



Highly porous single-ion conductive composite polymer electrolyte for high performance Li-ion batteries



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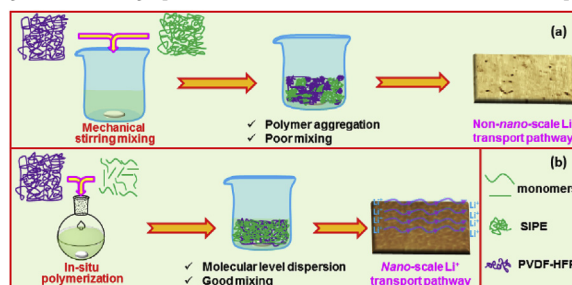
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HIGHLIGHTS

- A facile *in-situ* polymerization process to approach molecular mixing level of polymer blends.
- Highly porous SIPE displays excellent properties for high performance LIBs.
- The fast C-rate is obtained for single ion polymer electrolyte Li-ion batteries.

GRAPHICAL ABSTRACT

A Novel *in-situ* Polymerization Process is here carried out to overcome the drawbacks of poor mixing of the commercial mechanical stirring process. The obtained well-mixing of the PVDF-HFP binder and single ion polymer electrolyte is greatly beneficial for constructing the nanoscale lithium ion transport channels, which gives rise to high performance of Li-ion batteries at ambient temperature.



ARTICLE INFO

Keywords:

Lithium ion battery
Single ion polymer electrolyte
Porosity
In-situ polymerization
Thermal dimensional stability

ABSTRACT

A highly porous polymer electrolyte with good wettability and excellent thermal dimensional stability is of great importance to enable the high performance of lithium ion batteries (LIBs). This study reports a facile *in-situ* polymerization process to approach molecular mixing level of poly (vinylidene fluoride-hexa-fluoropropylene) (PVDF-HFP) and the fully aromatic single-ion conducting polymer (*fa*-SIPE). The molecular level mixing is greatly beneficial for promoting both macro and nanophase separation between the flexible aliphatic PVDF-HFP and the aromatic *fa*-SIPE. These occur because of the poor physical compatibility of the two polymers and leads to a macro/nano porous single-ion polymer electrolyte (SIPE). Filling the porosity with a Li⁺-ion coordinating solvent enables high Li⁺-ion mobility, which is favorable for the development of high power and fast charge LIBs. Remarkably, the highly porous SIPE membrane displays high mechanical stability, high electrolyte wettability and strong thermal dimensional stability, all possibly contributing to excellent stability and reliability of

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LIBs. This study provides an efficient way of fabricating porous, single-ion polymer electrolyte for LIBs application.

1. Introduction

Recently, there is an increasing demand for development of safe, cost-effective and efficient LIB technologies to power electric vehicles [1–6]. An efficient separator should possess high porosity and favorable electrolyte wettability to facilitate fast ion transport, high electrochemical and chemical stability to enable compatibility with electrodes, and high thermal and mechanical stability to ensure the safety and the enhanced operative temperature range of the batteries [7–10]. Unfortunately, the widely used commercial polyolefin separators, such as polyethylene (PE) and polypropylene (PP), still suffer from the drawbacks of slow electrolyte wetting and large shrinkage at high temperatures. Therefore, upon heating, the separator may not avoid the direct contact of the electrodes anymore, leading to the short circuit of the battery and an even larger generation of heat. This drawback is greatly limiting the use of conventional LIBs in the applications as power sources for electric vehicles and large-scale energy storage systems. In addition, the LiPF_6 electrolyte salt used in commercial batteries suffers from poor thermal stability above 80°C , is highly moisture sensitive, costly, and, due to the mobility of both Li^+ and PF_6^- ions, inherently leads to concentration polarization upon charge and discharge of LIBs.

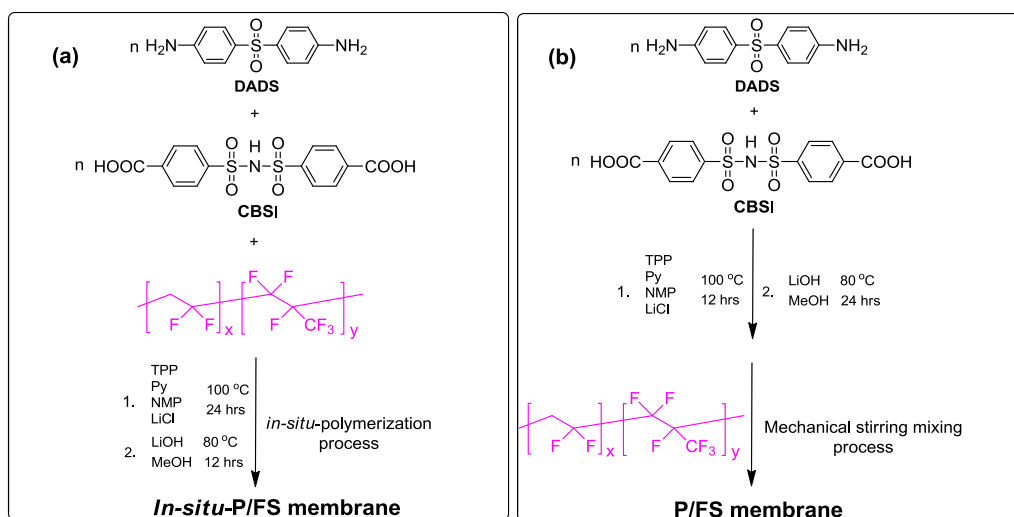
Great efforts have been made to overcome those problems by, for example, coating ceramic nanoparticle on the surface of the polyolefin separators. Although some performance, for example, ionic conductivity, electrolyte wettability and safety, was improved, they are still not available to operate at elevated temperatures ($> 100^\circ\text{C}$) due to degradation of the polyolefin substrate as well as of the organic binders. Another effective approach to solve the safety problems is to develop all-solid-state LIBs using solid-state electrolytes. Unfortunately though, their low ionic conductivity at room temperature has greatly limited their practical application. However, replacing the polyolefin based separators with heat-resistant polymer membranes could reduce the safety issue. To date, porous polyimide, polyetherimide and polybenzimidazole [11] membranes have been investigated for high safety and good wettability polymer separators.

Single-ion conductive polymer electrolytes (SIPes) are considered as one of the most appealing alternatives to conventional, Li salt-containing electrolytes due to high lithium ion transference number (close

to unity), high stability against water, excellent thermal, chemical and electrochemical stability, good mechanical strength and high safety [12–15]. In the past several years, great efforts have been made to develop novel SIPes following different strategies, such as the design of effective functional groups [16] and polymer backbones [17–24], or the fabrication of porous structures [25,26].

Poly (vinylidene fluoride) (PVDF) and its copolymers, a well-known class of membrane materials, have been widely considered as separators in LIBs because of their appealing properties in terms of electrochemical and thermal stability and affinity to electrolyte solutions [27,28]. In our previous work, a facile self-assembly process has been proposed to fabricate porous single-ion polymer electrolyte membrane with good mechanical strength [29,30]. The self-assembly process originates from the spontaneous phase separation of the rigid, fully aromatic SIPE (*fa*-SIPes) and the flexible aliphatic PVDF-HFP, due to their inherent poor physical compatibility. However, such a phase separation was significantly influenced by the degree of mixing of the PVDF-HFP and *fa*-SIPE. In fact, only molecular level mixing can generate nanophase separation, which is greatly favorable for the formation of continuous nanoscale Li^+ -ion transport channels. Unfortunately, the conventional mechanical mixing (stirring) process in organic solvents always leads to poor mixing with marked aggregation of polymers, largely obstructing the formation of continuous nanoscale Li^+ -ion transport channels and thus low ionic conductivity.

To overcome such a limitation we present herein a facile *in-situ* polymerization process in solution, involving pre-dissolved PVDF-HFP and the precursors of *fa*-SIPes. As the precursors of *fa*-SIPE are also dissolved in the PVDF-HFP solution, homogeneously surrounding the space polymer chains prior to polymerization. In this way, the molecular level dispersion of the *fa*-SIPE precursor in PVDF-HFP is achieved, giving rise to nanophase separation during polymerization and membrane fabrication. Thus, high efficient, nanoscale and continuous Li^+ -ion transport channels are formed in the membrane, leading to enhanced ionic conductivity. Surprisingly, we found that the interfacial resistance between electrolyte and electrodes is also reduced. The combination of high thermal and electrochemical stability, excellent dimensional stability at elevated temperature, and good wettability of the SIPE membrane enables the realization of LIBs exhibiting remarkable electrochemical performance.



Scheme 1. Fabrication of PVDF-HFP/*fa*-SIPE membranes via (a) *in-situ* polymerization process and (b) traditional mechanically stirring mixing process.

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