Fully flexible lithium ion battery based on a flame retardant, solid-state polymer electrolyte membrane

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A B S T R A C T

The safety issue of a portable battery has increasingly become paramount important because of intimate contact of wearable devices with the human body. In this study, a flame retardant, thermally stable polymer electrolyte membrane (PEM) has been fabricated based on crosslinkable polyurethane precursor, viz., polyethylene glycol-*bis*-carbamate dimethacrylate (PEGBCDMA). This PEGBCDMA based PEM is solvent-free, transparent, bendable, and twistable, which makes it an ideal candidate for a fully flexible battery application with safety attributes. Moreover, the above PEM exhibits high ionic conductivity close to the superionic level ($8 \times 10^{-4}\,S\,cm^{-1}$ at room temperature) and electrochemical stability in a large operating window of $-0.5\,V$ to $4.5\,V$. The PEM shows over 80% of specific capacity retention up to 250 cycles tested in the lithium iron phosphate ($LiFePO_4$)/PEM/graphite full cells. Of particular importance is that the present PEGBCDMA based PEM has met most of the application criteria for a flexible solid-state lithium ion battery.

1. Introduction

The fully flexible electronics have gained growing interest and worldwide demands in flexible displays, wearable devices, sensors, electronic papers, and among others [1–5]. These next-generation devices require flexible energy storage devices with safety attributes [6,7]. By virtue of its high energy density, cycling stability, lithium ion battery has long been a work-horse as the power source for flexible electronics and related applications [8]. Conventional lithium ion batteries operate based on a liquid electrolyte solvent consisting of mixtures of cyclic/acyclic organic carbonate derivatives that can concurrently dissolve lithium salt crystals. The major drawback is that these liquid electrolytes have an inherent risk of leakage due to low vapor pressure in conjunction with their low flash points, resulting in catching fire [9–11]. Hence, these liquid electrolytes must be contained in metal or robust plastic containers in order to alleviate the safety issue of solvent leakage and/or battery explosion. However, this flammable liquid electrolyte problem becomes increasingly severe at elevated battery operatures and more complex in assembling the fully flexible lithium ion battery. To improve the battery safety, there is a need for designing fully flexible solid polymer electrolyte membranes (PEM) for all solid-state flexible batteries, which must not contain any organic liquids (i.e., solvent-free) during fabrication as well as operation of flexible electronics [12,13].

The first primary non-rechargeable solid-state lithium-ion battery was introduced as early as 1972 based on a doped lithium iodide solid-state electrolyte [14]. This solid-state electrolyte was mixed with calcium iodide that exhibited an ionic conductivity of $2.3 \times 10^{-6}\,S\,cm^{-1}$ at room temperature. Since then, various types of solid-state electrolytes were introduced to the lithium ion batteries, noticeably lithium metal oxides, lithium metal phosphates, and polymer electrolyte [15–17]. Besides the improvement of thermal stability, the added advantage of the solid-state lithium ion batteries is that cycle-life performance is reported to be much longer. This prolonged battery life of solid lithium ion battery is ascribed to the absence of solvent (i.e., solvent-free) that was required in the case of liquid electrolytes, which is the source of the fire hazard of the conventional liquid electrolyte based lithium ion batteries [18]. While the solid-state PEM materials could provide an additional freedom in the battery design and integration into various devices, the major challenge with the solid polymer electrolyte is the poor ionic conductivity, which is significantly lower than that of its liquid electrolyte counterpart. For instance, the ionic conductivity of ether-based polymer electrolyte (lithium salt dissolved in polyethylene oxide (PEO)) is as low as 10^{-9}–$10^{-7}\,S\,cm^{-1}$ [19,20]. Some recent works have shown that the room temperature ionic conductivity of the solid PEM based on the photo-cured polyethylene glycol network has improved to the order of 8×10^{-4} to $10^{-3}\,S\,cm^{-1}$ with the aid of solid plasticizers such as succinonitrile (SCN) [21–23].

In this paper, polyethylene glycols (PEG) terminated with telechelic

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amine groups were reacted with cyclic ethylene carbonate (EC) via ring-opening reaction to afford polyethylene glycol-*bis*-carbamate. Subsequently, UV-curable methacrylate groups were further attached to the telechelic chain ends to form polyethylene glycol-*bis*-carbamate dimethacrylate (PEGBCDMA), i.e., polyurethane methacrylate, to afford crosslinking capability [24]. Combining properties of polyurethane (PU) and polyacrylate (PA) are anticipated to improve chemical resistance and hardness afforded by PA segment and improved elasticity, scratch resistance, flexibility and toughness provided by PU segment. Upon UV crosslinking, the PEGBCDMA network exhibits a low glass transition temperature ($-60\,°C$) with high tensile strength and elongation, which is an ideal polymer matrix for flexible solid PEM. With the addition of solid plasticizer and lithium salt into the polymer precursor, the melt-mixed ternary mixture was completely miscible over a wide compositional range. Upon photo-crosslinking, the cured ternary PEM network remained transparent and completely amorphous. The thermal stability and electrochemical performance including ion conductivity and capacity retention have been examined for the aforementioned solid-state PEMs. More importantly, the feasibility of fabricating flexible, flame-retardant, all solid-state lithium ion battery has been demonstrated.

2. Experimental section

2.1. Materials

Ethylene carbonate (EC, 99%), 4,7,10-trioxa-1,13-tridecanediamine (TTDDA, 97%, also known as PEG diamine), 4-(dimethyl-amino) pyridine (DMAP, 99%), hydroquinone (99%), triethyleneamine (TEA, 99%), methacrylic anhydride (MAA, 94%), lithium *bis*(trifluoromethyl) sulfonyl imide (LiTFSI) having a purity of 99.9% were purchased from Sigma-Aldrich Co. Organic solvents such as dichloromethane (99.9%) and 1-methyl-2-pyrrolidinone (NMP) were also obtained from Sigma-Aldrich. The electrode materials lithium iron phosphate (LiFePO$_4$), graphite, and carbon black (CB) powders were purchased from MTI Corp. Poly(vinylidene fluoride) (PVDF, having Mw ~534,000) was obtained from Sigma-Aldrich and used as electrode binder.

2.2. Sample preparation

In the fabrication of solid PEM, several selected compositions of PEGBCDMA/EC/LiTFSI were melt-blended to form isotropic mixtures. Melt-mixing was performed at room temperature by mechanically stirring without using any solvent. 2 wt% of Irgacure 819® with respect to the polymer weight was added to the above mixtures during melt-blending. The homogeneous mixture thus obtained was placed in a glass mold, and then covered with a transparent PET film and lightly rolled to spread uniformly using a rubber roller. Subsequently, UV polymerization was performed by illuminating using a UV Lamp (Bondwand 350 nm) at room temperature (25 °C) and an intensity of $5\,mWcm^{-2}$ for 15 min, inside a glove box under the argon gas circulation. The thickness of the photocured transparent film ranges from approximately 0.1–0.2 mm.

The cathode was prepared by mixing active material such as lithium iron phosphate (LiFePO$_4$), carbon black, and PVDF in NMP solvent at the weight ratio of 8:1:1. The mixed slurry was coated on an aluminum foil and then dried at 160 °C in a vacuum oven for 24 h. The graphite anode was fabricated in a similar manner, except that the slurry of anode mixture was coated on a copper foil.

In the flexible battery fabrication, polydimethylsiloxane (PDMS, Sylgard 184 from Dow Corning) was used as the flexible supporting substrate by mixing the base and curing agent in a mass ratio of 10:1 and pressed to remove the bubble inside if any, and subsequently cured at ambient temperature for 4 h followed by annealing at 120 °C for 2 h [25]. All the battery assembly was processed in the glovebox (LABstar Glove Box Workstation, MBraun) under argon atmosphere.

2.3. Sample characterization

Thermal properties of the samples were examined using a thermogravimetric analyzer (TGA; Model Q50, TA Instruments) at a heating rate of $10\,°C\,min^{-1}$ from room temperature to 500 °C under a nitrogen atmosphere. For solid PEM, tensile measurements were performed using a dynamic mechanical analyzer (DMA Q800 TA instruments) at a constant stress rate of $0.1\,MPa\,min^{-1}$. All tensile tests were conducted at ambient temperature.

Ionic conductivities of the solid PEM films were determined by using an AC impedance analyzer (HP4192A LF, Hewlett Packard). PEM films were sandwiched between two parallel polished stainless steel plates having an area of $10 \times 10\,cm^2$ and ~1 mm in thickness. Sample assembling was undertaken in a glovebox to prevent moisture absorption, if any. The frequency sweep was carried out from 13 MHz to 5 Hz with a voltage of 10 mV in amplitude. Temperature ramping was performed in a heating chamber for all solid PEMs at a rate of $1\,°C\,min^{-1}$. Cyclic voltammetry measurements were undertaken using SI 1260 Impedance/Gain Phase Analyzer in conjunction with SI 1287 Electrochemical Interface (Solartron Analytical Inc.). Galvanostatic charge/discharge cycling tests of the coin cells were conducting using MTI 8-channel battery cycler (MTI Corp.).

3. Results and discussions

In our previous work, we have reported the synthesis scheme of the UV-curable polymer PEGBCDMA as shown in Fig. 1(a), whereby polyethylene glycol (PEG) containing telechelic amine group was reacted with cyclic ethylene carbonate (EC) via ring-opening reaction [23]. The methacrylate groups were further attached to both chain ends to form PEGBCDMA and subsequently crosslinked by uniform UV irradiation. This crosslinked polymer containing urethane segments was shown to provide high tensile strength, high modulus, and high extensibility [23]. The chemicals structures of PEM constituents, viz., PEGBCDMA, EC, and LiTFSI are presented in Fig. 1(b). While the ether oxygen of PEGBCDMA can form strong complexation with the lithium cation, the lithium ions can be transported through these ion-dipole complexation sites [26,27]. Without plasticization, the ion diffusion through these complexation sites is rather slow and thus the ionic conductivity is low (i.e., $\sim 10^{-6}\,S\,cm^{-1}$) [24]. Hence, solid plasticizer such as succinonitrile (SCN) had been customarily used as a plasticizer to afford the chain mobility of the polymer matrix and to expedite the diffusion of the lithium cation while dissociating the lithium ions from their salt such as LiTFSI that serves as an ion source [28–32]. In the present case, EC having a crystal melting temperature of 36.4 °C, a high flash point (160 °C), and boiling point (248 °C) was chosen as solid electrolyte, since it can be readily dissolved in PEGBCDMA/LiTFSI mixture without requiring any solvent [9]. Moreover, the EC is part of the carbamate group of the as-synthesized PEGBC and thus their mutual solubility (or miscibility) can be anticipated.

As depicted in Fig. 1(c), the present photopolymerized PEM (i.e., PEGBCDMA/EC/LiTFSI 20/40/40) is completely isotropic and transparent having a smooth appearance, exhibiting good deformability such as bendability and twistability. Fig. 1(d) shows the tensile test results of the PEM. The elongation at break is around 27%. These shape-conformities make this solid-state PEM to be very desirable for a flexible solid lithium ion battery with diverse applications in flexible electronics.

The thermal stability of the PEM was investigated by means of TGA. Fig. 2(a) shows the TGA thermograms of neat EC (far left curve), LiTFSI (far right), crosslinked PEGBCDMA (3rd from the left) and their PEM composite having the 20/40/40 (PEGBCDMA/EC/LiTFSI) ratios (2nd from the left). The small molecule EC appears stable up to 120 °C (i.e., the intersection point of the two tangents which accidentally corresponds to 95% wt. loss) and thereafter, it undergoes thermal degradation. The crosslinked PEGBCDMA and LiTFSI are more stable up to