



Epoxy containing solid polymer electrolyte for lithium ion battery

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ABSTRACT

Solid polymer electrolyte based on the random copolymer PGO from the monomers of glycidyl methacrylate (GMA) and oligo (ethylene oxide) methyl ether methacrylate (OE) was successfully synthesized and investigated in detail aiming at applications in all solid lithium ion battery. Namely, four polymers PGO-60, PGO-70, PGO-80, PGO-90 with numbers indicating the percentage molar ratio of OE were mixed with LiClO₄, and studied for their Li conductivity and other electrochemical properties in order to understand the effects from the polar glycidyl moieties. Polymer PGO-70 showed the highest ionic conductivity of 2.08×10^{-5} S/cm when the LiClO₄ content was 50% and at 50 °C. PGO-60 had the largest lithium ion transference number of 0.549, and exhibited electrochemical stability up to 4.4 V vs. Li⁺/Li. When the epoxy groups in the polymer were hydrolyzed, two hydroxyl groups as side chain pendants were obtained. When tested, the ring-opening membrane HPGO-70 showed significantly higher ionic conductivity (2.26×10^{-6} S/cm, LiClO₄ = 30%) than the corresponding PGO-70 (2.58×10^{-7} S/cm, LiClO₄ = 30%) at room temperature. The maximum lithium ion transport number of ring-opening polymers is 0.693 for HPGO-60, however, it's stability was a little lowered to 4.0 V vs. Li⁺/Li. Generally, compared with the polymer electrolyte membrane before ring opening, the lithium ion conductivity and lithium ion transference number of the ring-opening polymer electrolyte membrane were improved, however, the electrochemical stability window was slightly reduced. In the preliminary test of the assembled half cell battery using HPGO-60 as the polymer electrolyte and LiFePO₄ as the anode, fairly good charge/discharge cycling can be achieved at 25 °C, but the capacity remained quite low (around 20 mAh/g). When temperature increased to 70 °C, the capacity increased considerably to 99 mAh/g at the first cycle, but quickly decreased to around 50 mAh/g.

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1. Introduction

Lithium-ion batteries (LIB) generally use liquid organic electrolytes, however, safety issues are consequently incurred due to such highly flammable organic liquid and also the formation of dendrite that are responsible for explosion hazards for mobile phone, laptop, electric vehicle and so on [1–3]. Therefore, the development of highly secured batteries becomes particularly urgent. Recent studies suggest that all-solid-state polymer electrolyte

is a promising solution not only to overcome the drawback of liquid electrolyte leakage, difficult processing and sealing, but also to inhibit the formation of lithium dendrites, the critical culprit for short circuit accident [4].

In 1973, Wright and Parker observed that the complex of alkali metal ions with poly(ethylene oxide) (PEO) had a characteristic ionic conductivity [5,6], then the study of polymers as solid electrolytes was kicked off [7]. Till now, many polymers with different chemical structures have been studied, as has been well reviewed [8]. Among them, PEO is still the most studied via pure form, blending, copolymerization, grafting and addition of fillers to improve the comprehensive electrochemical performance. In a very systematic and fundamental study, Bouchet and coll. investigated

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the mechanism of ion transport in PEO/LiTFSI complexes, attention was paid especially on the effect of temperature, molecular weight of PEO and the end groups such as hydroxyl or methyl [9]. They also developed a series of ethylene oxide- (EO-) containing block copolymers using polystyrene as the structuring component [10], the presence of EO moieties either in the main chain or in side chain can make a difference for properties. In another PEO-derived (as B block) ABA type triblock copolymers of single-ion-conductor containing anionic LiTFSI moieties from the same group [11,12], high electrochemical properties and excellent mechanical properties can be achieved. Compared to the styrene-based single-ion-conductor electrolytes, they found methacrylate-based ones can have even higher conductivity at high salt concentrations [12]. PEO can also be blended with other polymers to make electrolyte. Cui et al. [13] used a combined rigidity and flexibility strategy to construct new solid polymer electrolyte. They mixed PEO, poly(cyanoacrylate) (PCA) and lithium bis(oxalate)borate (LiBOB), and cast onto the homemade cellulose nonwoven film. The membrane had high mechanical strength, and the conductivity of lithium ion reached 3.0×10^{-4} S/cm at 60 °C. Colby et al. [14] introduced PEO segments to the side chain of polysiloxane, the conductivity increased from 10^{-11} S/cm to 10^{-6} S/cm at room temperature. Other interesting polymer architectures include silicon-based polymers which can have excellent thermal stability, low flammability, and non-toxicity [15]. A third type of attractive polymer is aliphatic polycarbonate whose idea was generated by the widely used carbonate small molecules in lithium battery as liquid electrolyte. The examples can be poly(vinylene carbonate) (PVC) [16], poly(ethylene carbonate) (PEC) [17], poly(propylenecarbonate) (PPC) [18], poly(trimethylene carbonate) (PTMC) [19], and other carbonate copolymers [20].

Oligo(ethylene oxide) methyl ether methacrylate (OE) has been a very useful monomer, especially in the design of comb-like and amphiphilic block copolymers especially using the well documented controlled radical polymerization method [21]. For instance, Zhang et al. [22] prepared a novel thermally responsive polydisulfides of a disulfide-bonded POE multi-block having redox-responsive properties. The length-tunable PEG side chains can offer a good amorphous host for transportation of lithium ion, and at the same time, crystallinity can be inhibited due to the short comb-like side chain. For example, in 1984 Xia et al. [23] reported the use of short side-chain PEG polymethacrylate to complex with alkali salts such as NaSCN, NaCF_3SO_3 and LiSO_3CF_3 , crystallinity of the salts is reduced, and conductivity can be enhanced by lowering the salt content or adding plasticizer like propylene carbonate and so on, which meant that the studied polymers can be viable alternatives for classic PEO materials. At almost the same time, Bannister et al. [24] reported the similar polymer mixed with LiSO_3CF_3 , high conductivity by $10^{-4} \Omega^{-1}\text{cm}^{-1}$ can be achieved at 373 K. Jannasch et al. [25] reported a semi-interpenetrating polymer networks synthesized from PEG mono- and di-methacrylates, PMMA and LiTFSI, the conductivity exceeded 10^{-5} S/cm when the PMMA content is lower than 85 wt% at 30 °C. Copolymer was using similar monomer by Bergman et al. [26] showed that ionic conductivity can exceed 10^{-3} S cm^{-1} at 110 °C, unfortunately a prototype half cell using LiFePO_4 and the solid polymer electrolyte showed surprisingly low capacity (<20 mAh g^{-1}) at 60 °C. More interesting architectures using block copolymer prepared from the similar monomer can be found in review paper by Young et al. [27] Mayes and coll. prepared series of poly(lauryl methacrylate)-b-POE block copolymer electrolytes which displayed conductivities exceeding 10^{-5} S/cm at room temperature [28]. They also used MMA and OE to prepare random copolymer and block copolymer, respectively [29]. The room temperature ionic conductivity of the random copolymer can be two orders of magnitude lower than that of the block copolymer

(2.18×10^{-8} S/cm vs. 2.06×10^{-6} S/cm). Epps and coll [30], prepared tapered block copolymer from OE and styrene monomers, the conductivity by 10^{-6} - 10^{-4} can be achieved between 20 °C and 90 °C for these block copolymer of unique nanostructures. To investigate the detailed nanostructure of PMMA-b-POE-PMMA, Bergfelt and coll [31], used deuterated PMMA- d_8 in synthesis, small-angle neutron scattering (SANS) showed no phase separation, and the assembled battery using LiFePO_4 showed fairly good discharge capacity by 120 mAh g^{-1} at 60 °C. They also studied another similar ABA type triblock copolymer using poly(benzyl methacrylate) as the A building block [32]. When mixed with LiTFSI, solid electrolyte can be prepared. Phase separation was observed via small-angle X-ray scattering (SAXS). Higa and coll [33], prepared a hyperbranched polymer electrolyte with POE as the branched side chain. When the POE content was 51 wt%, the conductivity was 2×10^{-5} S/cm at 30 °C. Watanabe and coll [34], used ring-opening polymerization to synthesize the polymer with PEO on both backbone and sidechains. The crystallinity of the polymer can be greatly reduced with the increasing comb-like PEO side chain components. The conductivity can be as high as 1.4×10^{-3} S/cm at 60 °C and even 3.3×10^{-4} S/cm at 30 °C.

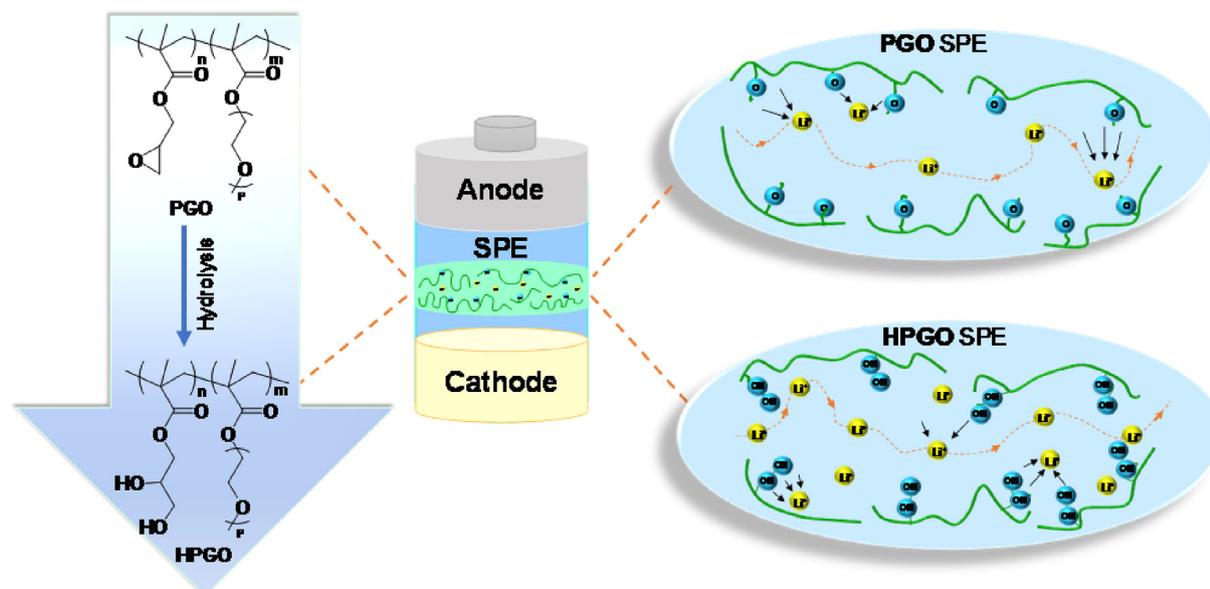
Epoxy resins have also been studied as polymer electrolytes. For example, Sequeira and coll [35], prepared an interpenetrating polymer network (IPN) electrolyte by mixing poly(ethylene oxide) with diglycidyl ether of bisphenol A (BPA) and poly(propylene oxide) triamine. The room temperature conductivity of the electrolyte can reach 6.1×10^{-5} S/cm. Lee and coll [36], prepared another cured epoxy system containing plastic crystal based on BPA, the conductivity can achieve 2×10^{-4} S/cm. Shaplov and coll [37], used polyepoxide monomer to make a reinforced network for the polycationic polymer. Browder and coll [38], prepared a PEO-based epoxy resin cured with amine and doped with lithium salt in propylene carbonate (PC), the conductivity can reach 10^{-3} S/cm at room temperature. In the above mentioned systems, epoxides were used as networking forming molecules when cured, and no epoxy-containing polymer was used as polymer electrolyte to date and to the best of our knowledge.

In this study, we focus on the lithium ionic conductivity and other electrochemical properties of the solid random copolymer (abbr. PGO) of glycidyl methacrylate (GMA) and OE, the reasons are as follows, (1) highly reactive epoxy-containing GMA moiety provides a lot of opportunities for further functionalization; (2) rigidity as found in the relatively high T_g (68 °C) of homopolymer of PGMA can help in film formation for copolymers; (3) The effect of polar epoxy group on lithium ion conductivity remains unknown; (4) further hydrolysis [39] of epoxy can result in two extra hydroxyl groups to increase the polarity of molecular chain (even soluble in water) [40], which may affect lithium ion conductivity. The idea and the synthetic route are shown in Scheme 1 and Scheme 2, respectively.

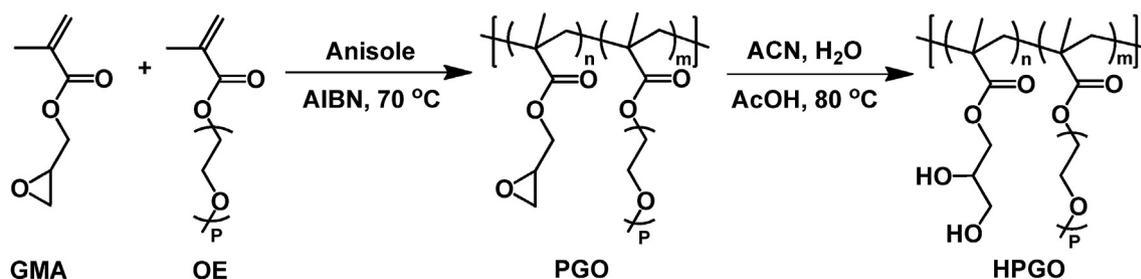
2. Experimental

2.1. Materials

Glycidyl methacrylate (GMA, 96%) was purchased from Behringer Technology Co., Ltd., oligo(ethylene oxide) methyl ether methacrylate (OE, $M_n = 300$) was from Sigma-Aldrich. They were passed through a basic alumina column before polymerization to remove inhibitor. Azobisisobutyronitrile (AIBN, AR) was from Sinopharm Chemical Reagent Ltd., and recrystallized from methanol and stored in the refrigerator before use. Anisole (99%) was from Aladdin Reagent, N-hexane (AR) was from Guanghua Chemical Reagent, anhydrous acetonitrile ($\text{H}_2\text{O} \leq 50$ ppm) was purchased from Energy Chemical Inc. Anhydrous high purity lithium



Scheme 1. PGO and the hydrolyzed product (HPGO) were investigated as solid polymer electrolytes for lithium conductivity aiming at safe lithium ion battery applications.



Scheme 2. The synthetic route of random copolymer of PGO and HPGO.

perchlorate (battery grade) was purchased from DoDo Chem Inc and used without further purification. Both of anhydrous acetonitrile (ACN) and lithium perchlorate were stored in glove box. Glacial acetic acid (AcOH, >99.9%, HPLC grade) was from Macklin Reagent.

2.2. Preparation of poly(glycidyl methacrylate-co-poly(oligo(ethylene oxide) methyl ether methacrylate) (PGO)

The reaction was carried out based on the predetermined molar ratio of GMA:OE (ex. PGO-60, number indicates the feed ratio of molar percentage of OE monomer, i.e. GMA:OE = 60:40). Below the example is given for the synthesis of PGO-60 copolymer. The monomer GMA (2.0000 g, 14.06 mmol), monomer OE (6.3270 g, 21.09 mmol), AIBN (28.86 mg, 0.18 mmol) and anisole (38.51 ml) were mixed in a 100 ml round bottom flask. Nitrogen was used to remove oxygen by bubbling for 30 min with magnetic stirring. The mixture was then heated in a preset oil bath at 70 °C and stirred for 16 h to allow polymerization. When the reaction finished, the copolymer was purified by precipitation in n-hexane. The products were dried in vacuum (<8 mbar, Welch type# 412722) for 24 h at 70 °C. Finally, transparent rubber-like solid was obtained (6.071 g, yield = 73%). The other three polymers were prepared by the same experimental method. The ratio of GMA/OE was calculated based on the integral ratio of 3.39 ppm and 3.21 ppm on NMR spectrum. ¹H NMR (400 MHz, CDCl₃) δ: 4.5–4.0 (broad, –COO–CH₂–), 4.0–3.5 (broad, –COO–CH₂–CH₂–O–), 3.39(s, –O–CH₃), 3.21(s, –COO–CH₂–

CH–), 2.84 and 2.63 (s, –CH–CH₂–), 2.2–1.5 (broad, backbone –CH₂–), 1.5–0.5 (broad, backbone –CH₃).

2.3. Hydrolysis of PGO (HPGO, also named poly(glycerol monomethacrylate))

The hydrolysis was made according to literature [39,40]. Typically, PGO-60 (1000 mg, 2.81 mmol) was weighed in a 50 ml round bottom flask and acetonitrile (4 ml) was added to dissolve the polymer completely. Then deionized water (0.91 ml, 50.55 mmol) and glacial acetic acid (0.52 ml, 9.08 mmol) were added. The turbid mixture was stirred at 80 °C for 6 h to finally turn into a uniform solution. Because the solubility would be poor when the solvent was stripped, the solution was concentrated in reduced pressure before use in the next step. PGO-x (X donates 70, 80 and 90) were hydrolyzed in the same manner, and the products were designated as HPGO-70, HPGO-80, and HPGO-90, respectively.

2.4. Preparation of polymer electrolyte membrane

Drying is important for the electrolyte membrane, as indicated also in the reviewing session of this manuscript. Sometimes, very stringent procedures have to be made [11]. Following procedures were used that are typical in literature [13,41–43]. Please also refer to the electronic supplementary information (ESI) for additional information.

2.4.1. Preparation of PGO polymer electrolyte membrane

The polymer was dried in vacuum again at 70 °C for 24 h, then quickly transferred to the glove box ($O_2 < 0.01$ ppm, $H_2O < 0.01$ ppm). The sample vial was then opened and allowed to stand till at least the next day for further operation (same for HPGOs). It was then added a certain amount of anhydrous lithium perchlorate and anhydrous acetonitrile to make a solution. The solution was cast on a Teflon plate, and dried in glove box for 3 days to obtain a transparent polymer electrolyte membrane (avg. 0.20 mm thick), as shown in Fig. 1.

2.4.2. Preparation of HPGO polymer electrolyte membrane

The concentrated reaction mixture in the synthesis of HPGO was directly poured onto a Teflon plate, allowed to evaporate in ventilation hood for one day, then in vacuum oven at 70 °C for one day, and finally the film was transferred into glove box and dried further for two days. To add $LiClO_4$, 1.00 M lithium perchlorate in acetonitrile stock solution was firstly prepared in a glove box. The mass of the dried film was weighed, and then specified amount of 1 M $LiClO_4$ solution was added onto the film using a pipette. In this way, the solid polymer electrolyte membranes containing 10%, 15%, 20%, 25% and 30% lithium perchlorate were obtained after acetonitrile vaporation in glove box (avg. 0.20 mm thick). The image of the membranes is shown in Fig. 1.

2.5. Characterization of polymer

The molecular weight of the polymers were measured using the gel permeation chromatography (GPC, Malvern MAX270) equipped with a VE 3580 refractive index (RI) detector. Two PolyAnalytik columns (LT3000L and LT6000L, Malvern) were used with THF as eluent at 35 °C at a flow rate of 1 mL/min. GPC was calibrated using polystyrene standards (from Malvern) before use. The chemical structure is characterized using the Avance III (400 MHz) model nuclear magnetic resonance (NMR) manufactured by Bruker. Fourier transform infrared spectroscopy (FTIR, Model: Alpha) was from Bruker and equipped with ATR accessory with diamond crystal of single reflection in the range 4000–400 cm^{-1} , the resolution is 0.8 cm^{-1} and the number of scans is 24. The glass transition temperature (T_g) of the polymer and its lithium salt containing samples were tested using a differential scanning calorimeter (DSC) from Mettler Toledo (DSC1). 5–10 mg of samples were weighed in 40 μ l standard aluminum crucible in glove box, and quickly transferred and clamp sealed in air. The scan range was from –90 °C to 100 °C at 10 °C/min in nitrogen atmosphere.

2.6. Electrochemical measurement

The electrochemical performances of the polymer electrolyte membrane were measured using an electrochemical workstation manufactured from Biologic (SP-300). To avoid the side effects from humidity and air, the measurements were all made in CR2032 button battery assembled in glove box.

2.6.1. Ionic conductivity measurement

Ionic conductivity of the solid polymer membrane was determined by electrochemical impedance spectroscopy (EIS) at room temperature with three membranes tested in parallel. Each membrane was measured three times. In the temperature dependent experiment, one of the three membranes was used in random, and the EIS was made in varied temperature from 25 °C to 50 °C. The membrane was placed in CR2032 cell (stainless steel/SPE/stainless steel). The impedance of the polymer electrolyte membrane (R_b) was measured by AC impedance method at the amplitude of 10 mV over a frequency ranged from 7 MHz to 1 Hz [44]. To control the thickness of the membrane, a PTFE 0.2 mm thick gasket spacer was used right between two stainless steel electrodes. The ionic conductivity was calculated based on equation (1) [45,46], where σ is the ionic conductivity of lithium ($S \cdot cm^{-1}$); d is the thickness of the membrane (cm); S is the area of electrolyte membrane (cm^2); R_b is as mentioned above (Ω). The results from varying temperature experiment were used to calculate the activation energy based on VTF equation (2) [8], where σ is the lithium ion conductivity ($S \cdot cm^{-1}$); A is the pre-exponential factor; E_a is the activation energy (J); k_B is Boltzmann constant ($1.38 \times 10^{-23} J K^{-1}$); T is temperature (K); T_0 is Vogel temperature and related to glass transition temperature, and usually set to be $T_g - 50 K$ [12,47–49].

$$\sigma = \frac{d}{R_b \cdot S} \quad (1)$$

$$\sigma = A \exp \left[-\frac{E_a}{R(T - T_0)} \right] \quad (2)$$

2.6.2. Electrochemical stability window measurement

The electrochemical stability of the electrolyte was studied using linear sweep voltammetry (LSV) on the Li/SPE/stainless steel cells at room temperature and a constant rate of 1.0 mV/s from 2 V to 6 V [50–52].

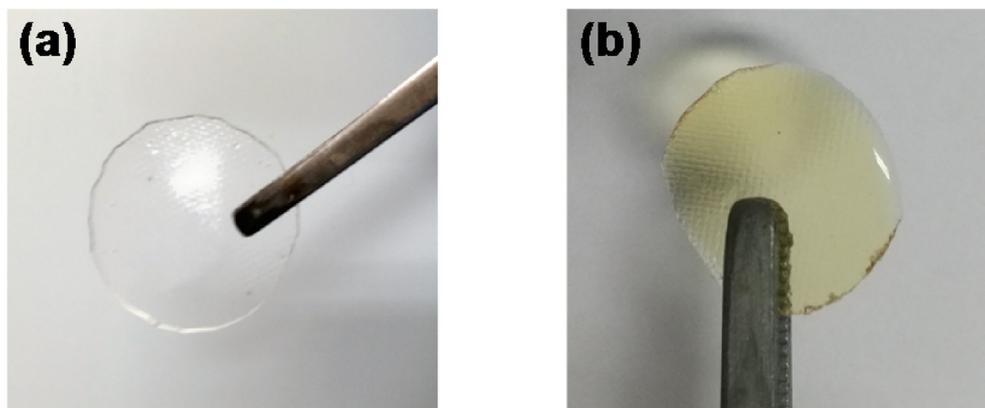


Fig. 1. PGO-60 (a) and HPGO-60 (b) polymer electrolyte membranes, both contain 30 wt % $LiClO_4$.

2.6.3. Lithium ion transference number measurement

The lithium ion transference number ($t_{Li^+}^+$) was measured from Bruce-Vincent-Evans equation (3) [4,16,53,54]. The sample was sandwiched between two Li electrodes, sealed in CR2032 battery, and kept at 40 °C overnight to equilibrate before measurement. The measurement is made at 25 °C, using a dc polarization voltage at $\Delta U = 50$ mV. Initial current (I_0) and initial interfacial resistance (R_0) before polarization were measured with EIS in advance at the amplitude of 10 mV over a frequency range from 7 MHz to 0.1 Hz. After polarization for 7200 s, the steady-state current (I_s) and interfacial resistance (R_s) were measured on the same condition again.

$$t_{Li^+} = \frac{I_s(\Delta U - R_0 I_0)}{I_0(\Delta U - R_s I_s)} \quad (3)$$

2.6.4. Electrochemical compatibility measurement

The electrochemical compatibility of solid polymer electrolyte membrane was estimated by monitoring the response of voltage with long-term lithium deposition/stripping cycles on Neware testing system (Shenzhen Neware CT-4008) at room temperature referring to the literature [16,54,55]. The cycling performance of symmetric Li/SPE/Li cells in CR2032 configuration at the current density of 5.0, 6.0, 7.0, 8.0 mA/cm² was tested in order for 10 h respectively, then back to 5.0 mA/cm² for another 10 h. The duration of each complete cycle took 1 h. Polarization voltage was recorded and plotted versus time.

2.6.5. Battery test

The half cell of LiFePO₄/HPGO-60/Li was assembled with the recipe LiFePO₄:PVDF:Ketjenblack = 8:1:1 according to the reported procedures [26,56,57]. A mixture of LiFePO₄, HPGO-60 and Ketjenblack and NMP solvent were blended and cast onto an aluminum current collector, dried in vacuum at 80 °C for 48 h and 110 °C for 3 h, and then transferred in glove box further dried at 80 °C for 24 h. Charge-discharge cycling was carried out over a voltage range of 2.5–4.0 V at a current rate of 0.1C. The cell was maintained at 80 °C for 4 h for aging prior to the test.

3. Results and discussion

3.1. Characterization by GPC, NMR and FTIR

The molecular weight (MW) and distribution of the polymers were measured by GPC, the results are shown in Fig. S1 and summarized in Table 1. From PGO-60 to PGO-90, M_n spans from 32.2 k to 52.8 k versus polystyrene standard in THF. The Polydispersity indexes (PDIs) were found to be between 3.12 and 3.40, that is common for polymers prepared via conventional free radical polymerizations. The NMR spectra are shown in Fig. 2(a), where PGO-

Table 1
Synthesis and selected properties of PGO-X copolymers.

	OE content (mol %)	Feeding ratio (mol %) Actual ratio ^a (mol %)	M_n	PDI	Yield (%)
PGO-60	60%	59%	32.2 k	3.35	73%
PGO-70	70%	69%	33.2 k	3.40	82%
PGO-80	80%	79%	47.8 k	3.16	79%
PGO-90	90%	86%	52.8 k	3.12	76%

^a Determined by NMR.

60 and its hydrolyzed product are shown as the typical example. The actual ratio of OE/GMA in polymer (PGO-60) can be calculated by integration of the protons from the end-capped methyl group (3.39 ppm) on OE and from the glycidyl group (3.21 ppm) on GMA. It was found the actual ratio of OE/GMA is very close to the value of feeding ratio, indicating similar rate of polymerization for both chosen monomers. This can be explained by similarity in the nature of reactive groups as both monomers have the same methacrylic functional groups.

Percentage of OE in polymer is only a little lower than that in the mixture of monomer, indicating the preferences for homo-polymerization and copolymerization of the two monomers are very close. The nearly perfect copolymerization may lie in the fact that the two monomers were all methacrylate, and should have similar reactivities, the difference may be caused by the a little bulky polyethylene glycol (PEG) side chain on OE.

When PGO was hydrolyzed in acidic condition, HPGO ("H" indicates hydrolysis) was obtained. The hydrolytic condition was as reported elsewhere [39,40]. The successful hydrolysis can be observed immediately for the complete solubility of products at the end of reaction (images in Fig. 2(b)), where a uniform solution was obtained after reaction was run for 6 h at 80 °C. In contrast, the raw materials before reaction was an unstable white mixture that has phase separated quickly after standing for a short while. After purification, HPGO also showed big difference from PGO. PGO is readily soluble in many organic solvents, such as THF, ACN, CHCl₃, Acetone and so on, but the corresponding HPGO was very hard to find a good solvent, especially after drying for unknown reasons, probably due to extensive hydrogen bonding. The NMR spectrum of HPGO-60 was made before it was completely dried, low signal/noise ratio also implied its poor solubility. To completely resolve the spectra of hydrolyzed polymeric samples is much more difficult than the monomers [40], especially when isomerization has to be considered [39]. In this contribution, much caution was made for HPGO to prepare water and oxygen free films in glove box as is required for lithium battery applications.

FTIR was also used to characterize the PGO and HPGO samples. As shown in Fig. 3, PGO and HPGO shows almost identical FTIR spectra, C–H stretching at 3000–2800 cm⁻¹; intense C=O stretching at 1730 cm⁻¹ and characteristic C–O absorption at 1100 cm⁻¹. By carefully examining the spectra, it can be found that HPGOs have typically higher intensity of broad O–H stretching peak centered around 3500 cm⁻¹ that can be attributed to the increase of intermolecular hydrogen bond [58]. As for PGOs, the intensity is much lower, and the position shifted to 3550 cm⁻¹, implying free hydroxyls [58] that could be due to the absorbed moisture. A critical issue is to resolve the spectra for epoxy and its ring-opened product. For example, by examining 840–750 cm⁻¹ [58], where 910 cm⁻¹ is believed to be related to the epoxy moiety [59], it turned out that the absorption at 910 cm⁻¹ was decreased for HPGO when compared to PGO. So, the successful opening of epoxy ring can be concluded.

3.2. T_g of polymers containing LiClO₄

To elucidate the effects of LiClO₄ on the thermal transition of polymers in this study, DSC was used to measure the glass transition temperature (T_g) of PGOs and HPGOs with different LiClO₄ contents, the thermograms were shown in Figs. S2 and S3, and the evolution of T_g vs. salt content is shown in Fig. 4, where PGOs and HPGOs were demonstrated respectively. All the samples showed typically amorphous structure in the range of scan (–90 to 100 °C) with only one glass transition being identified. Basically, all the samples showed an increase of T_g with the increase of LiClO₄. As for pure PGOs (LiClO₄ = 0 wt%), with the increase of OE, T_g decreased

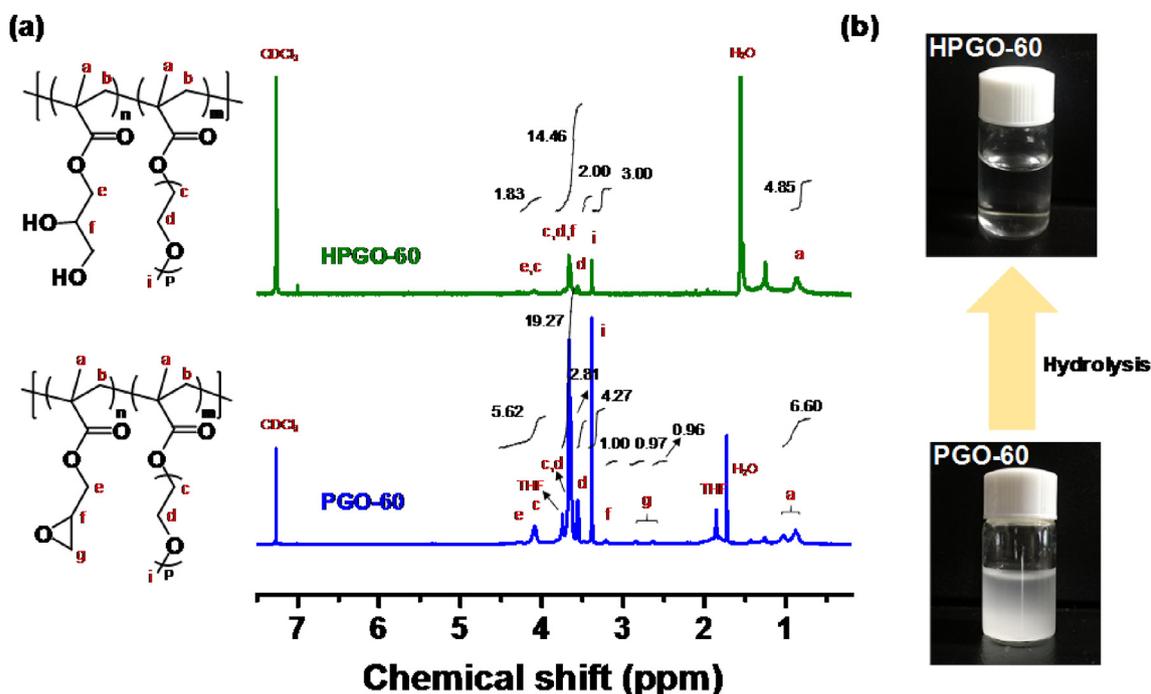


Fig. 2. NMR spectra (a) for PGO-60 and HPGO-60 and the pictures (b) for mixture of raw materials before and after hydrolysis of PGO-60.

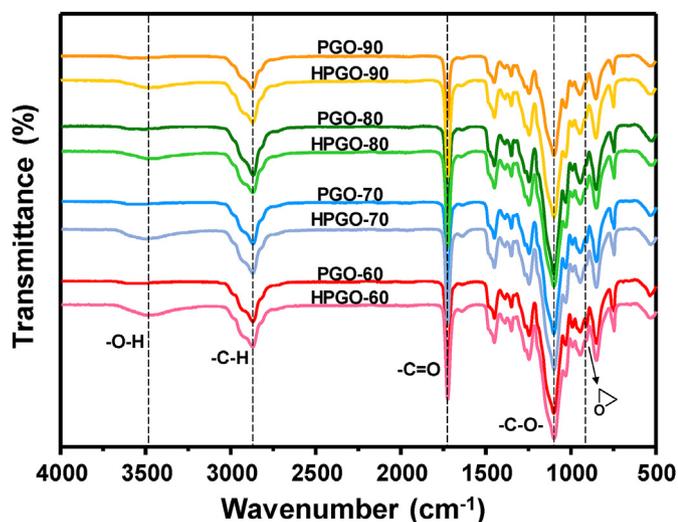


Fig. 3. FTIR spectra of PGOs and HPGOs, the spectra were normalized at 1730 cm^{-1} .

from $-29\text{ }^{\circ}\text{C}$ (PGO-60) to $-51\text{ }^{\circ}\text{C}$ (PGO-90). When 10 wt% of LiClO_4 was added, T_g increased considerably by more than $10\text{ }^{\circ}\text{C}$ averagely. With further increase of LiClO_4 , T_g increased more and more slowly, and reached around $20\text{ }^{\circ}\text{C}$ eventually at 50 wt% LiClO_4 . As for HPGOs, the phenomenon is similar. Pure samples showed decreasing T_g with the increase of OE content from $-24\text{ }^{\circ}\text{C}$ (HPGO-60) to $-53\text{ }^{\circ}\text{C}$ (HPGO-90). Then, with the increase of LiClO_4 content, T_g showed a quickly increase at the beginning followed by gradually approaching plateau. The increase of T_g was also observed in a similar ring-opened PGO copolymers, where it is explained by the formation of transient crosslinks due to solvation of lithium cation by ether oxygen [60]. It is noted that decrease of T_g can be sometimes observed with increase of lithium salt content [49,61–71], but in this research, generally monotonous increase is found.

3.3. Lithium ion conductivity

The lithium ion conductivity at room temperature was measured at different LiClO_4 concentrations. Three parallel experiments were made to check the data fluctuation. Fig. 5(a) shows the conductivity for PGOs at room temperature. Generally, the conductivity was in the order of 10^{-8} to 10^{-7} S/cm , and polymer that has higher OE content has higher conductivity. With the increase of LiClO_4 from 10 wt% to 50 wt%, the conductivity increased from 2.56×10^{-8} (PGO-60) to 5.81×10^{-7} (PGO-90). Higher data fluctuation for PGO-90 was found due to unknown reasons. As for HPGOs, it is more interesting to see that the trend is similar, but one order of magnitude higher than PGOs. In Fig. 5(b), it can be found that PGOs containing 10 wt% of LiClO_4 showed lower conductivity from 4.05×10^{-7} (HPGO-80) to 8.29×10^{-7} (HPGO-70). When LiClO_4 increased to 30 wt%, conductivity increased to a maximum of 2.26×10^{-6} (HPGO-70) and minimum of 1.85×10^{-6} (HPGO-90). When comparing between different HPGOs at a specific LiClO_4 content, it can be found that conductivity was not in the same order as OE content in HPGOs. The reason is hard to know so far, it seems that conductivity is more dependent on LiClO_4 concentration than OE for HPGOs, probably the two polar hydroxyls on the side chain took effects. Some references reported a maximum of conductivity in a moderate concentration of lithium salt, but is not observed in the current system [72].

The conductivity measured at different temperatures is shown in Fig. 6, polymers with LiClO_4 content of 30 wt% were tested. Generally, it was found that conductivity increased with the reciprocal of temperature roughly in linear mode. The results for PGO-60, PGO-70, PGO-80, and PGO-90 were 1.70×10^{-5} , 2.08×10^{-5} , 1.73×10^{-5} and $1.53 \times 10^{-5}\text{ S/cm}$ at $50\text{ }^{\circ}\text{C}$, respectively. The activation energy was found to be 0.175, 0.179, 0.209 and 0.205 eV, respectively. In contrast, the conductivities for HPGOs were higher than PGOs at low temperatures (see previous discussion with varied LiClO_4 concentration). Whereas, the conductivities were close for PGOs and PGOs at higher temperatures, for example,

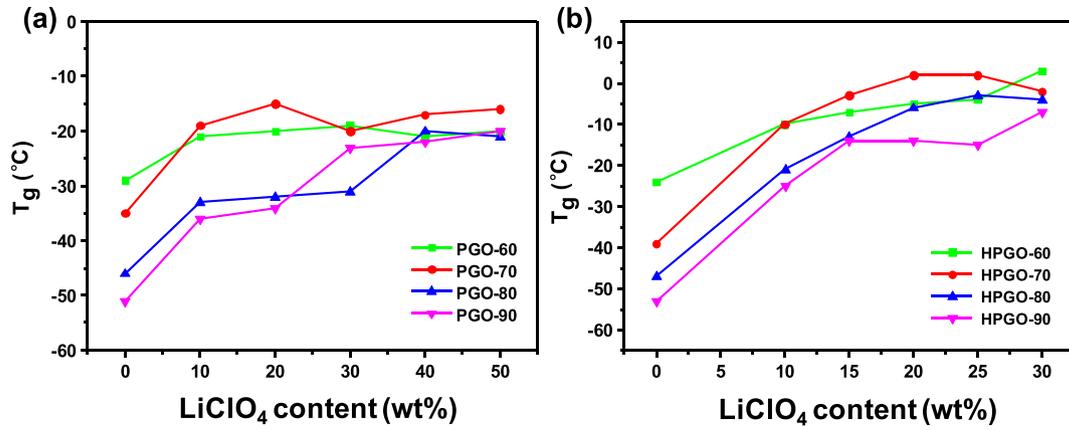


Fig. 4. T_g of PGOs (a) and HPGOs (b) at different LiClO_4 contents.

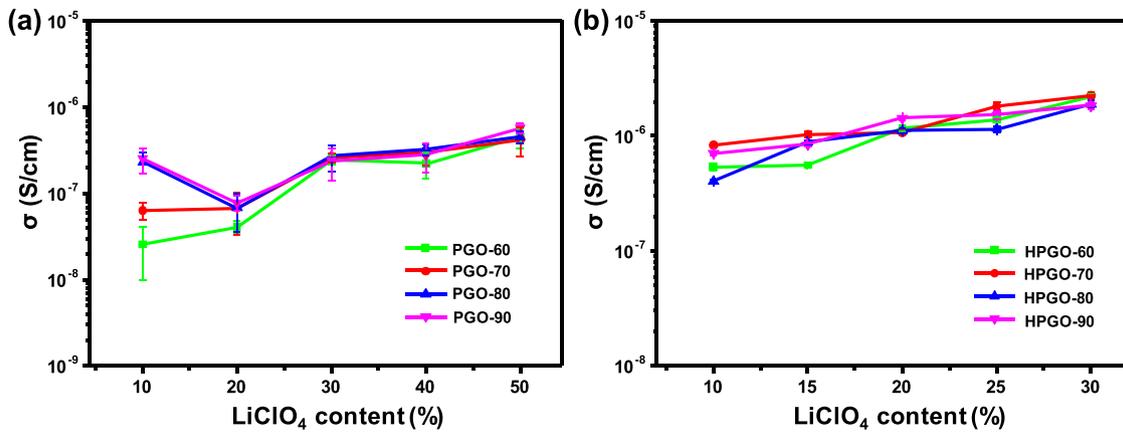


Fig. 5. Conductivity of different salt contents of PGO (a) and HPGO (b) polymer electrolyte at room temperature.

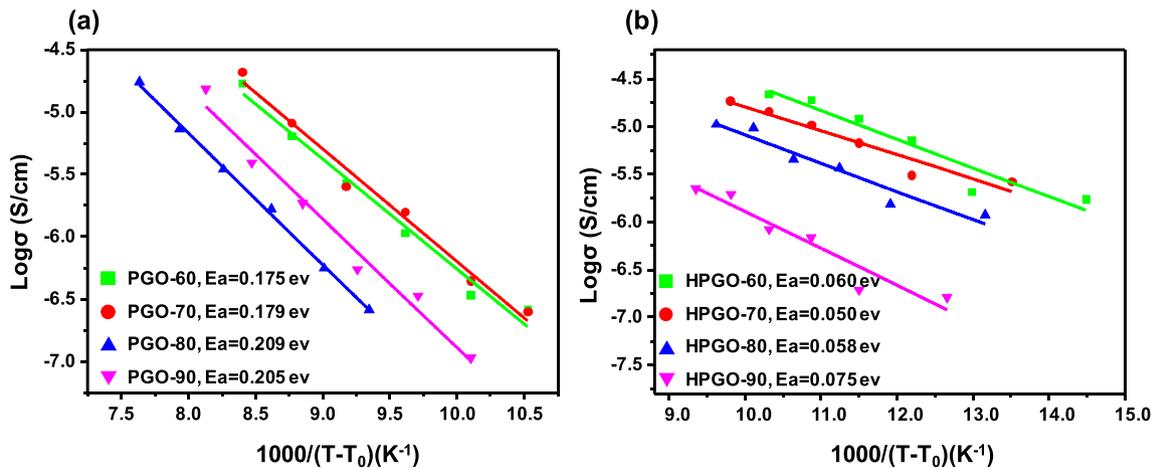


Fig. 6. Conductivities of PGO (a) and HPGO (b) at varied temperatures and fitted with VTF function, $\text{LiClO}_4 = 30$ wt %.

2.17×10^{-5} , 1.84×10^{-5} , 1.05×10^{-5} and 2.25×10^{-5} S/cm for HPGO-60, HPGO-70, HPGO-80 and HPGO-90 at 50°C , respectively. The reason is directly related to the relatively smaller slope on the curves for HPGOs, as seen the activation energy for HPGO-60, HPGO-70, HPGO-80 and HPGO-90 decreased considerably to 0.060, 0.050, 0.058 and 0.075 eV.

It is accepted that the increase of conductivity at higher temperature is due to the enhanced ionic mobility. The conductivity of PGO is close to PEO in the similar order of magnitude [73], for example, the conductivity of PEO ($\text{MW} = 10^6$) is 2.78×10^{-6} S/cm using lithium bis(oxalato)borate (LiBOB) or 1.48×10^{-6} S/cm using lithium hexafluorophosphate (LiPF_6) [74]. In a random copolymer

of methyl methacrylate (MMA) and OE, the conductivity was found to be 2.8×10^{-6} S/cm at low lithium trifluoromethanesulfonate (LiCF_3SO_3) concentration (2.2 wt%) at room temperature [29]. Compared to poly(trimethylene carbonate) whose conductivity was 10^{-7} S/cm at 60°C [19], the conductivities for PGOs and HPGOs were higher, but lower than poly(vinylene carbonate) = 9.82×10^{-5} S cm^{-1} at 50°C . The activation energy can be referred to the defect formation and the ion migration [75,76]. Low activation energy indicates a low energy barrier for the Li^+ transportation in the SPE sample [77]. So, the much lowered activation energy of HPGOs than PGOs indicates that ion migration is much easier in HPGO, which should be originated from the two extra hydroxyl groups after ring opening. However, it is still larger than the poly (vinylene carbonate) 0.03 eV [16].

3.4. Electrochemical stability window

Electrochemical stability window is an important parameter for the electrochemical performance of SPE membranes. The results are shown in Fig. 7.

The oxidation potential of PGOs were found to be from 4.2 V to 4.4 V. vs. Li/Li^+ respectively. Whereas, the oxidation potential of HPGO decreased a little to 4.0 V for HPGO-60 and HPGO-70. Other ring-opened SPE remained almost unchanged. The results are close to crosslinked PEG or blend of PMMA and PEO, from 4.0 to 4.5 V as measured from the graphs thereof [78,79], and lower than poly(vinylene carbonate) at 5.0 V [16]. However, the incorporation of hydroxyl group can be problematic for decreased electrochemical stability, as seen in hydroxyl abundant polymer systems such as polyHEMA or polyvinyl alcohol [80,81]. This may account for the slightly decrease of stability in HPGO-60 and -70, as compared to PGO-60 and -70, for the higher GMA content than -80 and -90.

3.5. Lithium ion transference number ($t_{\text{Li}^+}^+$)

High lithium ion transference number is important in lithium ion battery for lowering internal resistance and the concentration polarization of lithium ion during charge/discharge. The $t_{\text{Li}^+}^+$ of PGO and HPGO are shown in Fig. 8. It interesting to see that firstly, $t_{\text{Li}^+}^+$ decreased with the increase of OE component, and secondly, the $t_{\text{Li}^+}^+$ of PGO is high than the corresponding HPGO. For example, the $t_{\text{Li}^+}^+$ of PGO decreased from 0.549 to 0.180 for PGO-60 to PGO-90, and from 0.693 to 0.255 for HPGO-60 to HPGO-90. At the same time, PGO-60 is lower than HPGO-60, 0.549 vs. 0.693, same rule for other PGO-

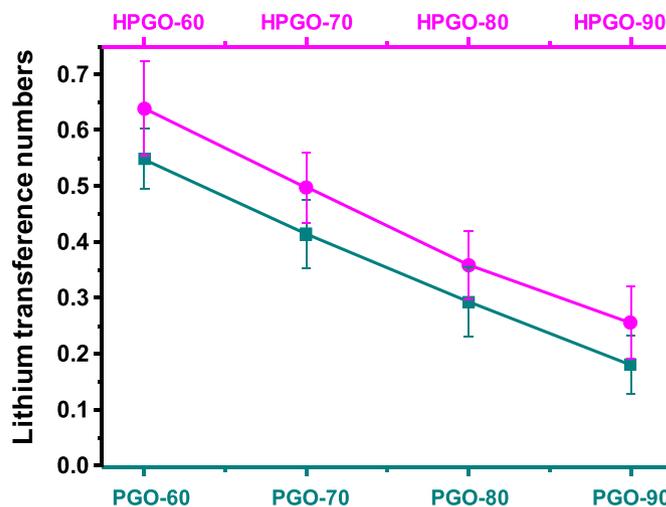


Fig. 8. Lithium ion transference number for PGOs and HPGOs at 25°C , $\text{LiClO}_4 = 30$ wt %.

HPGO pairs. PEO/LiTFSI membrane was reported 0.487, right in the range mentioned above [82]. From this point of view, the results of low OE content PGO and HPGO can be quite good. The reason of higher $t_{\text{Li}^+}^+$ for HPGO than corresponding PGO remains unsolved, it should be due to the utterly different molecular structure between epoxy and the hydrolyzed dihydroxyl moiety, which may be explained by a series of systematic studies by Zhu and coll. on separators in lithium ion battery that were chemically modified with polar groups, such as hydroxyl, carboxylate, amine and so on [83–86]. The transference number can increase to high values in these studies. Proof can also be obtained by measuring the $t_{\text{Li}^+}^+$ of hydroxyl-containing polymer, please refer to in ESI.

3.6. Electrochemical compatibility measurement

The typical cycling performance is shown in Fig. 9, using PGO-70 and HPGO-70 as examples. In the whole range of current density from 5, 6, 7, 8 and back to 5 mA/cm^2 , both samples showed stable cycling performance for a total of 50 h. HPGO-70 showed a little more noise than PGO-70 for unknown reasons. The fluctuation of voltage signal may also be a consequence of temperature fluctuation [16]. No gradually evolution of over-potential was observed, suggesting an equilibrated state, no further development of SEI was

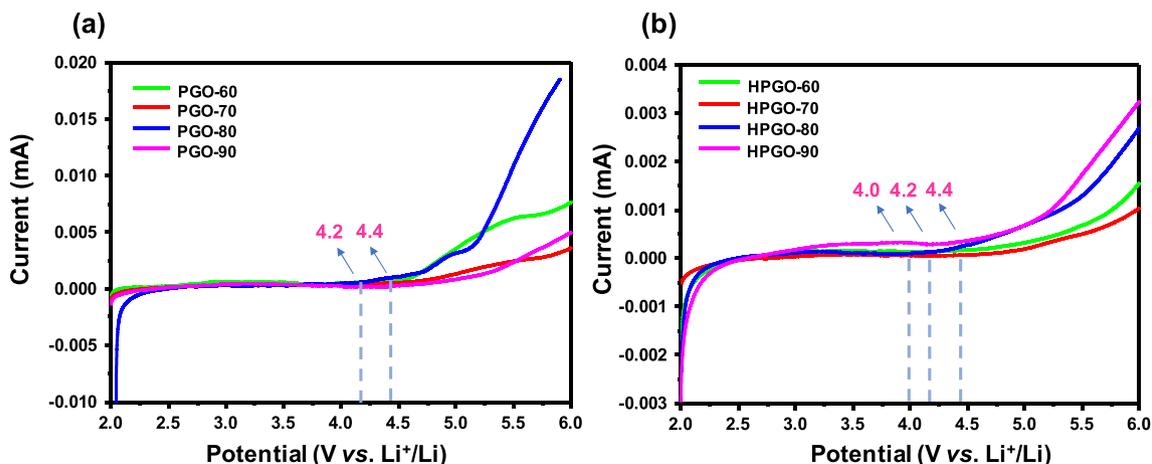


Fig. 7. Electrochemical stability measurement for PGO (a) and HPGO (b) SPE membranes at 25°C $\text{LiClO}_4 = 30$ wt %. (stainless steel as the working electrode and Li foil as the counter and reference electrodes, scan rate 1.0 mV/s).

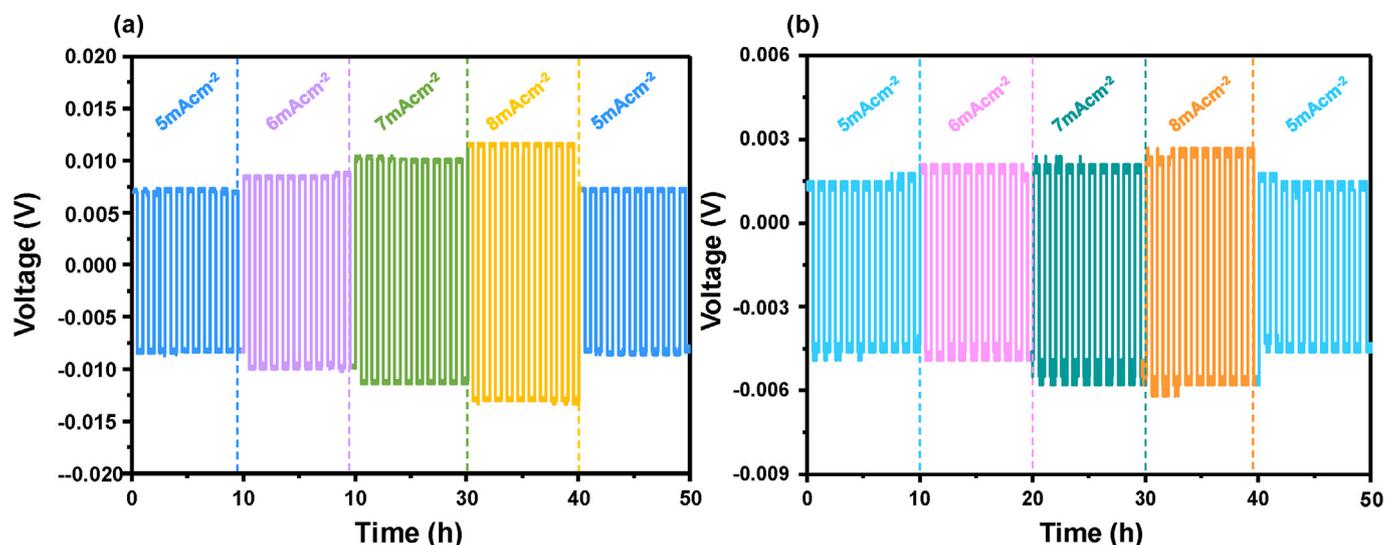


Fig. 9. Constant current polarization of PGO-70 (a) and HPGO-70 (b) at room temperature $\text{LiClO}_4 = 30 \text{ wt. \%}$.

expected [16]. In addition, there is no short-circuit phenomenon observed during the 50 h polarization with 5–8 mA/cm^2 cyclic current densities, indicating a good compatibility between polymer membranes and lithium anode, which means that dendrite cross-over was not observed during lithium deposition/stripping process, a critical point for the safety in the development of lithium ion batteries.

3.7. Electrochemical compatibility measurement

To test the performance of the polymer electrolyte, half cell

battery using HPGO-60 as electrolyte was assembled with the active material of LiFePO_4 . Shown in Fig. 10, one hundred charge/discharge cycles were recorded at room temperature. The charge capacity was found to be 24 mAh/g at the first cycle, and decreased to 17 mAh/g after 100 cycles. The low specific capacity of the cell may be due to the low conductivity of polymer electrolyte at room temperature for HPGO-60. When the temperature increased to 40 °C, the first charge capacity increased to 34 mAh/g and decreased to 31 mAh/g at the 5th cycle; when the temperature further increased to 70 °C, the first charge capacity increased considerably to 99 mAh/g , but quickly decreased to 51 mAh/g at the

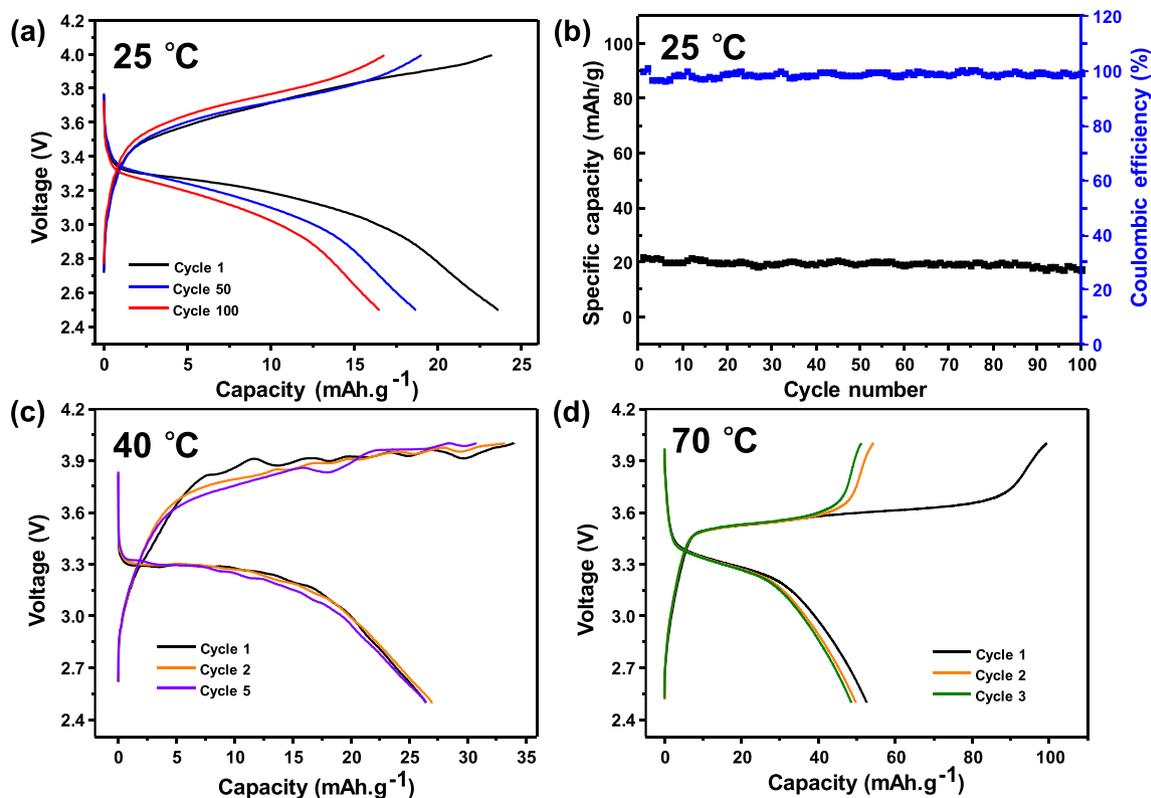


Fig. 10. The performance of the assembled half cell battery using HPGO-60 as the polymer electrolyte at 0.1C with LiFePO_4 as the anode and lithium foil as the cathode. (a) charge/discharge and (b) cycling performance at 25 °C; charge/discharge at (c) 40 °C and (d) 70 °C.

3rd cycle, implying some failure inside the battery probably due to high temperature instability. The improvement of capacity can be caused by the increased lithium ion conductivity at higher temperatures. Generally, the performance of the polymer electrolyte in this contribution is not good as polyethylene carbonate (PEC) as reviewed in literature except in some cases [87]. Such low capacity can also be found with similar copolymer which was attributed to poor electrode/electrolyte contacts [26].

4. Conclusions

In this contribution, epoxy-containing solid polymer electrolytes and their hydrolyzed counterparts were investigated carefully for the promising application in all solid lithium ion battery. The glass transition temperature of the polymers increased with increasing LiClO₄ content from below -50 °C to about freezing point. The conductivity increased with increasing LiClO₄ content either. At 50 °C, the ionic conductivity can be above 10⁻⁵ S/cm. When comparing PGO to HPGO, the conductivity of HPGO was generally higher than PGO at low temperatures, the HPGO's activation energy was much lower than PGO. Both electrochemical stabilities were similar, in the range from 4.0 to 4.4 V. The lithium ion transference number showed an interesting dependence on OE components, the higher OE content, the lower transference number. At the same time, PGO showed lower transference number than the corresponding HPGO. The highest transference number was found to be 0.549 for PGO-60 and 0.693 for HPGO-60, respectively. In the cycling lithium deposition/stripping experiment, both PGO and HPGO showed good compatibility with lithium electrode. The preliminary result of HPGO-60 in the assembled half cell battery using LiFePO₄ as the anode showed fairly good charge/discharge cycling property, but the capacity was quite low (around 20 mAh/g) at room temperature that may be attributed to the low conductivity and poor interface contact. When temperature increased to 70 °C, the capacity increased considerably to 99 mAh/g at the first charge step, but quickly decreased to about 50 mAh/g.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.electacta.2019.06.069>.

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