



# Highly conducting blend hybrid electrolytes based on amine ended block copolymers and organosilane with in-situ formed silica particles for lithium-ion batteries



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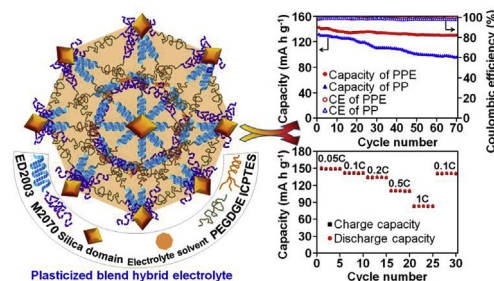
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## HIGHLIGHTS

- Solid and plasticized electrolytes are synthesized from the same blend hybrid matrix.
- The hybrid SPE exhibits maximum ionic conductivity of  $1.1 \times 10^{-4} \text{ S cm}^{-1}$  at 30 °C.
- The PPE membrane reveals an extremely high conductivity of  $24 \text{ mS cm}^{-1}$  at 30 °C.
- The cell delivers initial capacity of  $142 \text{ mAh g}^{-1}$  with 92% retention after 70 cycles.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

In this study, amine ended block co-polymers of ethylene oxide/propylene oxide units are reacted separately with poly(ethylene glycol) diglycidyl ether (PEGDGE) and (3-isocyanatopropyl)triethoxysilane (ICPTES) and then mixed in different weight ratios to obtain ion conductive and mechanically stable hybrid solid polymer electrolytes (SPEs). Various characterization techniques are employed to explore the morphology, thermal stability, molecular interaction, backbone structure and dynamic behavior of the blend hybrid SPEs. The hybrid SPE exhibits the maximum ionic conductivity of  $1.1 \times 10^{-4} \text{ S cm}^{-1}$  at 30 °C. The electrochemical stability window of hybrid SPEs varies from 4.5 to 4.7 V, depending on salt concentration. Moreover, the “salt free” hybrid membrane is plasticized in an organic electrolyte solvent to enhance the ionic conductivity to an exceptionally high value of  $2.4 \times 10^{-2} \text{ S cm}^{-1}$  at 30 °C and  $1.8 \times 10^{-1} \text{ S cm}^{-1}$  at 70 °C. The test cell consists of plasticized blend hybrid membrane delivers an initial discharge capacity of  $142.5 \text{ mAh g}^{-1}$  and retains 92% of initial capacity after 70 cycles with coulombic efficiency value of over 99%. Our results show that the blend hybrid electrolytes can be a promising electrolyte system for applications in high energy density lithium-ion batteries.

## 1. Introduction

The technological prowess and environmental concerns have prompted researchers to develop devices to use renewable energy

resources and/or effectively store them. Among storage devices, lithium-ion battery (LIB) is the most promising and increasingly demandable battery system due to its high energy density in comparison to other battery technologies, which finds applications from consumer

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electronic products to hybrid electric vehicles/electric vehicles (HEVs/EVs) [1,2]. However, with the continuous technological advancement in the consumer products, the development of more powerful batteries is utmost important. Electrolyte is one of the key components of battery that needs urgent attention to fulfil the goal of developing high power batteries. However, development of an efficient and high performance electrolyte for next generation lithium-ion batteries is still a challenge. The classical lithium-ion batteries presently available in the market mostly use lithium salts to be dissolved in organic solvents as electrolytes in order to offer ionic conductivity values on the order of  $10^{-3} \text{ S cm}^{-1}$  or higher. Still, high flammability of organic solvents, formation of lithium dendrite, thermal instability and solvents leakage have raised serious concerns on safety and overall performance of LIBs [3,4]. Solid polymer electrolytes (SPEs) are considered as effective alternatives to liquid electrolytes to overcome the drawbacks mentioned above [5–7]. SPEs have their advantages such as good flexibility, facile processability, low interfacial resistance and good interfacial contacts with electrodes. Since the pioneering works carried out by Wright and Armand groups on poly(ethylene oxide) (PEO) based SPEs, much research effort has focused on SPEs for acknowledging their potentials in rechargeable batteries [8,9]. However, poor ionic conductivity of PEO-based SPEs at room temperature, mostly from  $10^{-7}$  to  $10^{-5} \text{ S cm}^{-1}$  seriously impedes their applications in LIBs.

In an effort to address the issue of low ionic conductivity of PEO-based SPEs, several alternative strategies, such as semi-interpenetrating network polymer electrolytes, blend polymer electrolytes, branched polymer electrolytes, composite polymer electrolytes, block co-polymer electrolytes and salts dissolved in different types of polymeric matrices have been tested out and achieved mixed results in boosting ionic conductivity [10–16]. In addition, some of these electrolytes also entangle with deficiencies, for example, particle aggregation in composite SPEs, inferior mechanical strength and narrow electrochemical stability window that prohibits their practical use in LIBs. Poor mechanical properties of SPEs additionally raise safety concerns, due to the short circuit between the electrodes in the batteries at elevated temperature. Therefore, here is a great scope to explore new SPEs that can overcome these drawbacks. In search of high performance electrolytes, organic-inorganic hybrid electrolytes have gained considerable interests because of their higher ionic conductivity at room temperature [17–19]. Moreover, these organic-inorganic hybrids can improve the interfacial contact between electrolyte and electrodes due to their flexible design and adhesiveness. These hybrid SPEs can possess unique physical and chemical properties by changing the amount of organic and inorganic components according to requirements. Furthermore, the functionalization level can be easily controlled as the sol-gel process mainly involved in the synthesis of these hybrids. Therefore, the hybrid electrolytes could synergistically combine the beneficial properties of both organic and inorganic components to form a mechanically stable free-standing membrane. Another important fact is that these hybrid SPEs can be easily converted to plasticized polymer electrolytes (PPEs) by simply swelling the membranes in organic solvents without deterioration of mechanical properties. PPEs are safer than liquid electrolytes because they can uptake solvent efficiently and retain it inside the pores of the polymeric matrix without leakage, and thus prevent any fire or explosion hazards at the time of battery malfunction. Normally, the ionic conductivity of PPEs is in the ranges of  $10^{-3}$  to  $10^{-2} \text{ S cm}^{-1}$  and suitable for good charge-discharge and life cycle performance of battery systems [20–22]. In addition, well compatibility with the electrodes and wide electrochemical windows make PPEs the electrolyte of choice [20–22].

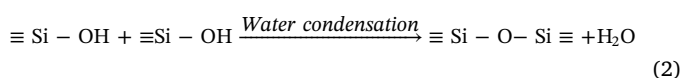
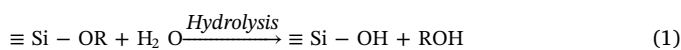
In the present work, we devote our effort to blend two polymer precursors with different chain lengths to make SPEs with in-situ formed silica particles to give the composite nature. Then the same blend hybrid membrane is employed to make PPEs that are further used as separators in lithium-ion batteries to evaluate the electrochemical performances. Blending eases the synthesis procedure of the hybrid

electrolytes while maintaining higher ionic conductivity as well as thermal and mechanical integrity. The blend hybrid electrolytes can be composed of the soft and hard components from two polymer precursors with the soft part mainly responsible for ionic conduction, while the hard part for thermal and mechanical strength [11,13]. Based on the above strategies, herein we reports a new type of blend organic-inorganic hybrid electrolyte that is formed by blending two different polymer precursors: one is formed by polymerization of polyetheramine (M-2070) and poly(ethylene glycol) diglycidyl ether (PEGDGE) (precursor I), and the other is from the reaction of polyetherdiamine (ED2003), PEGDGE and (3-isocyanatopropyl)triethoxysilane (ICPTES) (precursor II). The  $\text{N}=\text{C}=\text{O}$  functional group in the organosilane ICPTES is highly reactive towards the  $\text{NH}_2$  end groups of polyetherdiamine (ED2003), and thus allows these functional groups to bond covalently to make the stable hybrid structure. Further, it generates in-situ sub-micron sized silica particles after hydrolysis and condensation reactions, which have positive effects in improving the electrical and mechanical properties of the electrolyte. The blending amount of precursors and salt concentrations are varied and optimized to prepare the blend hybrid SPEs. The physical and chemical behaviors of the blend hybrid SPEs are characterized by DSC/TGA, wide angle XRD and FTIR analysis. The structural integrity and dynamic properties of the blend hybrid SPEs are analyzed with multinuclear ( $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^7\text{Li}$ ) solid-state NMR spectroscopy. The electrochemical characterizations, such as AC impedance and linear sweep voltammetry (LSV) are determined to obtain the ionic conductivity and electrochemical stability window of the blend hybrid SPEs. For testing the battery performance of the blend hybrid system, the pristine blend hybrid membrane (without salt) is swelled in different electrolyte solvents and its ionic conductivity and LSV are measured. To the end, the lithium-ion battery is assembled with the blend hybrid PPE using lithium metal and  $\text{LiFePO}_4$  electrodes and its cycle performance and capacity at different current rates are measured.

## 2. Experimental section

### 2.1. Synthesis of blend hybrid SPEs

For the preparation of the blend hybrid SPEs, two polymer precursors were synthesized in the first place. The synthesis procedure is schematically described in Fig. 1. In the first phase, 2 mol of polyetheramine M-2070 (Jeffamine M-2070 with  $M_w = 2000 \text{ g mol}^{-1}$ , Huntsman) and 1 mol of PEGDGE ( $M_w = 526 \text{ g mol}^{-1}$ , Aldrich) were dissolved in 15 mL of tetrahydrofuran (THF) separately and then mixed together and stirred at  $50^\circ\text{C}$  for 24 h to complete the reaction to form the precursor I. In the second phase, 2 mol of polyetherdiamine (Jeffamine ED2003,  $M_w = 2000 \text{ g mol}^{-1}$ , Huntsman) and 1 mol of PEGDGE were dissolved in 15 mL of THF separately and then mixed both the solutions and stirred at  $50^\circ\text{C}$  for 24 h to complete the reaction. Afterwards, 2 mol of ICPTES (Aldrich) was added to the reaction mixture and stirred at  $60^\circ\text{C}$  for 24 h to attach the silane chains to the polymeric matrix. Subsequently, a small amount of 1 M HCl (0.3 mL) was added to the mixed solution to facilitate the hydrolysis and condensation reactions of ICPTES in order to form the silica network architecture within the polymeric matrix. The resulting product was denoted as the precursor II. The hydrolysis and condensation reactions of the organosilanes took place as follows:



Silanol groups are generated from the hydrolysis of ICPTES. Condensation of these silanol groups forms the siloxane bridges ( $\text{Si}-\text{O}-\text{Si}$ ) that build the whole silica structure and finally forms the in-

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