Supplementary Information

Polar polymer-solvent interaction derived favorable interphase for

stable lithium metal batteries

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METHODS AND CHARACTERIZATION

Preparation of PPN

LiTFSI : EC electrolyte was prepared in argon-filled glove box with < 1 ppm oxygen and moisture by dissolving LiTFSI (99.95%, Sigma-Aldrich) in EC (Alfa Aesar) with a molar ratio of 1 : 6 (LiTFSI : EC) at 50 °C on a hot plate while stirring. For the PPN fabrication, 4 wt% of PAN (Mn = 150k, Sigma-Aldrich) was added in either LiTFSI : EC or 1M LiPF₆ in EC : DEC (76 wt%). After fully dispersed in sonicating bath, 20 wt% of PEGDA (Mn = 700, Sigma-Aldrich) was dissolved in the solution. To cross-link PEDGA oligomers, 1 wt% of thermal initiator (2,2'-Azobis(2-methylpropionitrile), Sigma-Aldrich) by weight of PEGDA was added in the solution and mixed by sonication. The prepared solution was casted on a glass substrate. After sandwiched by another glass substrate, PPN was thermally cross-linked at 90 °C for 10 min. The thickness was controlled by adjusting the distance between two glass substrates (40~200 µm).

PPN characterization

To investigate the electrolyte coordination, Raman spectroscopy was performed with Witec Micro-Raman Spectrometer Alpha 300 with a 600 grooves/mm grating (BLZ at 500 nm). Spectra were typically collected using a 2 sec exposure time with 10 accumulations. The Raman sample was prepared in argon-filled glove box by hermetical sealing. For the polymer-solvent interaction analysis, FTIR was carried out using Thermo Scientific Nicolet iS5. The sample was mixed with potassium bromide powder (KBr, FTIR grade, Alfa Aesar) with a weight ratio of 1 to 100 and pressed into a pellet. To investigate the thermal behavior, TGA was performed with a PerkinElmer TGA4000 thermogravimetric analyzer from 30 to 800 °C with a ramping rate of 5 °C min⁻¹ under air. DSC was conducted using Mettler Toledo DSC 3. The samples were closely sealed in Al crucible to prevent solvent evaporation and kept at -100 °C for 5 min to fully freeze. The measurement was conducted from -100 °C to 50 °C with a ramping rate of 5 °C min⁻¹ under nitrogen flow of 50 mL min⁻¹.

Li morphology/SEI characterization

SEM images were taken by Scanning Electron Microscopy (Hitachi, S5500) to observe the morphology and microstructure of the surface of Li-metal which was disassembled from coin cells after cycling test. *In-situ* optical microscopy was conducted using a symmetric Li | Li cell. Two strips of copper mesh were first placed on a glass slide on which half-cut Li chips were attached. After injecting either liquid electrolyte or PPN solution between Li chips, the cell was sealed by epoxy glue. In case of the PPN, the assembled cell was heated at 90 °C for 10 min to *in-situ* polymerize. Optical images were taken by Nikon Epiphot 200 equipped with Nikon Digital Sight DS-U3 after Li plating/stripping of 1, 5, 10 and 20 cycles under 5 mA cm⁻² for 1 mAh cm⁻². For the SEI's compositional analysis, XPS was performed using Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer equipped with a monochromatic Al K α X-ray source (1,486.7 eV) for excitation. For sample preparation, symmetric Li | Li cells were cycled with either LiTFSI : EC or PPN under 5 mA cm⁻² for 1 mAh cm⁻² of 10 cycles. After disassembled in argon-filled glove box, the surface of Li chip was cleaned by pure EC solvent then dried on hot plate at 50 °C. The samples were hermetically sealed in argon-filled glove box before transferred to XPS chamber.

Electrochemical measurements

Electrochemical analysis of symmetric Li | Li, Li | LCO, and Li | NCM cells was performed in 2032 coin cells. For the Li plating/stripping test, Li chips were polished to remove the native passivation layer. Symmetric Li | Li cell was tested under 1 mAh cm⁻² charge/discharge with

different current densities of 1, 5 and 10 mA cm⁻². To investigate the electrochemical performance of Li-metal batteries, half cells were assembled with LCO or NCM as the cathode while bare Li or PPN Li as anode. The cathode slurry was prepared by mixing LCO or NCM, super P and polyvinylidene fluoride (PVDF) with a weight ratio of 8 : 1 : 1 in N-methyl-2-pyrrolidone (NMP) which are coated on Al foil. The as-coated cathode was dried at 120 °C for 3 hrs followed by 100 °C drying in vacuum oven overnight and cut into a disk with a diameter of 12 mm before transferred in argon-filled glove box. The average areal loading of active material was 1~2 mg cm⁻². Glass fiber was used as a separator for LiTFSI : EC while Celgard was used for 1M LiPF₆ in EC : DEC. The rate performance and cycling stability were investigated using BST 8 channel battery analyzer from MTI with a cut off voltage of 2.8 V to 4.2 V for LCO and 2.8 V to 4.25 V for NCM. For the Li | LCO cycling test, a formation process was performed by 5 cycles at 0.2C while a cycle of 0.1C was conducted for the Li | NCM cycling test prior to increase discharge C rate to 1C or 5C.

Computational details

Electron configurations of all molecules were calculated by density functional theory (DFT) method within the framework of the Gaussian 09 package. The standard Pople basis set, 6-31G++(d,p), combined with the Lee–Yang–Parr exchange correlation functional (B3LYP) was used for all calculations. Various kinds of relative geometry combination between PAN, PEO and EC were explored, and the most energy favorable geometry is selected. For each combination, the geometry was fully optimized to achieve the lowest total energy before energy level calculation, and possible spin multiplicities were explored (S=3, 4, 5, 6), among which we chose the one with the lowest energy for analysis and comparison between different combination.



Fig. S1. The intensity ratio of free EC band (720 cm⁻¹) and LiTFSI band (745 cm⁻¹) in Raman spectra in terms of peak height (blue square) and integrated area (red circle) for LiTFSI in EC (1:6 molar ratio), PPN without PAN and PPN (both polymers were fabricated in the same LiTFSI in EC).

We have calculated the intensity ratio between free EC band (720 cm⁻¹) and LiTFSI band (745 cm⁻¹) of Raman spectra (Fig. 2f) by comparing the peak height or the integrated area. As shown in Fig. S1, liquid electrolyte (LiTFSI in EC with 1:6 molar ratio) shows the area ratio of 0.67. In case of PPN w/o PAN shows the highest area ratio of 1.04 indicating there are lots of free EC molecules. It is speculated that ether group (C-O-C) of cross-linked PEGDA polymer chains may coordinate with Li⁺ that may release free EC molecules. Interestingly, when PAN is added (PPN), the lowest area ratio (0.49) was obtained implying that polymer-solvent interaction effectively reduced the free EC solvents.



Fig. S2. Thermogravimetric analysis (TGA) of different electrolyte. 1M LiPF₆ in EC : DEC (1:1vol) (green), LiTFSI : EC (1 : 6 molar ratio) (red) and PPN (blue). Both LiTFSI : EC and PPN show higher boiling point than conventional 1M LiPF₆ in EC : DEC electrolyte due to higher boiling point of EC solvent than DEC. Meanwhile, PPN shows lower boiling point than LiTFSI : EC implying that PPN may interrupt EC-EC interaction facilitating evaporation.



Fig. S3. Differential Scanning Calorimetry (DSC) of different electrolytes. (a) LiTFSI: EC and (b) PPN. LiTFSI : EC shows a melting point of 6.47 °C. However, in PPN, a melting point shift was observed about 11 °C higher than that in LiTFSI : EC, indicating that the coordination of EC has been changed.



Fig. S4. SEM image of Li dendrites on bare Li surface. The image was taken from a disassembled symmetric Li | Li cell after cycling test under 5 mA cm⁻² for 1 mAh cm⁻². Electrolyte: LiTFSI in EC (1:6 molar ratio).



Fig. S5. SEM images for initial morphology of Li plating. (a) pristine Li (uncycled), (b) bare Li, and (c) PPN Li after plating Li under 1 mA cm⁻² for 2 mAh cm⁻². Electrolyte: LiTFSI in EC (1:6 molar ratio) was used for bare Li. PPN based on LiTFSI in EC (1:6 molar ratio) was used for PPN Li.



Fig. S6. Schematic illustration of fabrication process for *in-situ* **observation cell.** 1) Attaching two Li chips on Cu current collector on glass slide. 2) Injecting either liquid electrolyte or PPN solution between Li chips. 3) Sealing by sealant and drying. In case of PPN, the cell was heated at 90 °C for 10 min for *in-situ* polymerization. 4) In-situ observation of Li/electrolyte interface during 5 mA cm⁻² cycling (1 mAh cm⁻²). All the steps were conducted in an Ar filled glove box. The current density was calculated based on the cross-sectional area (~0.08 cm²). Electrolyte: LiTFSI in EC (1:6 molar ratio) was used for bare Li. PPN based on LiTFSI in EC (1:6 molar ratio) was used for PPN Li.



Fig. S7. *In-situ* optical microscopy images after cycling. Cross-sectional images of (a) bare Li cell and (b) PPN Li cell after 20 cycles under 5 mA cm⁻² for 1 mAh cm⁻². The dotted lines indicate the top of Li surface during cycling. Electrolyte: LiTFSI in EC (1:6 molar ratio) was used for bare Li. PPN based on LiTFSI in EC (1:6 molar ratio) was used for PPN Li.



Fig. S8. Generation of gases from electrolyte-lithium reaction. (a) Photographs of the cells with bare Li and PPN Li after 1 cycle and 10 cycles where significant amount of gas bubbles are observed in bare Li cell while no observable gas was found in PPN Li cell. *In-situ* optical microscopy images of (b) bare Li and (c) PPN Li after 1 cycle under 5 mA cm⁻² for 1 mA cm⁻². A dark sphere in (B) clearly indicates a gas bubble generated during the cycling. Electrolyte: LiTFSI in EC (1:6 molar ratio) was used for bare Li. PPN based on LiTFSI in EC (1:6 molar ratio) was used for PPN Li.



Fig. S9. Conductivity of electrolytes. Electrochemical impedance spectroscopy of (a) LiTFSI in EC (1:6 molar ratio) and (b) PPN fabricated in the same liquid electrolyte at 25 °C.



Fig. S10. XPS on lithium surface before sputtering. (a, d) C1s, (b, e) O1s and (c, f) F1s spectra for (a-c) bare Li and (d-f) PPN Li. The Li-metals were collected after 10 cycles under 5 mA cm⁻² for 1 mAh cm⁻² in a symmetric Li | Li cell. Electrolyte: LiTFSI in EC (1:6 molar ratio) was used for bare Li. PPN based on LiTFSI in EC (1:6 molar ratio) was used for PPN Li.



Fig. S11. LUMO and HOMO levels of different molecules. Calculated LUMO and HOMO levels of uncoordinated EC solvent (Free EC), uncoordinated PAN polymer (PAN), PEO-EC interaction (PEO-EC), antiparallel or vertical interaction of PAN-EC (PAN-EC (V)) and parallel interaction of PAN-EC (PAN-EC (P)).

There can be antiparallel PAN-EC (PAN-EC (V)) interaction and the parallel PAN-EC (PAN-EC (P)) interaction. These two types of coordination (antiparallel and parallel) can exist in the PPN layer, but the antiparallel PAN-EC interaction is the most stable coordination which will be the majority interaction. Therefore, we have focused on PAN-EC (V) interaction to design and investigate the PPN layer.



Fig. S12. XPS spectra on PPN Li. (a) C1s and (b) N1s XPS spectra of PPN Li. The sample was cycled at 5 mA cm⁻² for 1 mAh cm⁻² for 10 cycles. After disassembled, Li-metal was collected after carefully taking PPN layer off. The residual polymer was remained on the Li-metal. Electrolyte: PPN was fabricated in LiTFSI in EC (1:6 molar ratio).

XPS spectra of C1s and N1s are shown in Fig. S12. In C1s spectra (Fig. S12a), it was difficult to distinguish C=N and C-O bonds due to the overlapped peak positions. However, almost no CO₃ peak (288~290 eV) was observed indicating that XPS was successfully taken on PPN since CO₃ is mostly observed on SEI layer (i.e., Li₂CO₃). Strong C-C, C-H may come from the cross-linked PEGDA and PAN polymer chains. In N1s spectra (Fig. S12b), two strong peaks around 399 eV and 397 eV were observed. Based on the literature, these peaks indicate C=N and LiTFSI peak, respectively [Z. Yue et al., J. Mater. Chem., 15 (2005) 3142–3148]. Therefore, we speculate that PAN was hardly reduced on Li-metal in the presence of EC and cross-linked PEGDA which well agreed with the LUMO & HOMO calculation (Fig. S11). However, it is still possible PAN those in contact with Li metal can be reduced. But considering the amount of PAN added in PEGDA matrix (~20 wt%), we assumed that this amount can be negligible since reduction of PAN was not clearly shown in XPS spectra.



Fig. S13. Rate performance of Li | **NCM batteries.** Bare Li (red) and PPN Li (blue) (charge at 1C & discharge at increasing C rate). PPN was also fabricated in 1M LiPF₆ in EC:DEC.



Fig. S14. Electrochemical performance of Li | **LCO batteries**. (a) Li | LCO battery cycling performance at 1C with bare Li (red) and PPN Li (blue). (b) Rate performance of Li | LCO batteries with bare Li (red) and PPN Li (blue) (charge at 1C & discharge at increasing C rate). Discharge voltage profiles under different C rate with (c) bare Li and (d) PPN Li. Note that EC single solvent was used in this experiment to clearly show the effect of PPN under a highly reactive electrolyte. The cell performance can be affected by the high viscosity and reactivity of EC solvent.

In Fig. S10a, cycling stability at 1C clearly shows that the PPN Li effectively stabilized Li interface. A drastic capacity fade was observed in bare Li cell after ~120 cycles which may come from the depletion of electrolyte as well as buildup of dead Li and SEI.

In Fig. S10b, both bare and PPN Li cells exhibit a similar capacity close to the theoretical value of LCO, 140 mAh g⁻¹ at 0.2C. However, under higher discharge C rates (> 1C), PPN Li shows a better rate capability compared to bare Li cell. Bare Li cell exhibits drastically increasing overpotentials with increasing discharge C rate implying a large impedance caused by the highly resistive SEI layer on the Li surface and the severe consumption of the electrolyte (Fig. S10c). On the contrary, PPN Li shows much smaller overpotentials (Fig. S10d). The improved rate performance can be attributed to the thinner and favorable SEI layer induced by PPN Li.



Fig. S15. Cycling test of Li | LCO batteries at 5C. Bare Li (red) and PPN Li (blue). LiTFSI : EC = 1 : 6 electrolytes were used.



Fig. S16. SEM images of bare Li surface after cycling with NCM. The SEM was taken with different magnifications of (a) $\times 150$ and (b) $\times 400$. The cell was cycled at 5C for 1000 cycles. Electrolyte: 1M LiPF₆ in EC:DEC.



Fig. S17. Cycling stability of Li | NCM batteries with glass fiber as a separator. (a) Bare Li and (b) PPN Li at 1C charge and 1C discharge in $1M \text{ LiPF}_6$ in EC:DEC (1:1 vol) electrolyte. PPN was also fabricated in $1M \text{ LiPF}_6$ in EC:DEC.

| Notation | Strategy | C rate | Capacity retention @ 200 cycles | Capacity fade rate | Ref# |
|------------|-----------------------------|--------|---------------------------------------|-----------------------|------|
| A1 | Artificial SEI layer | 1C | 96.0% | 0.025% | 9 |
| A2 | Artificial SEI layer | C/2 | 93.9% | 0.028% | 10 |
| В | 3D host | 1C | 93.6% | 0.029% | 8 |
| C1 | Electrolyte additives | C/3 | 91.9% | 0.042% | 30 |
| C2 | Electrolyte additives | 1C | 82.3% | 0.089% | 13 |
| D1 | Gel polymer | C/10 | 85.1% | 0.078% | 31 |
| D2 | Polymer electrolyte | C/2 | *81.2% | 0.094% | 32 |
| D3 | Inorganic electrolyte | C/2 | *80.0% | 0.100% | 33 |
| This study | Polymer-solvent interaction | 1C | 96.5% | 0.013% | - |
| This study | Polymer-solvent interaction | 5C | **98.7% | 0.0013% | - |

Table S1. Cycling performance comparison of Li | NCM batteries

* Calculated based on capacity fade rate available from paper

** Capacity retention after 1000 cycles at 5C