



## Short communication

# A high-performance polymer composite electrolyte embedded with ionic liquid for all solid lithium based batteries operating at ambient temperature



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## ABSTRACT

A novel polymer composite electrolyte for lithium-based battery operating at room temperature was introduced. The proposed polymer composite electrolyte consisted of electrolyte using a 3-D cross-linked polymer matrix, which is synthesized with polyethylene glycol (PEG) and 3-glycidoxypropyltrimethoxysilane (GPTMS), and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) as a Li-ion transport medium. The proposed polymer composite electrolyte shows a high ionic conductivity of  $35 \times 10^{-2} \text{ mS cm}^{-1}$  and high decomposition temperature of  $250^\circ\text{C}$  with a 3-D cross-linked polymer matrix. The EMITFSI mass ratio is 1:0.7 at room temperature. In addition, when polymer composite electrolyte is applied to the solid battery consisting of Li metal as an anode and  $\text{LiFePO}_4$  as a cathode, it can be operated at room temperature with a high specific capacity of  $75.8 \text{ mAh/g}$  at 0.1C rate. Furthermore, the battery with a structure of Li/polymer composite electrolyte/ $\text{LiFePO}_4$  also has excellent capacity retention.

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## Introduction

Lithium-based batteries, including lithium-ion batteries (LIB), lithium sulfur batteries and lithium air batteries, are the most attractive energy storage equipment for electronic devices such as mobile phones, laptops, and electric vehicles (EVs) due to their high power and energy density [1]. Especially in LIB applications, EVs are extensively researched to prevent global warming and environmental pollution [2]. In comparison to conventional vehicles with internal combustion engines, most EVs with the LIB system significantly reduce the emissions of greenhouse gases and exhaust particles [3] such as  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NO}_x$ ,  $\text{SO}_x$  and fine dust. However, the durability and safety of liquid electrolyte-based LIB show insufficient performance for EVs. The problems are caused by organic solvents in forms of leakage, worn out and thermal

runaway because organic solvents for LIB are highly volatile and flammable [4]. To solve these problems, all-solid-state batteries including solid electrolytes are suggested as a promising approach [5]. Especially, solid electrolytes could provide solutions for overcoming safety issues.

The solid electrolyte not only effectively solves the problems of solvent leakage and thermal runaway but also dramatically improves the cycle performances of batteries [4]. Furthermore, the battery designs can be diversified because a metal container for the liquid electrolyte is unnecessary. As well known, solid electrolytes could be divided into the ceramic type and polymer type [6]. Although the ceramic electrolytes have a high thermal stability and a mechanical stability, the relatively small specific capacity by a poor contact between the electrode and the electrolyte is still a problem. Also, the ceramic electrolyte is hard to apply in the conventional roll-to-roll process due to its brittleness. These drawbacks have to be addressed for actual applications on LIB. In comparison, the polymer electrolytes sufficiently solve interfacial contact issues. In other words, polymer electrolytes provide excellent safety performance,

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outstanding mechanical stability, and remarkable lithium dendrite suppression than the liquid electrolyte. Furthermore, the polymer electrolytes exhibit superior capacity characteristics than ceramic electrolytes [4]. Particularly, polyethylene oxide (PEO) based polymer electrolytes are commonly investigated for the all-solid-state lithium-ion battery due to their high lithium-ion solubility. However, PEO-based polymers show poor ionic conductivity ( $<10^{-6} \text{ S cm}^{-1}$  at room temperature) because of their high crystallinity. Thus, PEO-based polymers have some restrictions when used as the electrolytes for energy-storage devices [7]. For these reasons, PEO-based polymer electrolytes are investigated at high temperature to achieve reasonable ionic conductivity. However, the high temperature is not suitable to use for real LIB applications. Therefore, many researchers suggested solutions to overcome this critical problem, such as reducing the molecular weight of the polymer, polymer blending [8,9], and the addition of fillers [10–13]. Recently, it was reported that the usage of cross-linked polymers with a 3-D network structure is considered to be simple and effective methods to enhance the ionic conductivity [14–18]. However, these suggested methods are still not enough in terms of operating at room temperature.

Herein, we proposed a new type of polymer composite electrolyte embedding ionic liquid (IL) to fabricate the high-performance all-solid-state battery when operated at room temperature. The 3-D cross-linked polymer was composed by the coupling of polyethylene glycol (PEG) of host polymer and 3-glycidoxypropyltrimethoxysilane (GPTMS) of cross-linker. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) are selected as an IL for the Li-ion transport medium due to their high ionic conductivity and relatively low viscosity [19–21]. The EMITFSI also play an important role as a plasticizer for the polymer to increase ionic conductivity by enhancing the relaxation of polymer chains [22]. Furthermore, the suggested polymer composite electrolyte is thermally stable up to 250 °C. Also, the LIB assembled with this polymer composite electrolyte shows a high discharge capacity of 75.8 mAh/g at 0.1C rate at room temperature.

## Experimental

### Materials

The 3-glycidoxypropyltrimethoxysilane (GPTMS), polyethylene glycol (PEG) (MW 600), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI), and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) were purchased from Sigma–Aldrich, poly(vinylidene fluoride) (PVdF, Kynar HSV 900) was received from Arkema. Toluene (99.5%), acetic acid (99.5%), *n*-methyl-2-pyrrolidone (NMP) was purchased from Daejung Chemical. Lithium iron phosphate ( $\text{LiFePO}_4$ ) was purchased from MTI Korea. Carbon black (Super P<sup>®</sup>) was purchased from Timcal. GPTMS, EMITFSI, and LiTFSI were kept in the glove box filled with a dried argon atmosphere. Every chemical are treated under vacuum before use to remove residual moisture.

### Preparation of polymer composite electrolyte

The polymer composite electrolyte was fabricated by mixing with ionic liquid and cross-linked polymer. First, the 15.2 g PEG and 4.0 g GPTMS were mixed with 10 ml toluene while stirring for uniform dispersion. After stirring, 80  $\mu\text{l}$  acetic acid as a catalyst with nitrogen protection was added into the solution. The mixed solution was stirred at 100 °C for 50 h for cross-linking reactions. After the coupling reaction, the solution changed to yellow with the solid phase, and then the products were heated to remove the toluene (solvent) and methanol (side product) under vacuum at

110 °C for 5 h. EMITFSI was dissolved in *N*-methyl pyrrolidone (NMP) and then added to the prepared cross-linked polymer and LiTFSI with various weight ratios. The mixed polymer was ground by a mortar in a glove box filled with argon gas, and highly viscous polymeric gels were obtained. The gels were casted on substrates and dried at 120 °C for 8 h to evaporate the NMP. Then, cross-linked PEO embedding EMITFSI could be obtained with rubbery state. We used two types of substrates: stainless steel electrodes (SUS) plate for investigating electrolyte performance and a cathode for analyzing cell performances.

### Characterization of polymer composite electrolyte

The chemical structure of polymer composite electrolyte was characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra with a range of 4000–600  $\text{cm}^{-1}$ . To investigate the thermal stability, thermogravimetric analysis (TGA) was used to determine the thermal decomposition temperature of the polymer composite electrolytes. Electrochemical properties are characterized in a coin cell (CR 2032). The ionic conductivity of polymer composite electrolytes was characterized by electrochemical impedance spectroscopy (EIS) using the CHI 600 system (CH Instruments, Inc.) at a frequency range from 0.1 Hz to 1 MHz with the alternative current (AC) amplitude of 5 mV using SUS/polymer composite electrolyte/SUS.

The cathodes were fabricated by the casting method with a Meyer rod. The slurry consisted  $\text{LiFePO}_4$  as an active material, Super P<sup>®</sup> as a conductive agent, and PVdF as a binder in the mass ratio of 8:1:1. The planetary centrifugal mixer (AR 100, Thinky mixer) was used to disperse the slurry uniformly with NMP solvent. The testing coin cells consisting of a prepared cathode, a polymer composite electrolyte, and a Li foil anode were assembled in a glove box filled with argon gas. The galvanostatic charge-discharge and cycling tests of coin cells were measured in a battery cycler system (WB3000, Wonattech Co., LTD.).

## Results and discussion

### Design of polymer composite electrolyte

The polymer electrolyte for the lithium-based battery was extensively studied since the first battery using polymer electrolyte based on PEO was proposed by Armand [23]. This polymer electrolyte consists of lithium salts and a polymer, which have a polar group that can interact with the lithium cation. However, various well-known candidates of polymer electrolytes, such as PEO, polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), and polyvinylidene fluoride (PVdF), could not satisfy the demand for a practical LIB application because of low ionic conductivity induced from their intrinsic crystalline structure caused by the interaction of the polar group between polymer chains [7]. In the case of PEO, the oxygen in PEO enhances the Li cation dissociation [24]. However, the ethylene oxide structure has a tendency to become crystalline, which suppresses ion transport in the polymer matrix [25]. For this reason, most polymer electrolytes have low ionic conductivity at room temperature. To achieve high ionic conductivity of polymer electrolyte, decrease of the crystalline region in polymer electrolyte was required because the ion transport in polymer electrolytes was related with a segmental relaxation of the polymer chain in the amorphous region [6]. Therefore, the crucial way to increase ionic conductivity is to enhance the relaxation of the polymer chain and movement of ions.

For these reasons, we adopted the addition of ionic liquids into a 3-D cross-linked polymer matrix as another approach to enhance the ionic conductivity of the polymer electrolyte, which effectively

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