s, all ECCs showed similar patterns in which peaks for inter– carbon bonding of sp<sup>2</sup> (~284.7 eV) and sp<sup>3</sup> (~285.2 eV) are most preponderated. However, while CNF mostly consisted of inter– carbon bonds, carbon black exhibited a noticeably large proportion of bonds corresponding to sp<sup>3</sup> and C–O/C=O. Comparing the XPS peak patterns, it can be seen that the C–O and C=O bond peaks increase along with the sp<sup>3</sup> peak. Furthermore, Figure 4–10(b) demonstrates that this difference in a C 1s pattern originated from C-O and C-OH bonds. Besides, an O 1s XPS peak pattern for the carbon black had a peak corresponding to C-OH (533.6 eV), contrary to other ECCs. As sulfide-based ISEs are vulnerable to oxygen and hydrogen either, especially water, functional groups related to oxygen and hydrogen can have harmful effects on the performance of sulfide-based solid cells. Therefore, when discussing the electrochemical performance of a sulfide-based cathode containing each ECC, the effect of the presence and the concentration of the C-O and C-OH bonds should be also considered.

Meanwhile, CNF had relatively a smaller C-O peak than the C=O peak, unlike other ECCs. This intensity difference in C-O and C=Opeaks comes from the crystallinity of ECC additives. In the manufacturing process of carbon materials at high temperatures, carbons are graphitized with  $C=C(sp^2)$  and  $C-C(sp^3)$  formation. If enough energy is continuously supplied, it allows the whole graphitization of the carbon materials and the higher concentration of C=C bonds. However, if sufficient energy is not supplied, the C-Cbond will be retained and applied to C-C(-O)-C chemical state formation. Furthermore, surface environments of carbon materials have relatively low carbon concentrations. Therefore, carbons have difficulty to more make bonds with other carbons and are easily combined with elements in the atmosphere. For these reasons, carbon black has a less-developed graphite structure and high sp<sup>3</sup> and carbonyl bonding, as verified through Raman spectroscopy, XRD, and XPS.[55] Despite having a well-developed graphitic crystal structure, high  $sp^2$  and carbonyl bond concentrations of CNT seem to originate from the inside and terminal of CNT. Since these areas in CNT have a large surface area, a lot of oxygen can be easily absorbed and combined.



**Figure 4–9** Atomic distribution for (a) C 1s and (b) O 1s in CNF and Carbon black through XPS depth profiling.



Figure 4-10 XPS spectra on (a) C 1s and (b) O 1s of CNF, CNT, and Carbon black.

#### 4.4.3 Electrochemical stability of ECCs

We examined the electrochemical stability of ECCs for an argyrodite sulfide-based ISE. Figure 4-11 provides LSV results for the mixture of argyrodite and ECCs. A cell for LSV analyses was prepared using a Li/In foil anode and an ECC-argyrodite (3-7 w/w)mixture. A reference cell without ECC was also assembled to verify the electrochemical reactivity of a pristine argyrodite. As a result, the carbon black cell exhibited the largest current changes for voltage scanning from OCV to 5.6 V (vs. Li/Li<sup>+</sup>). Meanwhile, the CNF mixture had the least changes. Since a reference cell did not show any peak, current peaks in LSV mean the reactivity between each ECC and argyrodite, or the responsiveness of ECCs for a voltage change. However, although there is a difference in the current scale, the location of peaks was the same regardless of ECCs. Just considering the current occurrence scale, carbon black can be regarded to have the lowest electrochemical stability among prepared ECCs. However, carbon black has the largest specific surface area (SSA), thus the responsiveness to electric changes might be much than other ECCs. That is, additional verification is required to compare the electrochemical stability of ECCs.

We next conducted a CV analysis to verify the progress of the electrochemical reaction in each argyrodite-ECC mixture. Furthermore, we checked the period required to form a stable interface between ECCs and an argyrodite. The CV analysis was performed in a range from 2.6 to 4.3 V (vs. Li/Li<sup>+</sup>), a cut-off voltage of the cell in this study. As shown in Figure 4-12 and Figure 4-13, all argyrodite-ECC mixtures exhibited a similar tendency with LSV

for the current occurrence. When the CV analysis is started, the current rapidly increased in all mixtures and gradually diminished as the cycle proceeded. In the first voltage ramp step, the carbon black mixture generated the most intensive current throughout the scan range, and the CNF mixture had the slightest current changes. Even in the voltage down step, argyrodite-ECC mixtures continuously generated a current. However, each argyrodite-ECC mixture was stabilized at a respectively different potential point in the voltage-down step. The CNF mixture was nearly stabilized at 4.2 V of the first cycle, and the carbon black, in contrast, lasted the reaction until the latest. This progress in the CV is related to the chemical state of each ECC additive.

As we verified in XPS, All ECCs consist of only carbon and oxygen. Therefore, we can suspect oxygen atoms as the cause that cause the current in CV by reacting with an argyrodite. That is, the relatively high oxygen concentration in the carbon black seems to raise and sustain reactions with argyrodite stronger and longer than ECCs. Besides, summarized together with the LSV result, the fierce initial current increase can be explained by the physical– and chemical state of ECCs. The higher concentration and SSA of the ECC let oxygen and its bonds react larger with an argyrodite for a long time. It cannot be denied that more electrons are accompanied by voltage changes due to the large SSA of the carbon black. However, the CV result demonstrates that reactions of an argyrodite with oxygen atoms are the major cause of the current transition indicating the electrochemical stability.



Figure 4-11 LSV results of each electronic conductive additive mixture with an argyrodite in a ratio of 7/3 (argyrodite/conductive additive w/w). The scan rate of LSV was set up at 0.1 mV s<sup>-1</sup>, and the cell consisted of the structure of the mixture|argyrodite|Li/In.



Figure 4-12 The 1st CV cycle profile and the reaction scale according to ECCs. CV was conducted at a scan rate of 1.0 mV s<sup>-1</sup>



Figure 4-13 CV results of argyrodite and each electronic conductive additive mixture (argyrodite/conductive additive=7/3, w/w). The cell was scanned at 1.0 mV s<sup>-1</sup> in a potential range from 2.6 to 4.3 V (Li/Li<sup>+</sup>).

	CNF-1*	CNF-2	CNT-1*	CNT-2	Carbon black*
Diameter (nm)	130	200-600	OD: 50 - 80 ID: 5 - 15	OD: 5 - 15 ID: 3 - 5	30 - 50
Length (µm)	20 - 200	20 - 50	10 - 30	~ 50	-
Tap density (g cm <sup>-3</sup> )	0.056	0.043	0.18	0.27	0.16
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	24	18	40	117	62

Table 4-1 Morphological features of ECCs

#### 4.4.4 Morphological estimation on ECC cathodes

Before the performance verification of sulfide-based cathodes with each ECC, we checked the morphology and atomic distribution in cathodes, as shown in Figure 4-14. Cathode samples were prepared in the shape of a pellet by mixing cathodic materials and pressurizing them. Cross-section SEM and BSE images show some NCA particles pulverized during a mixing process. That is, due to extending the surface area, NCA active material might undergo a more intense electro-chemical reaction including harmful side reactions. However, it also conversely means that active materials can have enough mass transport at interfaces with other materials. Thus, we can be less concerned about the degradation by space charge, which is caused due to the charge disproportion at the interface. Meanwhile, EDS results on each ECC composite cathode display the distribution of atoms consisting of cathodic materials. The EDS results on carbon (blue) display that ECC in all cathodes was dispersed well around NCA particles. Therefore, since electrons can sufficiently transfer across the cathode during the cell operation, electrochemical performance will not be degraded due to the lack of electron transport paths. Figure 4-15 shows the surface morphology of ECC:argyrodite(3:7) mixtures. Mixtures were fabricated through mixing and procedures as same with cathodic material preparation. In this Figure 4-15, ECCs were wrapped in argyrodite, and rarely broken and pulverized during the mixing process. Therefore, unlike active materials, ECCs can be anticipated that it will form electron transport paths as sustaining their shapes.



**Figure 4-14** Cross-section and atomic distribution images of composite cathodes contained each (a) CNF, (b) CNT, and (c) carbon black. These images were obtained by SEM, BSE mode@ SEM, and EDS analysis.



Figure 4-15 SEM images for (a) pristine CNF and (b) pristine carbon black and the mixture of (c) CNF and (d) carbon black with argyrodite (3:7).

### 4.4.5 Performance differences caused by ECCs

Following the previous evaluation of ECCs' characteristics, we verified the electrochemical performance of ECCs in the sulfidebased cathode. Furthermore, in this process, we attempted to interpret the electrochemical performance of ECCs by connecting them with their chemical state and shape. For this, we prepared cathodes by mixing cathodic materials in a glove box: NCA, argyrodite, and ECCs, as procedures written in a 4.2 experimental section.

First, we investigated the effect of the shape of ECCs on the longterm stability and the electrochemical performance of sulfidebased cathodes. Two CNF and CNT with different shapes were prepared, as shown in table 4-1. Two CNFs and CNTs were applied to cathode fabrication and examined their rate capability in the constant-temperature chamber at 25 °C. The rate capability test was organized in the order of 0.1C, 0.2C, 0.5C, 1.0C, and 0.1C, and an initial 0.1C step proceeded for 10 cycles to cell stabilization. Figure 4-16 demonstrates the result of the rate capability test. All CNT cathodes showed better rate capability than the cathode with CNTs. Although both ECCs work with similar capacity during lowrate steps, there was obviously a performance difference as the Crate increased. In high C-rate steps of 0.5C and 1.0C, CNF cathodes had a higher capacity than CNT cathodes. Thus, it can be seen that electrons or ions transport faster in CNF cathodes than in CNT cathodes. Electron generally has a faster transport speed than ions, thus this result means that the ionic resistance inside the CNF cathode is lower. Furthermore, the results in XPS and Raman

spectroscopy can explain the reason for different performances in CNF and CNT cathodes.

In Figure 4-8, both CNF and CNT had a low D/G intensity ratio indicating well-developed graphitic crystalline. Therefore, the electric conductivity of both ECCs has probably not a significant difference. However, CNF had slightly higher D/G intensity, which means a higher defect concentration than that of CNF. As we verified using XPS, the defect is related to bonds between carbon and oxygen atoms, such as carbonyl, carboxyl, and even carbonyl groups. These bonding might be reacted with sulfide-based ISEs to cause performance deterioration by forming a non-conductive passivation layer. In summary, due to the reactions on the CNT surface of oxygen atoms and an argyrodite, the interfacial resistance for lithium ions was increased. Higher ionic resistance eventually caused a lower rate capability performance of CNT cathodes than CNF cathodes. Meanwhile, the same type of ECCs did not show an apparent performance difference. CNF cathodes showed very similar performance as if they were the same materials. The difference between CNFs and CNTs was rather obvious. That is, in the same type of ECCs, it seems that the shape difference, like and diameters, does not significantly affect the lengths electrochemical performance of the sulfide-based cathode. CNTs and CNFs in this study were different in lengths, diameters, tap density, and even surface area. Nonetheless, the performance difference between CNTs was slighter than the difference according to the types of ECCs. Therefore, it can be concluded that the electrochemical performance between ECCs is more influenced by the material scale of ECCs like between fibers and tubes, than the shape scale of lengths and diameters.



**Figure 4–16** Rate capability test of two CNF and two CNT cathodes with different shapes and physical characters

#### 4.4.6 Understanding performance degradation

Until now, we discussed what factors in ECCs affect the performance degradation of a sulfide-based cathode. Finally, we checked the long-term stability of each ECC and verified how electrochemical degradation progressed through EIS and electrochemical estimations. The cell was fabricated applying each ECCs and operated above 50 cycles at high charge and discharge rates of 0.5C or 1.0C. Figure 4-17 demonstrates the capacity change for 100 cycles at 0.5C. Cathodes with each ECC had a similar initial capacity of ~175 mAh  $g^{-1}$ . Following the 0.5C step, the capacity of the carbon black cathode had a greater capacity decrease compared to other cathodes. Other cathodes exhibited a capacity of ~150 mAh g<sup>-1</sup>, but a carbon black cathode was ~120 mAh  $g^{-1}$ . As cycles proceeded, the capacity in all cathodes was linearly decreased. However, the respective slope in each cathode was different. Even though a CNT cathode showed a similar capacity to the CNF cathode at early steps, the capacity decrease in the CNT cathode was slightly faster than the CNF cathode.

The low capacity in a carbon black cathode can be explained in Figure 4-18(a). The initial slope in a charge/discharge curve means the activation of cathodic materials to transport lithium ions. Thus, a carbon black cathode underwent the slowest mass transfer among ECC cathodes. It can be inferred that a carbon black cathode had high interfacial resistance inside or already formed nonconductive layers by chemical reaction. Unlike CNT and CNF, carbon black is an amorphous and formless carbon powder. Therefore, carbon black has a lot of grain boundaries inside and interfaces with cathodic

materials. These factors impede electron transport in the cathode. On the other hand, carbon black had a relatively high oxygen-bond concentration on the surface. Besides, the hydroxyl group was also detected on the carbon black surface. These bonds related to oxygen can cause reactions with argyrodite electrolytes and generate resistive layers lowering the ionic transfer. It is also related to a performance decrease in the CNT cathode. The mass transport in the CNT cathode was smooth, as shown in Figure 4– 18(a). However, accumulated side reactions in the CNT cathode deteriorated the lithium ionic transfer, and eventually increased the internal resistance, as seen in Figure 4–18(c). The carbon black cathode underwent a more fierce reaction than the CNT cathode, thus the performance of the carbon black cathode was degraded more rapidly [Figure 4–18(d)].



**Figure 4-17** Comparison of long-term cycle stability at 0.5C of each composite cathode with ECCs.



**Figure 4–18** Charging/discharging profile at (a) 0.1C formation and 0.5C in (a) CNF cathode, (b) CNT cathode, and (d) carbon black.

To further understand the difference in the electrochemical stability according to ECCs, EIS analysis and long-term cycle test at 1.0C were conducted at the same time. Immediately after the cell assembly, we measured the internal resistance of cells for each ECC first. As shown in Figure 4-19(a), the bulk resistance of the argyrodite-electrolyte layer was a similar value of about 30  $\Omega$  ( $\sigma$  = 1.5 mS cm<sup>-1</sup>) in all cells. Meanwhile, since the carbon black cell showed a distinct semicircle in a Nyquist plot, it is inferred that there might be chemical reactions before the cell operation. After the formation step at 0.1C, all cells had changes in the Nyquist plot, as shown in Figure 4-19(c). In this figure, the Nyquist plot for each cell means that the side reactions and passivation layer inside the cathode cause interfacial resistance, thereby delaying the mass transfer through the interface. Therefore, we can recognize that ECCs undergo a larger intensity of side reactions in order of carbon black, NCT, and CNF (carbon black >CNT >CNF). In the long-term cycle stability test at 0.5C coming up next, the cell with CNF cathode exhibited the best performance and cycle stability among tested cells. Contrariwise, the carbon black cell had the worst initial capacity and remaining capacity at the 50th cycle.

During the cycle stability verification proceeded at 0.5C, we analogized the proceeding and causes for performance degradation through EIS analysis every 10th cycle. As seen in Figure 4-21, bulk resistance in the argyrodite electrolyte layer was rarely changed(starting point), whereas internal resistance rather was increased obviously(semi-circle). Therefore, it can be confirmed that the cell performance was mainly influenced by the condition of the cathode. That is, since the greatest side reaction among ECC cathodes occurred, a carbon black cell showed a Nyquist plot with the largest resistance and capacitance area. Besides, CNF and CNT had fewer changes during repeated cycles, contrastively a carbon black cell suffered an increase in internal resistance and capacitance until the 20th cycle. As the following cycle proceeded, Nyquist plots showed steadily the area decrease in all ECC cells. In conclusion, the changes in the Nyquist plot demonstrate that side reactions in CNF and CNT cathodes finished earlier than a carbon black cathode. However, carbon black cathode exhibits continuous side reactions, and internal resistance increase until the 20th cycle. As the reaction was diminished, the internal resistance of all ECC cathodes was decreased, and the mass transfer inside the cathodes became smooth.

Table 4-2 shows the resistance changes and an equivalent circuit for each ECC cell. First, R1 indicates the bulk resistance of an argyrodite electrolyte layer. The resistance values of the argyrodite layer were rarely changed but slightly increased as cycles progressed. It is due to the electrochemical degradation of the argyrodite layer itself. Meanwhile, R2 means the interfacial resistance between a Li-In anode and an argyrodite layer. After 0.1C formation, the interfacial resistance of each ECC cell decreased and stabilized. As cells operated, the surface of the Li-In anode or the interface shape of Li-In/argyrodite might be changed to facilitate the deposition and detachment of lithium ions. Thus, during initial cycles including 0.1C formation, R2 would decrease and then shows constant resistance values due to the surface optimization for lithium ion transport. R3 shows the interfacial resistance between cathodic active materials and surrounding argyrodite. After a 0.1C formation step, CNT had the lowest R3 resistance value while CNF showed the largest value. This result is related to the specific surface area of each ECC, as shown in Table 4-1. CNT has more large surface area than CNF and thus can have lower interfacial resistance with cathodic active materials. Meanwhile, although carbon black has the largest surface area, it can be judged that the interfacial resistance with cathodic active materials was increased due to the initial chemical resistance with argyrodite. As the cycle stability test progressed, R3 values in ECC cells generally decreased. However, CNT and carbon black cells showed the R3 increase until 0.5C 10th cycle, unlike a CNF cell. It caused the shape and tendency difference in the EIS results of each ECC cell, as shown in Figure 4-21. Lastly, R4 indicates the resistance and mass transfer in the cathode. Increased R4 values due to the side reaction between ECCs and argyrodite gradually reduced and became constant after the 10th cycle. That is, initial electrochemical side reactions between ECCs and argyrodite impeded mass transports and caused resistance increases in the cathode. In summary, side reactions in the ECC cathode impede mass transfer, thereby causing performance degradation. Even though the mass transfer is slightly recovered as the reactions finish, deteriorated performance does not recover due to accumulated side products in the cathode. Oxygen atoms on the surface of carbon black severely cause performance deterioration of the cathode, and other ECCs were also affected, albeit to a lesser degree.



**Figure 4–19** (a) Nyquist plots for ECC cells immediately after assembly. (b) Charge/discharge profiles of ECC cathodes at 0.1C formation step. (c) Nyquist plots for ECC cells after 0.1C formation.



Figure 4-20 Capacity change and retained capacity ratio of ECC cells during 50 cycles.



**Figure 4-21** Charge/discharge profiles and Nyquist plots at 1st and every 10th cycles for (a) CNF, (b) CNT, and (c) carbon black.

**Table 4–2** An Equivalent circuit and resistance element parameters for the Nyquist plots in each EIS analysis for the cell with (a) CNF, (b) CNT, and (c) carbon black. Each resistance element parameter respectively represents the bulk resistance of an argyrodite electrolyte layer(R1), the interface resistance between a Li–In anode and an electrolyte layer(R2), the interface resistance between cathodic active materials and surrounding argyrodite(R3), and total resistance and mass transfer in a cathode(R4).



(a) CNF

\* unit: Ω

	10th	20th	30th	40th	50th
R1	26.7	27.9	30.6	33.7	34.2
R2	15.3	13.7	14.8	13.6	17.4
R3	64.2	62.8	59.1	52.8	43.6
R4	140.5	146.1	151.9	146.6	148.3

# (b) CNT

\* unit: Ω

	10th	20th	30th	40th	50th
R1	28.7	31.8	32.4	34.4	35.7
R2	18.04	20.4	21.0	16.5	21.5
R3	109.3	102.7	98.3	100.0	88.6
R4	167.4	177.4	194.7	195.0	198.6

# (c) Carbon black

\* unit: Ω

	10th	20th	30th	40th	50th
R1	36.6	38.0	38.1	40.2	39.5
R2	19.8	36.7	33.8	28.3	21.5
R3	124.4	111.2	95.8	83.5	68.6
R4	215.8	244.1	235.0	239.4	235.0

### 4.5. Summary

In this study, we introduced two types of additives into the cathode of sulfide-based all-solid-state batteries. The first additives consist of ionic conductive polymers (ICPs), we adopted them as materials for a buffer layer and a protection layer. As a result, we confirmed that poly(ethylene oxide) - based ICPs are improper to the sulfide-based system, due to their electrochemical instability for sulfide-based electrolytes. Meanwhile, poly (ethylene carbonate)-based ICPs were electrochemically stable for sulfidebased electrolytes. Based on this result, we tried to apply poly(propylene carbonate) having high molecular weight into the cathode of sulfide-based cells. To wrap the active materials in a poly(propylene carbonate) ICP, we adopt the solution coating method. PPC-Coated active materials exhibited excellent cycle stability, even if the capacity slightly is lowered. Furthermore, to enhance the processability of PEC-based ICPs, we synthesized poly (trimethylene carbonate) and examined the performance of the PTMC-ICP composite cathode. As a result. We confirm that ICPs can enhance the cycle stability of sulfide-based ASSBs by protecting cathodic materials from harmful side reactions.

As the second additive for sulfide-based cathodes, we chose electronic-conductive carbons(ECCs). We prepared CNF, CNT, and carbon black as ECCs, and compared their crystallinity and chemical state through Raman spectroscopy, XRD, and XPS. As a result, we confirmed that each ECC has a different concentration of defects and oxygen on the surface. These defects and oxygen bonds with carbon atoms caused the electrochemical deterioration of sulfide-based cathodes. Among the ECCs in this study, carbon black exhibited the worst performance due to its high oxygen and defect concentration. Thus, well-developed graphitic structures and low oxygen concentration in ECCs enable long-term stable operation of sulfide-based ASSBs. Meanwhile, we compared two materials having different lengths and diameters in each CNF and CNT. Furthermore, by comparing each two CNF and CNT, we confirmed that the electrochemical performance of sulfide-based ASSBs is more affected by the type of material than the shape of the materials.

## **Chapter 5. Concluding remarks**

This dissertation dealt with various solid electrolytes consisting of polymers or inorganics. Polymer solid electrolytes showed considerably low ionic conductivity compared with liquid electrolytes. Thus, this dissertation suggested a gel polymer electrolyte as a compromise. Gel polymer electrolytes can obtain high ionic conductivity as a liquid electrolyte introduces. Meanwhile, a kind of inorganic solid electrolyte, sulfide-based solid electrolytes undergo problems in chemical instability and interface with materials of other cell parts, especially at the cathode. By applying different methods to remedy these problems, the cell with solid electrolytes was stably operated as electrochemical stability improved. For stable operation of solid electrolyte cells, methods introduced in each chapter are summarized as follows.

First, the designing of the polymeric structure was introduced to SPEs and GPEs. As well known, PEO-based polymers have a relatively low electrochemical oxidation potential. In chapter 2, a PO unit introduction into PEO structure resulted in enhancing the chemical stability and ionic conductivity of PEO-based SPEs. in addition, in chapter 3, as a crosslinker based on an ionic liquid is applied, an IL-based GPE showed better electrochemical performance than PEO-based GPEs. These results demonstrate that the polymer design is effective for adjusting the characteristics of polymer solid electrolytes.

Second, we explored various combinations and compositions of solid electrolytes or cathodes. In chapter 2, PEO-based and PEO/PPO-based plasticizers were mixed in different ratios to optimize performances in ionic conductivity and electrochemical stability. Meanwhile, an appropriate combination in a sulfide-based cathode was investigated in chapter 4. Conductive additives, which are necessary to all LIBs, can rather cause side-reaction in the sulfide-based cathode. Therefore, it is required to find less reactivity and proper physical characteristics suitable to sulfidebased ASSBs. In a study to find the proper combination of a sulfidebased cathode, it was verified that CNT is a stable cathodic material to the sulfide-based system. To conclude, Searching for combinations and compositions seems an easy method for performance optimization. By only adjusting the ratio or the kinds of materials, an electrolyte and electrodes can have various properties and exhibit better performance.

Third, we attempted to solve interfacial problems in solid– electrolyte-based LIBs. Solid electrolytes generally undergo problems related to interfaces due to their intrinsic physical characteristics like mechanical strength and viscosity. In studies on polymer solid electrolytes, the chapters 2 and 3, we applied the in– situ thermal crosslinking method to form enough interfaces between polymer electrolytes and cathodic materials. Using a liquid state of precursor, polymer electrolytes can easily penetrate the cathode inside. After heating, since the finished polymer electrolyte contacts enough with cathodic materials, the ion transport between cathodic materials and a polymer electrolyte becomes smooth. On the other hand, we introduced the ionic conductive polymer as a buffer layer to a sulfide-based cathode. Because a cathode with ionic conductive polymers exhibited better cycle stability, it was confirmed that ionic conductive polymers are enough to protect cathodic materials from side reactions in interfaces.

To sum up, this dissertation presents various methods to secure the long-term stability of solid electrolyte-based LIBs, while remedying the shortcomings of each solid electrolyte. The common necessary to solid electrolytes is electrochemical stability. Various factors disrupt the stable working of electrolytes. However, methods to improve stability also abound. That is, if further studies on solid electrolytes steadily proceeded, ASSBs will make gradual progress and expand their application fields and devices.

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## **Korean abstract**

오늘날 배터리는 지금까지의 스마트폰이나 스마트워치, 노트북과 같은 소형 전자 장치에만 국한되지 않고 자동차와 스마트 그리드와 같이 큰 규모까지 활용되고 있다. 다양한 규모와 적용 분야에 맞춰 여러 배터리들이 적용되고 있지만, 면적당 또는 질량당 요구되는 배터리의 에너지밀도가 점차 증가함에 따라서 리튬이온배터리의 수요가 점차 늘고 있다. 하지만 현재 리튬이온배터리에 적용되는 액체 전해질은 발화점이 낮고 증기압이 높은 유기 용매들로 구성된다. 또한 점차 가혹해지는 작동 조건에서 액체전해질은 부반응을 일으켜 가연성 기체를 발생시킬 수 있다. 따라서 만일 외부에 화재나 나거나, 작동 중에 스파크가 발생하다면 배터리가 발화하거나 폭발할 수 있다. 이러한 액체 전해질의 위험성은 전기자동차와 같이 규모가 큰 적용 분야에서는 심각하게 다뤄지고 있다. 따라서 리튬이온배터리의 안전성을 높이기 위해서, 액체 전해질은 반드시 높은 열에서도 안정한 전해질로 대체돼야 한다. 이를 위해서 많은 연구 그룹과 기업에서는 고온에서도 안정한 고체 전해질을 연구하고 있다. 이 논문에서는 이러한 고체 전해질에 대해 전반적으로 다루고 있으며, 특히 고체 전해질이 적용된 배터리 시스템의 전기화학적 안정성을 향상시키고자 하는 세 가지 연구들을 논의했다.

첫 번째로, 고분자를 기반으로 하는 고체상 고분자 전해질의 전기화학적 안정성을 높이기 위해, 구성 물질들의 구조를 설계하고 고체상 고분자 전해질들을 조합하여 전기화학적 성능을 최적화했다. 기존 문헌들에서 이온전도체로 많이 다루고 있는, poly(ethylene oxide)기반의 고분자 전해질의 문제점인 실온 결정성을 최대한 억제하는 동시에 전기화학적 안정성을 확보할 수 있는 고분자 구조를

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제안했다. 동시에 제안한 구조의 이온전도성 고분자를 활용하여 고체 고분자 전해질이 더욱 높은 성능을 오랫동안 유지할 수 있도록 했다.

하지만 고체상 고분자 전해질이 액체 전해질에 비해 매우 낮은 이온 전도도를 가지고 있기 때문에, 고체상 고분자 전해질의 상용화는 아직 시간이 걸릴 것이다. 따라서 고체상 고분자 전해질이 충분히 발전하기 까지 적용할 수 있는 대안을 두 번째 연구에서 제시했다. 이 연구에서는 고체상 고분자 전해질에서 사용했던 가교제를 이온성 액체 기반의 고분자로 제작하여, 상용 액체 전해질과 함께 겔 고분자 전해질을 제작했다. 이온성 액체는 이온전도체로써 많이 사용되면서 높은 전기화학적 안정성과 열적안정성을 증명해왔다. 이러한 이온성 액체를 가교제로 활용하여 다른 문헌에서의 겔 고분자 전해질보다 우수한 열적 안정성과 이온전도성을 보였다.

세 번째 연구 주제로 황화물 기반의 무기물 전해질을 다뤘다. 높은 이온전도도와 우수한 기계적 강도를 얻을 수 있는 황화물 기반 무기물 전해질은 액체 전해질을 대체할 만한 또 다른 선택지가 될 수 있다. 하지만, 황화물 자체의 낮은 화학적 안정성과 분말 형태이기에 발생하는 계면 문제가 복합적으로 작용하여, 황화물 기반 무기물 전해질이 완전한 성능을 발휘하는데 방해가 되고 있다. 이 연구에서는 황화물 기반의 무기물 전해질이 적용된 양극 내에 다양한 고분자 첨가제나 도전재를 적용하여, 양극의 전기화학적 안정성을 높이고 수명 특성을 향상하고자 했다. 이 연구과정을 통해 황화물 기반 무기물 전해질과 안정한 고분자 물질의 종류를 찾았고, 이를 버퍼층 또는 보호막으로 적용하여 황화물 기반 셀에서 양극이 안정적으로 구동하게끔 했다. 한편, 황화물 기반 셀에서 양극의 로딩 밀도를 높여 에너지 밀도를 높이기 위해 도전재는 반드시 양극 내에 포함돼야 한다. 따라서 다양한 도전재를 적용한 황화물 기반의 양극들의 성능을

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비교하고 성능 열화에 대한 요인을 탐색하여, 양극의 성능을 극대화하는데 적절한 도전재를 이 연구에서 제안했다.

본 논문의 내용을 다시 정리하면, 기존 리튬이온배터리 내 액체 전해질을 대체하여 배터리의 안전성을 높일 수 있는, 고분자 또는 무기물 기반의 고체 전해질들의 단점을 보완하는 동시에 이들 전해질을 포함하는 셀의 전기화학적 안정성을 향상시키고자 했다. 각각의 고체 전해질은 액체 전해질과 비교했을 때, 분명한 단점들이 있지만 점점 발전하는 리튬이온배터리가 안전하게 작동하기 위해선 고체 전해질의 적용은 반드시 필요하다. 이러한 고체 전해질의 적용 시기를 앞당겨 상용화하는데 본 논문에서 제시한 방법들이 도움이 될 것으로 기대한다.

핵심어: 고체전해질, 고분자 전해질, 황화물 기반 고체 전해질, 고체상 배터리, 차세대 리튬이온배터리

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