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Composite electrolyte membranes incorporating viscous copolymers with cellulose for high performance lithium-ion batteries

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ABSTRACT

A novel composite electrolyte membrane (CEM), consisting of a viscous PEGMEM-co-SMA copolymer, lithium salt and cellulose matrix, has been prepared as a new class of electrolyte for high performance lithium-ion batteries (LIBs). This CEM exhibits a wide electrochemical stability window (>5 V vs. Li/Li$^+$), reasonably high ionic conductivity and thermal stability up to 315 °C. At temperature above the melting temperature (31.98–35.71 °C), the viscous flow nature of the copolymer is beneficial to fully infiltrate the electrode materials like liquid electrolyte to maintain uniform contact with electrode surfaces during charge/discharge process. The interfacial resistance (R_{intf}) of the fresh cell based on this CEM is extremely low (3.8 Ω cm^{-2}) and the Li/LiFePO$_4$ cell deliveries a discharge capacity as high as 156.9 mA h g^{-1} with a current density of 1 C at 80 °C. It is anticipated that this work provides a new insight for designing advanced electrolyte materials for LIBs with enhanced interfacial contact and excellent cycling performance.

1. Introduction

Lithium-ion batteries (LIBs), with higher specific capacity and enhanced cycling performance compared with other battery technologies, have been widely used in a variety of portable electronic devices and electric tools, and are expected to be a prominent power source in the fields of transportation and grid-scale energy storage [1–3]. To meet this increasing demand, advanced electrolyte materials, possessing high ionic conductivity, good safety and mechanical properties and excellent contact/adhesion with electrodes, are urgently needed [4]. For traditional organic electrolytes, excellent interfacial contact with electrodes and electrochemical performance make it possible for practical application, however, safety concerns have been raised due to the leakage and explosive nature of volatile organic electrolytes at high temperature (>60 °C) [5]. Recently, solid polymer electrolytes (SPEs) for LIBs have attracted intensive attention due to the enhanced safety at high temperature. However, low ionic conductivity and poor interfacial contact between solid electrolyte and electrode materials limit the practical use of SPEs in LIBs [6,7].

The improvements pursued in SPEs for LIBs are mainly focused on high ionic conductivity. Most of the research works on SPEs have been dedicated to poly(ethylene oxide) (PEO) and its derivatives, which are recognized as typical representatives of the polymer matrix for SPEs due to PEO's ability to dissolve lithium salts and high segmental flexibility for lithium ion transport in the amorphous phase [8,9]. However, the application of pristine PEO-based electrolytes is still hindered by their low ionic conductivity ($10^{-7}-10^{-8}$ S cm^{-1}) owing to their crystallization propensity at temperatures below 65 °C [10,11]. Structural modifications of PEO segments *via* the methods of cross-linking and co-polymerization (block or graft copolymers), such as introducing the polar units (acrylonitrile [12], urethane [13], amide [14], maleic anhydride [15,16]) into the PEO matrix, are the common strategies to suppress PEO crystallization. Kota et al. prepared a semi-interpenetrating solid polymer electrolyte with a conductivity of $\sim 2\times10^{-5}$ S cm^{-1} at 25 °C by introducing the polar units of acrylonitrile [17]. Maleic anhydride was introduced into the PEO-based electrolytes as a polar units to form a comb-like solid polymer electrolyte with an ionic conductivity of $\sim 10^{-4}$ S cm^{-1} at 90 °C, indicating that this kind of solid polymer electrolyte can be used at high temperature [16]. However, the motion of EO segments is often hindered by van der Waals forces between the EO segments and the polar units, which are not beneficial to disrupt the crystallization of EO segments [11,18]. Thus, introduction of bulky non-polar units, such as hydrocarbon chains, is expected to weaken the van der Waals forces and break the regularity of EO

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chains. The bulky non-polar units could also expand the free volume of EO units, accelerate the movement of EO segments that provide channels for lithium ions transportion and, in turn, improve the ionic conductivity of polymer electrolytes.

More importantly, for SPEs, another crucial factor affecting the electrochemical performance of LIBs is the poor contact of electrode/electrolyte interfaces. As the electrode/SPE interfaces are non-fluid solid/solid contacts, i.e., SPEs cannot fully infiltrate the electrode materials like liquid electrolytes, prolonged electrochemical cycle degradation becomes evident in all solid-state LIBs [4,19,20]. Considerable efforts have been devoted to mitigate the interfacial stability, such as adding or grafting a certain amount of ceramic powders (SiO_2 [21], Al_2O_3 [22], ZnO [23], CeO [24], $ZnAl_2O_4$ [25]) into the SPEs. However, the rate capability and long-term cycling performance of the solid-state LIBs have not been greatly improved since the intrinsic disadvantage of non-fluid solid/solid contacts still remains. Hence, tuning the physical appearance of the SPEs to be more elastic or viscous to maintain uniform contact with electrode surfaces, would be an effective way to obtain an effective and stable interface between electrolyte and electrode to achieve remarkable rate capability and enhanced cycling performance simultaneously.

Inspired by these concepts, we developed a composite electrolyte membrane (CEM) by incorporating viscous copolymers with cellulose for high performance lithium-ion batteries. A highly viscous PEGMEM-co-SMA copolymer was specially designed by introducing a secondary block, SMA, with bulky non-polar units of C_{18}, which could suppress the crystallization propensity via creating defects in the PEO crystallization phase and accelerate the movement of EO segments. At temperature above the melting temperature (31.98–35.71 °C), the PEGMEM-co-SMA copolymers present a viscous-flow state that is beneficial to maintain good interfacial contact with electrodes like liquid electrolyte. In order to ensure the dimensional stability of the copolymer to separate the cathode from anode, various kinds of cellulose matrices were usually used to improve the mechanical properties of polymers [26–28]. In this study the NKK TF40 cellulose paper was selected to incorporate with the copolymer of PEGMEM-co-SMA and LiTFSI to form a viscous copolymer/cellulose composite electrolyte membrane. The experimental results confirm that such composite electrolyte membrane not only possesses high thermal stability and good ionic conductivity, but also yields excellent interfacial contacts with lithium electrode and outstanding cycling performance in LIBs.

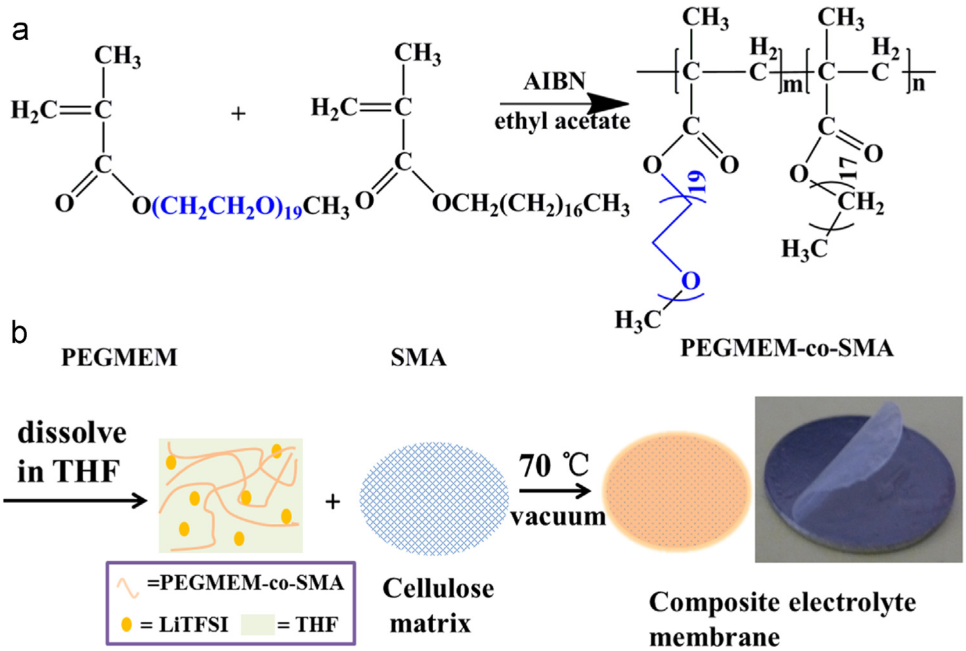
2. Experimental sections

2.1. Materials

Poly(ethylene glycol) methyl ether methacrylate (PEGMEM, $M_n = 936\ g\ mol^{-1}$) and stearyl methacrylate (SMA, $M_n = 338\ g\ mol^{-1}$), obtained from Sigma-Aldrich, were stored at 2–8 °C to prevent self-polymerization. The lithium salt, lithium bis (trifluoromethane sulfonamide) (LiTFSI), was purchased from Sigma-Aldrich and dried at 120 °C under vacuum condition for 12 h before use. Tetrahydrofuran (THF), 2,2-azobisisobutyronitrile (AIBN), ethyl acetate and petroleum ether, obtained from Sinopharm Chemical Reagent Co., Ltd., were used as received. The cellulose separator (NKK TF40, 40 μm thickness, low ESR type), purchased from Nippon Kodoshi Corp., Japan, is composed of solvent-spun regenerated cellulose fiber, with an average pore diameter of 0.3 μm and a porosity factor of 73%.

2.2. Preparation of CEMs

Firstly, PEGMEM-co-SMA copolymers were synthesized by a simple free radical method, as shown in Scheme 1a. Various stoichiometric mass ratios of PEGMEM and SMA monomers (95/5, 90/10, 85/15, 80/20 and 75/25) were dissolved in ethyl acetate with AIBN as the initiator (0.5 wt% of total mass). This solution was then heated to 70 °C in a water bath under constant stirring and N_2 atmosphere. After 10 h, the obtained viscous liquid was dissolved in THF and precipitated in petroleum ether for three times. The as-precipitated copolymers with various SMA contents were dried at 70 °C under vacuum condition to remove the residual solvent. Secondly, to obtain the designed CEMs, the PEGMEM-co-SMA copolymers with various SMA contents and LiTFSI, with a desired [Li]/[EO] molar ratio (1/25, 1/20, 1/15, 1/10, 1/8 and 1/5), were dissolved in a THF solution, and then dripped on a cellulose matrix



Scheme 1. (a) Synthesis of the PEGMEM-co-SMA copolymers and (b) preparation of the viscous copolymer/cellulose CEMs.