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Characterization of N-butyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide-based polymer electrolytes for high safety lithium batteries

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HIGHLIGHTS

- ► PVdF-HFP membrane was prepared by electrospinning.
- ► Py_{14}TFSI-based gel polymer electrolyte has good physical properties.
- ► Py_{14}TFSI-based gel polymer electrolyte shows excellent electrochemical properties.

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ABSTRACT

Poly(vinylidene difluoride-*co*-hexafluoropropylene) (PVdF-HFP) membrane was prepared by electrospinning. The membranes served as host matrices for the preparation of ionic liquid-based polymer electrolytes (ILPEs) by activation with non-volatile, highly thermally stable, and safe room temperature ionic liquid (RTIL) electrolytes; N-butyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (Py_{14}TFSI) complexed with 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). In this work, the first combination of electrospun PVdF-HFP fiber polymer host and pyrrolidinium-based ionic electrolyte was employed for highly stable lithium batteries. The ILPE exhibited low Li^+–TFSI coordination, low crystallinity, high thermal stability, high electrochemical stability, and high ionic conductivity with a maximum of 1.1×10^{-4} S cm^{-1} at 0 °C. The ILPE exhibited good compatibility with a $LiFePO_4$ electrode on storage and good charge–discharge performance in Li/ILPE/$LiFePO_4$ cells at room temperature, delivering specific capacities of 143 and 115 mA h g^{-1} at 0.1 and 1 C-rates. The ILPE also exhibited stable cycle properties and have therefore been demonstrated to be suitable for lithium battery applications.

1. Introduction

Lithium polymer batteries have received considerable attention in recent years since they offer versatility of shape, flexibility, lightness, and are intrinsically safe. Thus, they can be commercialized in miniature electronic device, as well as electric vehicles [1]. However, suitable polymer electrolytes must satisfy the following properties: high ionic conductivity, good mechanical, thermal, interfacial, and electrochemical stabilities.

Among the polymer electrolytes suggested for lithium batteries, polyethylene oxide (PEO) has been widely studied as a promising host polymer, because of the good thermal properties and interfacial stability. However, due to a high degree of crystallinity, PEO-based polymer electrolytes have very low ionic conductivities below room temperature [2,3]. Efforts have been made to increase the ionic conductivity at low temperatures, where plasticized or gel polymer electrolytes have attracted much attention, since they show high ionic conductivity at room temperature by immobilizing large amounts of liquid electrolyte in a polymer host [4–6]. The polymer hosts are membranes adapted specifically for the plasticized or gel polymer electrolytes with pores of nanometer to micrometer size that retain the liquid electrolyte. The membranes should have the capability to absorb the liquid electrolyte without leakage, be chemically compatible with electrode materials, and

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adhere well to the electrode. We prepared polymer membranes by an electrospinning process. The electrospun membranes appear to be particularly suitable as host matrices in microporous polymer electrolytes, because the fully interconnected pores have large surface areas that can function as efficient channels for ion conduction [6–8]. Among the few polymers for membranes that meet the necessary requirements is poly(vinylidene difluoride-*co*-hexafluoropropylene) (PVdF-HFP), which has a strong electron withdrawing function, a unique arrangement and a high dielectric constant. Thus, effectively dissociating lithium salts to generate a large quantity of charge carriers for conduction. Apart from the diffusion established by a plasticizer, such as ionic liquid electrolytes, it is highly likely that conduction occurs also through the swollen PVdF-HFP host, which makes this a very suitable host.

At present, room temperature ionic liquids (RTILs) are considered the most promising plasticizers to substitute for the organic solvents of lithium batteries. Consisting of an organic cation and an inorganic anion, RTILs have several advantages over organic solvents: high chemical and thermal stability, non-flammability, and negligible vapor pressure. In some cases also high electrochemical stability and hydrophobicity [9,10]. In addition, the use of RTILs in less controlled environments than ultra-dry, oxygen-free glove boxes would certainly benefit industrial electrochemical processes. An example of this type of RTIL is N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($Py_{14}TFSI$), which is stable in air, has a sub-ambient melting temperature, high ionic conductivity, and a wide electrochemical window. It generates a superoxide ion in the cathodic process and forms a solid electrolyte interface (SEI) that prevents undesired reactions between the carbon anode and electrolyte [10–14].

Here we have investigated the electrochemical performance of $LiFePO_4$ cathodes working together with the ionic liquid-based polymer electrolytes, since $LiFePO_4$ is inexpensive, non-toxic, thermally stable, and has a high specific capacity (170 mA h g^{-1}) [15,16]. Several research groups have already studied PVdF-HFP-based plasticized ionic liquid polymer electrolytes prepared by phase inversion and PEO-based ionic liquid polymer electrolyte for $LiFePO_4$ batteries [17–21]. However, for these polymer electrolytes physical and electrochemical properties, such as ion paring, ionic conductivity, low temperature stability, and electrochemical stability can still be improved. The ionic liquid-based polymer electrolyte (hereafter named ILPE) composited with a PVdF-HFP electrospun fiber membrane and $Py_{14}TFSI$, shows high electrochemical and thermal stability, and high cycling stability. Also, in particular, a high ionic conductivity showed at low temperatures.

2. Experimental

$Py_{14}TFSI$ and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were both obtained from Aldrich ($\geq$99% purity), stored under Argon atmosphere, and used as received. The moisture content of 1 M LiTFSI in $Py_{14}TFSI$ was measured by coulometric Karl Fischer titration to be 100 ppm. The value could not be sufficient but an influence was not discovered on this study. The PVdF-HFP fibrous membrane was prepared by electrospinning according to the method described previously [6,8]. A 16 wt.% solution of PVdF-HFP (Kynar Flex 2801) in a mixed solvent of acetone and N,N-dimethylacetamide (HPLC grades, Aldrich) in 7:3 wt. ratio was electrospun at room temperature. A homogenous film of $\sim$80 μm thickness was obtained. The membrane has a porous structure of entwined polymer fibers of $\sim$1.5 μm average thickness, forming a net with a mesh size of $\sim$5 μm. The ILPE was obtained by soaking the polymer membrane for 10 s in a solution of 1 M LiTFSI/$Py_{14}TFSI$ (mol L^{-1}) under argon atmosphere at room temperature. The weight ratio of polymer membrane and IL is 1:3.

Membrane electrolyte uptake was determined by soaking a circular piece of the membrane (diameter 1.6 cm) in ionic liquid electrolyte (ILE). The weight of the wetted membrane was determined at different soaking intervals, taking care to remove excess electrolyte remaining on the surface of the membrane by wiping softly with tissue paper. The electrolyte uptake (ε) was calculated using the relation:

$$\varepsilon(\%) = \frac{M - M_0}{M_0} \times 100$$

where M_0 is the mass of the dry PVdF-HFP membrane and M is the mass after soaking with ILE. The ILE uptake of the fibrous PVdF-HFP membrane in the present study is much higher ($\sim$300%) compared to that reported for Celgard separators ($\sim$130%) [7]. The $LiFePO_4$ cathode material, with 6 wt.% carbon coating, was prepared by a mechanical activation process under optimized condition [15,22].

Raman spectra of the ionic liquids and the ionic liquid electrolytes were recorded on a Bruker IFS66 Fourier Transform spectrometer, equipped with an FRA 106 Raman module and using the 1064 nm line of a Nd:YAG laser as excitation source. The laser power was set to 250 mW and the resolution was 4 cm^{-1}. ^7Li NMR measurements were performed using a Bruker DSX-300 solid state NMR spectrometer at room temperature. Differential scanning calorimetry (DSC) experiments were performed using a Q1000 from TA Instruments at a heating rate of 10 °C min^{-1} and a helium flow rate of 25 mL min^{-1}. The samples were sealed in aluminum DSC pans inside an argon atmosphere glove box (H_2O <10 ppm). Typically the samples were first cooled at a rate of 20 °C min^{-1} from 40 °C to −140 °C and then heated at 10 °C min^{-1} to 180 °C. The ionic conductivity of the ionic liquid-based electrolytes was measured from −70 °C to 80 °C in a gold-plated cell, over the frequency range 10^{-1}–10^6 Hz, using a Novocontrol broadband dielectric spectrometer. Thermal gravimetric analysis (TGA) of the samples was performed on an SDT-Q600 (USA) instrument under oxygen flow and at a heating rate of 10 °C min^{-1}.

Lithium transference numbers (t_+) were measured using the D.C. polarization method with Bruce and Vincent correction [23,24]. The frequency range for the EIS measurements was 500 kHz–100 mHz, with a 10 mV ac signal. Polarization was performed with a 20 mV dc signal. The lithium cation transference numbers were calculated as:

$$t_+ = \frac{I_S(\Delta V - R_0 I_0)}{I_0(\Delta V - R_S I_S)}$$

where ΔV is the polarization potential (20 mV); R_0 is the interfacial resistance of the lithium electrode before polarization; R_s is the interfacial resistance of the lithium electrode after polarization; I_0 is current at the start of polarization, and I_s is the steady-state current at polarization. The steady-state technique may be applied when the Li electrode/electrolyte interface resistance is negligible [23,25].

Every material was evaluated in three independently assembled samples. The cell assembly was made in glove box with oxygen and moisture level of below 1 ppm. Lithium electrodes were provided by Sigma–Aldrich (Lithium ribbon, 99.9% trace metal basis). All measurements were performed on a VMP3 multichannel potentiostat-galvanostat (Bio-Logic Science Instruments, France).

For the electrochemical measurements $LiFePO_4$ powder, carbon black and poly(vinylidene difluoride) (PVdF: Aldrich) binder were added to N-methyl pyrrolidone (NMP) solvent in the ratio 83:7:10, by weight. The viscous slurry was cast on aluminum foil and dried at 95 °C under vacuum for 12 h. The film was cut into circular discs of area 0.95 cm^2 and mass $\sim$3.0 mg for use as cathodes. Cyclic voltammetry (CV) measurements of Li/ILPE/Li cells were performed at a scan rate of 1 mV s^{-1}, between −1 and +1 V. Electrochemical