



Application of the imidazolium ionic liquid based nano-particle decorated gel polymer electrolyte for high safety lithium ion battery

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ABSTRACT

For the possible application in high safety lithium ion batteries, nano-particle decorated poly(methyl methacrylate-acrylonitrile-ethyl acrylate) (P(MMA-AN-EA)) based gel polymer electrolyte (GPE) using 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMITFSI) ionic liquid as plasticizer was developed in this paper for the first time. Characterization of thermal stability indicated that the MS5 (SiO₂: Al₂O₃ = 5:5 in weight) membrane presented better property of anti-thermal shrinkage, which in turn exhibited the excellent flame retardation performance for the corresponding GPE when incorporated with ionic liquid. The developed MS5 membrane had the strongest fracture strength of 160 MPa, much higher than that of polyethylene (PE) separator (138 MPa). Electrochemical analysis suggested that the GPE exhibited the enhanced ionic conductivity of $3.2 \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature, caused by its better porous structure with the highest porosity of 70%. The temperature dependence of ionic conductivity followed Vogel-Tamman-Fulcher (VTF) behavior. Oxidative potential of MS5 based GPE was significantly improved from 4.7 V (vs. Li⁺/Li) (PE saturated with ionic liquid) to 5.7 V. Theoretical calculation results showed that the stronger interaction between lithium ions and TFSI⁻ anions was responsible for the better compatibility of GPE with the electrodes. Thus, MS5 based GPE exhibited excellent cyclic stability, which kept 95.1% capacity retention after 100 cycles under 0.2C rate in LiFePO₄/GPE/Li type coin cell at room temperature, while retained 88.4% of initial discharge capacity at high temperature of 55 °C. Due to the enhanced transference number of lithium ion of the GPE, LiFePO₄ cathode in LiFePO₄/GPE/Li coin cell also presented superior rate performance.

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1. Introduction

Technological advancement has directly accelerated the development of higher efficient energy storage appliances [1–6]. Rechargeable lithium-ion battery (LIB) that owns high energy density and long cyclic life, has been widely used in various types of power and energy storage devices. The liquid electrolyte used in conventional LIB is formed by a certain concentration of lithium salt (lithium hexafluorophosphate) dissolved into the carbonated ester

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solvent (mixtures of ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), and so on) and a minority of additives. Although the liquid electrolyte system exhibits high ionic conductivity and good wettability with electrodes, the solvents that consist of linear and cyclic carbonates have low flash point and tend to burn easily. As the working temperature increases in the condition of incorrect usage or local overheating caused by aging, over charging or discharging, the fabricated battery is prone to combustion or triggering other safety accidents. Therefore, it could bring some hidden troubles when the liquid electrolyte is applied in large-scale power and energy storage devices.

In consideration of the comprehensive characterization, adsorbing carbonated liquid electrolyte into the polymer matrix to form the gel polymer electrolyte (GPE), could ensure the high ionic

conductivity of the GPE system and improve the safety of the carbonated electrolyte simultaneously. The traditional polymer matrix is composed of diversified functional compounds, such as polyethylene oxide (PEO), polymethylmethacrylate (PMMA), polyacrylonitrile (PAN), polyimide (PI), polyvinylidene fluoride (PVdF). However, the currently practicable homo-polymer matrix cannot satisfy the requirement of commercial LIBs, either tensile strength or ionic conductivity. For example, PMMA based GPE achieves super scalability but undesired film forming ability and poor mechanical strength [7]. PVdF based GPE generates high crystalline from its unique structure owing to the disciplinarian arrangement of $-\text{CH}_2-\text{CF}_2-$ repeated unit in the molecular chains [8,9]. Moreover, PAN based GPE has the excellent electrochemical properties but poor adhesion with the lithium metal anode [10]. To surmount the mentioned deficiencies of homo-polymer, copolymers with specific functional groups are fabricated via polymerization by cross-linking different monomers. To our knowledge, the comprehensive properties of ternary polymers based GPEs, such as poly(methyl methacrylate-butyl acrylate-vinylbenzyl chloride) (P(MMA-BA-VBC)) [11], poly(methyl methacrylate-butyl acrylate-2,2,2-trifluoroethyl methacrylate) (P(MMA-BA-TFEMA)) [12], are predominant over that of binary polymers or homo-polymers. Taking the satisfied performance into account, the poly(methyl methacrylate-acrylonitrile-ethyl acrylate) (P(MMA-AN-EA)) copolymer is chosen as the alternatively matched matrix. Here, the copolymer provides the enhanced electrolyte uptake ability, favorable compatibility with electrode and acceptable ionic conductivity for the GPE [13]. To further improve the mechanical strength of corresponding GPE, nano-SiO₂ and nano-Al₂O₃ are co-doped into P(MMA-AN-EA) matrix [14]. The nanoparticles decorated P(MMA-AN-EA) based GPE plasticized by carbonated solvent exhibits the remarkable mechanical strength and the lithium ion diffusion properties. However, in the extreme conditions, the liquid electrolyte tends to once again move freely by separating from the polymer matrix (or dehydration reaction) due to relatively weak reciprocity between the organic liquid component and the polymer matrix. Thus, the safety risk still exists in the carbonated solvent plasticized GPE [15,16].

To solve the safety problem from the source, it is necessary to avoid the use of flammable carbonated solvents. Room temperature ionic liquids (RTILs) are undoubtedly the best candidates because they will not burn or volatilize over the wide temperature range. RTIL generally comprises of organic cations with large molecular weights and organic/inorganic anions with small molecular weights. Due to their asymmetric structure, RTILs are liquid state at room temperature although they have relatively large molecular weight. According to the desired properties of specific application, the designed ionic liquids basically consist of infinite structural variations by the convenient synthesis [17,18]. As the main plasticizer for the GPE, the cationic ions of ionic liquid are usually imidazolium, pyrrolidinium, piperidinium and quaternary ammonium, while the anions are the same as that of lithium salt.

Because RTILs improve the amorphous regions and lithium ion transport of GPE by hindering the crystallization process of polymer chains [19–23], the literatures have reported the use of RTILs as electrolyte solvent or plasticizer in GPE system. The GPEs incorporated with RTILs generates considerable interests in view of favorable performances, including desired electrochemical stability, high ionic conductivity, negligible vapor pressure, inflammability and hydrophobicity. Furthermore, RTIL can prevent the formation of dendrite on high capacity lithium metal anode, which will enhance the energy density and broaden the application scope of the corresponding LIBs [24–26].

The choice of RTILs species, especially the cation molecules, is an important factor for the interface properties of the corresponding

batteries. Aromatic cation, 1-ethyl-3-methylimidazolium (EMIM⁺), which possesses lower viscosity and melting point [27–29], is selected as the cationic component in this paper. The bis(trifluoromethylsulfonyl) imide (TFSI⁻) is used as anions since the corresponding lithium salt of LiTFSI shows much higher ionic conductivity than that of LiPF₆ [30]. However, imidazolium based ionic liquid exhibits poor compatibility with electrode materials. With the aim to enhance the interfacial stability of electrolyte and electrode, interfacial film-forming additive is necessary to be added into ionic liquid system [31]. Vinylene carbonate (VC) is easy to form the solid electrolyte interface (SEI) layer on the surface of electrode before the ionic liquid electrolyte is decomposed, and then effectively prevents the side reactions of the electrolytes and electrodes. Thus, VC is proved to be a valid additive in imidazolium based ionic liquid system, since it exerts positive influence on the cyclic performance of LIBs [32–34].

In this paper, P(MMA-AN-EA) based ionic liquid type GPE is developed in order to build a practical and experimental viewpoint of the interaction between ionic liquid and P(MMA-AN-EA) copolymer. The characterizations of ionic liquid type GPE are evaluated by both electrochemical measurement and theoretical calculation. From the theoretical calculation of preferential potential, the excellent electrochemical stability of ionic liquid type GPE is attributed from higher decomposition potential of ionic liquid itself. Furthermore, the Li/GPE/LiFePO₄ type coin cells are assembled and characterized to demonstrate the possibility of further application the developed GPE in commercial LIBs.

2. Experimental

2.1. Preparation

Polyethylene (PE) (Celgard 2400, thickness: 16 μm, USA) supported poly(methyl methacrylate-acrylonitrile-ethyl acrylate) (P(MMA-AN-EA)) copolymer based membranes without and with 10 wt% nano-particles (Germany Degussa, average particle size: 100 nm) of copolymer weight, named as M0 (without nano-particles), MS10 (nano-particles of SiO₂: Al₂O₃ = 10:0), MS5 (SiO₂: Al₂O₃ = 5:5) and MS0 (SiO₂: Al₂O₃ = 0:10), were prepared by our previous reports [13,14]. The ionic liquid electrolyte was obtained by dissolving 0.5 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, ≥ 98.5%, Aldrich) into the ionic liquid solvent of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMITFSI, 99%, Aldrich). Vinylene carbonate (VC, ≥ 99.9%, Aldrich) additive was dissolved in the ionic liquid with contents of 10 wt%. By soaking the membranes into ionic liquid based electrolyte for 0.5 h, the corresponding nanoparticles decorated gel polymer electrolytes (GPEs) were prepared. The PE separator and the corresponding PE saturated with ionic liquid electrolyte were prepared and served as control.

To verify the safety property of ionic liquid electrolyte, the organic carbonated electrolyte was also obtained by dissolving 1 M LiPF₆ into the solvent of dimethyl carbonate and ethylene carbonate (DMC: EC = 1: 1, v/v, battery grade, Samsung Cheil Industry, Korea). The prepared membranes were soaked into the carbonated electrolyte to form the corresponding GPEs as well. All the procedures and handles were carried out in an argon-filled glove box (Mbraun Unilab MB20, Germany).

2.2. Characterization

To determine the thermal stability, the membranes were heated to 150 °C, and then maintained at that temperature for 1 h to observe the sharp change after heat treatment. The MS5 based GPE that contained different electrolytes was vertically ignited by a

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