

Enabling wide temperature battery operation with hybrid lithium electrolytes

Experimental

Materials

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, $\geq 98\%$), was purchased from TCI America. N-methylpyrrolidine (97%), Iodoethane (99.5%), ethyl acetate (ACS grade, dichloromethane (ACS reagent, $\geq 99.5\%$). Methanol (ACS reagent, $\geq 99.8\%$), Magnesium sulfate (ACS reagent, $\geq 98\%$), and propylene carbonate (anhydrous, 99.7%) were purchased from Millipore Sigma. LCO, LTO, Polyvinylidene fluoride (PVDF-5130), Super C65 conductive carbon black, and 2032 coin cell parts were purchased from Gelon Lib company.

Synthesis of 1-ethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [PYR12][TFSI]

PYR12-I precursor was synthesized by reacting N-methylpyrrolidine (100 mmol, 8.5 g) with iodoethane (110 mmol, 17.2 g) in a round bottom flask with 200 mL of ethyl acetate. The solution was allowed to vigorously stir for 16 h at room temperature. This solution was then vacuum filtered and washed several times with ethyl acetate resulting in a colorless viscous ionic liquid. The ionic exchange was performed by dissolving the ionic precursor and LiTFSI (110 mmol, 28.7 g) in water separately in 100 mL (each) of deionized water. The ionic-liquid precursor was then placed in a round bottom flask and stirred while the LiTFSI solution was added slowly. This solution was then mixed for 16 h. The resulting solution was then phase separated with ethyl acetate and dried over magnesium sulfate. The solution was concentrated under reduced pressure using a rotoevaporator. Once concentrated, the final solution was purified using flash chromatography using a 90:10 dichloromethane:methanol mixture. The final product was then dried in a vacuum oven for 12 h at 120 °C. The final result is a colorless liquid/semi solid at room temperature. Finally, the ionic liquid was mixed at a 1:1 weight ratio with 0.3 m, 1.0 m, 2.5 m LiTFSI in PC. The hybrid electrolytes were mixed in a humidity controlled dry room (≤ 100 ppm water).

Electrochemical Characterization

To measure the ionic conductivities of the electrolyte solutions, liquid electrolyte was soaked into glass fiber separators (18 mm dia., 190 μm thick per layer, 2 layers), sandwiched between two stainless steel discs (15.5 mm dia., 0.5 mm thick, Gelon Lib Group), placed into a 2032-coin cell case with one stainless steel wave spring (Gelon Lib Group), and crimped at 700 psi (MTI MSK-110 Hydraulic Crimping Machine). Coin cells were placed into an ESPEC BTZ-133 Environmental Chamber, after which Electrochemical Impedance Spectroscopy (EIS) measurements were performed at -60 °C, -40 °C, -20 °C, 0 °C, 23 °C, 40 °C, and 60 °C (20 mV RMS, 1 MHz to 0.2 Hz, Gamry Instruments Reference 3000 Potentiostat/Galvanostat/ZRA). The coin cells were allowed to equilibrate at each temperature for 2 hours before measurement. Reference measurements of the short-circuited setup were performed using the same EIS settings and temperature profile. “Electrolyte + setup” resistance was taken from the high frequency intercept of the electrolyte Nyquist plots if no high frequency semi-circle was present, or taken from the low frequency intercept of the high frequency semi-circle if it was present. “Setup” resistance was taken from the low frequency intercept of the short-circuited setup Nyquist plots. After subtracting the “setup” resistance from the “electrolyte + setup” resistance, the calculated “electrolyte” resistance was converted to “electrolyte” total conductivity using the total glass fiber separator thickness and the stainless steel disc diameter.

Supporting Information

LCO and LTO electrodes were prepared by uniformly mixing the active powder with SUPER C65 carbon black, and PVDF at a mass ratio of 92: 4: 4 in N-methyl-2-pyrrolidone (NMP) to prepare the electrode slurry. Slurries were then blade coated onto Al foil and dried in a vacuum oven at 120 °C. LTO||LCO full cells were assembled with areal capacities of 2.0 and 2.2 mA h cm⁻² for the LTO and LCO, respectively (N/P ratio of 0.9). LTO was then punched into 12 mm disks and paired with 14 mm LCO and filled with electrolyte using GF/C as the separator.

LTO||LCO full cells were formation cycled at room temperature (23 °C) from 1.0–2.8 V for 3 cycles using a C/10 cycling rate, based on the theoretical capacity of the limiting electrode (LTO) in the cell. The discharge capacity after the 3rd formation cycle was taken to be the true capacity of the cell, and all subsequent cycling rates were calculated based on this discharge capacity. The formation cycled cells were then cycled either at room temperature (23 °C), at –20 °C in an environmental chamber, or at 60 °C in an environmental chamber. The cells cycled at –20 °C/60 °C were allowed to equilibrate at each temperature for 4 h before cycling. Cycle life tests were carried out by cycling the cells at a C/10 cycling rate for 100 cycles at the designated temperature. Rate capability tests were carried out by cycling the cells for 5 cycles each at C/10, C/5, C/2, 1C, and 2C cycling rates, then cycling at a C/10 cycling rate for 5 additional cycles, all at the designated temperature. Cells were analyzed with LANDT potentiostats.

Self-extinguishing measurements were made by igniting an initial electrolyte mass of ~0.5 g in a stainless steel container. The ignition time and the total test time (e.g. until fire naturally extinguishes) were recorded, along with the final mass of the electrolyte. The flammability index was calculated by taking the difference between the total test time and the ignition time, then normalizing to the final electrolyte mass.

| Solvent | Short Name | Melting Point (°C) | Flash Point (°C) | Viscosity (cP) |
|---|---------------|--------------------|------------------|----------------|
| Ethylene Carbonate | EC | 36.4 | 132 | 1.92* |
| Ethyl Methyl Carbonate | EMC | -55 | 23 | 0.65 |
| Propylene Carbonate | PC | -48.8 | 32 | 2.51 |
| 1-Ethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide | [PYR12][TFSI] | 90 | n/a | solid |

*Viscosity temperature 40 °C.

Table S1. Physical and chemical characteristics of select solvents and ionic liquid.

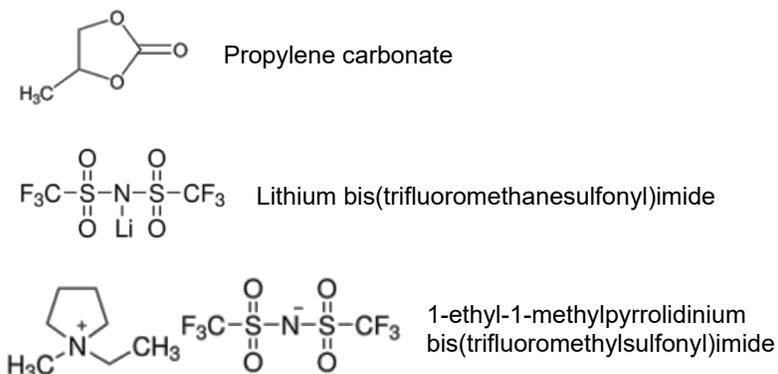


Figure S1. Chemical structure of propylene carbonate, lithium bis(trifluoromethanesulfonyl)imide, and 1-ethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. These chemicals combined is what comprises our lithium-ion conducting hybrid electrolyte.

Supporting Information

| Full Name | Abbreviated | PYR12(W/W) | LiTFSI (W/W) | PC (W/W) | Total |
|--------------------------------------|-------------|------------|--------------|----------|-------|
| 0.3 m LiTFSI in PC in PYR12 | 0.3-PC-PYR | 13.57 | 40.38 | 46.03 | 100 |
| 1.0 m LiTFSI in PC in PYR12 | 1.0-PC-PYR | 13.57 | 47.57 | 38.85 | 100 |
| 2.5 m LiTFSI in PC in PYR12 | 2.5-PC-PYR | 13.57 | 57.30 | 29.11 | 100 |
| 2.5 m LiTFSI in PC | 2.5-PC | 0 | 71.75 | 28.25 | 100 |

Table S2. Weight ratios between PYR12, LiTFSI, and PC for 2.5-PC, 0.3-PC-PYR, 1.0-PC-PYR, and 2.5-PC-PYR.

Ionic Conductivity ($mS\ cm^{-1}$)

Supporting Information

| Electrolyte | -60°C | -40°C | -20°C | 0°C | 23°C | 40°C | 60°C |
|---|-------|-------|-------|------|------|------|------|
| 1.0 m LiPF₆ in EC:EMC (3:7) | 0.15 | 0.75 | 1.83 | 3.41 | 3.92 | 2.54 | 3.23 |
| 2.5 m LiTFSI in PC | 0.01 | 0.14 | 0.32 | 1.17 | 2.20 | 2.60 | 5.15 |
| 2.5 m LiTFSI in PC:PYR12 | 0.005 | 0.07 | 0.29 | 0.56 | 1.05 | 1.94 | 2.89 |
| 1.0 m LiTFSI in PC:PYR12 | 0.02 | 0.29 | 0.92 | 2.44 | 4.59 | 5.42 | 6.61 |
| 0.3 m LiTFSI in PC:PYR12 | 0.03 | 0.41 | 1.52 | 3.47 | 6.54 | 7.72 | 7.91 |

Table S3. Ionic conductivity at respective temperature measured for this series of electrolytes: (i) 1.0 m LiPF₆ in EC:DMC (3:7) (1.0-EC/EMC); (ii) 2.5 m LiTFSI in propylene carbonate (2.5-PC); (iii) 2.5 m LiTFSI + PYR12 (2.5-PC-PYR); (iv) 1.0 m LiTFSI + PYR12 (1.0-PC-PYR); and (v) 0.3 m LiTFSI + PYR12 (0.3-PC-PYR).

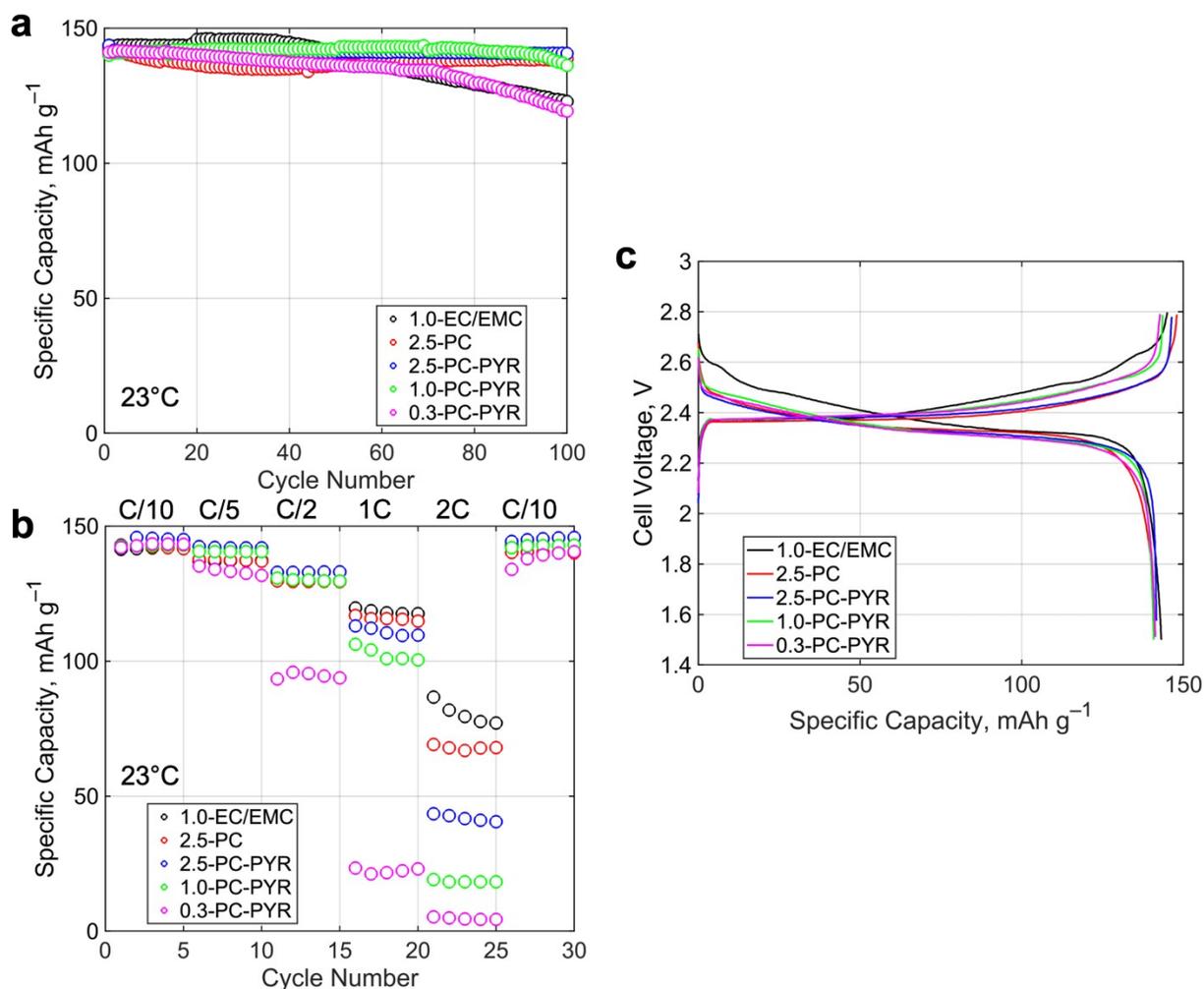


Figure S2. Room-temperature (23 °C) performance for this series of electrolytes: (i) 1.0 m LiPF6 in EC:DMC (3:7) (1.0-EC/EMC); (ii) 2.5 m LiTFSI in propylene carbonate (2.5-PC); (iii) 2.5 m LiTFSI + PYR12 (2.5-PC-PYR); (iv) 1.0 m LiTFSI + PYR12 (1.0-PC-PYR); and (v) 0.3 m LiTFSI + PYR12 (0.3-PC-PYR). **(a)** C/10 life/cycle tests and **(b)** corresponding rate capability at imposed cycling rates of C/10, C/5, C/2, 1C, 2C, and reversal back to C/10. Coulombic efficiency plots are shown in **Fig. S3**. **(c)** Cell voltage versus specific capacity at C/10.

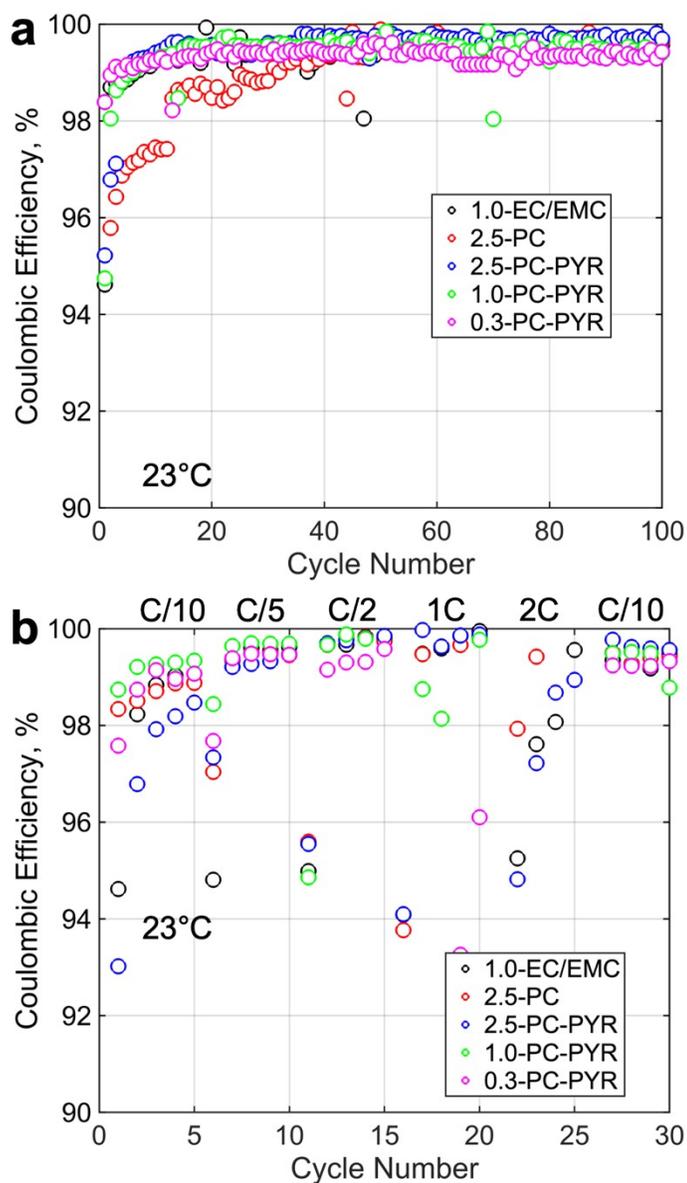


Figure S3. Room-temperature (23 °C) performance for this series of electrolytes: (i) 1.0 m LiPF₆ in EC:DMC (3:7) (1.0-EC/EMC); (ii) 2.5 m LiTFSI in propylene carbonate (2.5-PC); (iii) 2.5 m LiTFSI + PYR12 (2.5-PC-PYR); (iv) 1.0 m LiTFSI + PYR12 (1.0-PC-PYR); and (v) 0.3 m LiTFSI + PYR12 (0.3-PC-PYR). Coulombic efficiencies of (a) C/10 life/cycle tests and (b) rate capability at imposed cycling rates of C/10, C/5, C/2, 1C, 2C, and reversal back to C/10.

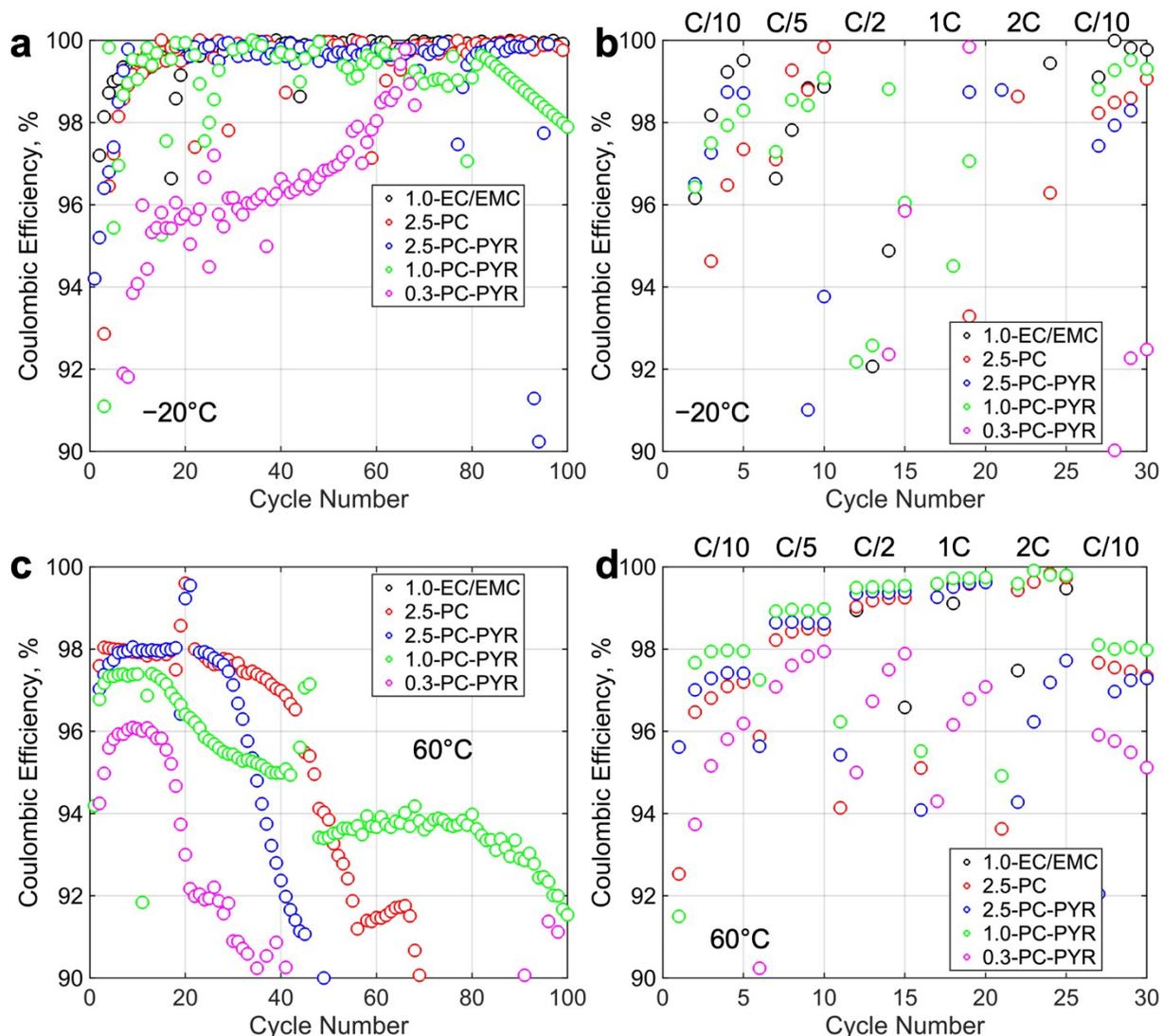


Figure S4. (a,b) Low-temperature ($-20\text{ }^{\circ}\text{C}$) and (c,d) High temperature ($60\text{ }^{\circ}\text{C}$) performance for this series of electrolytes: (i) 1.0 m LiPF₆ in EC:DMC (3:7) (1.0-EC/EMC); (ii) 2.5 m LiTFSI in propylene carbonate (2.5-PC); (iii) 2.5 m LiTFSI + PYR12 (2.5-PC-PYR); (iv) 1.0 m LiTFSI + PYR12 (1.0-PC-PYR); and (v) 0.3 m LiTFSI + PYR12 (0.3-PC-PYR). Coulombic efficiencies of (a,c) C/10 life/cycle tests and (b,d) rate capability at imposed cycling rates of C/10, C/5, C/2, 1C, 2C, and reversal back to C/10.

Supporting Information

| Electrolyte | Ignition Time (s) | Time to Extinguish (s) | Flammability Index (s g ⁻¹) |
|--------------|-------------------|------------------------|---|
| 1.0-EC/EMC | 3 | 22.5 | 77.0 |
| 2.5-PC | 8 | 15.4 | 51.2 |
| 2.5-PC-PYR12 | 8 | 8.6 | 22.9 |
| 1.0-PC-PYR12 | 8 | 11.4 | 35.1 |
| 0.3-PC-PYR12 | 8 | 15.3 | 50.4 |

Table S4. Flammability index for this series of electrolytes: (i) 1.0 m LiPF₆ in EC:DMC (3:7) (1.0-EC/EMC); (ii) 2.5 m LiTFSI in propylene carbonate (2.5-PC); (iii) 2.5 m LiTFSI + PYR12 (2.5-PC-PYR); (iv) 1.0 m LiTFSI + PYR12 (1.0-PC-PYR); and (v) 0.3 m LiTFSI + PYR12 (0.3-PC-PYR).