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In situ 3D crosslinked gel polymer electrolyte for ultra-long cycling, high-voltage, and high-safety lithium metal batteries

Jie Zhu^{a,c}, Jinping Zhang^{a,c}, Ruiqi Zhao^{a,c}, Yang Zhao^{a,c}, Jie Liu^{a,c}, Nuo Xu^{a,c}, Xiangjian Wan^{a,b,c}, Chenxi Li^{a,c}, Yanfeng Ma^{a,c}, Hongtao Zhang^{a,c,*}, Yongsheng Chen^{a,b,c,*}

^a The Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

^b State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

^c Renewable Energy Conversion and Storage Center (RECAST), Nankai University, Tianjin 300071, China

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ABSTRACT

The commercialization of lithium metal batteries (LMBs) highly relies on developing high-performance solid electrolytes, which should possess high Li⁺ conductivity comparable to liquid electrolytes, efficient suppression of dendrite growth, nonflammability, intimate electrode/electrolyte contact, and compatibility with the state-ofart lithium batteries industrial fabrication. Herein, we develop an in situ crosslinking method via cationic ringopening polymerization (CROP) using a four-armed cross-linker and fabricate a crosslinked gel polymer electrolyte (c-GPE), where the more densely and efficiently three-dimensional (3D) crosslinked polymer network renders the c-GPE high solvent uptake and improved oxidative stability. Moreover, the strong interaction between the crosslinked polymer network and the solvent is proved to reduce the desolvation energy barrier of Li⁺, which facilitates homogeneous Li⁺ deposition. Thus, the Li||LiFePO4 battery with this in situ fabricated c-GPE demonstrates one of the longest lifespans among polymer electrolyte-based batteries at high rate (2C) so far (2000 cycles with 78% retention). Furthermore, when this in situ 3D crosslinked gel polymer electrolyte is applied together with high voltage cathode material Ni_{0.6}Mn_{0.2}Co_{0.2}O₂, the Li|c-GPE|Ni_{0.6}Mn_{0.2}Co_{0.2}O₂ battery could deliver the best cycling performance with high nonflammability among CROP-based batteries so far (300 cycles with 80% retention). These results demonstrate that by the dedicated design of in situ polymerization, a high-performance c-GPE could be achieved to meet the requirements for practical, safe, and high-energy-density LMBs.

1. Introduction

The rapid growth of electrically powered devices requires rechargeable batteries with higher energy density, safety, and so on. Lithium metal batteries (LMBs) have been considered as one of the promising next-generation rechargeable batteries due to the high theoretical specific capacity (3860 mAh g⁻¹) and lowest negative redox potential (-3.040 V vs. standard hydrogen electrode) of lithium metal anode [1–4]. However, the parasitic reactions between common organic liquid electrolyte (LE) and lithium metal anode result in an unstable solid electrolyte interface (SEI) and Li dendrite. These factors seriously limit the cycling stability of LMBs [1,5]. Additionally, the highly flammable solvent in LE aggravates the safety hazards [6,7]. Using gel polymer electrolytes (mixtures of polymer matrix and liquid solution, denoted as GPEs) is a promising strategy for developing LMBs suitable for practical application. Compared to LEs, GPEs are nonvolatile and possess high thermal and improved electrochemical stability [8–12]. More importantly, GPEs can be fabricated by the *in situ* polymerization method, which is compatible to the state-of-art lithium ion batteries (LIBs) fabrication industry [13,14]. In this method, a precursor solution containing LE and monomer is injected into an assembled cell and subsequently polymerizes under certain external conditions. Thus, this method ensures that the electrodes are fully wetted by the LE before and after polymerization, largely avoiding the high interfacial resistance in the batteries using conventional solid electrolytes.

In general, in terms of polymerization mechanism, *in situ* polymerization methods mainly include radical polymerization and cationic ringopening polymerization (CROP) [15–20]. In recent years, CROP has

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^{*} Corresponding authors at: College of Chemistry, Nankai University, Tianjin 300071, China. *E-mail addresses:* htzhang@nankai.edu.cn (H. Zhang), yschen99@nankai.edu.cn (Y. Chen).

attracted great interest due to the outstanding electrochemical performance of the fabricated polymer electrolytes, which can be attributed to the following reasons: (1) CROP uses Li salt and solvent in LE as the initiator and monomer, respectively, avoiding the introduction of additional reagents in the batteries; (2) the generated polymer matrix is composed of polyether, which has excellent flexibility, high ionic conductivity, and compatibility toward Li anode. For example, Guo et al. first reported a GPE by using LiPF₆ to induce the *in situ* gelation of a traditional LE (1 M LiTFSI in DOL/DME), and Archer et al. prepared a solid-state polymer electrolyte by using Al(OTf)₃ to initiate the polymerization of LE (2 M LiTFSI in DOL) [18,21]. These works reported the polymer electrolytes with room temperature (RT) ionic conductivity at the mS cm⁻¹ level and intimate electrolyte/electrode contact, realizing excellent battery cycling performance. However, the polymer matrics of most CROP-based GPEs obtained by dioxolane (DOL) homopolymerization are polyether. Linear polymers generally have poor mechanical strength and less efficient network formation, so the polymer matrixes of GPEs are only capable of a low solvent uptake (solvent/(solvent+polvmer) < 50 wt% in most cases). Otherwise, the GPEs would transform into an uncured liquid-like state [19,22,23]. Low solvent uptake is detrimental to the dissociation and transport of Li ions in GPE [24]. Therefore, the electrochemical performances of CROP-based GPEs are still inferior to that of LEs. Moreover, the oxidative stability of GPEs is impaired by the terminal hydroxyl groups in linear polyether and the residual DOL, which exhibit electrochemical instability, limiting their applications in high-voltage batteries [25-28].

Herein, we develop a four-armed cross-linker based in situ crosslinking strategy to fabricate a crosslinked GPE (c-GPE) via Li saltinitiated CROP. The polyfunctional pentaerythritol glycidyl ether (PEE) with four epoxy groups is, for the first time, used as a cross-linker to efficiently construct a three-dimensional (3D) crosslinked PEE-DOL copolymer network in c-GPE by in situ PEE crosslinking with the electrolyte solvent DOL. Such c-GPE enables an extremely high solvent uptake (solvent/(solvent+polymer) = 91 wt%) due to the densely 3D crosslinked polymer network. Thus, a high ionic conductivity above 2.36 mS cm^{-1} is achieved for our c-GPE. Furthermore, the introduction of such a four-armed cross-linker into this 3D crosslinked network can significantly improve the oxidative stability of our designed c-GPE (oxidation potential = 4.5 V). When introducing the solvent of fluoroethylene carbonate (FEC) into the 3D crosslinked c-GPE, the c-GPE exhibits even better nonflammability and outstanding compatibility with high-voltage cathode materials. The strong polymer-solvent interaction, which reduces the desolvation energy of Li⁺ and the LiF-rich interfaces originating from FEC further enhance the cycling stability of the battery using c-GPE. All these together render the LMBs assembled with our designed c-GPE ultra-long cycling stability, a wide operating voltage range, and high safety. Thus, the Li|c-GPE|LiFePO₄ (LFP) battery achieves one of the longest lifespans of 2000 cycles at 2 C among all previously reported polymer electrolyte-based batteries. Moreover, the high-voltage Li|c-GPE|LiNi0.6Mn0.2Co0.2O2 (NMC622) battery delivers the best cycling stability of 300 cycles compared with other LMBs fabricated by CROP. These results indicate that by choosing a suitable in



Fig. 1. (a) Schematic illustration of the *in situ* fabrication process of c-GPE and the crosslinking polymerization mechanism of PEE and DOL initiated by BF₃ (originated from LiDFOB). (b) RT ionic conductivities of GPEs with various cross-linker molar ratios and solvent uptakes. (c) Optical image of c-GPE-50. (d) LSV curves of c-GPE-50 and h-PE.

situ polymerization system, a practical approach compatible with the industrial LIBs fabrication could be developed for LMBs with high performance and safety.

2. Results and discussion

2.1. In situ polymerization for c-GPEs preparation

The in situ crosslinking process and proposed CROP mechanism are shown in Fig. 1a. First, the precursor solution, composed of lithium salts (lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) and lithium difluoro(oxalate)borate (LiDFOB)), solvent (FEC), monomer (DOL), and the four-armed cross-linker (PEE) with designed ratios shown in Table S1, was injected into the assembled battery. Next, LiDFOB undergoes a partial disproportionation reaction at the heating condition and generates a small amount of lithium bis(oxalate)borate (LiBOB) and lithium tetrafluoroborate (LiBF₄) [29]. The generated LiBF₄ provides Lewis acid BF₃, which further initiates the cationic crosslinking polymerization of PEE and DOL [30]. Finally, the 3D crosslinked polymer network in c-GPE is *in situ* generated inside the battery directly. Clearly, this process is compatible to the current industrial LIBs fabrication. As additional initiators and expensive additives are unnecessary, the cost of our c-GPE is similar or even lower than other reported works. The detailed comparison is shown in Tables S2 and S3.

2.2. Composition, ionic conductivity, and electrochemical stability of prepared c-GPEs

To optimize the solvent uptake and achieve the best ionic conductivity of c-GPE, the ratios of cross-linker PEE, monomer DOL, and solvent FEC were systematically varied. Meanwhile, the concentration of LiD-FOB and LiTFSI was fixed at a moderate value of 0.68 mol L^{-1} , a typical value reported by the literature [19,23]. The various precursor compositions and the ionic conductivities of these obtained c-GPEs are detailed in Fig. 1b and Table S1. To maintain the gelation state of the electrolyte, the maximum solvent uptake of GPE fabricated by only homopolymerized DOL (0 mol% PEE) is 50 wt% (an uncured liquid-like state is obtained when the solvent uptake is 60 wt%), and the ionic conductivity of this homopolymerized GPE is 1.50 mS cm^{-1} (as shown in Fig. 1b). In sharp contrast, after adding the four-armed cross-linker PEE (50 mol% PEE) into the precursor solution, the maximum solvent uptake of c-GPE fabricated by PEE-DOL crosslinking under the same conditions increases to as high as 91 wt% (an uncured liquid-like state is formed when the solvent uptake is 98 wt%), leading to a highly improved ionic conductivity of 2.36 mS cm⁻¹. As shown in Table S4, our crosslinking method endows c-GPE based on four-armed cross-linker with much higher solvent uptake than those reported previously. However, under the same conditions, using two- or three-armed cross-linkers can only result in uncured liquid-like electrolytes under such a high solvent uptake of 91 wt% (Fig. S1). These results indicate that the 3D crosslinked polymer network is more capable and efficient for immobilizing solvent than other homopolymerized DOL or crosslinked matrices using cross-linkers with lower functionality. However, as shown in Fig. 1b, with further increases in the content of cross-linker PEE, the ionic conductivity decreases due to the more densely crosslinked polymer network, while the solvent uptake kept steady. Therefore, we have chosen and focused on the c-GPE with 50 mol% cross-linker PEE and 91 wt% FEC (denoted as c-GPE-50) as the optimal candidate for further investigation.

As shown in Figs. 1c and S2a, a semi-transparent and flexible c-GPE-50 membrane could be obtained after performing the PEE-DOL crosslinking on a commercial glass fiber (GF/A) separator. The tensile modulus of c-GPE-50 is more than 6 times higher than that of the GF/A separator (Table S5 and Fig. S2a). The thermogravimetric analysis also indicates that the thermal stability has been greatly improved after transferring uncured homopolymerized electrolyte (0 mol% cross-linker

PEE and 91 wt% FEC, denoted as h-PE) to crosslinked GPE (c-GPE-50) (Fig. S2b). Scanning electron microscope (SEM) images show that the thickness of the c-GPE-50 is 180 µm (Fig. S3). NMR confirms that the polymer matrix of h-PE and c-GPE-50 is a polyether and crosslinked polymer network, respectively (Fig. S4). Our c-GPE also exhibits high and stable ionic conductivity at mS cm⁻¹ level in the temperature range of 298 - 363 K with a low activation energy of 18.57 kJ mol^{-1} , as shown in Fig. S5. In addition, c-GPE-50 displays a high Li⁺ transference number (t_{Li}^+) of 0.6, which is higher than that (0.54) of h-PE (Fig. S6). Linear sweep voltammetry (LSV) measurements and electrochemical floating analysis were used to investigate the effect of crosslinking on the electrochemical stability window of the obtained electrolytes. The oxidation potential of the c-GPE-50 with a crosslinked network is 4.5 V (Fig. 1d), which is significantly higher than that of the uncured homopolymerized DOL electrolyte without any cross-linker (4.2 V). This result is consistent with that obtained from electrochemical floating tests (Fig. S7). Compared to homopolymerized DOL, introducing four-armed crosslinker PEE in our c-GPE-50 could provide a more robust 3D crosslinked polymer network, thus significantly improving oxidative stability. All these experimental results demonstrate that using four-armed crosslinker is a very effective strategy for enhancing crosslinking and network formation, leading to improved oxidative stability of CROP-based GPE.

2.3. Long cycling performance of batteries with c-GPEs

The stability of c-GPE-50 with lithium metal anode was assessed by galvanostatic polarization experiments using Li||Li symmetric cell. As shown in Fig. 2a, under a current density of 0.5 mA $\rm cm^{-2}$ with the area capacity of 0.5 mAh cm⁻², the Li||Li symmetric cell with c-GPE-50 maintains a quite stable voltage polarization with a small overpotential of 15.2 mV over 2800 h, and the overpotential starts to increase substantially only around 3100 h (Fig. S8). Fig. S9 indicates that the Li|c-GPE-50|Li cell exhibits a high critical current density (defined as the highest current density at which the battery is short-circuited) value up to 3 mA cm⁻². Moreover, the Li|c-GPE-50|Cu cell exhibits a stable columbic efficiency of \approx 97% over 300 cycles (Fig. S10). The excellent compatibility of c-GPE-50 with Li should be ascribed to the intimate interface contact and the highly robust 3D polymer network constructed by in situ crosslinking. In contrast, the overpotential of the Li||Li symmetric cell with commercial liquid electrolyte (1 M LiPF₆ in EC/DEC, denoted as cm-LE) increases rapidly to 125 mV and fails to work after 1130 h due to dendrite-induced short circuits. LillLi symmetric cells of homopolymerized electrolyte (h-PE) and basic liquid electrolyte (0.68 mol L⁻¹ LiDFOB and 0.68 mol L⁻¹ LiTFSI in FEC, denoted as b-LE) were also tested and displayed much more polarization compared with that of c-GPE-50 (Fig. S11). The overpotential of Li|c-GPE-50|Li symmetric cell keeps steady overall and increases by 25% even after 2800 h, while the overpotential of Li|h-PE|Li and Li|b-LE|Li symmetric cell greatly increases by 125% and 282% after 2800 h, respectively. As shown in the SEM images of the cycled Li electrode (Fig. S12) with the controlled electrolytes (h-PE and b-LE), the increased overpotential may result from the continuous dendrite growth and isolated lithium loss. In contrast, the cycled Li electrode in Li|c-GPE-50|Li symmetric cell maintains a smooth surface without obvious Li dendrites and shows much smaller volume expansion. The above results confirm that the c-GPE-50 is highly compatible with the Li anode.

To further evaluate the long cycling performance, the Li||LFP batteries based on different electrolytes were assembled and tested. As shown in Fig. 2b, the Li|c-GPE-50|LFP battery achieves a high capacity of 134 mAh g⁻¹ and an ultra-long lifespan of 2000 cycles with an excellent capacity retention of 78% at a high rate of 2 C. The corresponding voltage profiles are shown in Fig. 2c and exhibit extremely low polarization and high coulombic efficiency. As far as we know, this is one of the best cycling stability (2000 cycles and 78% retention) of Li|| LFP batteries at a high rate of 2 C among all the polymer electrolytebased batteries reported so far (Table S6 and Fig. S13). The cycling



Fig. 2. (a) Polarization tests of Li||Li symmetric cells with cm-LE and c-GPE-50. (b) Cycling performances of Li||LFP batteries with cm-LE (blue),b-LE (black), c-GPE-50 (red), and h-PE (green) at 2 C. Corresponding voltage profiles of (c) Li|c-GPE-50|LFP, (d) Li|b-LE|LFP and (e) Li|h-PE|LFP batteries at 2 C.

stability of Li|c-GPE-50|LFP battery even exceeds that of a battery using commercial liquid electrolyte, which has a low capacity retention of 50% after only 1000 cycles (Fig. 2b). In sharp contrast, without the special 3D crosslinked polymer network, both the Li||LFP battery using homopolymerized electrolyte (h-PE) or basic liquid electrolyte (b-LE) display increasing voltage polarization and inferior cycling performances, as their capacity retentions fall rapidly to 57% after only 150 cycles (h-PE) and 59% after 1000 cycles (b-LE) (Fig. 2b, d, and e), respectively. These results indicate that the cycling stability of LMBs has been significantly improved by adopting PEE-DOL crosslinking strategy, compared with both homopolymerized DOL and liquid electrolyte.

Electrochemical impedance spectroscopy (EIS) was used to investigate the interfacial resistances during cycling at 2 C (Fig. S14). The Li|b-LE|LFP battery based on the basic liquid electrolyte shows a drastically increased interfacial resistance after 250 cycles, due to the unstable SEI formed in a FEC-based liquid electrolyte [31]. The interfacial resistance of Li|h-PE|LFP battery based on the uncrosslinked homopolymerized electrolyte without any cross-linker also increased rapidly due to lower stability of linear polymer. In contrast, with the four-armed cross-linker, the Li|c-GPE-50|LFP battery displays a rather stable interfacial resistance across 500 cycles. The EIS results are consistent with the cycling behavior of LMBs based on these electrolytes (Fig. 2b), confirming that the crosslinked polymer network fabricated by four-armed cross-linker can enhance the cycling stability of LMBs.

Moreover, the Li|c-GPE-50|LFP battery also displays an outstanding rate performance and achieves high discharge capacities of 152, 147, 140, 131, 112, and 80 mAh g^{-1} at 0.2, 0.5, 1, 2, 5, and 10 C, respectively (Fig. S15). Under lower rates, the Li|c-GPE-50|LFP batteries still display high capacities and excellent capacity retentions of 92% at 0.5 C and 91% at 1 C after 600 cycles (Fig. S16). These performances surpass those of Li|b-LE|LFP batteries significantly. Even under a higher current

density of 850 mA g⁻¹ (5 C), Li|c-GPE-50|LFP still exhibits an ultrastable cycling performance of 2000 cycles with 83% capacity retention (Fig. S17). Recently, polymer electrolytes based on three-armed crosslinker have been reported to improve the electrochemical performance of homopolymerized DOL [32,33]. However, our designed c-GPE fabricated by the four-armed cross-linker PEE enables the LMBs with a much superior rate and cycling performance, which is due to the more densely crosslinked polymer network than those fabricated by other cross-linkers. Furthermore, the general applicability of this in situ crosslinking strategy was also studied by using commercial nonfluorinated solvent (EC/DEC) as shown in Fig. S18. Li||LFP battery assembled with this nonfluorinated solvent-based c-GPE also displays rather high cycling stability at 2 C (78% retention after 1350 cycles). These experimental results indicate that our designed 3D crosslinked c-GPE with either fluorinated or nonfluorinated solvent could realize excellent cycling performance.

2.4. Impact on Li deposition and the mechanism of the improved performance

Scanning electron microscopy (SEM) was used to study the morphology of the deposited lithium on the Cu current collector in Li|| Cu batteries using different electrolytes. In the Li|b-LE|Cu battery, the deposited Li exhibits a loose and dendritic morphology with high tortuosity (Fig. 3a). In sharp contrast, in the Li|c-GPE-50|Cu battery with a crosslinked network, the Li particles grow larger and are more compactly fitted together to form a flat and seamless deposition morphology on the Cu current collector (Fig. 3b). The Li deposition morphology implies that the crosslinked polymer network may guide the homogeneous Li deposition and inhibits dendritic Li growth, which is in good agreement with the ultra-long cycling stability of the Li|c-



Fig. 3. (a,b) Morphological evolution of Li deposition on Cu current collector using b-LE and c-GPE-50. The areal capacity from the counter Li metal electrode is 5 mAh cm⁻¹. (c) Raman spectra of FEC, b-LE, and c-GPE-50. EIS results of fresh symmetric Li||Li cells using (d) b-LE and (e) c-GPE-50 at different temperatures. (f) Arrhenius behavior of Li⁺ desolvation in c-GPE-50 and b-LE. (g) Binding energies of FEC with PP and p(PEE-DOL) obtained from quantum chemistry simulation. (h) Schematic illustration of the electrolyte structures and proposed desolvation mechanisms in different electrolyte systems.

GPE-50|LFP battery.

The Li deposition morphology and corresponding ion desolvation mechanism of LMBs heavily depend on the solvation structure electrolyte [34]. As previous studies have indicated that Li⁺ desolvation dominates the Li deposition process, we hypothesize that the desolvation behavior is the direct result of the inherent solvation structure of the electrolyte, which holds the key to describing the performance discrepancy between the different electrolytes of b-LE and c-GPE-50 systems. Raman spectroscopy was used to investigate the solvation structure of electrolytes. As shown in Fig. 3c, pure FEC shows three strong absorption bands at 730 $\rm cm^{-1}$ (ring breathing mode, $\rm o_{O-C-O}$), 867 cm^{-1} (C-F stretching vibration, v_{C-F}), and 905 cm^{-1} (ring skeletal deformation mode, β_{C-C}). After LiTFSI dissolved in FEC, the o_{O-C-O} and β_{C-C} bands of b-LE have blue-shifted to 742 and 922 cm⁻¹, respectively, attributing to the FEC-Li⁺ coordination. In the spectrum of c-GPE-50, the band intensities (742 and 922 cm^{-1}) related to the FEC-Li⁺ coordination decrease, indicating that the PEE-DOL copolymer chain (denoted as p (PEE-DOL)) in c-GPE-50 weakens the coordination between FEC and Li⁺. The desolvation energy, representing the activation energy of Li⁺ when desolvating at the SEI/electrolyte interface, was further calculated by fitting the temperature-dependant EIS of fresh Li||Li symmetric cells (Fig. 3d,e,f) [35-37]. The desolvation energy is reduced by 26% in c-GPE-50 (39.07 kJ mol⁻¹), compared with a larger desolvation energy in b-LE (52.74 kJ mol⁻¹). Therefore, it can be concluded that the weakened FEC-Li⁺ coordination in c-GPE-50 lowers the energy barrier of Li⁺ desolvation, which enables homogeneous Li deposition. As represented in the proposed mechanism shown in Fig. 3g,h, the interaction between polymer and FEC was assessed via DFT calculation. The binding energy of FEC with p(PEE-DOL) is -0.29 eV. For comparison, the binding energy between FEC and another polymer without polar functional group, polypropylene (PP), was calculated to be -0.065 eV. The binding energy of the p(PEE-DOL)-FEC in c-GPE-50 is higher than that of the PP-FEC system, indicating that the polymer network in c-GPE-50 has a stronger interaction with FEC due to the polar groups in p(PEE-DOL).

Based on the above experimental and calculation results, the mechanism of Li⁺ desolvation and plating in c-GPE-50 is represented in Fig. 3h. In the liquid electrolyte (the left panel in Fig. 3h), the dissociated Li⁺ would coordinate with the FEC solvent. However, the FEC-Li⁺ coordination may lead to a higher desolvation barrier and increase the local charge-transfer impedance, thus resulting in dendritic Li growth in a tip-driven manner [38]. Conversely, in c-GPE-50 (the right panel in Fig. 3e), the solvent competition induced by the stronger p (PEE-DOL)-FEC interaction would weaken the FEC-Li⁺ coordination, which is consistent with the Raman spectra results [39]. Therefore, the

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energy barrier of desolvation is decreased and Li^+ desolvation occurs more easily in the weak-binding FEC system in c-GPE-50, realizing a homogenous Li^+ deposition behavior.

X-ray photoelectron spectroscopy (XPS) depth profiling using Ar ion etching was performed to characterize the spatial distribution of the chemical components in the SEI (Fig. 4). The B 1s and F 1s spectra of both the c-GPE-50 and b-LE systems (Fig. 4a,c,e,g) indicate the presence of B- and F-containing species in the SEI that derived from the decomposition of LiDFOB and FEC. In the C 1 s spectra (Fig. 4b,f), the O-C-O peaks in the c-GPE-50 system are ascribed to the -CH2CH2OCH2- unit that originated from the PEE-DOL copolymer [40]. In comparison, C=O, CO_3^{2-} , and poly(CO₃) peaks with higher binding energies in the b-LE system are attributed to the decomposition of FEC [41]. The absence of these peaks in the c-GPE-50 system demonstrates that the solvent decomposition is inhibited. Moreover, the LiNxOv signal (Fig. 4d, h), which implies the complete decomposition of the TFSI⁻ anion, is only detected in the c-GPE-50 system. This may be explained as follows: as p (PEE-DOL) weakens FEC-Li⁺ coordination, TFSI⁻ anions would enter the Li⁺ solvent sheath and then coordinate with Li⁺. Thus, in the c-GPE-50 system, TFSI⁻ anions are predominantly reduced and deposited in the SEI [42-44].

The atomic ratios of the SEI obtained from the XPS depth profiles are shown in Fig. S19a,c. The mass ratio of the components in the SEI that varied with depth is summarized in Fig. S19b,d. Compared to the b-LE system, the SEI formed in c-GPE-50 is composed of an inner layer enriched with B-O/B-F species and LiF, and an outer layer enriched with a LiN_xO_y and polyether (Fig. S19a,b). Both the high modulus of LiF and the crosslinked covalent skeleton formed by B-O bond contribute to a robust SEI. Furthermore, as an electrical insulator with low diffusion energy and high surface energy for Li⁺, LiF exhibits an overwhelming advantage in inhibiting dendrite growth and solvent decomposition [45]. The LiN_xO_y and polyether enriched in the outer layer have beneficial effects for fast Li⁺ ion transfer, contributing to homogeneous Li⁺ deposition [46,47]. This unique SEI structure formed in c-GPE-50 contributes to the outstanding ultra-long cycling performance of the Li| c-GPE-50|LFP battery.

2.5. Performance of high-voltage batteries with c-GPEs

Owing to the excellent oxidative stability of our designed c-GPE-50, a high-voltage cathode ($\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$, NMC622) was used in the battery to realize a high-energy-density battery system. As shown in Fig. 5a, the Li|c-GPE-50|NMC622 battery exhibits a high discharge capacity of 160 mAh g⁻¹ at 0.5 C. After 300 and 400 cycles, the Li|c-GPE-50|NMC622 battery displays an excellent cycling performance with 80% and 74% capacity retention, respectively, which is higher than that of



Fig. 4. XPS depth profiles of the SEI obtained from the Li||Cu batteries using (a-d) c-GPE-50 and (e-h) b-LE after depositing 5 mAh cm⁻² of Li.



Fig. 5. (a) Cycling performances of the Li||NMC622 batteries with b-LE and c-GPE-50 at 0.5 C. (b) SEM images and (c,d) XPS analyses of the cycled NMC622 cathodes with b-LE and c-GPE-50 after 100 cycles.

the Li|b-LE|NMC622 battery with liquid electrolyte (only 45% capacity retention after 400 cycles). Notably, the cycling stability of Li|c-GPE-50| NMC622 battery has surpassed most of the LMBs assembled with CROPbased polymer electrolytes, as shown in Table S7. Meanwhile, Lill NMC622 batteries assembled with cm-LE and h-PE display much worse cycling performances (Fig. S20). Under higher rates of 1 C, the Li|c-GPE-50 NMC622 battery still displays excellent cycling stability of 300 cycles with 74% capacity retention (Fig. S21). Furthermore, the crosslinked c-GPE-50 was extendedly investigated in LMBs using other commercial high-voltage cathode materials, including LiCoO2 (LCO) and LiNi_{0.3}Mn_{0.3}Co_{0.3}O₂ (NMC111). As shown in Fig. S22, both Li|c-GPE-50| LCO and Li|c-GPE-50|NMC111 batteries deliver initial discharge capacities of 135 mAh g⁻¹ at 0.5 C. These batteries also exhibit high capacity retention of 80% and 78% after 650 and 500 cycles, respectively. In comparison, rapid capacity fading is observed for the Li||LCO and Li|| NMC111 batteries assembled with other electrolytes (b-LE, cm-LE, and h-PE).

SEM and XPS were used to characterize the morphologies and chemical compositions of the surface of high-voltage NMC622 cathode after cycling in Li|c-GPE-50|NMC622 and Li|b-LE|NMC622 batteries. As shown in Fig. 5b, the cycled NMC622 particles from Li|c-GPE-50| NMC622 battery exhibit well-preserved mechanical integrity without visible cracks, while an extensive integranular cracking in the cycled NMC622 particles from the Li|b-LE|NMC622 battery could be observed, indicating the presence of more side reactions and faster electrolyte consumption. In the C 1s spectra (Fig. 5c), the CEI layers on cycled NMC cathode from both c-GPE-50 and b-LE show dominant XPS peaks corresponding to C-C, C-O, and C=O groups. However, the CEI on cycled

NMC cathode from b-LE shows an apparent CO_3^{2-} peak corresponding to Li₂CO₃, suggesting severe solvent consumption in the b-LE system. In addition, in the F 1s spectra (Fig. 5d), the detected C-F peak on cycled NMC cathode from b-LE is consistent with the continuous decomposition of fluorinated solvent in b-LE. The B 1s spectra (Fig. S23) demonstrate that more B-O species are presented in the CEI of cycled NMC cathode based on c-GPE-50 due to the decomposition of LiDFOB. These B-O species help stabilize the surface of the NMC cathode, mitigate side reactions between the NMC cathode and the electrolyte, and protect the Al current collector [48–51]. Benefiting from these inorganic species (LiF and B-O) in CEI, the generated stable CEI inhibits the side reactions between c-GPE-50 and the NMC622 cathode. This indicates that the crosslinked polymer network improves the compatibility of the CROP-based GPE with the high-voltage cathodes.

2.6. Full batteries performance

Furthermore, to demonstrate the potential of our designed c-GPE for practical applications, Li|c-GPE-50|LFP and Li|c-GPE-50|NMC622 full batteries with low negative/positive capacity ratios (N/P ratio, 5.5:1 and 5:1, respectively) were assembled with thin Li foil (50 μ m, 10 mAh cm⁻²) and high-loading LFP cathode (10.5 mg cm⁻², 1.8 mAh cm⁻²) /NMC622 cathode (10 mg cm⁻², 2 mAh cm⁻²) [52,53]. Li|LFP and Li| NMC622 batteries using c-GPE-50 maintain high capacity retentions of 82% and 79% after 300 cycles, respectively (Fig. 6a, b). However, under the low N/P ratio, the Li|LFP and Li|NMC622 full batteries using b-LE show dramatic capacity decay due to their rapid anode degradation and electrolyte consumption.



Fig. 6. Cycling performances of (a) Li||LFP and (b) Li||NMC622 batteries with b-LE and c-GPE-50 under low N/P ratios of 5.5:1 and 5:1, respectively. (c) Flame test of c-GPE-50 and b-LE (infiltrated into the seperator). (d) Safety test of Li|c-GPE-50|NMC622 pouch cell under various conditions including bending, cutting, and punching.

2.7. Fire-Retardant property and safety test

In addition to rigorous working conditions, high safety is also an essential requirement for developing of LMBs. Therefore, the nonflammability of c-GPE-50 was evaluated by the flame test. As shown in Fig. 6c and Video S1,2, the c-GPE-50 membrane does not combust even when directly exposed to the flame, demonstrating the superior fire-retardant property. This can be attributed to the much-reduced volatility of FEC in the c-GPE with densely crosslinked polymer network. In sharp contrast, b-LE (infiltrated into the seperator) bursts into flame as soon as contacting the fire. Furthermore, a Li|c-GPE-50|NMC622 pouch cell was also assembled to demonstrate the safety and flexibility of our designed c-GPE-50 for the destructive test. As shown in Fig. 6d, a blue light-emitting diode (LED) lamp is powered by the assembled pouch cell.

keeps constant. The excellent safety and flexibility of the pouch cell are attributed to the intimate contact interface of the cathode/electrolyte/ anode and densely crosslinked polymer network in our designed c-GPE.

3. Conclusion

In summary, we developed a 3D crosslinked c-GPE with densely crosslinked polymer network via *in situ* Li salt-initiated CROP by using a four-armed cross-linker PEE for the first time. The crosslinked polymer network not only significantly improved the solvent uptake of GPE to 91 wt%, but also effectively reduced the energy barrier of Li⁺ during desolvation. Thus, the obtained c-GPE-50 exhibited a high ionic conductivity of 2.36 mS cm⁻¹ at RT and excellent interfacial compatibility with the Li anode, LFP, and high-voltage cathodes. As a result, the Li||LFP battery with c-GPE-50 delivered an excellent cycling performance of

2000 cycles with a remarkably high capacity retention of 78%, exhibiting one of the longest lifespans (2000 cycles) at a high rate of 2 C among the reported polymer electrolytes. The cycling performance of high-voltage Li||NMC622 battery with c-GPE delivered the best cycling performance among CROP-based batteries, delivering a high capacity retention of 80% after 300 cycles at 0.5 C. The Li||LFP and Li||NMC622 full batteries based on the *in situ* crosslinked c-GPE with low N/P ratios were also assembled, which exhibited stable cycling performances for 300 cycles. In addition, a pouch cell assembled with this c-GPE-50 exhibited superior safety even after cutting, punching, and bending. Overall, the 3D crosslinked c-GPE fabricated by *in situ* crosslinking strategy, which is practical and compatible with the industry LIBs fabrication approach, is promising for the commercialization of LMBs with both high performance and safety.

CRediT authorship contribution statement

Jie Zhu: Conceptualization, Data curation, Formal analysis, Investigation, Validation, Writing – original draft, Writing – review & editing. Jinping Zhang: Conceptualization, Validation, Formal analysis, Investigation. Ruiqi Zhao: Formal analysis. Yang Zhao: Formal analysis. Jie Liu: Formal analysis. Nuo Xu: Formal analysis. Xiangjian Wan: Supervision, Formal analysis. Chenxi Li: Supervision, Formal analysis. Yanfeng Ma: Supervision, Formal analysis. Hongtao Zhang: Conceptualization, Supervision, Writing – review & editing. Yongsheng Chen: Conceptualization, Data curation, Formal analysis, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ensm.2023.02.012.

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