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Effect of temperature on electrochemical performance of ionic liquid based polymer electrolyte with Li/$LiFePO_4$ electrodes

Himani Gupta, Shalu, Liton Balo, Varun Kumar Singh, Shishir Kumar Singh, Alok Kumar Tripathi, Yogendra Lal Verma, Rajendra Kumar Singh*

Ionic Liquid and Solid State Ionics Lab, Department of Physics, Institute of Science, Banaras Hindu University, Varansi 221005, India

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ABSTRACT

Poly ethylene oxide based polymer electrolytes containing salt lithium bis(trifluoromethylsulfonyl)imide and ionic liquid 1-butyl-3-methyl pyridinium bis(trifluoromethylsulfonyl)imide are synthesized. The prepared polymer electrolytes are found to be thermally stable up to 340–360 °C. Ionic conductivity is observed $\sim 2.5 \times 10^{-5}$ S cm^{-1} at 25 °C and 2.3×10^{-4} S cm^{-1} at 40 °C for 30% IL containing polymer electrolyte. Also, ionic transference number > 0.99 and cationic transference number ~ 0.41 with electrochemical window ~ 5.2 V at 25 °C is observed for the electrolyte containing 30% IL. The highest Li^+ ion conducting polymer electrolyte is further optimised for battery application. The specific discharge capacity of the prepared cell (Li/polymer electrolyte/$LiFePO_4$) is found to be 106 mAh g^{-1} at 25 °C and 160 mAh g^{-1} at 40 °C up to 25 cycles with 0.1 C current rate. The increment in discharge capacity at higher temperature may be due to the better electrode-electrolyte contact. Decrement in cell resistance is also observed at higher temperature.

1. Introduction

The requirement of high performance rechargeable lithium metal polymer batteries (LMPBs) is continuously increasing as they are the best option for next generation electrochemical power sources for portable electronic devices, electric vehicles and telecommunication equipment [1]. LMPBs indicate the excellent choice because of their high energy density, flexibility, good cyclability and safety [2–5]. Conventional LMPB system includes a number of components with active materials for cathode and anode. These materials decide the energy capacity and voltage of the battery. A wide variety of active materials with high voltage were examined for LMPBs for increasing energy density [6–8]. Numerous cathode materials were synthesized; in particular, lithium manganese oxide ($LiMn_2O_4$) for LMPBs. Spinel $LiMn_2O_4$ is the fastest cathode material because of its unique 3-D structure which provides multi-direction ion diffusion. But, now days, it cannot be considered as the most suitable cathode material because of the shortage of stable electrolyte which can be used at its operating voltage [9–10]. $LiMn_2O_4$ material has relatively low stability and practical capacity (110–120 mAh g^{-1}) especially at higher temperature. This material also suffers from the problem of Mn-ion dissolution. Also, the surface oxygen atoms of $LiMn_2O_4$ cathode are nucleophilic which react with the electrophilic species present in electrolyte [11]. To overcome the drawbacks of $LiMn_2O_4$, lithium iron phosphate ($LiFePO_4$) cathode is used because of its low operating potential as compared to $LiMn_2O_4$. $LiFePO_4$ has good thermal stability, safety and excellent rate capacity. It is the commercial material whose practical capacity can be obtained near to theoretical one (165 mAh g^{-1} vs. 170 mAh g^{-1}) [12]. Also, the oxygen atoms present in $LiFePO_4$ cathode, are less reactive with electrolyte as compared to $LiMn_2O_4$ which provides the stability of cathode material [13].

Except the electrode materials, electrolyte also plays the major role in battery system. Since, it provides the path for ion transportation between the electrodes. The electrolyte system in LMPBs acts as a separator to prevent any physical contact between cathode and anode. The cell capacity, cyclability, safety and working temperature range are significantly affected by the selected electrolyte [14]. Many researches on polymer electrolyte system are carried out world-wide. Particularly, Poly ethylene oxide (PEO) based polymer electrolytes are selected for LMPBs application because of their high chain flexibility [15]. Also, it can easily dissolve lithium salt by coordinating lithium ion from ether oxygen of PEO [14]. But, the performance of PEO based LMPBs at room temperature is limited because of the low ionic conductivity (10^{-7} S cm^{-1}) [16–17] and this low ionic conductivity is due to the restricted segmental motion of PEO chain at room temperature [18–21].

To enhance the ionic conductivity of polymer electrolyte, general approach is the incorporation of lithium salt with a large anion (LiTFSI,

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* Corresponding author.
E-mail address: rksingh_17@rediffmail.com (R.K. Singh).

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LiBETI etc.) which reduces the crystallinity of polymer chain and promotes the Li ion transportation in polymer electrolyte [22–23]. Although, this approach increases the ionic conductivity about one order of magnitude yet room temperature ionic conductivity is low for battery application [24]. To further increase the room temperature ionic conductivity of polymer electrolytes, a very promising approach is accepted, i.e. addition of room temperature ionic liquid (RTIL) into PEO-salt (PEO-LiX) system. RTILs are molten salts having dissociated organic cation and organic/inorganic anion. RTILs are selected because of their desired properties such as high thermal stability, high conductivity, non-volatility, non-flammability and high potential for electrochemical stability [25–28]. Many research works are done on imidazolium cation based IL because of its low viscosity and high ionic conductivity [29–30]. But the acidic proton, present at imidazolium cation ring reacts with the lithium metal anode and shows poor stability [31–32].

In our previous paper, we have chosen phosphonium cation and TFSI anion based IL in PEO-LiTFSI complex system to synthesize polymer electrolytes [33]. The room temperature ionic conductivity of synthesized polymer electrolytes was found to increase with IL concentration up to 20% IL in polymer electrolyte. Above this concentration, ion pair formation was observed in polymer electrolyte. So, 20% IL containing polymer electrolyte is optimised for application purpose. For battery application, better lithium ion transportation and electrochemical stability was reported using prepared $LiMn_2O_4$ cathode with respect to Li reference anode.

In the present study, flexible, free standing polymer electrolyte films are prepared by solution cast technique using polymer PEO, salt Lithium bis(trifluoromethanesulfonyl)imide) (LiTFSI) and IL 1-butyl-3-methyl pyridinium TFSI. We have chosen hydrophobic pyridinium based IL because they provide related structure motif [34–35]. Only a few studies have been reported for battery application with pyridinium based IL using polymer PEO [1]. Most of the studies are carried out on density, surface tension [36], viscosity [37–38], structure [39], synthesis [40], conductivity [35] and toxicity [41] of pyridinium based IL. PEO has been selected because of its high solvation capability and ability to dissolve high concentration of lithium salt [15]. LiTFSI salt is chosen because of its numerous desirable properties including conductivity [35]. It is thermally strong and more stable towards oxidation process on electrode [42–43]. Li and $LiFePO_4$ have been used as anode and cathode respectively because of high energy density of Li anode [44] and high capacity, low operating voltage and good cyclability of $LiFePO_4$ cathode [13].

In this framework, RTIL containing polymer electrolyte has been optimised on the basis of high Li ion conductivity. The optimised polymer electrolyte is used as a separator for Li/$LiFePO_4$ and performance of the cell (Li/polymer electrolyte/$LiFePO_4$) is recorded at two different temperatures 25 and 40 °C.

2. Experimental techniques

2.1. Materials

Polymer PEO (molecular weight = 6×10^5 g mol^{-1}), salt LiTFSI, IL (1-butyl 3-methyl pyridinium TFSI) and Li foil (0.38 mm thickness) were purchased from sigma Aldrich, Germany. PEO and IL were vacuum dried at 10^{-6} Torr for 2 days before the synthesis of electrolyte. Li foil was kept in argon filled glove box (MBRAUN ABstar, H_2O and $O_2 < 0.5$ ppm). *N*-methyl-2-pyrrolidonel (NMP) (anhydrous, 99.5%) and methanol ($H_2O < 0.02\%$) were used as solvent for electrode and electrolyte preparation respectively.

2.2. Polymer electrolyte synthesis

Polymer electrolyte films PEO + 20% LiTFSI + X% IL (X = 0, 5, 10, 20, 30) were synthesized by solution cast technique. In this process, initially PEO was dissolved into dried methanol and stirred for 2 h at 50 °C to obtain homogeneous viscous solution. Then 20 wt% LiTFSI salt was added into the above solution and again stirred for 2–3 h. After complete dissolution of lithium salt into the polymer PEO, an appropriate amount of IL was added into this solution and again stirred for 3–4 h at 50 °C until a homogeneous viscous solution was obtained. After that, the solution was poured into polypropylene petri-dishes to slowly evaporate the solvent at room temperature for few days. When solution evaporated, free standing polymer films of thickness 180–240 μm were obtained. The prepared polymer films were vacuum dried at 10^{-6} Torr for 2–3 days to the complete evaporation of solvent. Then dried polymer electrolyte films were used for further studies.

2.3. $LiFePO_4$ cathode preparation

Cathode was prepared with $LiFePO_4$ active material, PVdF (poly (vinylidene fluoride)) binder and carbon black to improve the electronic conductivity of electrode. NMP was used as a solvent for cathode preparation. Initially, $LiFePO_4$ (80%), PVdF (10%), carbon black (10%) were mixed in mortar and then above mixture was stirred with NMP solvent until a viscous slurry was obtained. This slurry was uniformly coated onto the aluminium foil which was used as a current collector for cathode. After coating, it was vacuum dried at 110 °C for 48 h. Then the prepared cathode was pressed by 3 Ton pressure and transferred into glove box for further characterization.

2.4. Cell assembly

The cell was assembled by sandwiching polymer electrolyte film between $LiFePO_4$ cathode and Li metal anode. Before using Li metal foil as an anode, it was cleaned by stainless steel blade. Aluminium was used as a current collector for cathode. The assembled cell was laminated twice by thermal adhesive plastic sheet using lamination machine. The cell was thermally stabilised for 1 h at selected temperature (40 °C) before the measurement. The whole process was carried out inside the argon filled glove box (H_2O and $O_2 < 0.5$ ppm).

3. Experimental

The differential scanning calorimetry (DSC) was performed by using Mettler DSC 1 system within temperature range − 100 to 100 °C at a heating rate 10 °C min^{-1} under continuous purging of N_2 gas. Thermogravimetric analysis (TGA) was carried out by Mettler Toledo DSC/TGA 1 system within the temperature range 30–500 °C at 10 °C min^{-1} heating rate under the N_2 filled environment. The ionic conductivity of prepared polymer electrolyte was studied by complex impedance spectroscopic technique using Novo control impedance analyser within 1 Hz–40 MHz frequency range. To analyse ionic conductivity, polymer electrolyte was sandwiched between two gold plated electrodes of 20 mm diameter. Electrical conductivity (σ) has been calculated by using the formula [45].

$$\sigma = L/(R_b \times A) \tag{1}$$

where, L is the thickness, R_b is bulk resistance and A is the cross-sectional area of polymer electrolyte.

The electrochemical stability, total ionic transference number (t_{ion}), Li cationic transference number (t_{Li+}) and galvanostatic charge-discharge studies were performed by using AUTOLAB PGSTAT 302 N controlled by NOVA 1.8 software version (Metrohm Lab). The t_{ion} was calculated by using dc polarization technique. In this process, polymer electrolyte was sandwiched between two stainless steel (SS) electrodes and corresponding current was recorded as a function of time after applying 10 mV voltage for 1 h across the cell (SS/polymer electrolyte/SS).

Total ionic transference number (t_{ion}) of prepared electrolyte can be calculated by the relation [45].