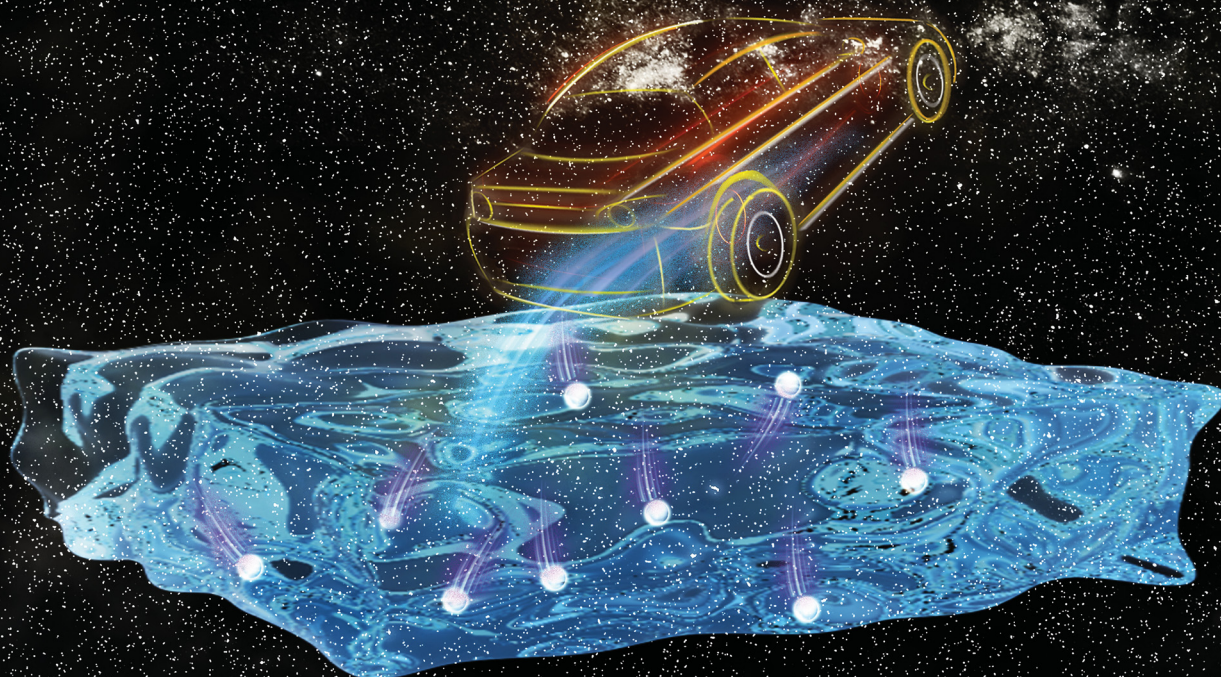


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Fiber-reinforced quasi-solid polymer electrolytes enabling
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enabling stable Li-metal batteries†Shilun Gao,[‡] Youjia Zhang,[‡] Mengxiang Ma,^a Zhenxi Li,^a Zongxue Sun,^b
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With high ionic conductivity and good contact/adhesion with electrodes, quasi-solid polymer electrolytes (QPEs) are considered as one of the most promising options to address the safety concerns of next-generation rechargeable batteries. A trade-off exists between mechanical strength and ionic conductivity, e.g., a high electrolyte uptake ratio leads to high ionic conductivity while low mechanical strength, and *vice versa*. Constructing QPEs with integrated high ionic conductivity and mechanical robustness is crucial in promoting the practical use of safe and long-cycling lithium (Li)-metal batteries (LMBs). Herein, by integrating the poly(propylene) fiber (PPF) and a rationally designed polymer network, i.e., poly[poly(ethylene glycol) methyl ether methacrylate]-*r*-(2-ethylhexyl acrylate)-*r*-sodium (*p*-styrene sulfonate)-*r*-polyethylene glycol dimethacrylate] (PPES), a mechanically reinforced PPES@PPF film is obtained with a decent Young's modulus of ~190 MPa. This fiber reinforced QPE (rQPE) exhibits a high ionic conductivity of 1.1 mS cm⁻¹ at 60 °C. The resulting Li/rQPE/LiFePO₄ (LFP) cell shows excellent cycling stability with a capacity retention of 91% over 900 cycles. Moreover, a cell with ultra-thin QPE (tQPE, ~10 μm) and a high-voltage LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) cathode was also assembled, and delivers stable cycling performance over 300 cycles with a capacity retention of 80%. The current design of fiber-reinforced QPE not only surpasses the mechanical strength–ionic conductivity trade-off of QPEs, but also sheds light on the application of solid electrolytes for high-energy density LMBs.

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1. Introduction

With the ever-increasing demand for high-energy density energy storage devices including small portable electronics and large-scale energy storage devices, the state-of-the-art lithium ion batteries (LIBs) based on the graphite anode cannot meet future applications, triggering huge research attention in the exploration of alternative electrode candidates.^{1–5} Metallic Li with ultrahigh theoretical specific capacity (3860 mA h g⁻¹) and the lowest electrochemical potential (−3.040 V vs. standard hydrogen electrode) is regarded as an ideal anode material for high-energy density rechargeable batteries.^{6–10} Unfortunately, three drawbacks severely impede the application of liquid electrolytes in Li-metal batteries (LMBs): (1) Arising from the

non-uniform Li deposition, the uncontrollable growth of Li dendrites can even penetrate the separator, leading to short-circuits (or micro short-circuits) of the batteries.^{11,12} (2) Due to the high reactivity of metallic Li, the side reactions between the Li electrode and liquid electrolyte result in the formation of an intrinsic solid electrolyte interphase (SEI) layer, which is mechanically brittle and cannot accommodate the volume variation of the Li electrode.^{13–16} The repeated formation/destruction of this intrinsic SEI layer will continuously consume the electrolyte and Li electrode, rendering low coulombic efficiency (CE) and poor cycling stability. (3) The Li electrode in an organic liquid electrolyte also leads to serious safety issues, such as electrolyte leakage, gas formation and even explosion.^{17–20}

Solid electrolytes, including inorganic solid electrolytes and solid polymer electrolytes, have been considered as more promising candidates to inhibit the Li dendrite growth and address the safety issues of LMBs.^{21–25} Generally, an ideal solid electrolyte should possess high ionic conductivity, good mechanical strength, and an intimate electrode/electrolyte interface.^{26–28} Nevertheless, the low ionic conductivity (much lower than that of a liquid electrolyte) and poor electrode/electrolyte contact severely impede their practical applications.^{29,30} Comparatively, by eliminating the leaking risk of liquid electrolytes while retaining intimate interfacial contact, the quasi-solid polymer

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electrolyte (QPE) shows great advantages in high safety and low electrolyte/electrode interfacial resistance. Moreover, by bipolar stacking, the overall energy density can also be improved significantly.^{31–34} However, for a typical QPE, a trade-off exists between mechanical strength and ionic conductivity. For example, to ensure high ionic conductivity, the QPE normally needs to uptake enough liquid electrolyte, which dramatically weakens the mechanical strength. During the repeated charge/discharge process, the QPE with a low mechanical strength inevitably leads to short circuit. Although numerous strategies, including embedding the organic/inorganic fillers in the polymer matrix,^{21,35,36} chemically cross-linking the polymer to increase the dimensional stability,^{17,37} and reducing the amount of liquid electrolyte being doped, have been developed, an efficient strategy to surpass trade-off between the mechanical strength and ionic conductivity for QPE remains a thorny issue.

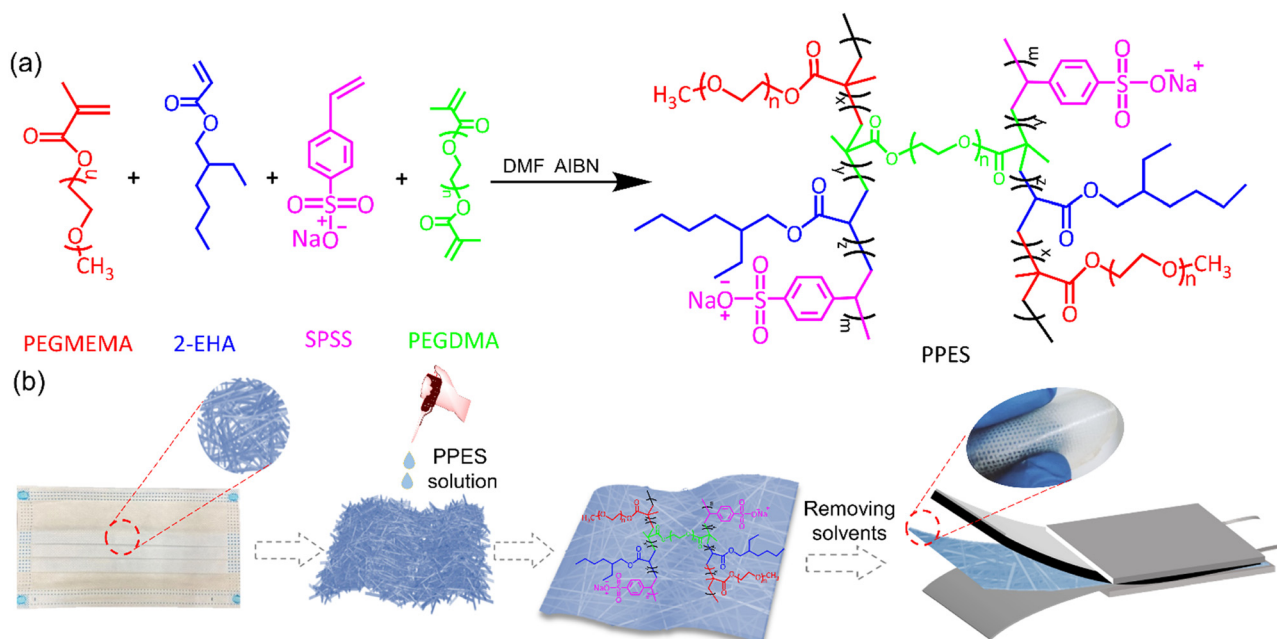
Herein, by incorporation of the poly(propylene) fiber (PPF) with a rationally designed elastic polymer network, *i.e.*, poly[poly(ethylene glycol) methyl ether methacrylate)-*r*-2-ethylhexyl acrylate-*r*-sodium (*p*-styrene sulfonate)-*r*-polyethylene glycol dimethacrylate]] (PPES, as shown in Scheme. 1a), a mechanically reinforced QPE (rQPE) is developed as shown in Scheme. 1b. The combination of flexibility, high ionic conductivity and high mechanical strength into a single polymer electrolyte enables efficient Li dendrite inhibition and significantly improved electrochemical performance. The assembled Li/rQPE/LiFePO₄ (LFP) cell exhibits stable cycling performance with a capacity retention of 91% over 900 cycles. Towards high-energy density LMBs, a full cell with commercial standard LFP (areal capacity of >2 mA h cm^{−2}) was also assembled, which shows stable cycling performance over 300 cycles with a capacity retention of 97%. Moreover, with ultra-thin QPE (tQPE, ~10 μm) and a high-voltage LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) cathode, the Li/tQPE/NMC811 cell still delivers stable

cycling performance over 300 cycles with a capacity retention of 80%. With such demonstration in surpassing the trade-off between ionic conductivity and mechanical strength, our demonstration will provide guidance on the design and utilization of QPEs towards safe and high-energy density batteries with a prolonged lifetime.

2. Results and discussion

2.1. Synthesis and characterization of PPES

PPES is chemically synthesized *via* the radical copolymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMEMA), 2-ethylhexyl acrylate (2-EHA) and sodium (*p*-styrene sulfonate) (SPSS) with poly(ethylene glycol)dimethacrylate (PEGDMA, 15 mol%) as a cross-linker as shown in Scheme. 1a. Generally, for the fabrication of QPEs, polymers endowed with high ionic conductivity and high mechanical strength are always preferred. In the current design, PEGMEMA with strong Li⁺/EO affinity is selected as the side chain of PPES to provide fast segmental dynamics and mechanical flexibility, leading to improved ionic conductivity. To improve the mechanical strength, SPSS monomer with a rigid molecular structure was also utilized for copolymerization followed by chemically cross-linking with PEGDMA to form a robust polymer network. To study the effect of crosslinking density, a series of polymers with different molar ratios of crosslinkers were synthesized and evaluated as shown in Fig. S1 (ESI[†]). The PPES with 5 mol% of PEGDMA is soft with low mechanical strength and can even be dissolved in an organic solvent. In contrast, with 25 mol% of the crosslinker, the polymer film becomes brittle and cannot form a free-standing film. Herein, PPES with 15 mol% of PEGDMA is selected in this study for further evaluation.



Scheme 1 (a) Synthesis scheme of PPES. (b) Schematic illustration of the fabrication process of rQPE.

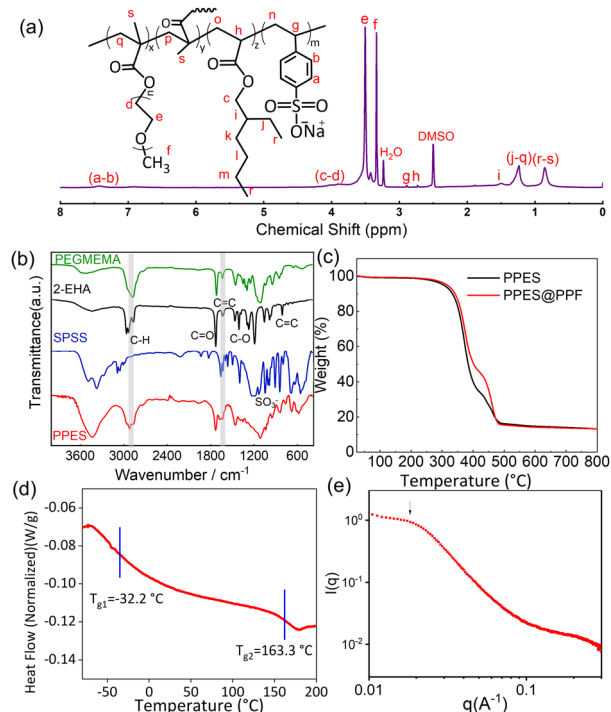


Fig. 1 Characterization studies of monomers and the as prepared polymer. (a) ^1H NMR spectra of the prepared PPES. (b) FT-IR spectra of PEGMEMA, SPSS, 2-EHA monomers and the resulting polymer network PPES. (c) The thermogravimetric analysis of PPES and PPES@PPF. (d) DSC curve of PPES. (e) SAXS spectrum of PPES.

The chemical structure of the as-prepared PPES was characterized by ^1H NMR and FT-IR spectra. As illustrated in the FT-IR spectra in Fig. 1b, the peaks lying at $\approx 2950\text{ cm}^{-1}$ for all samples correspond to the stretching vibration of C–H units. For PEGMEMA, 2-EHA and PPES, the peaks at $\approx 1720\text{ cm}^{-1}$ are assigned to the stretching vibration of $\text{C}=\text{O}$. The characteristic peaks at 1630 cm^{-1} assigned to the $\text{C}=\text{C}$ unit are obvious in the FT-IR spectra of PEGMEMA, 2-EHA and SPSS monomers. While in the spectrum of PPES, much weaker peaks around 1630 cm^{-1} can be observed, suggesting the polymerization of monomers, which can also be confirmed in the ^1H NMR results. As shown in comparative ^1H NMR spectra of PPES and monomers in Fig. 1a and Fig. S2 (ESI †), the absence of proton signals between 5 and 6.5 ppm corresponding to the alkene group indicates the near complete reaction of feeding monomers. The characteristic peak of methyl units at the chain end of 2-EHA (peak i in Fig. S2 (ESI †) and peak r–s in Fig. 1a) manifests the successful chemical bonding of 2-EHA to the polymer network, which could provide spontaneous adhesion with the compositing fibers.³⁸

The thermal stability of samples was measured using a simultaneous thermal analyzer at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from room temperature to $800\text{ }^\circ\text{C}$ in a N_2 atmosphere. The result demonstrates that the as-prepared PPES shows good thermal stability without significant weight loss until $350\text{ }^\circ\text{C}$ (Fig. 1c). Moreover, by thermally treating the rQPE and commercial separator under the same conditions (Fig. S3, ESI †), the

separator becomes significantly wrinkled while the rQPE retains the original shape, demonstrating excellent thermal stability. Generally, as polymer electrolytes, the glass transition temperature (T_g) should be lower than the operating temperature of the battery to endow fast segmental dynamics.³⁹ Herein, as identified using the differential scanning calorimetry (DSC) curve shown in Fig. 1d, two glass transition processes lying at $-32.2\text{ }^\circ\text{C}$ and $163.6\text{ }^\circ\text{C}$ separately are observed. The presence of two T_g s manifests the microphase separation between polar and nonpolar units. At ambient temperature, the soft segments contribute to film flexibility that can accommodate the volume variation of the Li electrode whereas the rigid component shows mechanical robustness. The microphase separation is confirmed by the small-angle X-ray scattering (SAXS) spectrum with a broad peak at 0.18 nm^{-1} (Fig. 1e), corresponding to a characteristic length of $\sim 33\text{ nm}$.

As shown in Fig. 2a, a freestanding, optically clear, flexible PPES film can be obtained after casting the as-prepared PPES polymer solution into a Teflon dish and then removing the solvent under vacuum. The PPES film exhibits a Young's modulus of 52 MPa (an ultimate tensile strength of 4 MPa as shown in Fig. 2e). Employed as a QPE, a high mechanical strength, especially after swelling with a large amount of liquid electrolyte, is crucial for the cell to prevent the potential (micro) short circuit under abused operation.^{40,41} To improve the mechanical strength, the PPF with a diameter of $\approx 20\text{ }\mu\text{m}$ was employed (Fig. 2b). It can be seen that PPF films composed of

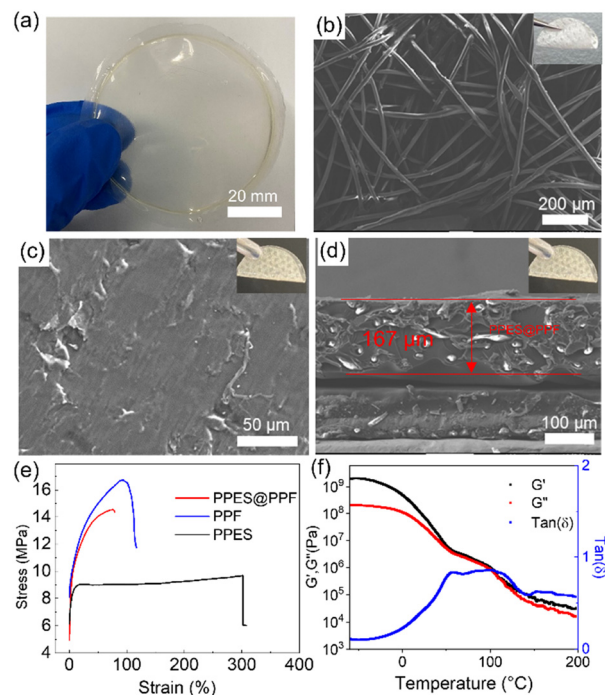


Fig. 2 (a) Optical photo of the as prepared PPES film. (b) SEM image of PPF from face mask. (c) Surface morphologies of PPES@PPF. The inset is the optical photo of the PPES@PPF film. (d) Cross-sectional SEM images of PPES@PPF. (e) Tensile test of PPES, PPF and PPES@PPF. (f) Temperature sweep of DMA of PPES. The blue line is the loss tangent ($\tan\delta$).



entangled fibers show a Young's modulus of ~ 190 MPa (an ultimate tensile strength of 16.7 MPa).

The fiber-reinforced polymer film can be successfully fabricated by imbedding the PPF into the PPES solution, followed by drying in a vacuum oven. As shown in Fig. 2c, the flexible and freestanding PPES@PPF film demonstrates a smooth and compact surface. The cross-sectional SEM image (Fig. 2d) shows that the thickness of the as-prepared fiber-reinforced polymer electrolyte is ~ 167 μm with the PPF uniformly distributed in the PPES polymer matrix. Tensile test demonstrates that the obtained flexible PPES@PPF has a fracture strain of 77% with an ultimate tensile strength of ~ 14.5 MPa (comparable Young's modulus to PPF). The mechanical properties of PPES are also evaluated by dynamic mechanical analysis (DMA) in a temperature range of -60 to 200 $^{\circ}\text{C}$. As shown in Fig. 2f, the higher storage modulus (G') than loss modulus (G'') ($\tan \delta < 1$) in the evaluated temperature range suggests the solid-like behavior of the synthesized PPES.⁴² In the temperature range of 50 – 100 $^{\circ}\text{C}$, the modulus of PPES exhibits a plateau-like behavior with comparable values of G' and G'' ($\approx 10^6$ Pa), indicating the high mechanical strength of PPES. The robust mechanical strength of PPES@PPF is attributed to the chemically crosslinked structure of PPES and the physically reinforced entangled fiber structure of PPF. With such mechanically reinforced properties, when the film is swelled with a liquid electrolyte, “well-connected” Li^+ transport channels can

be formed in the rQPE, rendering high ionic conductivity and uniform Li^+ transport. Moreover, with both physical and chemical reinforcement, these “well-connected” channels can be retained even under high charging/discharging current density or suffering from huge volume variation of Li electrode.

2.2. Electrochemical performance of rQPE

Apart from high mechanical strength, an ideal QPE should also possess high ionic conductivity, which is closely related to the electrolyte uptake ratio. As shown in Table S1 (ESI[†]), the as-prepared PPES@PPF film has a high electrolyte uptake ratio of $(83.7 \pm 2.1)\%$ with a high ionic conductivity of 1.1 and 0.45 mS cm^{-1} at 60 $^{\circ}\text{C}$ and 25 $^{\circ}\text{C}$, respectively (Fig. 3a and Fig. S4, ESI[†]). The high electrolyte uptake ratio can be ascribed to the unique chemical component and cross-linked structure of PPES, in which, high binding affinities can be formed between the abundant ethylene oxide (EO) units and the liquid electrolyte.³⁴ Due to this strong EO-solvent interactions, the solvent molecules are confined to the polymer network, creating stable “well-connected” Li^+ transport channels for facilitating ion transport. Moreover, the PPF in the cross-linked polymer chains can better stabilize this “well-connected” structure. All these factors contribute to a high electrolyte uptake ratio and superior ionic conductivity. As shown in Fig. 3b, the temperature-ionic conductivity curve fitted by Vogel-Fulcher-

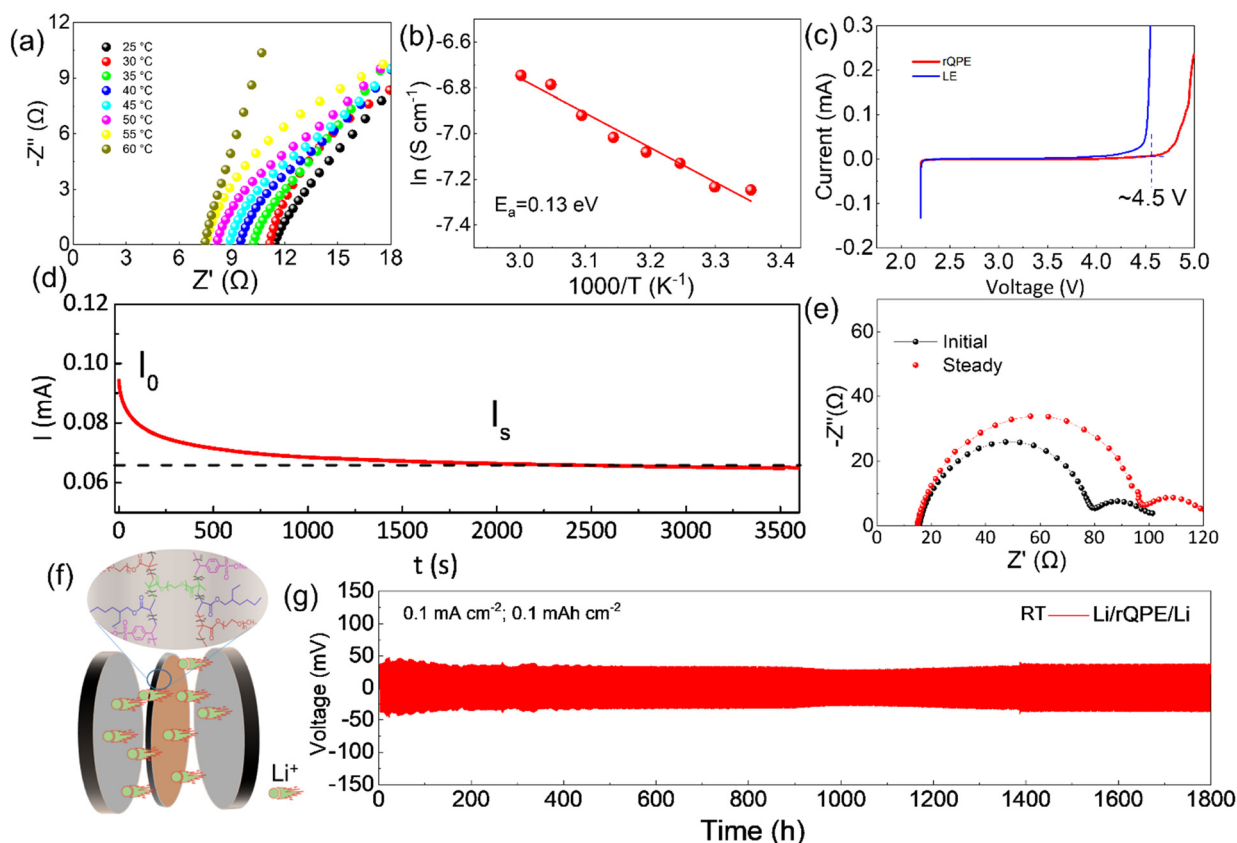


Fig. 3 (a) EIS curves of rQPEs from 25 $^{\circ}\text{C}$ to 60 $^{\circ}\text{C}$. (b) The temperature-ionic conductivity fitted by Vogel-Fulcher-Tammann (VFT) behavior. (c) LSV curve of rQPE from 2.0 – 5.2 V. (d) Potentiostatic polarization curve with applied potential of 10 mV and (e) the corresponding EIS curves of symmetric cells. (f) Schematic illustration of Li^+ transport through the rQPE in Li/rQPE/Li symmetric cell. (g) Cycling performance of Li/rQPE/Li symmetric cell.

- 3 M. Du, K. Liao, Q. Lu and Z. Shao, *Energy Environ. Sci.*, 2019, **12**, 1780–1804.
- 4 Z. Yu, X. Zhang, C. Fu, H. Wang, M. Chen, G. Yin, H. Huo and J. Wang, *Adv. Energy Mater.*, 2021, **11**, 2003250.
- 5 Q. Zhao, S. Stalin, C. Z. Zhao and L. A. Archer, *Nat. Rev. Mater.*, 2020, **5**, 229–252.
- 6 S. Gao, Z. Li, N. Liu, G. Liu, H. Yang and P. F. Cao, *Adv. Funct. Mater.*, 2022, **32**, 2202013.
- 7 C. Song, Z. G. Li, J. Peng, X. H. Wu, H. Peng, S. Y. Zhou, Y. Qiao, H. Sun, L. Huang and S. G. Sun, *J. Mater. Chem. A*, 2022, **10**, 16087–16094.
- 8 Y. Qiao, H. J. Yang, Z. Chang, H. Deng, X. Li and H. S. Zhou, *Nat. Energy*, 2021, **6**, 653–662.
- 9 J. Wu, S. Liu, F. Han, X. Yao and C. Wang, *Adv. Mater.*, 2021, **33**, 2000751.
- 10 W. Lu, M. Xue and C. Zhang, *Energy Storage Mater.*, 2021, **39**, 108–129.
- 11 S. Gao, A. Cannon, F. Sun, Y. Pan, D. Yang, S. Ge, N. Liu, A. P. Sokolov, E. Ryan, H. Yang and P.-F. Cao, *Cell Rep. Phys. Sci.*, 2021, **2**, 100534.
- 12 F. He, W. Tang, X. Zhang, L. Deng and J. Luo, *Adv. Mater.*, 2021, **33**, 2105329.
- 13 S. Gao, F. Sun, N. Liu, H. Yang and P.-F. Cao, *Mater. Today*, 2020, **40**, 140–159.
- 14 Y. An, Y. Cheng, S. Wang and J. Yu, *ACS Appl. Energy Mater.*, 2022, **5**, 2786–2794.
- 15 Z. Yu, P. E. Rudnicki, Z. Zhang, Z. Huang, H. Celik, S. T. Oyakhire, Y. Chen, X. Kong, S. C. Kim, X. Xiao, H. Wang, Y. Zheng, G. A. Kamat, M. S. Kim, S. F. Bent, J. Qin, Y. Cui and Z. Bao, *Nat. Energy*, 2022, **7**, 94–106.
- 16 S. H. Hong, D. H. Jung, J. H. Kim, Y. H. Lee, S. J. Cho, S. H. Joo, H. W. Lee, K. S. Lee and S. Y. Lee, *Adv. Funct. Mater.*, 2020, **30**, 1908868.
- 17 Q. Lu, C. Wang, D. Bao, H. Duan, F. Zhao, K. D. Davis, Q. Zhang, R. Wang, S. Zhao, J. Wang, H. Huang and X. Sun, *Energy Environ. Mater.*, 2023, e12447.
- 18 X. Zou, Q. Lu, Y. Zhong, K. Liao, W. Zhou and Z. Shao, *Small*, 2018, **14**, 1801798.
- 19 J. Wu, Z. Rao, Z. Cheng, L. Yuan, Z. Li and Y. Huang, *Adv. Energy Mater.*, 2019, **9**, 1902767.
- 20 J. H. Sun, J. Y. Peng, T. R. Y. Ring, L. Whittaker-Brooks, J. E. Zhu, D. Fraggadakis, J. Niu, T. Gao and F. Wang, *Energy Environ. Sci.*, 2022, **15**, 5284–5299.
- 21 Z. Li, S. Wang, J. Shi, Y. Liu, S. Zheng, H. Zou, Y. Chen, W. Kuang, K. Ding, L. Chen, Y.-Q. Lan, Y.-P. Cai and Q. Zheng, *Energy Storage Mater.*, 2022, **47**, 262–270.
- 22 S. Hao, L. Li, W. Cheng, Q. Ran, Y. Ji, Y. Wu, J. Huo, Y. Yang and X. Liu, *J. Mater. Chem. A*, 2022, **10**, 4881–4888.
- 23 L. Ye and X. Li, *Nature*, 2021, **593**, 218–222.
- 24 L. Fan, S. Wei, S. Li, Q. Li and Y. Lu, *Adv. Energy Mater.*, 2018, **8**, 1702657.
- 25 S. K. Vineeth, M. Tebyetekerwa, H. Liu, C. B. Soni, Sungjemmenla, X. S. Zhao and V. Kumar, *Mater. Adv.*, 2022, **3**, 6415–6440.
- 26 N. Meng, F. Lian and G. Cui, *Small*, 2021, **17**, 2005762.
- 27 W. Zhou, S. Wang, Y. Li, S. Xin, A. Manthiram and J. B. Goodenough, *J. Am. Chem. Soc.*, 2016, **138**, 9385–9388.
- 28 Y. Ma, Q. Sun, Z. Wang, S. Wang, Y. Zhou, D. Song, H. Zhang, X. Shi, C. Li, L. Zhang and L. Zhu, *J. Mater. Chem. A*, 2021, **9**, 3597–3604.
- 29 Y. Liu, L. Hou, Y. Jiao and P. Wu, *ACS Appl. Mater. Interfaces*, 2021, **13**, 13319–13327.
- 30 L. Yang, J. Zhang, W. Xue, J. Li, R. Chen, H. Pan, X. Yu, Y. Liu, H. Li, L. Chen and X. Huang, *Adv. Funct. Mater.*, 2022, **32**, 2200096.
- 31 X. He, Y. Ni, Y. Hou, Y. Lu, S. Jin, H. Li, Z. Yan, K. Zhang and J. Chen, *Angew. Chem., Int. Ed.*, 2021, **60**, 22672–22677.
- 32 D. Zhou, R. Liu, Y.-B. He, F. Li, M. Liu, B. Li, Q.-H. Yang, Q. Cai and F. Kang, *Adv. Energy Mater.*, 2016, **6**, 1502214.
- 33 T. T. Zuo, Y. Shi, X. W. Wu, P. F. Wang, S. H. Wang, Y. X. Yin, W. P. Wang, Q. Ma, X. X. Zeng, H. Ye, R. Wen and Y. G. Guo, *ACS Appl. Mater. Interfaces*, 2018, **10**, 30065–30070.
- 34 Q. Lu, Y. B. He, Q. Yu, B. Li, Y. V. Kaneti, Y. Yao, F. Kang and Q. H. Yang, *Adv. Mater.*, 2017, **29**, 1604460.
- 35 Y. H. Li, Z. J. Sun, D. Y. Liu, Y. Y. Gao, Y. K. Wang, H. T. Bu, M. T. Li, Y. F. Zhang, G. X. Gao and S. J. Ding, *J. Mater. Chem. A*, 2020, **8**, 2021–2032.
- 36 Z. Zhang, Y. Huang, C. Li and X. Li, *ACS Appl. Mater. Interfaces*, 2021, **13**, 37262–37272.
- 37 X. Zhang, S. Zhao, W. Fan, J. Wang and C. Li, *Electrochim. Acta*, 2019, **301**, 304–311.
- 38 S. Gao, Y. Pan, B. Li, M. A. Rahman, M. Tian, H. Yang and P. F. Cao, *Adv. Funct. Mater.*, 2022, **33**, 2210543.
- 39 S. Gao, Z. Li, Z. Zhang, B. Li, X. C. Chen, G. Yang, T. Saito, M. Tian, H. Yang and P.-F. Cao, *Energy Storage Mater.*, 2023, **55**, 214–224.
- 40 C. Monroe and J. Newman, *J. Electrochem. Soc.*, 2003, **150**, A1377–A1384.
- 41 Z. Zeng, X. Chen, M. Sun, Z. Jiang, W. Hu, C. Yu, S. Cheng and J. Xie, *Nano Lett.*, 2021, **21**, 3611–3618.
- 42 Y. Pan, S. Ge, Z. Rashid, S. Gao, A. Erwin, V. Tsukruk, K. D. Vogiatzis, A. P. Sokolov, H. Yang and P.-F. Cao, *ACS Appl. Energy Mater.*, 2020, **3**, 3387–3396.
- 43 J. Zhu, Z. Zhang, S. Zhao, A. S. Westover, I. Belharouak and P. F. Cao, *Adv. Energy Mater.*, 2021, **11**, 2003836.
- 44 H. O. Ford, B. Park, J. Jiang, M. E. Seidler and J. L. Schaefer, *ACS Mater. Lett.*, 2020, **2**, 272–279.
- 45 Z. Chen, D. Steinle, H.-D. Nguyen, J.-K. Kim, A. Mayer, J. Shi, E. Paillard, C. Iojoiu, S. Passerini and D. Bresser, *Nano Energy*, 2020, **77**, 105129.
- 46 P. Kuray, W. Mei, S. E. Sheffield, J. Sengeh, C. R. F. Pulido, C. Capparelli, R. J. Hickey and M. A. Hickner, *Front. Energy Res.*, 2020, **8**, 569387.
- 47 X. Shan, S. Zhao, M. Ma, Y. Pan, Z. Xiao, B. Li, A. P. Sokolov, M. Tian, H. Yang and P. F. Cao, *ACS Appl. Mater. Interfaces*, 2022, **14**, 56110–56119.
- 48 E. R. Parnham and R. E. Morris, *J. Mater. Chem.*, 2006, **16**, 3682–3684.
- 49 M. V. O'Reilly, H. Masser, D. R. King, P. C. Painter, R. H. Colby, K. I. Winey and J. Runt, *Polymer*, 2015, **59**, 133–143.
- 50 S. L. Gao, M. X. Zhang, C. Gainaru, A. P. Sokolov, H. B. Yang and P. F. Cao, *Matter*, 2022, **5**, 2457–2460.



- 51 Y. Guo, X. Qu, Z. Hu, J. Zhu, W. Niu and X. Liu, *J. Mater. Chem. A*, 2021, **9**, 13597–13607.
- 52 H. Huo, J. Gao, N. Zhao, D. Zhang, N. G. Holmes, X. Li, Y. Sun, J. Fu, R. Li, X. Guo and X. Sun, *Nat. Commun.*, 2021, **12**, 176.
- 53 W. Lin, X. Zheng, S. Ma, K. Ji, C. Wang and M. Chen, *ACS Appl. Mater. Interfaces*, 2023, **15**, 8128–8137.
- 54 X. Zeng, L. Dong, J. Fu, L. Chen, J. Zhou, P. Zong, G. Liu and L. Shi, *Chem. Eng. J.*, 2022, **428**, 131100.
- 55 H. Xu, S. Huang, J. Qian, S. Liu, L. Li, X. Zhao and W. Zhang, *Colloids Surf., A*, 2022, **653**, 130040.
- 56 J. Wang, C. Tao, J. Cao, X. Jiao, L. Wang and T. Liu, *ChemElectroChem*, 2022, **9**, 202200957.
- 57 J. Ma, X. Ma, H. Zhang, F. Chen, X. Guan, J. Niu and X. Hu, *J. Membr. Sci.*, 2022, **659**, 120811.
- 58 Y. Jin, X. Zong, X. Zhang, Z. Jia, H. Xie and Y. Xiong, *Energy Storage Mater.*, 2022, **49**, 433–444.
- 59 X. Fu, M. J. Hurlock, C. Ding, X. Li, Q. Zhang and W. H. Zhong, *Small*, 2022, **18**, 2106225.
- 60 S. Chai, Y. Zhang, Y. Wang, Q. He, S. Zhou and A. Pan, *eScience*, 2022, **2**, 494–508.
- 61 P. Liu, L. Zhong, S. Wang, S. Huang, D. Han, Z. Huang, M. Xiao and Y. Meng, *Energy Storage Mater.*, 2023, **58**, 132–141.
- 62 Z. Wang, H. Shi, W. Zheng, W. Sun, L. Zhao and W. Yuan, *J. Power Sources*, 2022, **524**, 231070.
- 63 Y. Sun, Y. Zhao, J. Wang, J. Liang, C. Wang, Q. Sun, X. Lin, K. R. Adair, J. Luo, D. Wang, R. Li, M. Cai, T. K. Sham and X. Sun, *Adv. Mater.*, 2019, **31**, 1806541.
- 64 J. Zhao, L. Liao, F. Shi, T. Lei, G. Chen, A. Pei, J. Sun, K. Yan, G. Zhou, J. Xie, C. Liu, Y. Li, Z. Liang, Z. Bao and Y. Cui, *J. Am. Chem. Soc.*, 2017, **139**, 11550–11558.
- 65 K. Leung, F. Soto, K. Hankins, P. B. Balbuena and K. L. Harrison, *J. Phys. Chem. C*, 2016, **120**, 6302–6313.
- 66 Z. A. Yu, D. G. Mackanic, W. Michaels, M. Lee, A. Pei, D. W. Feng, Q. H. Zhang, Y. C. Tsao, C. V. Amanchukwu, X. Z. Yan, H. S. Wang, S. C. Chen, K. Liu, J. Kang, J. Qin, Y. Cui and Z. N. Bao, *Joule*, 2019, **3**, 2761–2776.

