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Electrochemical and cycling performances of novel nonafluorobutanesulfonate (nonaflate) ionic liquid based ternary gel polymer electrolyte membranes for rechargeable lithium ion batteries

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ABSTRACT

A new-fangled nonaflate anion based ionic liquid ternary gel polymer electrolytes was prepared and their function as an active separator for lithium ion battery applications has been characterized. The ionic liquid gel polymer electrolytes (IGPEs) were prepared using facile solution cast technique by incorporating electrolyte mixtures such as lithium nonafluorobutanesulfonate (LiNfO) and 1-butyl-3-methylimidazolium nonafluorobutanesulfonate (BMImNfO) in poly vinylidenefluoride-*co*-hexafluoropropylene (*PVdF-co-HFP*) matrix. The electrochemical performance and the interactions between *PVdF-co-HFP*, LiNfO and imidazolium-based ionic liquid BMImNfO are comparatively investigated. IGPEs obey Arrhenius relation and its ionic conductivity is found to be maximum of 10^{-2} S cm^{-1} at 100 °C. At low current rate, IGPE also exhibits good cycling performance with $LiCoO_2$ and achieved a maximum discharge capacity of 138.1 mA h g^{-1}.

1. Introduction

In the past two decades, gel polymer electrolytes (GPEs) have worldwide become materials of massive interest due to their use as an excellent alternates of the liquid electrolytes in electrochemical and portable devices such as batteries, super capacitors, fuel cells, electronic devices and hybrid electric vehicles [1–6]. The main advantages of GPEs in lithium ion batteries (LIBs) lies with its non-leakage nature, higher ionic conductivity as compared to those observed for liquid electrolytes, and possibility of preparation of flexible, thinner and smaller electrochemical devices. However, the main drawback is their poor thermal and electrochemical properties with organic solvents that are volatile in nature, and their relatively narrow electrochemical potential window [7]. A promising way to overcome these problems is using room temperature ionic liquids (RTILs), which has several attractive features, such as chemical and thermal stability, non-volatility, and intrinsic high ionic conductivity at room temperature which results in improved safety in case of overcharging [8–11]. ILs also functions as solvent and promotes ensuing number of charge carriers in gel polymer matrix [8–14]. These examples highlight the importance of ILs and their derivatives which projects them as a potential candidate for advanced electrolytes in LIBs.

An extensive research has been devoted towards imidazolium-based ILs and electrolytes. Compared to other “onium” ionic liquids, Imidazolium-cationbased electrolytes show higher conductivities due to their quasi-planar, two-dimensional structure which leads to lower viscous drags [14]. Besides, imidazolium cations based ILs exhibit a wider cathodic stability and good compatibility with lithium anode [15–17].

Quite a lot of electrolytes based on GPEs such as poly (methyl methacrylate) (PMMA), poly(oxyethylene) (PEO), poly(acrylonitrile) (PAN), poly(vinylidene fluoride) (PVdF) and poly vinylidenefluoride-hexafluoropropylene (*PVdF-co-HFP*) are successfully used as matrix material in lithium-ion battery [12,17–19]. Among them, *PVdF-co-HFP* is believed to be the most promising matrix as separator material, because it has relatively lower crystallinity due to the copolymerization effect between VdF and HFP compared to PVdF [20]. In addition,

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PVdF-co-HFP shows high electrochemical stability and ease to dissolve lithium salts in amorphous phase thus acts as a better polymer host in LIBs.

The commercially available $LiPF_6$ is unstable at elevated temperature and sensitive to trace amounts of water [21–23]. The decomposition temperature of $LiPF_6$ in EC/DMC (ethylene carbonate/Dimethyl carbonate) lies in the range of 85–100 °C. Moreover for long storage times, it is unsuitable [23]. In order to avoid these issues, lots of efforts has been made to replace $LiPF_6$ with other traditional lithium salts [23]. Hence our ultimate aim is to focus to choose lithium salt with weak cation-anion interaction, which can be achieved by choosing bulky anions based lithium salts. Therefore, here we report lithium nonafluoro-1-butanesulfonate (LiNfO) as an electrolyte salt with the aim to replace $LiPF_6$.

We observed that the synthesized IL (BMImNfO) shows a promising performance in terms of interfacial stability, cycle life and electrochemical stability when tested in a lithium ion battery. To the best of our understanding, there are no previous reports on both LiNfO and BMImNfO as active materials for electrolytes in LIB applications. The ionic conductivity and transport properties of the samples are investigated by impedance spectroscopic studies. Further, we report on the performance of $Li/LiCoO_2$ batteries with the ionic liquid gel polymer electrolytes at room temperature, and study the compatibility of the gel electrolyte film and the electrodes.

2. Experimental

2.1. Materials

LiNfO salt (purity: >95%) and potassium nonafluorobutanesulfonate (KNfO) was purchased from TCI Chemicals, Tokyo. The lithium and potassium salts were kept under *vacuum* at 70 °C for 12 h. The polymer host *PVdF-co-HFP* (kynar flex, 2801) was obtained from Arkema, Japan. The other precursor materials namely 1-butyl-3-methylimidazolium bromide (BuMeImBr), acetonitrile (anhydrous) and dichloromethane were purchased from Sigma Aldrich and were used without further purification. 1-butyl-3-methylimidazolium nonafluorobutane-1-sulfonate was prepared via a metathesis reaction between BuMeImBr and KNfO. The details procedure is discussed herein.

2.2. Synthesis of 1-butyl-3-methylimidazolium nonafluorobutane-1-sulfonate (BMImNfO)

The 1-butyl-3-methylimidazolium nonafluorobutane-1-sulfonate (BMImNfO) was prepared and purified according to the procedure published earlier by Michael Gratzel [24]. Briefly, 50 mL solution of 43 mmol BuMeImBr was mechanically mixed with 100 mL solution of 41 mmol KNfO at 70 °C. In the whole process, the de-ionized water was used as solvent. The IL was washed thrice with dichloromethane to remove precipitates and then vacuum-dried at 100 °C for 12 h before use. After decantation, the liquid salt was washed twice with 30 mL H_2O and dried for 2 h at 150 °C under 0.1 mbar of pressure to afford 13.6 g of BMImNfO. After evaporation of the residual solvent, the colorless BMImNfO was further vacuum dried at 120 °C for 24 h and stored in a glove box that gives a yield of 72%. The excellent purity of the synthesized BMImNfO was confirmed by ^1H and ^{19}F NMR.

2.3. Gel polymer electrolytes preparation

The electrolyte mixture LiNfO/BMImNfO was prepared by dissolving 0.25 M of LiNfO in the neat ionic liquid BMImNfO and it was subjected to constant magnetic stirring at 70 °C until homogeneous solution was obtained. The gel polymer electrolytes were prepared by solution casting technique as reported earlier [25]. In this work, the system is expanded to mixtures of *PVdF-co-HFP* with one of three different compositions of LiNfO/BMImNfO electrolyte mixtures prepared by combining different cations and fluorinated sulfonates. In brief, the precursor *PVdF-co-HFP* was dissolved in appropriate amount of anhydrous acetonitrile in a one-necked 100 mL flask with magnetic stirring. After *PVdF-co-HFP* was fully dissolved in acetonitrile, desired amounts of LiNfO/BMImNfO mixtures were added and the mixture was heated and kept at 100 °C for 10 h with vigorous stirring in a nitrogen atmosphere. The different weight percentage of *PVdF-co-HFP* and LiNfO/BMImNfO were tabulated in Table 1. The mixture was then poured on to a polypropylene dishes and then vacuum dried at 120 °C for24h to remove trace amount of solvents. The resulting self-standing ionic liquid gel polymer electrolytes (IGPEs) were kept in vacuum desiccators for further characterizations.

2.4. Electrode preparation and $Li/GPE/LiCoO_2$ Swagelok cell assembly

The $LiCoO_2$ cathode was prepared by casting a well-homogenized slurry of $LiCoO_2$ (Sigma Aldrich) (80 wt%), binder poly vinylidenefluoride (PVdF) (10 wt%), super-P carbon and KS-6 carbon (5:5) onto a copper foil. N-methyl-2-pyrrolidone (NMP) was used as slurry forming reagent. In order to obtain the improved electric contact between $LiCoO_2$ particles and current collector, the carbon mixtures of super-P and KS-6 were used. The coated cathode material was dried under vacuum for 24 h at 120 °C. The dried electrode was roll pressed for 1 min before being cut into discs with diameter of 1.3 cm. The cathode discs were further dried at 70 °C under *vacuum* for 12 h before transferring into the glove box for battery assembly. The batteries were assembled as Swagelok cells inside an argon-filled glove box by using $LiCoO_2$ electrode as the cathode, lithium metal as the counter electrode and the prepared IGPE as the electrolyte.

2.5. Characterization techniques

The structures of synthesized BMImNfO were confirmed by nuclear magnetic resonance (^1H NMR, ^{19}F NMR, Mercury plus 300 MHz NMR spectrometer [Varian, USA]) spectroscopy using tetramethylsilane (TMS) as an internal reference for the analyses. For the drying procedure and the verification of the water content was determined by Karl Fisher titration using a Mettler DL21 KF auto-titrator. The viscosity of BMImNfO was analyzed using Modular compact rheometer (Physica MCR 301, Anton Paar).

At 25 °C, the viscosity of the synthesized BMImNfO was found to be 121 *cP* (see Supplementary Fig. S1). The amount of water content in the ionic liquid was determined using Karl-Fischer auto-titrator and it was found to be ~30 ppm. The purity of the ionic liquid BMImNfO

Table 1
Composition of IGPES and its corresponding values of T_g, T_m, % α, E_a, σ, σ_0 and $t_{Li}{}^{+}$.

Gel electrolytes	E_a (eV)	$\sigma_0 \times 10^3$ (S cm^{-1})	σ at 373 K (Scm^{-1})	($t_{Li}{}^{+}$)	T_g (°C)	T_m (°C)	Crystallinity % α
IGPE1	0.241	5.435	3.87×10^{-3}	0.24	−53.4	141.7	16.3
IGPE2	0.225	4.113	1.54×10^{-3}	0.32	−56.2	130.7	14.4
IGPE3	0.223	3.722	2.61×10^{-2}	0.44	−57.0	123.7	10.6

IGPE1 (60% LiNfO/IL +40% PVdF-HFP), IGPE2 (70% LiNfO/IL +30% PVdF-HFP) and IGPE3 (80% LiNfO/IL +20% PVdF-HFP).