A Room Temperature Ionic Liquid-based Superionic Conductive Polymer Electrolyte with High Thermal Stability for Long Cycle Life Lithium Batteries

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Abstract

A room temperature ionic liquid-based polymer electrolyte (RTIL-PE) was developed by mixing 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMPy][TFSI]), lithium bis(trifluoromethanesulphonyl)imide salt (LiTFSI), lithium bis(oxalate)borate (LiBOB) and poly(ethylene glycol) diacrylate (PEGDA). Quasi-solid, free-standing electrolyte membranes can be fabricated by photo-initiated cross-linking. The RTIL-PE exhibits outstanding thermal stability up to 270 °C and high ionic conductivity of 3.4 mS/cm at 80 °C. The ionic liquid [BMPy][TFSI] and the additive salt LiBOB significantly improved the electrochemical stability of the electrolyte at high temperature, achieving long-cycle stability in plating/stripping experiments. Half cells of lithium-ion batteries with RTIL-PE and lithium iron phosphate cathode were also investigated. The reversible capacity of the cell reaches 137 mAh/g at 0.2 C. After 500 cycles, the cell exhibited a capacity retention rate of 52.2% and an average Coulombic efficiency of 99.4%.

Keywords

Ionic liquid, Polymer electrolyte, Lithium ion batteries, Superionic conductive

Introduction

Rechargeable lithium ion batteries (LIBs) are the most successful electrochemical energy storage devices and have been widely used in portable electronics, hybrid/electric vehicles and large grid storage systems.[1–5] However, the commercial flammable liquid electrolytes used in current LIBs pose significant safety concerns in these applications, especially for large-scale devices with high operating temperatures. Under elevated temperatures, liquid electrolytes can leak and produce gaseous byproducts, which reduce battery cycle life and even lead to dangerous issue like explosion.[6–8] In order to improve the safety properties of LIBs, novel electrolyte systems, have been intensively researched in the past few decades, including polymer electrolytes and various ceramic solid-state electrolytes.[9–13] Among these investigated systems, polymer electrolytes stands out for their low manufacturing costs, processing flexibility, and good mechanical properties. In addition, polymer electrolytes have no leakage issues since they are solid at the battery operating temperatures, making them ideal for safe batteries. Poly(ethylene oxide) (PEO) is the most common polymer matrix in polymer electrolytes and has been extensively investigated since its first discovery in the 1970s.[14–16] PEO is able to dissolve different kinds of lithium salts and provide mechanical strength to the electrolyte membrane. However, PEO-based polymer electrolytes exhibit low ionic conductivity (10^{-6}-10^{-5} S/cm at room temperature) due to the high crystallinity of the polymers.[17,18] In order to improve the ionic conductivity, organic liquid plasticizers such as dimethyl carbonate (DMC), 1,2-dioxolane, propylene carbonate (PC) and ethylene carbonate (EC) were often added to PEO to form a gel polymer electrolyte (GPE) to reduce its crystallinity.[19–22] However, these liquid organic molecules also significantly reduce the mechanical strength of electrolyte composites. To improve the mechanic strength of polymer electrolyte, solid-state plastic crystal materials were introduced, which resulted in free-standing electrolyte membranes with good ionic conductivity.[23–26] Unfortunately, most solid-state plastic crystal materials exhibit low melting points and low thermal stability, presenting potential risks when battery operating temperatures are increased.[27–29] To address this issue, room temperature ionic liquids (RTIL) are a good option. RTILs usually exhibit high thermal stability, wide electrochemical window, non-flammability, ultralow-volatility and low toxicity.[30–33] In addition, RTIL can improve the Li^+ diffusion and promote the contribution of Li^+ ions transport to the measured collective ionic conductivity.[34] These unique properties render RTILs potential plasticizers in polymer electrolyte.

In this work, we report a RTIL-based polymer electrolyte consisting of lithium bis(trifluoromethanesulphonyl)imide salt (LiTFSI), lithium bis(oxalate)borate (LiBOB), RTIL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMPy][TFSI]) and crosslinked poly(ethylene glycol) diacrylate (PEGDA). [BMPy][TFSI] has been reported to have high ionic conductivity (3.93 mS/cm) at room temperature.[35,36] By integrating the RTIL with a polymer matrix, a free-standing RTIL-based polymer electrolyte membrane was prepared through an efficient photopolymerization method. The composition of the RTIL-based PE was optimized based on the ionic conductivity and the electrochemical stability measurements. Electrochemical and thermal characterizations were then carried out at to investigate the high temperature stability of RTIL-based polymer electrolyte (RTIL-PE). Further electrochemical performance evaluation of $LiFePO_4$ (LFP)|RTIL-PE|Li batteries demonstrated that RTIL-PE exhibited excellent high-temperature electrochemical stability in long cycle tests.

Experiments and methods

Materials

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMPy][TFSI], IoLiTec), poly(ethylene glycol) diacrylate (PEGDA, Sigma Aldrich, 99%) with molecular weight of 700 g/mol, and photoinitiator *bis*(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Irgacure® 819, Sigma Aldrich, 97%), lithium bis(trifluoromethanesulphonyl)imide (LiTFSI, Matrix Scientific). Lithium bis(oxalate)borate (LiBOB, Sigma Aldrich) were purchased without further purification. Lithium iron phosphate ($LiFePO_4$[LFP], MTI Corp.), carbon black (Timcal Super P, MTI Corp.) and poly (vinylidene fluoride) (HSV900 PVDF, Arkema, >99.5%) were placed in the vacuum oven at 80 °C overnight before use. Battery fabrication components: aluminum current collector (MTI Corp.), anhydrous 1-methyl-2-pyrrolidone (NMP, Alfa Aesar, 99%), round punched lithium metal pieces (Li, MTI Corp.) were used as purchased.

Polymer Electrolyte membrane preparation

The membrane of RTIL-based polymer electrolyte was prepared by polymer precursor-casting followed with a photopolymerization process in the Ar-filled glovebox. First, the polymer precursor was prepared by blending PEGDA, [BMPy][TFSI] with LiTFSI with a vortex mixer (VWR International) for at least 10 min until the homogeneous solution was obtained. LiBOB was then added into the polymer precursor and the electrolyte was blended for additional 5 min. Then, 1 wt% Irgacure® 819 photoinitiator (regarding to the mass of PEGDA) was added into the precursor followed by stirring for 5 min. Finally, the as-prepared precursor was poured in a desired size stainless-steel mold and photopolymerized via UV irradiation (350 nm with intensity of 0.02 mW/cm^2, 25W Mineralight®, UVP LLC) for about 3 min. The transparent, free-standing polymer electrolyte membrane was obtained by removing the electrolyte film from the mold.

Thermal properties characterization

Thermal gravimetric analysis (TGA) was obtained using a Q50 analyzer (TA Instruments Inc.). The experiment was carried out under N_2 atmosphere from room temperature to 600 ^oC at a scan rate of 10 $^oC/min$, which gave an indication of mass loss as well as thermal degradation on heating. To measure glass transition temperature and crystallinity of the polymer electrolyte, the differential scanning calorimetry (DSC, TA Q200, TA Instruments Inc.) was conducted. The measurement was performed under N_2 atmosphere from -60 ^oC to 80 ^oC at a constant cooling/heating rate of 5 $^oC/min$.

Electrochemical properties characterization

Ionic conductivity of the polymer electrolyte was tested by using the following blocking cell configuration: stainless steel (SS)|RTIL-PE|SS. In this measurement, electrochemical impedance spectroscopy (EIS) test was conducted by applying a perturbation potential of 5 mV AC signal of frequency range 1 Hz – 100 KHz. To explore the ionic conductivity at different temperatures, the blocking cells were placed in an isothermal chamber, connected to a temperature controller (Omron E5AK). The measurement was performed in the temperature range from -20 ^{o}C to 100 ^{o}C, with the system thermally equilibrated at each selected temperature for at least 30 min. Linear sweep voltammetry (LSV) was conducted to investigate the electrochemical stability limit of the polymer electrolyte membrane, by using the electrochemical workstation (CHI608E Electrochemical Analyzer, CH Instruments) at room temperature and 50 ^{o}C, with SS|RTIL-PE|Li cell configuration. In the LSV test, the potential range was 0 - 6 V (*vs*. Li^+/Li) with a scan rate of 0.5 mV/s. For further electrochemical stability characterization, the cyclic voltammetry (CV) measurements were conducted, by utilizing the same blocking cell configuration as the LSV. The CV was performed at a scan rate of 5 mV/s from open circuit potential (OCP) to 5 V (anodic limit) and -0.5 V (cathodic limit) *vs*. Li^+/Li. The compatibility of polymer electrolyte with lithium metal was investigated by "plating/stripping" test. In this experiment, symmetric cells with the Li|RTIL-PE|Li configuration was galvanostatically cycled (1.5 hrs for charge and discharge, respectively) at a current density of 0.1 mA/cm^2 in an isothermal chamber (50 ^{o}C). The thickness of polymer electrolyte membranes for plating/stripping experiment was 250 μm. The deterioration of the polymer electrolyte membrane was determined by sudden drop or irregular time dependence curve shape of the potential vs. time curve.

Lithium-ion battery fabrication

The LFP cathode was prepared by casting a slurry with a composition of the active electrode materials/super P/PVDF in weight ratios of 80/10/10 in the presence of NMP onto Al foil using a doctor blade. The slurry was prepared by grinding the mixture with a ball milling machine (MTI Corp.). The casted LFP electrode was dried in an oven at 80 ^{o}C overnight. The active material mass loading of the LFP electrode was controlled at around ~1.5 mg/cm^2. All cells were assembled in an oxygen-free and humidity-free Ar-filled glovebox. The LFP electrodes were pre-soaked into initiator-free electrolyte precursor for overnight. The soaked electrodes were placed in a stain steel well mold (diameter = 19.05 mm and height = 500 μm). The mold was subsequently filled with electrolyte precursors (with photoinitiator), which were further photo-crosslinked via UV exposure to obtained the free-standing polymer composite and cathode assembly. Metallic Li was used as the counter electrode and was laminated with the composite cathode to build up 2032 coin-type cells (LFP|RTIL-PE|Li).

Battery Testing

The cycling performance of the LFP|RTIL-PE|Li cells was evaluated by galvanostatic charge/discharge method using the 8 Channel Battery Analyzer (BST-8A, 5V, 1 mA, MTI Corp.) in an isothermal chamber (50 ^{o}C). The first five cycles were tested in a potential range between 2.5 and 3.7 V (*vs*. Li^+/Li) at 0.05 C (1C=170 mAh/g) and the following cycles were conducted with a potential window of 2.5 to 3.9 V (*vs*. Li^+/Li) at the designed current density.

Results and discussion

For a ternary polymer electrolyte system, the ratio between crosslinked PEGDA:RTIL ([BMPy][TFSI]):Lithium Salt is determined by several key factors: (1) acceptable mechanical property for polymer electrolyte to remain free-standing state; (2) ionic conductivity and (3) broad electrochemical window. In order to guarantee the film-forming ability, the weight percentage of PEGDA needs to be at least 20 % regarding to the total mass of polymer electrolyte, while the weight percentage of RTIL ([BMPy][TFSI]) should be less than 60 % since too much IL would adversely affect the physical strength of the composite.[26] Figure 1a shows a transparent and self-standing RTIL/PEGDA/LiTFSI membrane. In this ternary polymer electrolyte system, the ionic liquid component acts as the plasticizer that decreases the crystallinity of the polymer and promotes the Li^+ ion conduction.[37] A possible ionic transport mechanism in the polymer electrolyte system is proposed and illustrated in Figure 1b. The bulky $[BMPy]^+$ cations are trapped in the PEGDA matrix due to strong ion-dipole interaction, which decreases the attraction forces between polymer chains and reduces the crystallinity. As a results, the amorphous region in the polymer matrix increases, which will improve the intra- and interchain hoping of Li^+ ions, leading to the enhanced ionic conductivity.[38] Polymer electrolyte membranes with five different ratios were prepared to investigate the composition-property relationship of the composite electrolyte. The ionic conductivity values of polymer electrolytes were measured between -20 ^oC and 100 ^oC by using electrochemical impedance spectroscopy (EIS) analysis. Figure 1c exhibits average ionic conductivity of each polymer electrolyte at different temperatures, revealing that the ionic conductivity is significantly affected by the ratio of the IL. Except the electrolyte with mass ratio of 35:35:30 (PEGDA:RTIL:LiTFSI), other electrolytes exhibited good ionic conductivity over 0.1 mS/cm at 30 °C. Among all the tested electrolyte, the electrolyte with ratio of 25:40:35 has the highest ionic conductivity (3.4 mS/cm) at 80 °C. Further comparison of electrochemical stability between these electrolytes was evaluated by Linear Sweep Voltammetry (LSV) measurement, showing in Figure 1d. The mixture of RTIL and LiTFSI (1:1 in mass ratio) was also measured as the reference in LSV tests, shown as the purple curve in the Figure 1d. From LSV results, it is clear that the electrolyte with ratio of 30:40:30 (PEGDA:RTIL:LiTFSI) exhibited the best electrochemical stability up to 5.5 V (*vs*. Li^+/Li). Other electrolytes exhibited electrochemical stability up to 5 V (*vs*. Li^+/Li). To further investigate the electrochemical stability of electrolyte films at high voltage, the electrolyte samples (30:40:30 and 20:60:20) was treated at 5.2 V constant voltage for 2 hours using the same cell structure as the LSV test. A smoother current-time profile is observed for the electrolyte with ratio of 30:40:30 (Figure S1 in supporting information). The stability of electrolyte may be affected by the association status of three components: lithium salt, polymer and RTIL. This salt-mediator association was also observed in high-concentration electrolytes, showing improved electrochemical stability. Considering both ionic conductivity and electrochemical stability, the electrolyte with ratio of 30:40:30 was chosen for the further study.

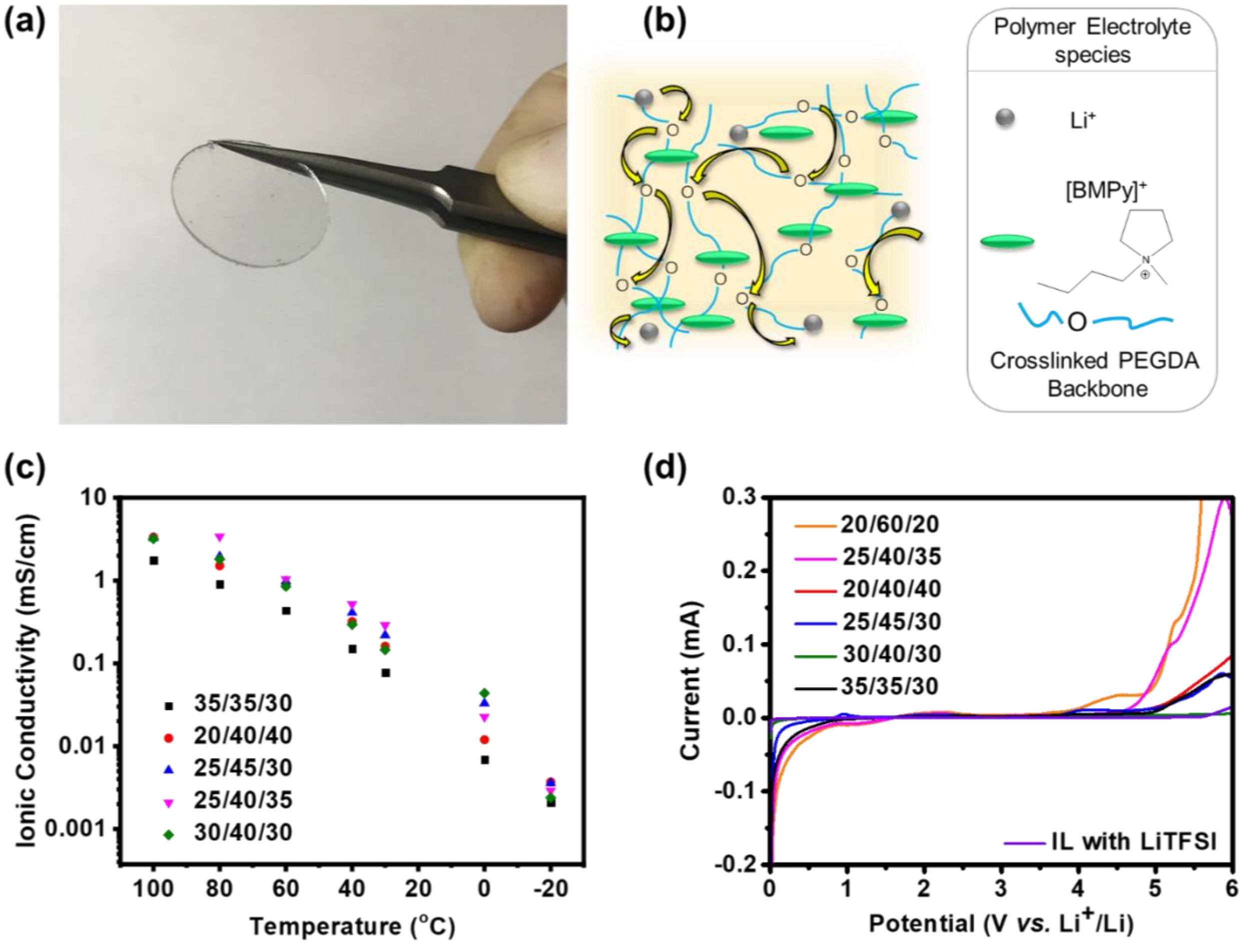

Fig. 1 (**a**) The photo of the free-standing RTIL-based polymer electrolyte membrane. (**b**) Schematic illustration of Li+ ions transport mechanism in the RTIL-based polymer electrolyte. (**c**) The temperature-dependent ionic conductivity of the RTIL-based polymer electrolyte with different ratios of components (ratio showed as crosslinked PEGDA:RTIL:LiTFSI). (**d**) LSV of the RTIL-based polymer electrolyte with different ratios of components

The thermal properties of optimized polymer electrolyte (PEGDA:RTIL:LiTFSI = 30:40:30) were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The decomposition behavior of polymer electrolyte is shown in Figure 2a. From the weight loss curve and dW/dT peak, the first degradation stage is observed around 270 ^oC, as shown by the dashed line in the figure. This degradation can be attributed to the decomposition/evaporation of RTIL. The second degradation is between 390 ^oC and 440 ^oC, which belongs to the decomposition of cross-linked PEGDA. The final degradation stage is around 470 ^oC, where lithium salts degrade. The TGA results showed the high temperature thermal stability of RTIL-PE. DSC measurement was conducted to determine the crystallinity and amorphousness nature. As shown in Figure 2b, there is one peak observed at -8 ^oC in the heating process, which could be identified as the melting temperature (Tm) of the ionic liquid ([BMPy][TFSI]). No other peak is found in the continuous DSC scan, indicating an amorphous state of composite electrolyte above -8 ^oC. The results suggest that the ionic liquid ([BMPy][TFSI]) can effectively plasticize the crosslinked PEGDA, which will lead to the improvement in the chain mobility and the ionic conductivity of the electrolyte.[39]

LiBOB was used as an additive salt based on the recent report in liquid electrolytes[40,41] and our previous work of polymer electrolyte.[26,42] Therefore, LiBOB was added as co-salt in this work to improve electrochemical stability of the polymer electrolyte at elevated temperatures. The solubility of LiBOB in the pre-crosslinked polymer electrolyte system is up to about 1%wt of the total polymer electrolyte mass. Thus, a mixed salt with a molar ratio of LiTFSI:LiBOB equal to 1:0.0488 was used in the following tests, while keeping the polymer electrolyte ratio (PEGDA:RTIL:Lithium salt = 30:40:30) as a constant. It is worth to note that the mixed salt-based electrolytes also exhibited a higher ionic conductivity as shown in Figure 2c. The ionic conductities of the electrolytes are 0.48 mS/cm, 1.57 mS/cm and 2.9 mS/cm at 30 ^oC, 50 ^oC and 80 ^oC, respectively. The electrochemical working potential range of the polymer electrolyte with mixed salts was investigated by LSV measurement at 30 °C and 50 °C (Figure 2d). The electrolyte showed similar stability as the single salt electrolyte at room temperature. (up to 5.5 V (*vs*. Li^+/Li) at 30 °C). Even at 50 °C, the increase of oxidative current starts from 5.0 V (*vs*. Li^+/Li), indicating a high electrochemical stability at higher temperatures. Further cyclic voltammetry (CV) evaluation was carried out to study the oxidation and the reduction of electrolyte within the potential range of -0.5-5 V (*vs*. Li^+/Li) at 50 °C. As shown in the Figure 2e, the symmetric peaks between -0.5-0.5 V (*vs*. Li^+/Li) are ascribed to the lithium plating and stripping processes.[43] At high potential range (2.5-5.0 V *vs*. Li^+/Li), the CV curve of the electrolyte remained flat, suggesting that the electrolyte is resistant to oxidative side reactions. For small current responds between 0.5-2 V (*vs*. Li^+/Li), they may be related to the reduction of impurities (i.e. H_2O) in the RTIL-based electrolyte,[44] which stabilized after a few initial cycles. From both LSV and CV performance, it could be concluded that the incorporation of ionic liquid [BMPy][TFSI] and LiBOB enhanced the electrochemical stability of PE at high temperature range.

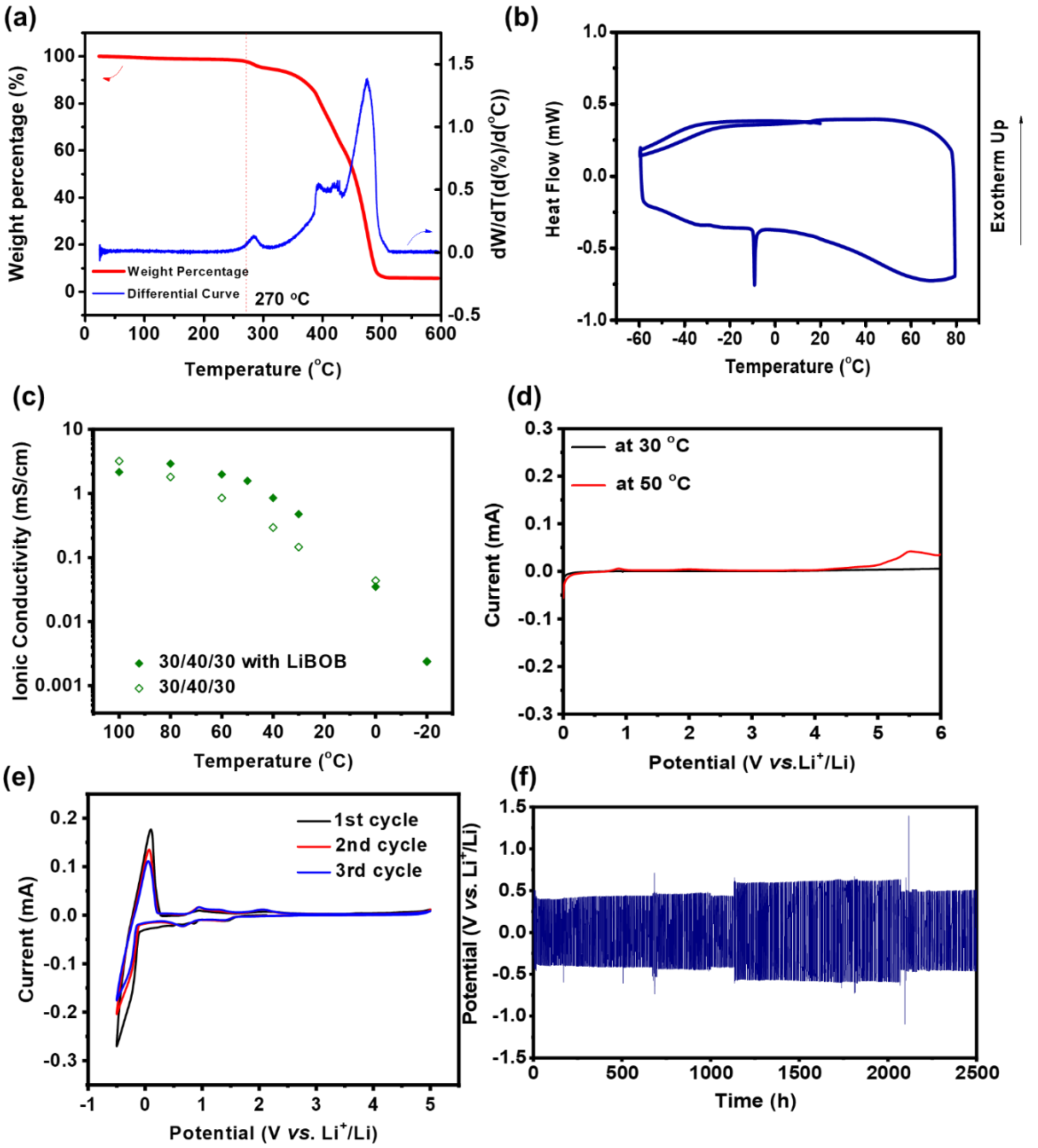

Fig. 2 (**a**) The TG/DTG thermogram of the polymer electrolyte (PEGDA:RTIL:Lithium salt = 30:40:30). (**b**) The DSC thermogram of the polymer electrolyte film (PEGDA:RTIL:Lithium salt = 30:40:30). (**c**)

Comparison of ionic conductivities of RTIL-PE with/without LiBOB salt. (**d**) LSV of the polymer electrolyte (PEGDA:RTIL:Lithium salt = 30:40:30) at 30 °C and 50 °C. (**e**) CV of the polymer electrolyte (PEGDA:RTIL:Lithium salt = 30:40:30) at 50 °C. (**f**) Lithium plating/stripping test conducted at a current density of 0.1 mA/cm^2 at 50 °C. The charge and discharge time were fixed at 1.5 hrs.

The electrochemical compatibility of the RTIL-based polymer electrolyte membrane against lithium dendrite formation was further evaluated by the plating/stripping test, using a symmetric lithium cell with the configuration of Li|RTIL-PE|Li. The symmetric cell was periodically charged and discharged with 1.5 hrs, with a specific current density of 0.1 mA/cm^2 under 50 °C. In Figure 2f, a stable potential file could be observed, revealing a uniform lithium deposition process. The plating/stripping process was stable up to 2500 hrs, demonstrating excellent high temperature electrochemical stability and durability of the RTIL-PE. During the cycling, a few fluctuations of potential were also observed, which are caused by the connection changes or environmental temperature variations.

In order to determine electrochemical property of the polymer electrolyte membrane in lithium ion batteries, LFP|RTIL-PE|Li half cells were fabricated. In these cells, metallic Li was used as the anode while the $LiFePO_4$ (LFP) was used as the cathode. The details of cell fabrication and testing procedure were described in the supporting information. The rate performance test of the LFP|RTIL-PE|Li half cells were conducted at 50 °C within the chemical window of 2.5-3.9 V (*vs.* Li^+/Li) and illustrated in Figure. 3a. The cells exhibited reversible specific capacities of ~137 mAh/g, ~118 mAh/g, ~96 mAh/g, ~78 mAh/g, 60 ~mAh/g and 15 ~mAh/g at corresponding current densities at 0.2C, 0.4C, 0.6C, 0.8C, 1C and 2C. After the current was returned to 0.2C, the specific capacity after rate test was ~135 mAh/g. Figure 3b shows the corresponding charge/discharge curves during the rate tests. The polarization effect was obvious when compared to conventional LFP liquid cells, which could be explained by relatively thick PE membranes (~500 µm) used in this work. Further, the long cycle galvanostatic charge/discharge experiments were conducted at 0.2C and 0.5C (under 50 ^{o}C) to investigate the cycle stability of the cells. In Figure 3c, the LFP/RTIL-PE/Li cell gave an initial specific capacity of ~127 mAh/g with the current density at 0.2 C. The average coulombic efficiency was over 99.4% with a ~ 52.2% capacity retention after 500 cycles. Particularly, there was no obvious deterioration in the first 170 cycles. For the cells tested under 0.5 C (Figure 3d), the reversible capacity was ~115 mAh/g at the beginning of the test. After 160 cycles, a capacity retention of ~88.5% was recorded. The average coulombic efficiency was over 99.7%. These excellent cycling performances of LFP/RTIL-PE/Li cells validated the outstanding high temperature electrochemical stability of the RTIL-based polymer electrolyte.

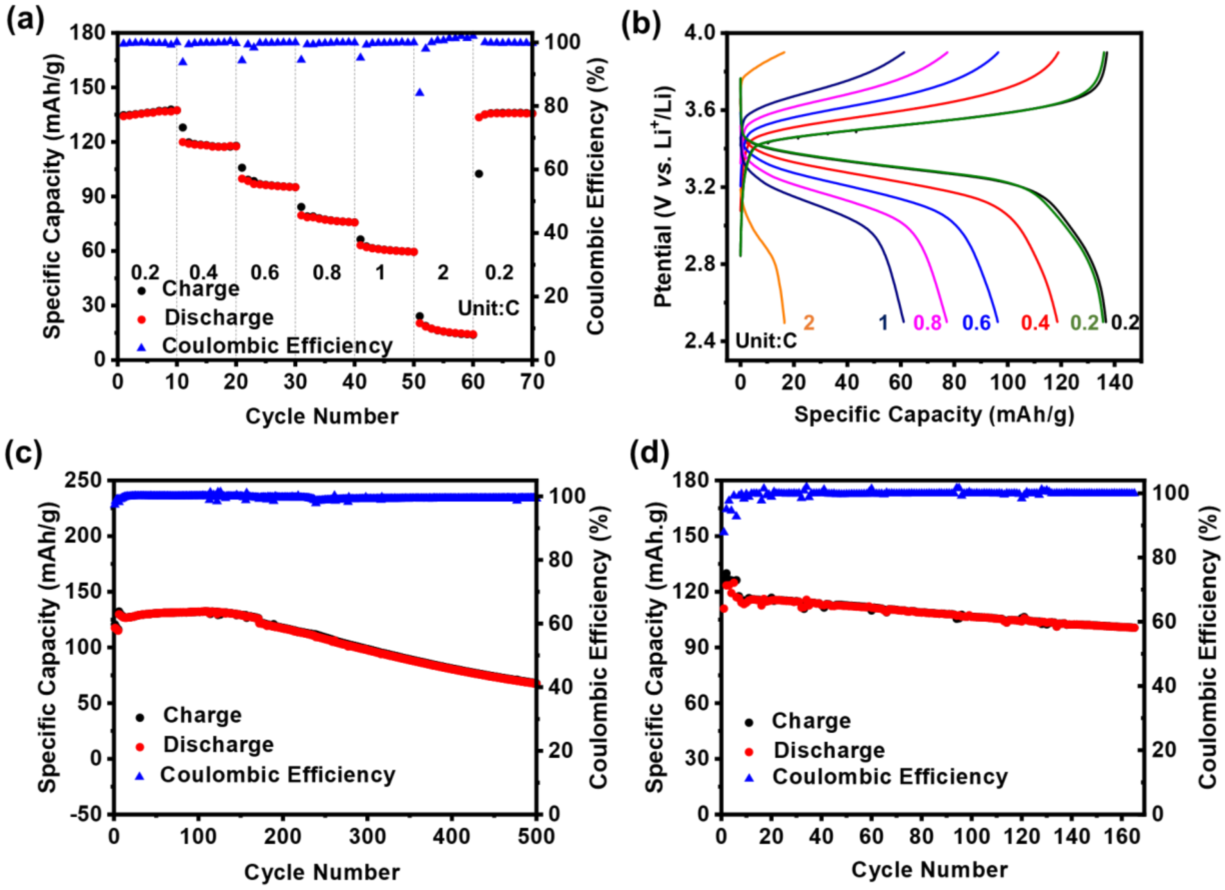

Fig. 3 (**a**) The rate performance of RTIL-PE (PEGDA:RTIL:Lithium salt = 30:40:30, with 1 % LiBOB) based LIB at 50 ºC from 0.2 C to 2 C as indicated. (**b**) The corresponding charge/discharge profiles of LIBs with RTIL-PE at different rates. (**c**) The long cycle performance of LIB at 0.2 C under 50 ºC. The cycles were operated from 2.5 V to 3.9 V at 0.1 C. (**d**) The long cycle performance of LIB at 0.5 C under 50 ºC. The cycles were operated from 2.5 V to 3.9 V at 0.5 C.

Conclusions

In summary, a free-standing RTIL-based polymer electrolyte with an optimized composition (PEGDA:RTIL:Lithium salt = 30:40:30, with 1 % LiBOB) has been successfully demonstrated in this work. Plasticizing with ionic liquid ([BMPy][TFSI]) reduces the overall proportion of crystalline PEG in the polymer electrolyte membrane, promotes the formation of amorphous region and increases ionic conductivity. High ionic conductivity up to 3.4 mS/cm at 80 ^{o}C was observed. RTIL-based polymer electrolyte also exhibits good thermal stability (~ 270 ^{o}C) and a wide electrochemical stability window (5.0 V *vs*. Li^+/Li at 50 ^{o}C). In the plating/stripping test at 50 ^{o}C, the electrolyte membrane remained stable for more than 2500 hrs at a current density of 0.1 mA/cm^2, indicating its outstanding high-temperature electrochemical stability. LFP|RTIL-PE|Li half cells were fabricated and delivered a reversible specific capacity of 137 mAh/g at 0.2C. For the long cycle performance at 0.2 C under 50 ^{o}C, the RTIL-PE-based cell was able to exhibit an average coulombic efficiency was over 99.4%, with a capacity retention rate of approximately 91.1 % at its 100th cycle and around 52.2% at its 500th cycle. The excellent high-temperature electrochemical stability and cell performance of RTIL-PE render it potential safe electrolyte for future advanced electrochemical energy storage devices.

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Author Contributions All authors have given approval to the final version of the manuscript.

Conflict of interest

The authors declare no competing financial interest(s)

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References

1. Scrosati B, Hassoun J, Sun YK (2011) Lithium-ion batteries. A look into the future. Energy Environ Sci 4: 3287–3295. https://doi.org/10.1039/C1EE01388B
2. Enany E, Roberts M, Johns P, Owen J, Brandell D, Edstrom K, El Enany G, Guery C, Golodnitsky D, Lacey M, Lecoeur C, Mazor H, Peled E, Perre E, Manikoth Shaijumon cd M, Simon P, Taberna P-L (2011) Open Archive Toulouse Archive Ouverte (OATAO) 3D lithium ion batteries-from fundamentals to fabrication. J Mater Chem 21: 9876–9890. https://doi.org/10.1039/c0jm04396f
3. Choi NS, Chen Z, Freunberger SA, Ji X, Sun YK, Amine K, Yushin G, Nazar LF, Cho J, Bruce PG (2012) Challenges Facing Lithium Batteries and Electrical Double-Layer Capacitors. Angew Chemie Int Ed 51: 9994–10024. https://doi.org/10.1002/ANIE.201201429
4. PbSO P, Koh N, - -e, Li Si V, LiX S (2008) Building better batteries. Nat 2008 4517179 451: 652–657. https://doi.org/10.1038/451652a
5. Wu F, Maier J, Yu Y (2020) Guidelines and trends for next-generation rechargeable lithium and lithium-ion batteries. Chem Soc Rev 49: 1569–1614. https://doi.org/10.1039/C7CS00863E
6. Cao C, Li Z Bin, Wang XL, Zhao XB, Han WQ (2014) Recent advances in inorganic solid electrolytes for lithium batteries. Front Energy Res 2: 25.

https://doi.org/10.3389/FENRG.2014.00025/BIBTEX

7. Liu S, Imanishi N, Zhang T, Hirano A, Takeda Y, Yamamoto O, Yang J (2010) Effect of nano-silica filler in polymer electrolyte on Li dendrite formation in Li/poly(ethylene oxide)–Li(CF3SO2)2N/Li. J Power Sources 195: 6847–6853. https://doi.org/10.1016/J.JPOWSOUR.2010.04.027

8. Oh P, Lee H, Park S, Cha H, Kim J, Cho J (2020) Improvements to the Overpotential of All-Solid-State Lithium-Ion Batteries during the Past Ten Years. Adv Energy Mater 10: 2000904. https://doi.org/10.1002/AENM.202000904

9. Zhou W, Zhang M, Kong X, Huang W, Zhang Q (2021) Recent Advance in Ionic-Liquid-Based Electrolytes for Rechargeable Metal-Ion Batteries. Adv Sci 8: 2004490. https://doi.org/10.1002/ADVS.202004490

10. Nagata H, Akimoto J (2021) All-oxide solid-state lithium-ion battery employing 50Li2SO4–50Li2CO3 glass electrolyte. J Power Sources 491: 229620. https://doi.org/10.1016/J.JPOWSOUR.2021.229620

11. Ping W, Wang C, Wang R, Dong Q, Lin Z, Brozena AH, Dai J, Luo J, Hu L (2020) Printable, high-performance solid-state electrolyte films. Sci Adv 6: 8641–8659. https://doi.org/10.1126/SCIADV.ABC8641/SUPPL_FILE/ABC8641_SM.PDF

12. Xiao Y, Turcheniuk K, Narla A, Song AY, Ren X, Magasinski A, Jain A, Huang S, Lee H, Yushin G (2021) Electrolyte melt infiltration for scalable manufacturing of inorganic all-

solid-state lithium-ion batteries. Nat Mater 2021 207 20: 984–990. https://doi.org/10.1038/s41563-021-00943-2

13. Zhu J, Zhang Z, Zhao S, Westover AS, Belharouak I, Cao PF (2021) Single-Ion Conducting Polymer Electrolytes for Solid-State Lithium–Metal Batteries: Design, Performance, and Challenges. Adv Energy Mater 11: 2003836. https://doi.org/10.1002/AENM.202003836

14. Wright P V (1975) Electrical conductivity in ionic complexes of poly (ethylene oxide). Polym Int 7: 319–327

15. Rietman EA, Kaplan ML, Cava RJ (1985) Lithium ion-poly (ethylene oxide) complexes. I. Effect of anion on conductivity. Solid State Ionics 17: 67–73

16. Gorecki W, Jeannin M, Belorizky E, Roux C, Armand M (1995) Physical properties of solid polymer electrolyte PEO (LiTFSI) complexes. J Phys Condens Matter 7: 6823

17. Buriez O, Han YB, Hou J, Kerr JB, Qiao J, Sloop SE, Tian M, Wang S (2000) Performance limitations of polymer electrolytes based on ethylene oxide polymers. J Power Sources 89: 149–155

18. Wright P V (2002) Developments in polymer electrolytes for lithium batteries. Mrs Bull 27: 597–602

19. Kim JR, Choi SW, Jo SM, Lee WS, Kim BC (2004) Electrospun PVdF-based fibrous polymer electrolytes for lithium ion polymer batteries. Electrochim Acta 50: 69–75. https://doi.org/10.1016/j.electacta.2004.07.014

20. Das S, Ghosh A (2015) Effect of plasticizers on ionic conductivity and dielectric relaxation of PEO-LiClO4 polymer electrolyte. Electrochim Acta 171: 59–65

21. Song JY, Wang YY, Wan CC (1999) Review of gel-type polymer electrolytes for lithium-ion batteries. J Power Sources 77: 183–197

22. Pitawala H, Dissanayake M, Seneviratne VA, Mellander B-E, Albinson I (2008) Effect of plasticizers (EC or PC) on the ionic conductivity and thermal properties of the (PEO) 9 LiTf: Al 2 O 3 nanocomposite polymer electrolyte system. J Solid State Electrochem 12: 783–789

23. He R, Echeverri M, Ward D, Zhu Y, Kyu T (2016) Highly conductive solvent-free polymer electrolyte membrane for lithium-ion batteries: Effect of prepolymer molecular weight. J Memb Sci 498: 208–217. https://doi.org/10.1016/J.MEMSCI.2015.10.008

24. Li S, Chen YM, Liang W, Shao Y, Liu K, Nikolov Z, Zhu Y (2018) A Superionic Conductive, Electrochemically Stable Dual-Salt Polymer Electrolyte. Joule 2: 1838–1856. https://doi.org/10.1016/J.JOULE.2018.06.008

25. Ha HJ, Kil EH, Kwon YH, Kim JY, Lee CK, Lee SY (2012) UV-curable semi-interpenetrating polymer network-integrated, highly bendable plastic crystal composite electrolytes for shape-conformable all-solid-state lithium ion batteries. Energy Environ Sci 5: 6491–6499. https://doi.org/10.1039/C2EE03025J

26. Liang W, Shao Y, Chen Y-M, Zhu Y (2018) A 4 V Cathode Compatible, Superionic

Conductive Solid Polymer Electrolyte for Solid Lithium Metal Batteries with Long Cycle Life. ACS Appl Energy Mater 1: 6064–6071

27. Tan J, Ao X, Dai A, Yuan Y, Zhuo H, Lu H, Zhuang L, Ke Y, Su C, Peng X, Tian B, Lu J (2020) Polycation ionic liquid tailored PEO-based solid polymer electrolytes for high temperature lithium metal batteries. Energy Storage Mater 33: 173–180. https://doi.org/10.1016/J.ENSM.2020.08.009

28. Li R, Wu D, Yu L, Mei Y, Wang L, Li H, Hu X (2019) Unitized Configuration Design of Thermally Stable Composite Polymer Electrolyte for Lithium Batteries Capable of Working Over a Wide Range of Temperatures. Adv Eng Mater 21: 1900055. https://doi.org/10.1002/ADEM.201900055

29. Tao T, Lu S, Chen Y, Lu SG, Tao T, Chen Y (2018) A Review of Advanced Flexible Lithium-Ion Batteries. Adv Mater Technol 3: 1700375. https://doi.org/10.1002/ADMT.201700375

30. Zhang F, Sun Y, Wang Z, Fu D, Li J, Hu J, Xu J, Wu X (2020) Highly Conductive Polymeric Ionic Liquid Electrolytes for Ambient-Temperature Solid-State Lithium Batteries. ACS Appl Mater Interfaces 12: 23774–23780. https://doi.org/10.1021/ACSAMI.9B22945/ASSET/IMAGES/LARGE/AM9B22945_0005.JPEG

31. Costa LT, Sun B, Jeschull F, Brandell D (2015) Polymer-ionic liquid ternary systems for Li-battery electrolytes: Molecular dynamics studies of LiTFSI in a EMIm-TFSI and PEO blend. J Chem Phys 143: 024904. https://doi.org/10.1063/1.4926470

32. Zhou T, an Zhao Y, ang Wook Choi J, Coskun A (2021) Ionic Liquid Functionalized Gel Polymer Electrolytes for Stable Lithium Metal Batteries. Angew Chemie 133: 22973–22978. https://doi.org/10.1002/ANGE.202106237

33. Li R, Fang Z, Wang C, Zhu X, Fu X, Fu J, Yan W, Yang Y (2022) Six-armed and dicationic polymeric ionic liquid for highly stretchable, nonflammable and notch-insensitive intrinsic self-healing solid-state polymer electrolyte for flexible and safe lithium batteries. Chem Eng J 430: 132706. https://doi.org/10.1016/J.CEJ.2021.132706

34. Ye Y-S, Rick J, Hwang B-J (2013) Ionic liquid polymer electrolytes. J Mater Chem A 1: 2719–2743

35. Safna SH, Thayyil MS, Deshpande SK, T.V J, Kolte J (2017) Development of ion conducting ionic liquid-based gel polymer electrolyte membrane PMMA/BMPyr.TFSI - With improved electrical, optical, thermal and structural properties. Solid State Ionics 310: 166–175. https://doi.org/10.1016/J.SSI.2017.08.012

36. Sánchez-Ramírez N, Assresahegn BD, Bélanger D, Torresi RM (2017) A Comparison among Viscosity, Density, Conductivity, and Electrochemical Windows of N-n-Butyl-N-methylpyrrolidinium and Triethyl-n-pentylphosphonium Bis(fluorosulfonyl imide) Ionic Liquids and Their Analogues Containing Bis(trifluoromethylsulfonyl) Imide Anion. J Chem Eng Data 62: 3437–3444. https://doi.org/10.1021/ACS.JCED.7B00458/ASSET/IMAGES/LARGE/JE-2017-00458F_0006.JPEG

37. Polu AR, Rhee H-W (2017) Ionic liquid doped PEO-based solid polymer electrolytes for lithium-ion polymer batteries. Int J Hydrogen Energy 42: 7212–7219

38. Reddy MJ, Chu PP (2002) Optical microscopy and conductivity of poly (ethylene oxide) complexed with KI salt. Electrochim Acta 47: 1189–1196

39. Wu J, Xia G, Li S, Wang L, Ma J (2020) A Flexible and Self-Healable Gelled Polymer Electrolyte Based on a Dynamically Cross-Linked PVA Ionogel for High-Performance Supercapacitors. https://doi.org/10.1021/acs.iecr.0c04741

40. Nayak PK, Grinblat J, Levi M, Aurbach D (2015) Understanding the Effect of Lithium Bis(oxalato) Borate (LiBOB) on the Structural and Electrochemical Aging of Li and Mn Rich High Capacity Li1.2Ni0.16Mn0.56Co0.08O2 Cathodes. J Electrochem Soc 162: A596–A602. https://doi.org/10.1149/2.0251504jes

41. Zhang SS, Xu K, Jow TR (2006) LiBOB-based gel electrolyte Li-ion battery for high temperature operation. J Power Sources 154: 276–280

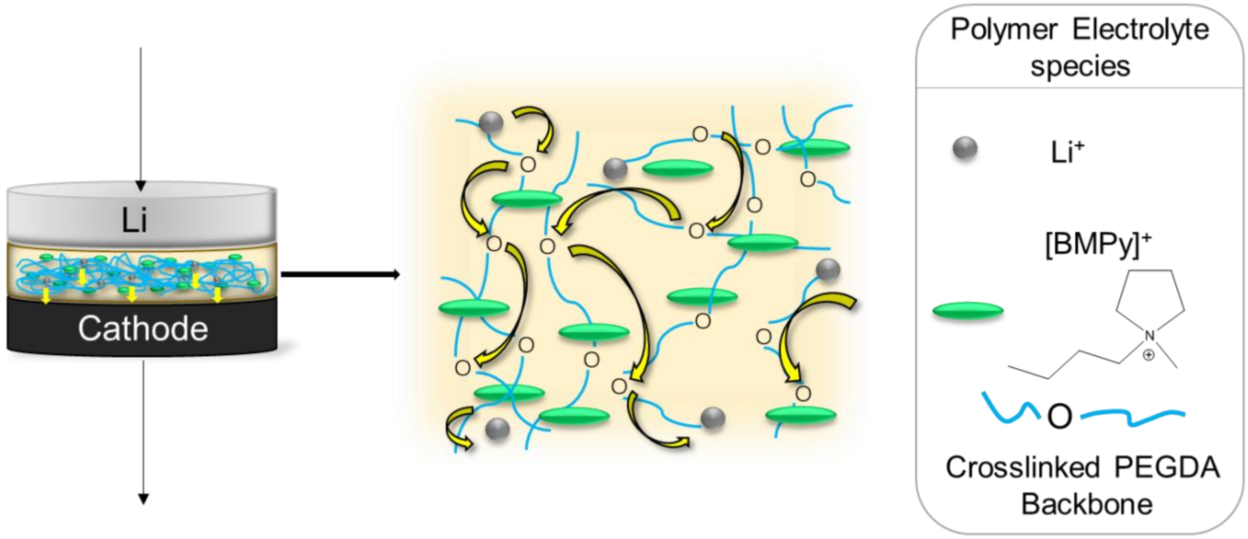
42. Li S, Chen Y-M, Liang W, Shao Y, Liu K, Nikolov Z, Zhu Y (2018) A Superionic Conductive, Electrochemically Stable Dual-Salt Polymer Electrolyte. Joule

43. Zhou W, Wang S, Li Y, Xin S, Manthiram A, Goodenough JB (2016) Plating a dendrite-free lithium anode with a polymer/ceramic/polymer sandwich electrolyte. J Am Chem Soc 138: 9385–9388

44. Lane GH (2012) Electrochemical reduction mechanisms and stabilities of some cation types

used in ionic liquids and other organic salts. Electrochim Acta 83: 513–528

TOC


Li
Cathode
O
Polymer Electrolyte species
Li+
[BMPy]+
N
⊕
O
Crosslinked PEGDA Backbone