In Situ Copolymerized Gel Polymer Electrolyte with Cross-Linked Network for Sodium-Ion Batteries

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High thermal stability, nonflammability, and no liquid leakage are indispensable capabilities for electrolytes in sodium-ion batteries toward large-scale energy storage systems. The use of solid-state or gel polymer electrolytes has proven to be one of the enabling tools to bring about these advancements; however, their application suffer from tedious synthesis procedure and/or low ionic transport to ensure a battery operation. Herein, a novel gel polymer electrolyte with a cross-linked polyether network (GPE-CPN) was crafted through a self-catalyzed strategy, where in situ copolymerization of two monomers, 1,3-dioxolane and trimethylolpropane triglycidyl ether is realized successfully, with the use of sodium hexafluorophosphate (NaPF6) as an initiator, at room temperature. We demonstrate that the resultant GPE-CPN possesses a superior electrochemical stability window up to 4 V versus Na+/Na, a considerable ionic conductivity, of $8.2 \times 10^{-4}$ S cm$^{-1}$ at room temperature, which is a capability good enough to suppress the growth of sodium dendrites and thus, stabilize the interface of electrolyte/sodium anode. Considering the benefit from its facile fabrication and superior characteristics, the as-generated GPE-CPN reveals a potential application for future rechargeable sodium batteries.

Keywords: sodium-ion batteries, gel polymer electrolytes, full-cell, in situ polymerization, cationic mechanism
Introduction

Gel polymer electrolytes (GPEs) inherit both high ionic conductivity and wettability, which is unique, as compared with liquid electrolytes. They also exhibit high-voltage/temperature stability similar to all-solid-state electrolytes. Therefore, GPEs are identified as excellent electrolytes for developing high-performance energy storage batteries. A classical GPE consists of a gel polymer host as the backbone and a liquid electrolyte as a filler. Of them, the polymer network could be classified into one-dimensional (1D) and three-dimensional (3D) types, according to the molecular chain structure. Typical representatives of 1D polymer backbones include poly(ethylene oxide), poly(methyl methacrylate), poly(ethylene glycol), poly(acrylonitrile), poly(vinylidene fluoride), and poly(vinylidene fluoride-co-hexafluoropropylene), which are the most widely studied. Nonetheless, they suffer inadequacies such as poor thermal/electrochemical stability, moderate compatibility with electrolytes, serious interface reaction, and others. As a result, many design concepts based on polymer skeleton structure have been proposed successively, which include copolymerization, blending, and cross-linking, to promote the transformation of a polymer skeleton from 1D to 3D. In the light of current successful advancements, some novel 3D polymer hosts have also been developed using a one-pot approach with more than one monomer. However, so far, only a few of such concepts have been employed in sodium-ion batteries (SIBs).

Besides screening for polymer hosts for good performance of batteries, their tailoring strategies should also be considered in their practicability. Current methods for preparing polymer frameworks include solution casting and hot pressing, which, at a glance, have many deficiencies such as cumbersome processing, wasted organic solvents, unfriendly environments, and reliance on additional equipment. Therefore, developing high-safety, solid-state SIBs still hinges on constructing GPEs with 3D polymer frameworks through a simple and economical process. Notably, the routine procedure for preparing GPEs starts from the synthesis of the polymer backbone, followed by an introduction of the electrolyte salt and solvent by soaking. To break through such habitual thought, we proposed an in situ polymerization process to prepare highly effective GPEs with a facile approach to fabricate compatible interfaces within a battery system via existing manufacturing techniques and infrastructures. Herein, a novel GPE with 3D cross-linked polyether network (GPE-CPN) was developed for SIBs, using an in situ polymerization of two distinct monomers, which are, 1,3-dioxolane (DOL) and trimethylolpropane triglycidyl ether (TMPTGE), with sodium hexafluorophosphate (NaPF6) as an initiator. The resultant in situ GPE formed revealed a broad operating voltage window and good thermal stability. In particular, it possessed a good capability for suppressing the growth of sodium dendrites, thus stabilizing the interface of electrolyte/sodium anode. The resultant quasi-solid-state batteries delivered admirable specific capacity and cyclic stability at room temperature when paired with Na3V2(PO4)3 or Na(Li0.05Ni0.3Mn0.5Cu0.1Mg0.05)O2 cathodes and metallic sodium or hard carbon anode. Benefiting from its unique features, such as free of impurities, ambient polymerization condition, good compatibility toward metallic sodium anode, the GPE showed great potential as a dependable electrolyte for highly secured sodium-rechargeable batteries.

Experimental Methods

Preparation of electrolyte containing organic copolymer

A 2.6 g of NaPF6 was dissolved sufficiently in a mixed solvent containing 70 vol % organic monomers (95% DOL + 5% TMPTGE, vol/vol) and 30 vol % conventional organic solvents, viz, propylene carbonate and fluorinated ethylene carbonate (95% PC + 5% FEC) to prepare a solvent containing 70 vol % organic monomers (95% PC + 5% FEC). The resultant solution was added dropwise to 400 mL of a copolymer electrolyte solution consisting of solely 70% organic monomers of DOL (PDOL) as a control. Note that all reagents are dewatered using molecular sieves (4 Å) or by vacuum drying prior to use.

Extraction of polymer

Each of the prepared gel electrolytes derived from the cross-link or PDOL, was fully dissolved in water, and the resultant solution was added dropwise to 400 mL of ethanol solvent to form a uniform suspension, followed by high-speed centrifugation to collect the precipitant, and drying at room temperature for 72 h to obtain white, solid-type polymers of cross-linked polyether network (CPN), named GPE-CPN and pure PDOL, respectively.

Synthesis and source of electrode materials

The electrode materials used in this report included Na3V2(PO4)3, Na(Li0.05Ni0.3Mn0.5Cu0.1Mg0.05)O2, and NaTi2(PO4)3, and were prepared according to the methods reported in related literature, and hard carbon anode coated material were obtained from a commercial channel (KUREHA Corporation, Chuo-ku, Tokyo, Japan).
Chemical characterization

Fourier-transform infrared (FTIR) spectrometer (TENSOR-27; Bruker, Shanghai, China) was used to characterize the pure polymers in the range of 4000–400 cm\(^{-1}\). We performed the \(^{13}\)C NMR experiments on a Bruker Avance II 500 MHz NMR spectrometer (11.7 T; Bruker). X-Ray diffraction (XRD) data were obtained with a Rigaku Microdiffactometer (D/max 2500, Beijing, China) using Cu Ka radiation (\(\lambda = 1.5406\) Å). We observed the morphologies and microstructures of the as-synthesized materials by using a field-emission scanning electron microscopy (FESEM; JSM-6701F; JEOL, Peabody, MA). Considering the damage caused by electromagnetic radiation to the conventional Celgard membrane, the influence of the liquid electrolyte on the morphology of the membrane before and after copolymerization of the two monomers, DOL and TMPTGE, was investigated based on a cellulose membrane. X-Ray photoelectron spectroscopy (XPS) measurements were carried out on a spectrometer (Escalab 250xi; Thermo Fisher Scientific, Shanghai, China). For ex-situ XPS analysis, the cycled electrodes were disassembled from the batteries and washed with dimethyl carbonate in an argon-filled glove box. Thermogravimetric (TG) calorimeter (Thermo plus EVO2; Rigaku, Beijing, China) was utilized to perform TG analysis with a temperature range between 30 °C and 400 °C at 10 °C min\(^{-1}\) rate, under atmospheric nitrogen to determine temperature-dependent conductivity of the electrolytes.

Electrochemical measurements

Electrochemical performances of the CR2032-type coin cell assembly were evaluated by initially preparing the electrode, mixing the obtained active material (GPE-CPN), carbon black, and polyvinylidene fluoride (PVDF), according to their specific mass ratio, followed by the addition of N-methyl-2-pyrrolidone (NMP) as a solvent to prepare a homogeneous slurry. In particular, the mass ratios of Na\(_3\)V\(_2\)(PO\(_4\))\(_3\), Na\((Li_{0.05}Ni_{0.3}Mn_{0.5}Cu_{0.1}Mg_{0.05})\)O\(_2\), NaTi\(_2\)(PO\(_4\))\(_3\), and hard carbon electrode were 80:10:10. The control material (PDOL) was also used to prepare a cell battery in a parallel fashion. Coin cells were created by assembling the slurry containing the organic polymers as electrolytes with addition of polypropylene films, in an argon-filled glove box, using Celgard 2400 as the separators (Linyi Gelon LIB Co., Mainland, China) to sandwich between the gel polymer electrolyte, GPE-CPN, or PDOL, and a carbon-coated aluminum foil, and dried overnight at 80 °C to create GPE-CPN or PDOL cathodes. For comparison, we prepared three types of liquid cell electrolyte cathodes from 1 M NaClO\(_4\) or NaPF\(_6\) dissolved in propylene carbonate (PC) or ethylene carbonate (EC) and diethyl carbonate (DEC) with 5% volume fluoroethylene carbonate (FEC) as the electrolytes and glass fiber (Whatman, GF/D) as the separator. We created half-cells by using sodium foils as anodes, whereas full-cells were generated by using hard carbon as anodes. The typical loading of the electroactive material per electrode was \(-1.8\) mg. Before assembling the full-cells, the hard carbon electrode was presodiated in the half-cells with disks of sodium foil as anodes at a current density of 50 mA g\(^{-1}\) until the cells underwent four charge and discharge cycles, and finally stopped at a discharge of 0.01 V. Then, the presodiated electrode was unpacked and paired with the cathode to assemble SiB in the glove box. Linear sweep voltammetry (LSV) was used to study the electrochemical stability window of the electrolyte at 0.1 mV s\(^{-1}\) scan rate, and between 0 and 5 V. The ionic conductivities of the gel electrolytes were analyzed by performing alternating current (AC) electrochemical impedance spectroscopy (EIS; PARSTAT3000A; Princeton Applied Research, USA) at a frequency range of 0.1 Hz–1 MHz. AC impedance measurements were performed with an amplitude of 5 mV at temperatures ranging from 20 °C to 70 °C. For the full-cells, the EIS experiments were conducted in the frequency range of 0.01-100 kHz. We conducted potentiostatic polarization experiments with an applied voltage of 10 mV and a polarization time of 10,000 s, using the EIS potentiostat/galvanostat system (PARSTAT3000A; Princeton Applied Research, USA) to measure electrolyte charge/discharge performance of the fabricated battery types.

Results and Discussion

A novel GPE-CPN SIB was constructed through copolymerization of DOL and TMPTGE monomers after optimizing the volume ratio of each monomer, based on the preliminary experimental result of in situ polymerization of either DOL alone (PDOL) or DOL plus the TMPTGE cross-linker (GPE-CPN). The concept of in situ liquid electrolyte gelation benefitted the cross-linked battery by virtue of the presence of traces of H\(_2\)O in the electrolyte solution and the hydrolysis characteristics of the sodium salt, compared with the PDOL control. We identified the cross-linking of the two monomers of the GPE cell by initially characterizing the polymerization products by X-ray diffraction (XRD), as well as FTIR, and compared with the PDOL cell control. The results showed that the diffraction peak of the CPN moved from low to high angle, and the half-peak width was narrowed, compared with the polymer PDOL, but the peak shapes of the two systems were almost the same (Supporting Information Figure S1). These results implied that the addition of a small amount of TMPTGE did not only change the long-range disorderliness of DOL in the polymer, but also, extended the polymer chain length, enlarged the volume, and shortened the distance between the segments, which indicated that TMPTGE played an essential role in connecting multiple segments in this system.
Further FTIR analysis revealed that CPN and PDOL had similar functional group environments (Supporting Information Figure S2), having peaks around 2875, 1454, 1350, and 1110 cm$^{-1}$, attributable to the C–H stretching, asymmetric stretching, bending vibration in $-\text{CH}_2$ and $-\text{CH}$, and C–O–C stretching, respectively. However, the CPN revealed a unique C–C stretching vibration at a characteristic absorption peak of quaternary carbon at 1080 cm$^{-1}$, indicating that the TMPTGE was introduced successfully into the copolymer system.

The NMR analysis of the two monomers and the corresponding copolymer systems found that the characteristic peaks of the carbon atoms of the monomers disappeared after polymerization, suggesting that the polymerization process in the electrolyte was thorough and sufficient (Supporting Information Figure S3). There was no significant difference in the carbon spectrum between the cross-link and the linear polymer systems. Typically, the resonances at $\sim$68 and $\sim$95.4 ppm were attributable to $-\text{OCH}_2\text{CH}_2\text{O}$– and $-\text{OCH}_2\text{O}$– functional groups on the long-range linear chain, respectively, which demonstrated further that polymerization had occurred. Also, the CPN system had fewer peaks at $\sim$68 ppm, demonstrating that the addition of TMPTGE significantly increased the molecular weight of the polymer. Collectively, we postulated that the copolymerization mechanism of our system occurred in the following order of processes (Figure 1; Supporting Information Figure S4): (1) Since the monomer DOL concentration was much higher than that of TMPTGE, DOL first polymerized to form a chain of anion–cation initiator during polymerization. Specifically, PF$_5$ was hydrolyzed to form an anion–cation pair, and then the as-formed ion pair attacked the ether oxygen atom of the DOL monomer, thus, easily subjecting it to ring-opening to initiate cat-ionic polymerization with the resultant generation of oxonium ions (Figure 1). (2) The resultant oxonium ions further cross-linked with the TMPTGE monomer to form a CPN in situ. (3) The organic solvents (e.g., PC, FEC) or electrolyte salt that could not be polymerized were stabilized within this 3D framework to form a novel GPE (Figure 1). Favorably, with this cross-linked polymerization mode, the gelation time of the electrolyte solution was considerably shortened (<12 h; Supporting Information Figure S5). Further, the gelation properties in ether solvents, such as diethylene glycol dimethyl ether (DEGDME), were also compared. We found no signs of gelation, even after 130 h, which was probably related to several factors, including the ether solvent used, salt type, salt concentration, and kinetic differences, in fabrication of the electrolyte-containing cell cathode.

We visualized the establishment of the in situ polymerization by analyzing FESEM images of the surface and cross-section of the cellulose and composite membrane, as well as optical images of liquid electrolyte-containing monomers and the GPE-CPN (Figure 2). We found that the cellulose membrane was formed by interlacing fibers, and gaps of different sizes were formed therebetween. When the precursor electrolyte solution was injected into the separator membrane for 10 h, the gap of the membrane was completely filled by the GPE, and there was no noticeable gap in the cross-sectional view, further proving that the gelation of the solution electrolyte in the membrane was successful and sufficient. Additionally, TG measurements demonstrated that the cross-linked polymerized electrolyte maintained its gelation characteristics from 20 °C to 80 °C, promulgating that the system had good thermal stability (Supporting Information Figure S6). It should be noted that, as the temperature was increased above 80 °C, the electrolyte underwent a slight color change, which was mainly due to the decomposition of NaPF$_6$ initiator at such a high temperature.

Figure 1 | Cross-linking polymerization mechanism of two liquid electrolyte monomers, 1,3-dioxolane (DOL) and trimethylolpropane triglycidyl ether (TMPTGE), induced by sodium hexafluorophosphate (NaPF$_6$) for the generation of the gel electrolyte.
The TG analysis (Supporting Information Figure S7) also revealed that the resulting GPE skeleton was stable below 100 °C, and the slight weight loss was attributable to the presence of solvent components, consistent with the evolution of optical thermal properties, and suggested that our generated GPE was adaptable to higher temperatures, preferably, in suitable solvents like ester and sodium salts.

When the prepared three liquid electrolyte types were each dropped onto fresh sodium metal (Supporting Information Figures S8a1–c1), the monomer-containing electrolyte (1 M NaPF₆ with PC-FEC-DOL-TMPTGE, Supporting Information Figure S8c2) caused the metallic sodium to gradually change color, while this behavior was not observable in the other two electrolytes (1 M NaClO₄ with PC-FEC, Supporting Information Figure S8a2) and (1 M NaPF₆ with EC-DEC-FEC, Supporting Information Figure S8b2), indicating that a protective layer of metallic sodium could also be formed in situ during the polymerization. Remarkably, benefitting from the presence of ether solvents (DOL and TMPTGE), good wetting of monomer-containing electrolytes with conventional Celgard membrane could be achieved (Supporting Information Figure S8c3) without the addition of low-viscosity solvents such as diethyl carbonate (DEC; Supporting Information Figure S8a3,b3).

To verify the practicality of the GPE-CPN described above in the electrochemical cell, we compared the electrochemical window of the liquid and the GPE coin cells by EIS (Figure 3a). We found that the GPE had an electrochemically stable window of up to 4 V, similar to the liquid electrolyte (1 M NaPF₆ in EC-DEC with 5% FEC), but the liquid system decomposed slowly above 4 V, mainly due to oxidation of the solvent EC and FEC, compared with the GPE, which remained intact above 4 V. Thus, the GPE sustained better stability than the liquid electrolyte, a phenomenon comparable to ether electrolytes, in which there is reduction in the amount of ether to increase its electrochemical stability.²¹ Besides, the ionic conductivity of the GPE reached 8.2 × 10⁻⁴ S cm⁻¹ at room temperature (Figure 3b and Supporting Information Figure S9), indicating that it is feasible for it to operate as an effective electrolyte. Further, a polarization test results (Supporting Information Figure S10) showed that the transference number of sodium ion in the GPE was 0.46, which was significantly higher than that in the liquid electrolytes (0.12). This result suggested that the GPE system is more favorable for inhibition of growth of dendrites, which tend to short-circuit batteries, causing their function to deteriorate.

The electrochemical cycle performed by LSV at a current density of 0.5 mA cm⁻² showed that the GPE system exhibited better cycle stability than the conventional

Figure 2 | FESEM images of (a and b) cellulose membrane and (d and e) gel composite membrane. Optical images of (c) liquid electrolyte-containing monomers and (f) cross-linked gel electrolyte.
liquid electrolyte system; also, the latter underwent an increased polarization and was short-circuited after 170 h, whereas the former maintained good stripping-deposition characteristics, even after 400 h (Figure 3c). After the cycles test, the surface topography observation of the metallic sodium in the liquid system displayed rough, cracked, and porous, as well as a large amount of sodium scrap which fell off easily, and adhered to the glass fiber membrane (Figure 3d,e). Likewise, the liquid system fabricated by using Celgard membrane also exhibited corresponding poor characteristics (Supporting Information Figure S11). Strikingly, cycle testing of Na-symmetric cells based on the Celgard membrane often failed, mainly because the sodium dendrites easily pierced through the membrane causing a short circuit. In sharp contrast, the surface of the metallic sodium, based on GPE, appeared smoother and flatter (Figure 3f,g), without appreciable appearance of dendrites, suggesting that GPE was efficient in inhibiting the growth of sodium dendrites.

In general, the inorganic component in the interfacial film of a battery cell forms a dense layer, which plays a major role in inhibiting the growth of dendrites. Thus, to gain insight into the capability of GPE to suppress the growth of sodium dendrites, the surface composition of the metallic sodium in the liquid and GPE electrolyte systems were subjected to ex-situ XPS analysis, after the cycles test (Supporting Information Figure S12) to analyze comparatively, the inorganic components of the metallic sodium surfaces of the two systems, which both contained Na$_2$CO$_3$ and NaF. Our results showed that, while the inorganic component of the liquid system was mainly Na$_2$CO$_3$ (13.1%), that of the GPE gel system was mainly NaF (4.92%). Obviously, the NaF content in the gel system was approximately four times as high as that in the liquid system, which was mainly related to the gelation process. Thus indicating that the NaF-rich interface film was denser and endowed the system with the sustainability of prolonged cycle stability, consistent with other reports, thereby, promising that the resultant GPE could have potential application prospects in sodium-metal batteries or sulfur electrochemistry with high-safety and high-energy density.

Moreover, electrochemical behaviors of the above two electrolyte systems were studied in half-cell configurations with Na$_3$V$_2$(PO$_4$)$_3$ as the cathode and the use of commercial Celgard membrane. When the assembled liquid cell, without gelation, was examined using a potentiostat/galvanostatic testing system, its charge and discharge process failed (Supporting Information Figure S13), accompanied by electrochemical oxidation of the monomers. Furthermore, these two Celgard
membrane-based liquid system demonstrated a persistent short-circuit phenomenon during the charge and discharge process, resulting in the battery failure (Supporting Information Figure S14). Favorably, the Celgard membrane-based gel system was capable of undergoing multiple charges and discharge cycles without being short-circuited or depreciation, indicating that the gelation process was appropriate for the cells tested and that our in situ gelation strategy is promising for future manufacturing of sodium-rechargeable batteries.

Consequently, we chose a glass fiber separator in the liquid system to compare with the GPE gel counterpart. Preceding the electrochemical test, the morphology changes of the Na3V2(PO4)3 electrode before and after gelation were compared by FESEM (Supporting Information Figure S15). The results showed that the GPE covered the surface of the electrode and filled its inherent voids after gelation, which aided in improving the kinetics of the sodium ions. Although our LSV analysis showed that both systems were capable of releasing a specific capacity of ~90 mAh g⁻¹ at a current density of 0.1 C (Figure 4a, b), the gel system exhibited a slightly larger electrochemical polarization, related to the very low ionic conductivity of GPE, compared with the liquid electrolyte. Notably, a voltage-step phenomenon could be observed on the discharge curve (dashed rectangle) in Figure 4a, mainly due to the presence of the passivated layer, which reflects the anode corrosion resistant property of GPE and the ultimate long shelf-life of the corresponding battery. After 100 cycles at a discharge rate of 0.2 C, the two systems exhibited comparable capacity retention of ~96% (Figure 4c). The morphology analysis after the cycles showed that the surface of the metallic sodium in the liquid system was rough and easy to fall off.

**Figure 4** | Electrochemical performances of half-cells based on Na3V2(PO4)3 cathode, analyzed by electrochemical potentiostat/galvanostat system. Charge–discharge profiles based on (a) gel and (b) liquid electrolyte at 0.1 C. (c) Comparison of cycle performance of liquid and gel electrolyte at 0.2 C. (d) Cycle performance of full-cells based on Na3V2(PO4)3 cathode and hard carbon anode with liquid and gel electrolyte at 0.1 C.
ions caused a sharp increase in its impedance (including cycle progressed, irreversible consumption of sodium ions, which, in turn, led to deterioration of cycle durability.

**Conclusion**

We have constructed a cross-linked 3D GPE battery by a self-catalyzed strategy via an in situ facile cationic polymerization initiated by sodium salts. The GPE possesses good thermal stability, high ionic conductivity at room temperature, and good electrochemical compatibility toward both cathode and anode, such as the metallic sodium anode. The sodium-rechargeable battery based on the resultant GPE exhibited superior interfacial stability, compared with the conventional liquid electrolyte system. Our results demonstrated that this reliable, in situ synthetic chemistry strategy, derived via a cationic copolymerization mechanism is very promising in the preparation of high-performance polymer electrolytes and would facilitate the prospects of highly durable and safe, solid-state sodium-rechargeable batteries.

**Supporting Information**

Supporting Information is available.

**Conflict of Interest**

The authors declare no competing financial interests.

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