



# Polymeric Ionic Liquid Gel Electrolyte for Room Temperature Lithium Battery Applications



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## ABSTRACT

Free-standing gel polymer electrolytes (GPE) composed of the polymeric ionic liquid poly[diallyldimethylammonium] bis(trifluoromethane) sulfonimide, the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethane) sulfonimide, and lithium salt are reported for their use in lithium batteries. The GPEs are thermally stable and contain ionic liquid and salt contents of up to 80 wt.% which results in highly ionically conductive electrolyte films with  $\sigma = 3.35 \text{ mS cm}^{-1}$ . The affinity of the polymeric ionic liquid with the ionic liquid and salt components of the GPE allows wide electrochemical stability window  $-0.1$ – $4.9 \text{ V}$  and increased lithium ion transference number. In addition, the GPEs suppressed dendrite formation compared to ionic liquid electrolytes and in turn enabled the use of these GPEs in batteries with lithium anodes. Galvanostatic charge/discharge cycling of Li/GPE/LiFePO<sub>4</sub> cells shows discharge capacity of  $169.3 \text{ mAh g}^{-1}$  at C/10,  $126.8 \text{ mAh g}^{-1}$  at 1C, and impressive capacity retention capability for 40 cycles at up to 5C rate, at  $22^\circ\text{C}$ .

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## 1. Introduction

Lithium ion batteries (LIBs) have been extensively studied as energy sources for devices ranging from portable electronics to electric vehicles (EVs). LIB safety remains one of their biggest concerns due to flammable organic liquid electrolytes [1–3]. In recent years, the emergence of polymer electrolytes (PE) opened up an avenue for safer battery technology [4–6]. The main advantage of all solid-state batteries is their ability to overcome drawbacks such as electrolytes leakage and gas evolution during solvent decomposition. Since the introduction of polymer electrolytes, numerous polymers and polymer/solvent couples have been reported with improved electrochemical and mechanical properties for applications in LIBs.

PEs are mainly of two types, solid polymer electrolyte (SPE) and gel polymer electrolyte (GPE). The former consists of a lithium salt dissolved in high concentrations in a polymer and the latter consists of polymer gelled by electrolyte solutions containing lithium salt. Early research by Armand et al. [7] investigated the performance of SPEs based on polyethylene oxide (PEO) for the first time for potential lithium-ion battery applications. These

electrolytes had ionic conductivities as high as  $10^{-5} \text{ S cm}^{-1}$  at  $40$ – $60^\circ\text{C}$ . Since then, numerous researches have been reported using SPEs in lithium-ion batteries, based on PEO [8,9], polyacrylonitrile (PAN) [10,11], poly(vinyl alcohol)(PVA) [12,13], polyethylene carbonate (PEC) [14,15], polymethylmethacrylate (PMMA) [16,17], polyvinylidene fluoride-co-hexafluoro propylene (PVDF-HFP) [18–20], and polyvinylidene fluoride (PVDF) [21,22] and its copolymers. SPEs however generally have poor ionic conductivities without additives ( $\sim 10^{-8}$ – $10^{-5} \text{ S cm}^{-1}$ ) [3,23] at room temperature due to their high crystallinity causing ion diffusion restrictions. These problems have led to their predominant utilization in low power applications, or in high temperature applications exceeding their glass transition temperatures [24,25].

To overcome the diffusional problem, GPEs take advantage of low viscosity liquids containing high concentration of lithium salts. The introduction of a liquid affords GPEs as many as 100 folds of improvement in ionic conductivity, especially at low temperatures. Other advantages of GPEs over SPEs are better interfacial contact with the electrodes and improved mechanical flexibility. Tarascon et al. reported the first GPE with PVDF-HFP activated by 1 M LiPF<sub>6</sub> in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 v/v) in LiMn<sub>2</sub>O<sub>4</sub>/C battery with a rate capability of  $115 \text{ mAh g}^{-1}$  [26]. Typical solvents used in GPEs include EC, DMC, 1,2-dioxolane, dimethoxymethane [27]. Although these solvents provide better

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performance for GPEs compared to SPEs, they still suffer from problems observed in liquid electrolytes such as evaporation, leakage, and flammability. The search for a non-flammable solvent with high electrochemical stability, low volatility, and capable of dissolving high lithium salt concentrations is therefore essential to GPE research.

Room temperature ionic liquids (ILs) have been regarded as ideal solvents for GPEs due to their ultralow-volatility, general non-flammability, and impressively wide electrochemical stability window. Watanabe and Noda reported on the first use of the IL based on imidazolium [EMIM][BF<sub>4</sub>] and pyridinium [BP][BF<sub>4</sub>] that were combined with a polyvinyl [28] with ionic conductivities of  $2 \times 10^{-2}$  and  $3 \times 10^{-3}$  mS cm<sup>-1</sup> at 30 °C, respectively. The most used imidazolium based ionic liquid is 1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonylimide) [EMIM][TFSI] due to its high fluidity and ionic conductivity at room temperature. To serve as an electrolyte for lithium-ion batteries, binary mixtures of ILs and a lithium salt are necessary. Lithium salt, LiTFSI is a commonly used salt because of the plasticizing ability of TFSI<sup>-</sup> anion and since it promotes amorphous phase fraction [29]. Armand et al. [30] reported on a Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/EMIMTFSI-1M LiTFSI/LiCoO<sub>2</sub> with more than 90% capacity retention after 200 cycles at 1-C rate with 106 mAh g<sup>-1</sup> capacity. Yang et al. reported on a GPE of [EMIM][TFSI] IL with PVDF-HFP polymer with 141.9 mAh g<sup>-1</sup> discharge capacity at the initial cycling and maintained 93.1% retention after 20 cycles at C/10 rate at 20 °C [20]. Ohno et al. [31] proposed the utilization of polymeric ionic liquids (PIL) which are essentially polymers of the IL monomers used as matrices for GPEs. These PILs have been reported to have high chemical affinity with ILs leading to the improved performance of the resulting GPEs. In addition, PILs show low phase separation and leakage problem, very simple processability (such as solvent casting), good electrochemical and thermal properties [32,33]. Marcilla et al. and Pont et al. suggested in their studies alternative approaches to synthesizing PILs [34,35]. Imidazolium and pyrrolidinium based PILs were synthesized by an anion-exchange reaction with the halide form of the polymer using a lithium salt, such as LiTFSI in water. These types of PILs were generally hydrophobic, thermally stable, and have a wide electrochemical stability window (ESW). Early reports on PILs performance in a lithium-ion battery yielded capacities of 140 mAh g<sup>-1</sup> at 40 °C for 70 cycles at C/10 rate [36].

In this work, we report on the preparation of a free-standing GPE composed of the pyrrolidinium-based PIL poly[diallyldimethylammonium bis(trifluoromethane) sulfonimide] (PDADMATFSI), the imidazolium-based IL [EMIM][TFSI], and the lithium salt LiTFSI. Thermal and electrochemical properties of the GPE were evaluated to determine the utility of the synthesized GPE in lithium-ion battery applications. Cyclability study of Li/GPE/LiFePO<sub>4</sub> batteries were also performed at room temperature (22 °C) for rates up to 5C charge and discharge rates.

## 2. Experimental

### 2.1. Materials

Poly(diallyldimethylammonium chloride) (MW=200,000–350,000 Dal), bis(trifluoro methane) sulfonimide lithium salt (LiTFSI), 1-ethyl-3-methylimidazolium chloride (≥95%) and poly(vinylidene fluoride) PVDF (MW=530,000 Dal) pellets were purchased from Sigma-Aldrich. Acetone and 1-methyl-2-pyrrolidone (NMP) were purchased from Fisher Scientific. Lithium metal chips and carbon pre-coated LiFePO<sub>4</sub> powder were purchased from MTI Corporation. Carbon Black, acetylene (99.9+ %, bulk density 170–230 gL<sup>-1</sup>) was purchased from Alfa Aesar. Celgard 2400 was purchased from Celgard LLC.

### 2.2. Synthesis of PIL

Polymerized ionic liquid PDADMATFSI was synthesized by simple anion exchange reaction between the chlorinated polymer and LiTFSI previously reported by Pont et al. [35]. The synthesized PIL was insoluble in water but readily soluble in acetone. Fig. 1(a) depicts the chemical structure of the PIL.

### 2.3. Synthesis of [EMIM][TFSI]

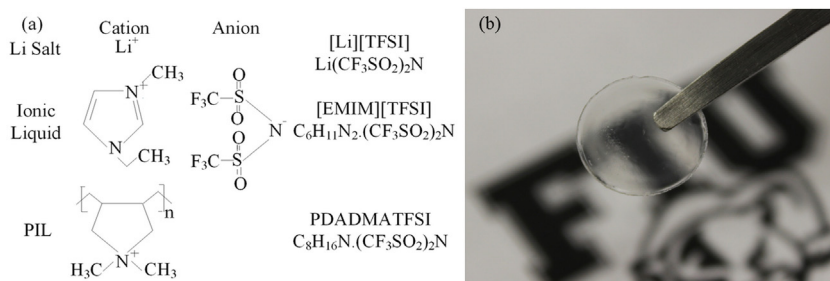
Ionic Liquid [EMIM][TFSI] was synthesized by reacting [EMIM][Cl] and LiTFSI salt in deionized water as described elsewhere [37]. The obtained IL was dried in a vacuum oven (60 °C under vacuum for 2 hours) then was stored in an oxygen-free and humidity-free glovebox until later use. The prepared IL was colorless, odorless, and fluid at room temperature.

### 2.4. Preparation of gel polymer electrolyte (GPE)

For the preparation of GPE, first 1 M LiTFSI in [EMIM][TFSI] was prepared followed by mixing with 20 wt.% of PIL (final composition 80:20 electrolyte:PIL by weight). The mixture was then dissolved in acetone and stirred/sonicated until fully dissolved. The solution was then drop-casted in 0.5" circular PDMS template layered on a glass slide. Acetone was allowed to evaporate at room temperature conditions for 20 minutes followed by vacuum drying at 90 °C for 72 hours. The resulting films were transparent and free-standing as can be observed in Fig. 1(b).

### 2.5. Cathode preparation

The cathode was prepared using 78 wt.% carbon pre-coated LiFePO<sub>4</sub>, 10 wt.% PVDF, and 12 wt.% carbon black. Before making the cathode slurry, LiFePO<sub>4</sub> was baked at 140 °C for 2 hours to remove moisture. Then LiFePO<sub>4</sub> and carbon black were added to pre-



**Fig. 1.** a) Chemical structures of the GPE and ILE components: [Li][TFSI], [EMIM][TFSI], and PDADMATFSI. b) Photograph of a half inch diameter GPE demonstrating its free-standing property.

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