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Electrochemical study of Ionic Liquid based polymer electrolyte with graphene oxide coated $LiFePO_4$ cathode for Li battery

Himani Gupta, Shalu Kataria, 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

Ionic Liquid (IL) based polymer electrolytes using polymer poly ethylene oxide (PEO), salt lithium bis(fluoromethylsulfonyl)imide and IL *N*-propyl-*N*-methylpyrrolidinium-bisfluorosulfonylimide ($PYR_{13}FSI$) are synthesized by solution cast method. Using different experimental techniques, good thermal stability and wide electrochemical window are observed for synthesized polymer electrolytes. Maximum Li^+ conductivity is found for 10% IL containing polymer electrolyte so, it is used in Li cell preparation. $LiFePO_4$ (LFP) cathode and graphene oxide wrapped LFP cathode (GO-LFP) are also prepared to observe the effect of graphene oxide coating in electrochemical performance of the Li cell. From charge –discharge process, high specific discharge capacity (~163 mAh g^{-1} at 0.1 C) is found for GO-LFP as compared to LFP cathode. GO-LFP cathode shows good cyclability and Coulombic efficiency up to 100 cycles. High charge-discharge capacity of GO-LFP is noticed even at higher current rate.

1. Introduction

The serious climate change and rapidly increasing demand for energy are focusing the research in the development of sustainable energies such as wind energy, solar energy, wave energy etc. These energies need to be stored in devices for future use. Over the last decade, invention in energy storage devices with high power and capacity are still in progress. Among them, Li battery is one of the most promising replacements of these energy storage systems due to its high energy density, capacity and good electrochemical performance [1–4]. To improve the capacity, cyclability and energy density of Li battery, discovery of suitable cathode and anode materials are in progress. $LiFePO_4$ (LFP) is one of the most popular cathode materials for Li battery which fulfils the requirement of energy storage such as high capacity, good stability, low cost and environmental capability [5,6]. But some factors such as intrinsic material property and defects in structure reduce the Li^+ diffusion in electrodes which results in lowering the actual capacity of LFP cathode. Also the electrochemical performance of LFP decays at high charge/discharge rate because of its low electronic conductivity and Li^+ diffusion rate [7]. Current approach to boost up the electrochemical performance of LFP cathode is being used such as metal doping [8–10], carbon coating [11–13] and reduction in LFP particle size [14]. Metal doping is able to increase the voltage of LFP based Li battery by expanding the Li^+ diffusion path. The carbon coating on LFP particle are extensively used in industry because this conducting carbon coating enhances the rate of electron migration during charge/discharge process. The reduced LFP particle size shortens the Li^+ diffusion path but it has a disadvantage that the reduction in LFP particle size results higher surface area which requires large amount of binder to bind the small LFP particles. The addition of high loading binder further reduces the capacity.

Recently, Graphene oxide is in focus for Li battery due to its excellent electronic conductivity and large surface area which improves the electrochemical performance of LFP cathode. Wei et al. reported that graphene wrapped LFP increases electron transport and fast ion diffusion [15]. Improved rate capability and cycling stability were also reported when some metal oxide [16,17] and metal [18] based anode materials were modified by graphene. Because of such beneficial properties of graphene, in present paper, we coated LFP particles with graphene oxide to observe its electrochemical behaviour in lithium polymer battery.

Capacity, cyclability and rate performance of Li battery are also affected by electrolyte used. Since only electrolyte is responsible for ion migration from cathode to anode and vice versa. Generally, liquid electrolytes offer low resistance for ion transportation but due to corrosion, leakage and portability problems, liquid electrolyte is replaced by polymer electrolytes which provide several advantages over liquid electrolytes such as increased resistance to change the volume of

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* Corresponding author.
E-mail addresses: rksingh_17@rediffmail.com, rajendrasingh.bhu@gmail.com (R.K. Singh).

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electrodes during charge/discharge process, improved safety, good flexibility and processability [19]. Even dendrite growth could also be minimized using polymer electrolytes. Polyethylene oxide (PEO) with alkali metal salts (LiX) are the best candidate for polymer electrolytes in which polymer matrix dissolves Li salt by co-ordinating Li^+ with ether oxygen. However, its poor Li^+ transport nature provides barrier to use it in battery application. In order to enhance its Li^+ transference number and/or ionic conductivity, recent approach is the use of Ionic Liquid (IL). ILs are molten salt containing self-dissociated organic cation and organic/inorganic anion. IL increases the ionic conductivity of polymer electrolyte since it acts as a plasticizer and also provides free charge carriers. These bulky, asymmetric ions/charge carriers enhance the empty space or free volume available for segmental motion of polymer chain and ion conduction and thus enhance ionic conductivity. IL is selected because of its high ionic conductivity, good thermal stability, non-flammability, non-volatility and wide electrochemical stability [20–25].

On the basis of their electrochemical stability, these ILs are classified into two categories. The first category includes piperidinium, pyrrolidinium, phosphonium and ammonium based ILs. They exhibit good electrochemical stability and lower cathodic limiting potential to permit the lithium deposition [26,27]. The second category contains guanidinium and imidazolium based ILs. They have higher cathode limiting potential and lower electrochemical window compared to the first. Although, varies studies have been reported on imidazolium based ILs due to its low viscosity. But when these ILs are used in battery application, the acidic proton at C2 position of imidazolium cation ring leads to electrode corrosion [25,28]. To overcome this drawback, the C2 position proton was replaced by C_2H_5, CH_3 group and other rings but these groups start to decrease the conductivity [29]. In our previous papers, we have reported phosphonium and pyridinium IL based polymer electrolytes [24,25] and found that phosphonium IL based polymer electrolyte shows ionic conductivity (σ) $\sim 4.2 \times 10^{-5}\,S\cdot cm^{-1}$, lithium ion transference number ($t_{Li}{}^+$) ~0.38 and electrochemical stability ~3.34 V at 30 °C. While the pyridinium IL based polymer electrolyte results σ $\sim 2.5 \times 10^{-5}\,S\cdot cm^{-1}$ with $t_{Li}{}^+$ ~0.41 and electrochemical stability ~5.2 V at 30 °C. In this study, we have studied Pyrrolidinium IL based polymer electrolyte.

In present study, polymer electrolytes are synthesized using polymer PEO, salt lithium bis(fluorosulfonyl)imide (LiFSI) and IL *N*-propyl-*N*-methylpyrrolidinium-bisfluorosulfonylimide ($PYR_{13}FSI$). PEO was selected due to its salt dissolution ability and good mechanical stability [30]. While LiFSI salt was chosen because of its good chemical stability, high ionic conductivity, anti-corrosive property and ability to form stable SEI (solid electrolyte interface) layer on various electrodes [30–32]. Pyrrolidinium based IL was used due to its high ionic conductivity, low viscosity, suitable electrochemical stability [33]. These flexible, free standing synthesized polymer electrolyte films are used as ion conductor and separator for Li cell. LFP cathode and graphene oxide coated LFP (GO-LFP) cathode are prepared and their electrochemical performance is recorded using polymer electrolyte film for the cell (Li/LFP and Li/GO-LFP).

2. Experimental

2.1. Materials

Polymer PEO, salt LiFSI, IL $PYR_{13}FSI$, Li foil (0.38 mm thickness), LFP, graphene oxide, carboxymethyl cellulose (CMC) binder and carbon black were purchased from sigma Aldrich, Germany. All above materials were vacuum dried for 10^{-6} Torr before further use. Li foil which is used as anode was already kept inside the argon field glove box (MBRAUN ABstar, H_2O and $O_2 < 0.5$ ppm) for safety purpose. Distil water and methanol were used as solvent for cathode and electrolyte synthesis respectively.

2.2. IL based polymer electrolyte synthesis

Solution cast technique was used to prepare polymer electrolyte films, PEO + 20% LiFSI + X% $PYR_{13}FSI$ (X = 0, 2.5, 5, 7.5, 10). In this mechanism, polymer PEO was dissolved into dried methanol. This mixture was stirred for 2 h at 50 °C to obtain homogeneous viscous solution. Then 20 wt% LiFSI salt was added into above solution and stirred for 2 h at the same temperature. When salt was completely dissolved into above solution, appropriate amount of IL was added and stirred for 2–3 h at 50 °C until homogeneous viscous solution was achieved. This solution was poured into petri-dishes (polypropylene) and allows evaporating the solvent at room temperature for few days. When maximum solvent was evaporated, it was vacuum dried at 10^{-6} Torr for 2–3 days to complete evaporation of remaining solvent and volatile substances. After complete drying, flexible, free standing polymer electrolyte films of thickness 100–330 μm were obtained.

2.3. Cathode preparation

2.3.1. GO-LFP particle preparation

Wet chemical method was used to prepare graphene oxide coated LFP active material. Initially, graphene oxide was dissolved into absolute alcohol ($1\,mg\cdot ml^{-1}$). This solution was kept under ultrasonic treatment for ½ h for complete mixing of graphene oxide and LFP active material was added into above solution under moderate stirring. The resulting solution was heated at 70 °C for complete evaporation of remaining alcohol. Finally, this mixture was vacuum dried at 150 °C for 24 h. As a result, GO-LFP particle was obtained.

2.3.2. LFP/GO-LFP cathode preparation

Cathode was prepared by LFP active material which determines the energy of cathode. Carbon black to enhance the electronic transportation of cathode and CMC binder was used to glue the carbon black and active material together with aluminium (Al) current collector. Distilled water was used as a solvent. Firstly, CMC binder (5%) was dissolved into distil water and stirred at room temperature until complete mixing. After that carbon black (5%) and active material LFP and/or GO-LFP (90%) were added into the above solution and stirred at room temperature until homogeneous, viscous slurry was obtained. This slurry was coated on Al foil current collector. After coating, it was vacuum dried at 110 °C for 2 days. This prepared cathode was pressed under 3 Ton pressure and moved into glove box for further study.

3. Experimental techniques

Thermogravimetric analysis (TGA) was performed by Mettler Toledo DSC/TGA 1 system within temperature range 30–500 °C at $10\,°C\,min^{-1}$ heating rate under N_2 environment. The measurement of ionic conductivity of synthesized polymer electrolytes was carried out by complex impedance spectroscopic technique using Novo control impedance analyser within frequency range 1 Hz-40 MHz. To study the ionic conductivity, polymer electrolyte was sandwiched between two gold plated electrodes having 10 mm diameter. The ionic conductivity of polymer electrolytes has been calculated using formula [34].

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

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

Total ionic transference number (t_{ion}), Li^+ cationic transport number (t_{Li+}), electrochemical stability along with galvanostatic charge-discharge process of polymer electrolyte were studied by using AUTOLAB PGSTAT 302N controlled by NOVA 1.8 software version (Metrohm Lab). t_{ion} of polymer electrolyte was calculated by using d.c polarization technique. In this process, a constant d.c potential was applied across the cell SS/polymer electrolyte/SS (SS: stainless steel) and corresponding current was recorded as a function of time for 1 h.