Electrochimica Acta 133 (2014) 529–538

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Lithium bis(fluorosulfonyl)imide/poly(ethylene oxide) polymer electrolyte

Heng Zhang[a], Chengyong Liu[a], Liping Zheng[a], Fei Xu[a], Wenfang Feng[a], Hong Li[b], Xuejie Huang[b,*], Michel Armand[c], Jin Nie[a,*], Zhibin Zhou[a,**]

[a] Key Laboratory for Large-Format Battery Materials and System, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, China
[b] Institute of Physics, Chinese Academy of Sciences, 3rd South Street, Zhongguancun, Beijing 100080, China
[c] CIC energigune, Alava Technology Park, Albert Einstein, 4801510 MIÑANO Álava, Spain

ARTICLE INFO

Article history:
Received 17 February 2014
Received in revised form 16 April 2014
Accepted 19 April 2014
Available online 24 April 2014

Keywords:
Lithium bis(fluorosulfonyl)imide
Poly(ethylene oxide)
Solid polymer electrolytes
Lithium polymer battery

ABSTRACT

New solid polymer electrolytes (SPEs) comprising of lithium bis(fluorosulfonyl)imide (LiFSI) and high molecular weight poly(ethylene oxide) (PEO, $M_v = 5 \times 10^6$ g mol^{-1}) have been prepared and characterized, and are comparatively studied with the representative SPEs, Li[N(SO$_2$CF$_3$)$_2$] (LiTFSI)/PEO, at a molar ratio of EO/Li$^+$ = 20. Their physicochemical properties have been investigated in terms of phase transition behavior, ionic conductivity, lithium-ion transference number ($t_{Li}{}^+$), electrochemical stability, and with particular attention to the interfacial behavior between lithium electrode and SPEs. It has been demonstrated that the ionic conductivities of LiFSI/PEO electrolyte are higher than those of LiTFSI/PEO one above 60 °C, and exceeds 10^{-3} S cm^{-1} at 80 °C. The interface resistances of Li symmetric cell (Li metal | polymer electrolytes | Li metal) using LiFSI/PEO electrolyte are much lower than those using LiTFSI/PEO. The Li/LiFePO$_4$ cell using LiFSI/PEO electrolyte exhibits good cycling performance at 80 °C. These outstanding properties of the LiFSI/PEO electrolyte make it attractive as SPEs for Li battery.

1. Introduction

Over the past 30 years, solid polymer electrolytes (SPEs) have been intensively studied as electrolytes for application in solid state lithium rechargeable batteries [1–8]. This is mainly motivated by their superior advantages over conventional liquid electrolytes, such as good flame-resistance, excellent flexibility and low cost in design, as well as functioning as a separator [1–8]. Conventional SPEs are generally prepared by dissolving lithium salt into polymer matrix, in some cases, additionally containing plasticizers. The polymer matrix must contain a unit of Lewis base, usually ethylene oxide unit (-OCH$_2$CH$_2$-), to solvate lithium salt. It is generally accepted that the motion of Li$^+$ ions is coupled to the motion of the polymer backbone and/or segment through the coordinating interactions between mobile Li$^+$ cations and Lewis base (e.g., ether oxygen atoms) [9], and facile ion transport occurs in the amorphous phase of polymer matrix with a high molecular weight [6,10].

So far, various lithium salts have been investigated as conducting salt for the PEO-based polymer electrolytes, which mainly includes those with weakly coordinating nature, such as hexafluorophosphate (PF$_6{}^-$) [11–13], tetrafluoroborate (BF$_4{}^-$) [14,15], perchlorate (ClO$_4{}^-$) [16–19], triflate (CF$_3$SO$_3{}^-$) [20–22], bis(trifluoromethanesulfonyl)imide ([N(SO$_2$CF$_3$)$_2$]$^-$, TFSI$^-$) [23–25], bis (pentafluoroethanesulfonyl)imide ([N(SO$_2$C$_2$F$_5$)$_2$]$^-$, BETI$^-$) [26–32], and so on. Among them, LiTFSI has been most extensively studied as conducting salt for SPEs. This is mainly attributed to several intrinsic features of TFSI$^-$, including (1) the high flexibility of -SO$_2$-N-SO$_2$- of TFSI$^-$, being favorable for reducing the crystallinity of PEO matrix (plasticizing effect); (2) the highly delocalized charge distribution of TFSI$^-$, being pivotal for effectively reducing the interactions between Li$^+$ and TFSI$^-$, thus increasing the dissociation and solubility of LiTFSI in PEO matrix; and (3) excellent thermal, chemical and electrochemical stability, being required for stable electrolytes. These important natures of TFSI$^-$ are helpful for developing reliable conductive SPEs for Li battery and other electrochemical devices. The success of LiTFSI is well manifested by its application as conducting salt of Li-polymer battery for an electric car, Autolib®, in Paris.

In recent years, lithium bis(fluorosulfonyl)imide (Li[N(SO$_2$F)$_2$], LiFSI), an analogue of LiTFSI, has been intensively studied as

---

[*] Corresponding authors.
[**] Corresponding author. Tel.: +86 27 87559427; fax: +86 27 87543632.
E-mail addresses: xjhuang@iphy.ac.cn (X. Huang), niejin@mail.hust.edu.cn (J. Nie), zb-zhou@mail.hust.edu.cn (Z. Zhou).

http://dx.doi.org/10.1016/j.electacta.2014.04.099
0013-4686/© 2014 Elsevier Ltd. All rights reserved.

electrolyte salt for Li and Li-ion batteries [33–37], because of its excellent compatibility with various electrodes, such as Li metal [34,36], graphitized carbon [33,35], and silicon [39] anodes and $LiFePO_4$ and $LiCoO_2$ cathodes in room temperature ionic liquids [33–37], ambient temperature molten salt [40–42], and conventional liquid carbonate electrolyte systems [38,39]. Furthermore, it has also been demonstrated that a novel sulfonyl (FSO_2)-containing salt, LiFNFSI ($Li[(FSO_2)(nC_4F_9SO_2)N]$), can effectively improve the performances of both $LiCoO_2$ and $LiMn_2O_4$ cells at elevated temperatures [43,44]. All these results clearly indicate that having an FSO_2- group of the imide anion has a significant impact on the improvement of electrode/electrolyte interface, though the mechanism behind this improvement still remain to be understood well. On the other hand, it has been reported that the interfacial stability of Li metal electrode/electrolyte of LiTFSI-PEO electrolyte is relatively poor and could be improved with ceramic fillers [45,46], and the membrane of the SPEs using LiTFSI is very sticky and difficult to process [45]. With above known knowledge on both LiTFSI and LiFSI for electrolytes in minds, and also as part of our work to explore new lithium salts for Li (Li-ion) battery, we try to investigate the application of LiFSI in SPEs.

In this study, we wish to report a new type of SPEs, LiFSI/PEO, which was simply prepared by dissolving LiFSI and PEO in organic solvent, respectively, followed by mixing and solvent-casting process for forming electrolyte membrane. A molar ratio of ethylene oxide ($-CH_2CH_2O-$, EO) unit/Li^+ (i.e., a molar ratio of [EO] to [lithium salt]) of 20 was chosen for LiFSI/PEO, since the concentration of lithium salt for LiTFSI/PEO electrolyte around this ratio region has been found to afford relatively high ionic conductivities in medium-high temperatures, and its ionic conduction is little affected by its heat history [23]. The physicochemical and electrochemical properties of LiFSI/PEO ($EO/Li^+ = 20$ by mole) electrolyte, including phase transitions, ionic conductivity, lithium-ion transference number ($t_{Li}{}^+$), oxidation potential, the interfacial behavior of Li metal electrode/electrolyte, and the performance of Li/$LiFePO_4$ were investigated. For comparison, the respective properties of the corresponding LiTFSI/PEO ($EO/Li^+ = 20$ by mole) electrolyte were also measured and comparatively studied under the same experimental conditions, with particular attention being paid to the interfacial behaviors of Li metal electrode/electrolyte.

2. Experimental

2.1. Materials

Poly(ethylene oxide) (PEO, $M_v = 5 \times 10^6$ g mol^{-1}, Huagao Fine Chemicals, China) was dried at 50 °C for 10 h under vacuum conditions before use. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, battery grade, Rhodia, China), lithium bis(fluorosulfonyl)imide (LiFSI, battery grade, Suzhou Fluolyte, China) were used as received. Conductive carbon blacks (super P, Timcal), polyvinylidene fluoride (PVDF), aluminum foil and lithium iron phosphate ($LiFePO_4$) cathode material were gratis from Suzhou Phylion, China. All other reagents and solvents were dried and purified using standard procedures before use [47]. All the procedures related to the moisture or oxygen sensitive materials were carried out in an argon-filled glove box (Mikrouna, H_2O and $O_2 < 1$ ppm).

2.2. Preparation of polymer electrolyte membrane

The polymer electrolytes of lithium salt (LiX, X = FSI and TFSI)/PEO were prepared in a glove box (H_2O and $O_2 < 1$ ppm) under argon atmosphere by mixing and dissolving pre-weighed amounts of PEO and the corresponding lithium salt in acetonitrile. The concentration of lithium salt in the polymer electrolytes was determined by the molar ratio of $-CH_2CH_2O-$ (EO)/Li^+ (i.e., [EO unit] to [Li^+]). Since the heat history of SPEs has an impact effect on their phase behavior, precaution was taken to not heat the electrolyte samples during their preparation process, as described in literature [48]. The membranes of the polymer electrolytes were prepared by casting the solutions into Teflon dish (2 cm in diameter), following by evaporation and drying at room temperature at least 48 h under high vacuum conditions.

2.3. Phase behavior

The phase transition behavior of the electrolyte was measured on a differential scanning calorimeter (Netzsch 200 F3). The prepared electrolyte sample (in Section 2.2) with average weight of ca. 5 – 10 mg was hermetically sealed in an aluminum pan in a glove box (H_2O and $O_2 < 1$ ppm). The sample was measured for two successive cooling-heating scans at a cooling and heating rate of 10 °C min^{-1} in the temperature of −150 to 150 °C, except for the initial cooling scan from room temperature. At the temperature scanning to the low (−150 °C) and high (150 °C) ends in each scan, the sample was allowed to stand for five minutes. The glass transition temperature (T_g) was taken at the onset of the heat capacity change, while the melting (T_m) and crystallization (T_c) points were taken at the peak of the heat capacity change.

2.4. Electrochemical measurements

The measurements of ionic conductivity were carried out on an Autolab PGSTAT302 N electrochemical workstation (EcoChemie, Netherland) by the complex impedance method. The electrolytes were sandwiched between a pair of stainless steel blocking electrodes (area of disc: 0.2 cm^2). Before measurement, the sandwiched cell was heated to 80 °C for 4 h for obtaining good contact, and then were allowed to stand for 24 h at room temperature (20–25 °C). Afterwards, the measurements were carried out between 30 to 100 °C at an interval of 10 °C for the first heating scan. At each temperature of measurement, the cells were allowed to equilibrate for at least 1 h for good contact. The ac impedance spectra were recorded in the frequency range from 1 to 10^6 Hz. The ionic conductivity (σ, in S cm^{-1}) was derived from the value of resistance (R, in Ω) of the bulk electrolyte obtained in the complex impedance diagram, according to the equation: $\sigma = L/(RS)$, where L (cm) is the thickness of membrane of the polymer electrolyte, and S (cm^2) is the area of the membrane.

To monitor the effect of aging time of the sample on conductivity, the sample after subjecting to the first heating scan was allowed to stand at room temperature for one week, and its conductivities were measured, again, as described above for the first heating scan.

The lithium-ion transference number ($t_{Li}{}^+$) of the polymer electrolyte at 80 °C was measured by a combination measurement of ac impedance and dc polarization using a symmetric cell of Li | polymer electrolytes | Li, as described by Watanabe and Bruce [49–51]. The surface of lithium metal was shaved with a scalpel before use. The cell was assembled in a glove box (H_2O and $O_2 < 1$ ppm). The temperature of the cell was accurately controlled by using a JULABO F12 oil bath (±0.1 °C). The cell was firstly heated to 80 °C for 4 h for obtaining good contact, as well as for forming a stable interface between the electrolyte and electrodes. Then, the cell at 80 °C was applied a dc voltage (ΔV (mV), and 10 mV in this study) until a steady current was obtained (usually 3–5 hours in this study), and the initial (I_o) and steady (I_s) currents (μA), which flow through the cell, were measured. Simultaneously, the impedance spectra of the cell were recorded in the frequency range from 0.01 to 10^6 Hz with an oscillation voltage of 5 mV, before and after the dc polarization, to obtain the initial (R_i) and final (R_f) resistances (Ω) of the