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Flexible gel polymer electrolyte based on ionic liquid EMIMTFSI for rechargeable battery application

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ABSTRACT

Development of high performance lithium polymer batteries (LPBs) with high thermal and electrochemical stabilities is now being intensively pursued for various applications like personal electronics, grid storage etc. In the present study, we report synthesis and characterization of a gel polymer electrolyte (GPE) based on polymer polyethylene oxide (PEO), salt lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and different amounts of added ionic liquid (IL) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI). Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), complex impedance spectroscopy, ionic transference number studies, linear sweep voltammetry (LSV) and cyclic voltammetry (CV) studies exhibit promising characteristics of prepared GPEs for suitable application in LPBs. The GPEs show high thermal stability (i.e. no weight loss up to 310 °C), high ionic conductivity ($\sim 2.08 \times 10^{-4}$ S cm^{-1} at 30 °C), high lithium transference number ($t_{Li^+} = 0.39$) and high electrochemical stability window (~4.6 V). A low cost simple thermal lamination technique was used to encapsulate whole LPB assembly by sandwiching best performing GPE between a $LiMn_2O_4$ cathode and lithium metal anode. In galvanostatic charge/discharge cycles the prepared cell showed good electrochemical performance.

1. Introduction

The increasing level of pollution due to combustion of conventional fossil fuel is forcing us to the renewable green energy like solar energy, wind energy, geothermal energy etc. These renewable energy sources rely on weather for power supply which can be unpredictable and inconsistent. So storage and efficient delivery of these sustainable green energies is highly important. Rechargeable batteries are one of the most promising candidates for this purpose [1]. Li batteries have highest volumetric and gravimetric energy density among all the secondary batteries [2–4]. They also have long cycle life [5]. However, improvement in safety, energy density, cycle life and many other aspects are required. The electrodes, electrolyte materials and their interfaces are the main components of a battery. While new electrode materials are being synthesized and studied for better energy density and good electrode-electrolyte contact, the problems with liquid electrolytes also need to be minimized [6–8]. The problem of corrosion, portability and leakage arising due to liquidus nature of electrolytes can be avoided in gel polymer electrolytes (GPEs) [9–11].

In GPEs, mobile ionic species are incorporated into polymers. Compared to liquid electrolytes, GPEs are more mechanically and thermally stable and can be fabricated into thin, flexible films [12]. Earlier, many polymer electrolytes have been synthesized by complexing ionic salts (like $LiBF_4$, $LiClO_4$, NH_4ClO_4 etc.) with polar polymers like polyethylene oxide (PEO), polyvinylidene fluoride (PVdF), polyvinyl acetate (PVA) etc. But their room temperature ionic conductivity was very low ($\sim 10^{-7}$ S/cm) [13]. Different approaches have been adopted to enhance the ionic conductivity of GPEs. One of them is to incorporate low molecular weight plasticizers such as ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC) etc. with GPEs. This method may increase conductivity of GPEs but decreases their mechanical and thermal stability [14]. It also narrows the electrochemical potential window which limits their use in device application. Another method is to use nano size ceramic fillers like Al_2O_3, SiO_2, TiO_2 etc. into polymer electrolytes [15].

A new technique to enhance the ionic conductivity is to incorporate Ionic Liquids (ILs) into GPEs [16]. Recently, ILs have attracted much attention as a substitute for conventional plasticizers due to their distinct properties like high ionic

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conductivity, wide electrochemical window, non-volatility, non-flammability, negligible vapour pressure, wide liquidus range, excellent thermal stability etc. [17–19]. ILs are basically room temperature molten salts entirely composed of bulky asymmetric organic cations and organic/inorganic anions. ILs act as plasticizers which increase the amorphicity of the GPEs and enhance Li^+ ion conduction [9,20].

For preparing GPEs, PEO is the most studied polymer because of its high solvation property and its ability to dissolve high concentration of dopant salts [21]. Almost all commercial lithium batteries use $LiPF_6$ salt in electrolyte but it has poor thermal and chemical stability. Lithium imide salts can be good alternatives to $LiPF_6$ due to their relatively high thermal and chemical stability. Among the common lithium imide salts, lithium bis-fluoromethylsulfonyl imide (LiFSI) and lithium bis(trifluoromethylsulfonyl) imide (LiTFSI) are possibly the most promising salts for lithium battery application. But LiTFSI was found to corrode the aluminum current collector at a higher potential than the onset potential of aluminum corrosion for LiFSI salt [22]. Also LiTFSI salt has low lattice energy. We choose 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI) IL due to its high thermal stability, large electrochemical window, high ionic conductivity etc [23,24].

In our present study, free standing films of PEO + 20 wt. % salt LiTFSI with different amounts of added IL EMIMTFSI were prepared by solution cast technique. Thermal stability, electrochemical stability and ionic conductivity of the prepared samples were studied. Finally, we assembled a cell using prepared GPE with Li metal foil as anode and a standard cathode. $LiMn_2O_4$ was used in standard cathode as active cathode material because it has high energy density (~ 148mAh/g), high potential (4.1 V vs. Li/Li^+), low cost and high environment acceptability [2,25]. Battery performance of this cell was studied and electrochemical performance was investigated comprehensively.

2. Experimental

2.1. Materials

The polymer PEO (molecular weight 6×10^6 g/mol), ionic liquid EMIMTFSI ($\geq$98%), salt LiTFSI (99.95%) and Lithium foil (99.9%) were purchased from Sigma Aldrich, Germany. All these chemicals were kept and handled inside an Argon gas filled glove box (MBRAUN ABstar) where water and oxygen levels were maintained below 0.5 ppm. PEO and EMIMTFSI were vacuum dried at $\sim 10^{-3}$ Torr for 24 hours before sample preparation. Solvent methanol (analytical grade, H_2O <0.02%) and N-methyl-2-pyrrolidonel (anhydrous, 99.5%) were used as received without further purification.

2.2. Electrolyte Synthesis

PEO + 20 wt. % LiTFSI + x wt. % EMIMTFSI (x = 0, 2.5, 5, 7.5, 10 & 12.5) films were prepared by solution casting technique. In this process, appropriate amount of PEO was dissolved in methanol under constant stirring at 500 rpm at 50 °C for 2 hours to obtain a clear homogenous solution. Then 20 wt. % of LiTFSI was added and the solution was stirred for another 2 hour. After that different amounts of EMIMTFSI (i.e. 0, 2.5, 5, 7.5, 10 and 12.5 wt. %) were added in the above solution and stirred for another 4 hours at 50 °C until a highly viscous and homogenous solution was obtained. This viscous solution then poured into polypropylene petri dishes for casting and the solvent was allowed to evaporate in dry ambient condition. After solvent evaporation for few days, free standing films of thickness ~ 150–200 μm were obtained which were vacuum dried for 3 days at ~ 10^{-3} Torr for complete solvent evaporation. These dried samples were then kept inside the glove box and used for further studies. A typical photograph of prepared freestanding and flexible GPE is shown in Fig. 1(A). It may be mentioned here that on further increasing the amount of EMIMTFSI into the GPEs, the mechanical integrity of the films became very poor.

2.3. Electrode Preparation

For preparation of cathode, a slurry of 80 wt. % $LiMn_2O_4$, 10 wt. % carbon black and 10 wt. % polyvinylidene fluoride (PVdF) binder was prepared. N-methyl-2-pyrrolidone (NMP) was used as solvent. This slurry was coated uniformly onto an aluminum foil by using doctor's blade and then vacuum dried at 110 °C for 48 hours. After drying, prepared cathode was put between 2 butter papers and pressed by applying 3 ton pressure. Few rectangular shaped cathodes of dimension 2 cm x 4 cm were cut and transferred to the glove box. Mass loading of the cathode was nearly 1 mg/cm^2. Lithium metal foil was used as anode. Before using, surface of the Li foil was cleaned by a stainless steel blade.

2.4. Cell Preparation

Prepared GPEs were sandwiched between cathode and anode. Aluminum and copper foil were used as current collectors at cathode and anode sides respectively. Two long strips of aluminum and copper foil were kept with current collectors for future external electrical connection. This whole assembly was wrapped

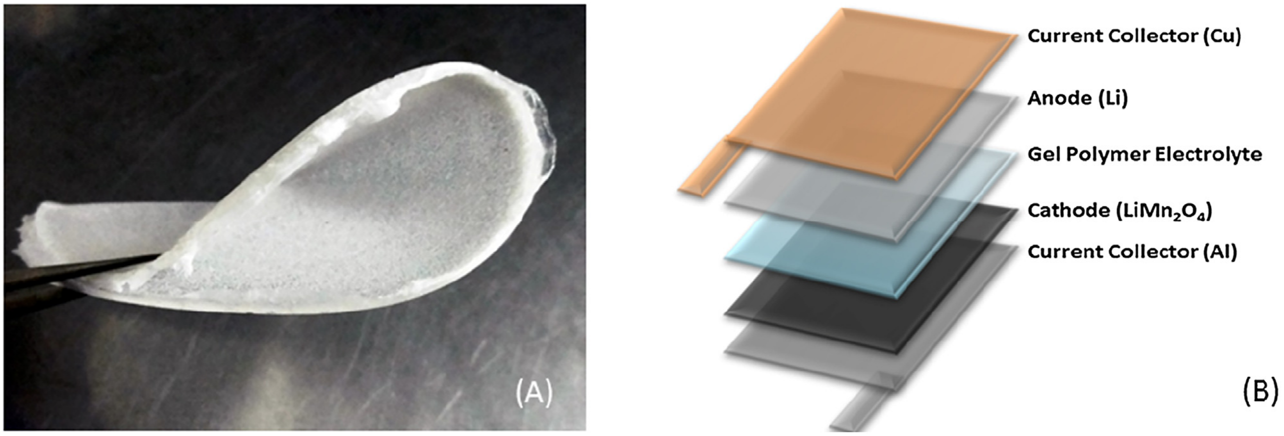

Fig. 1. (A) A typical photograph of prepared GPE which shows mechanical stability and flexibility; (B) Schematic diagram of the prepared LPB cell.