

Supporting Information

A fluorine-substituted pyrrolidinium-based ionic liquid for high-voltage Li-ion battery

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1. Materials and Electrochemical Testing

1.1 Electrode and electrolyte preparation

LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ cathodes (90% NMC532 (Toda Kogyo Corp.), 5% C45 conductive carbon (Timcal), and 5% PVdF (Solvay 5130) by weight), graphite composite anode (91.8% CPG-A12, 6% PVdF (Kureha 9300), 2% C45 conductive carbon and 0.17% oxalic acid) were fabricated by Cell Analysis, Modeling, and Prototyping (CAMP) Facility at Argonne National Laboratory. Active material loading is 10.26 mg/cm² for NMC532 cathode and 5.56 mg/cm² for graphite anode. The electrolytes were prepared in an argon-filled glovebox by mixing testing ionic liquid with LiFSI (Nippon Shokubai Co., Ltd.). The water content was <20 ppm, measured by using Mettler Toledo coulometric Karl-Fischer titrator C30. The viscosity was measured by ViscoLab 4000 at room temperature.

1.2 Electrochemical characterization

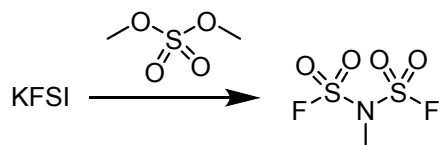
Electrolyte conductivity (σ) was calculated using the resistance data obtained by electrochemical impedance spectroscopy (EIS) using Solartron Analytical 1400 Cell test station. The distance between the electrodes (l) was kept equal to 0.172 cm using a Teflon spacer ring with the inner area (A) of 0.502 cm². Cell impedance was measured the frequency range of 1 MHz to 0.1 Hz at the open circuit potential (OCV).

Cyclic voltammetry was performed using a Gamry Instrument potentiostat reference 600+. The measurements were carried out in a 3-electrode cell with Pt (0.5 mm diameter) as working electrode, two lithium strips as counter and reference electrodes. The scan rate was 10 mV/s.

Galvanostatic charge-discharge cycling tests were conducted on Maccor Electrochemical Analyzer (MIMSciEnt) with Al-coated 2032-coin cells (Pred Materials International). All cells were assembled using NMC532 as cathode and lithium metal foil or graphite as the anode with a cutoff voltage of 4.2-3.0 V, 4.3-3.0 V or 4.7-3.0 V. The separator was a glass micro-fiber disc. The effective electrode area was 1.54 cm² for cathode and 1.77 cm² for anode. The cells were formed by three C/20 cycles followed by 100 cycles at C/10 (C = 2.3 mAh, 1 C current = 2.3 mA). All electrochemical experiments were conducted at 30°C. The N/P ratio for the NMC532/graphite cell is around 1.1 - 1.2. The specific capacity (mAh/g) was calculated by the obtained cell capacity (mAh)/active cathode material weight (*i.e.* weight of NMC532 material in gram).

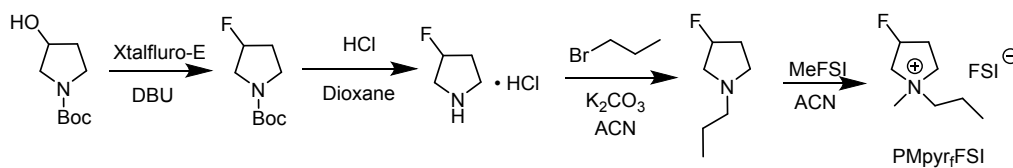
2. Precursor and PMpyr_r-FSI Synthesis

2.1 Methyl bis(fluorosulfonyl)imide - CH₃FSI



Scheme 1. Synthesis of CH₃FSI.

A 2 L round bottom flask was charged with potassium bis(fluorosulfonyl)imide (60 g, 276 mmol) and 1,4-dioxane (24 mL, 276 mmol), and dimethyl sulfate (400 mL, 4.2 mol) were added slowly. The mixture was heated to 100°C for 3 h. After cooling back to 70°C, ice cold water (900 mL) was added into the flask slowly and the mixture was stirred at 70°C for 1 h. After cooling down to room temperature, the mixture was extracted with CHCl₃ (200 mL x 3). The combined organic layer was washed with H₂O (150 mL) and dried with Na₂SO₄. The volatiles were removed under vacuum to get the crude product. The final product was isolated by vacuum distillation to yield as colorless liquid (26.8 g, 50%, b.p. 70-75 °C/50 torr). ¹H NMR (300 MHz, Acetone-*d*₆) δ 3.85 (t, J = 1.6 Hz, 3H). ¹⁹F NMR (282 MHz, Acetone-*d*₆) δ 53.83 (q, J = 1.8 Hz).



Scheme 2. Synthesis of PMpyr_F-FSI.

2.2 1-Boc-3-fluoropyrrolidine

A flask was charged with 1-boc-3-hydroxypyrrolidine (1.87 g, 10 mmol) and dichloromethane (DCM) (30 mL) and cooled to -78°C. XtalFluro-E (3.45 g, 15 mmol) and DBU (2.25 mL, 15 mmol) were added at -78°C and the mixture was stirred at -78°C for 2 h and then the temperature was allowed to warm up to room temperature and stirred overnight. The reaction was quenched

with NaHCO₃ (sat., 50 mL) and the aqueous layer was extracted with DCM (50 mL x 3). The combined organic layer was washed by brine solution and dried with Na₂SO₄. The volatiles were removed under vacuum to yield a brown oil and the crude was purified by silica gel chromatography (5-10 % ethyl acetate in hexanes) to give 0.9 g product (47.6%) as yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 5.21 (dt, J = 52.9, 3.7 Hz, 1H), 3.59 (ddd, J = 51.5, 26.4, 15.0 Hz, 4H), 2.35 – 2.11 (m, 1H), 1.95-1.85 (m, 1H), 1.47 (s, 9H). ¹⁹F {¹H} NMR (282 MHz, CDCl₃) δ -177.0, -177.4.

2.3 3-Fluoropyrrolidine hydrochloride

A flask was charged with 1-boc-3-fluoropyrrolidine (0.9 g, 4.7 mmol) and 1,4-dioxane (25 mL) and HCl solution (8 mL, 4 M in 1,4-dioxane) was added and the mixture was stirred at room temperature overnight in Ar-filled glovebox. The product was collected by filtration and rinsed with Et₂O as a light brownish solid (0.36 g, 60 %) and used in the next step without further purification. ¹H NMR (300 MHz, D₂O) δ 5.48 (dt, J = 51.7, 3.9 Hz, 1H), 3.88 – 3.11 (m, 4H), 2.69 – 1.68 (m, 2H). 1.47 (s, 9H). ¹⁹F {¹H} NMR (282 MHz, D₂O) δ -177.0.

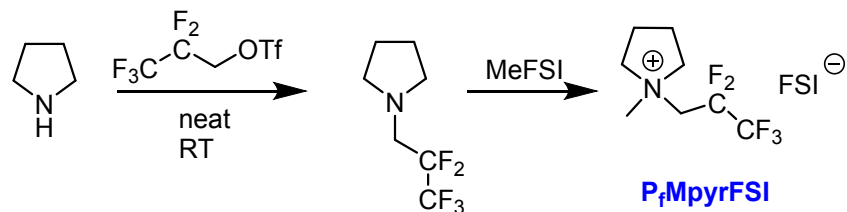
2.4 1-Propyl-3-fluoropyrrolidine

A flask was charged with 3-fluoropyrrolidine hydrochloride (2.01 g, 16 mmol), K₂CO₃ (6.60 g, 48 mmol), 1-bromopropane (1.6 mL, 18 mmol) and acetonitrile (50 mL) and the mixture was heated to 50 °C and stirred for 2 days. The solid was filtered off and HCl solution (4 mL, 4 M in 1,4-dioxane) was added to the filtrate. The volatiles were removed under vacuum to yield a yellow solid and the solid was taken up into water (20 mL) and neutralized by NaOH (aq. 2.5 M). The aqueous layer was extracted with Et₂O (30 mL x 3) and the combined organic layer was washed with brine solution. The majority of Et₂O was removed by distillation and the product

was isolated by vacuum transfer as an Et₂O solution (5.0 g, with 3 eq. Et₂O and 0.1 eq. 1,4-dioxane per product, yield 88%) for the next step without further purification. ¹H NMR (300 MHz, Acetone-*d*₆) δ 5.13 (dddt, J = 56.2, 6.9, 5.1, 1.8 Hz, 1H), 2.81 – 2.46 (m, 3H), 2.40 – 2.10 (m, 4H), 1.98 – 1.71 (m, 1H), 1.70 – 1.37 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H), (1,4-dioxane is observed at δ 3.58 as singlet and Et₂O is observed at δ 3.40 and 1.11 as quartet and triplet, respectively). ¹⁹F{¹H} NMR (282 MHz, Acetone-*d*₆) δ -168.3.

2.5 *1-Methyl-1-propyl-3-fluoropyrrolidinium bis(fluorosulfonyl)imide (PMpyr_F-FSI)*

To the Et₂O solution of 1-propyl-3-fluoropyrrolidine (5.0 g, with 3 eq. Et₂O and 0.1 eq. 1,4-dioxane per 1-propyl-3-fluoropyrrolidine), MeFSI (2.75 g, 14 mmol) was added slowly and the mixture was stirred at room temperature for 2 h. The volatiles were removed under vacuum to yield a light-yellow oil. The crude was taken up in ethyl acetate (50 mL) and activate charcoal (4 g) was added and the mixture was stirred overnight. The activate charcoal was removed by filtration and the volatiles were removed under vacuum to yield colorless oil (3.9 g, 85%). The resulted IL was dried in lyophilizer for at least 2 days, then stored over 4 Å molecular sieves and filtered before use. ¹H NMR (300 MHz, Acetone-*d*₆) δ 5.68 (d, J = 54.6 Hz, 1H), 4.31 – 3.77 (m, 4H), 3.74 – 3.49 (m, 2H), 3.42 and 3.39 (s, 3H), 3.05 – 2.43 (m, 2H), 2.07 – 1.82 (m, 2H), 1.02 and 1.01 (t, J = 7.2 Hz, 3H). ¹⁹F{¹H} NMR (282 MHz, Acetone-*d*₆) δ 51.4, -168.9, -172.4. ¹³C{¹H} NMR (75 MHz, Acetone-*d*₆) δ 92.79 (d, J = 177.6 Hz), 71.47 – 69.82 (m), 68.34 (d, J = 3.6 Hz), 64.68 (d, J = 3.6 Hz), 51.08 (d, J = 3.6 Hz), 31.52 (d, J = 2.0 Hz), 17.87 (d, J = 2.0 Hz), 10.82 (d, J = 2.0 Hz).



Scheme 3. Synthesis of P_fMpyr-FSI.

3. Precursor and P_fMpyr-FSI Synthesis

3.1 1-(2,2,3,3,3-Pentafluoropropyl)pyrrolidine¹

A flask was charged with pyrrolidine (50 mL, 600 mmol) and cooled to 0°C. 2,2,3,3,3-Pentafluoropropyl trifluoromethanesulfonate (33 mL, 200 mmol) was added at 0°C and the temperature was allowed to warm up to room temperature and stirred overnight. The solids were removed by filtration and washed with Et₂O. The filtrate was diluted with Et₂O to a total volume of 120 mL and then the Et₂O layer was washed by 5% HCl (aq.) solution (120 mL x 2). The Et₂O was removed by distillation and the product was isolated by distillation (36 g, 89%, b.p. 114-115°C). ¹H NMR (300 MHz, CDCl₃) δ 3.12 (t, J = 15 Hz, 2H), 2.73 (br, 4H), 1.82 (br, 4H). ¹⁹F NMR (282 MHz, CDCl₃) δ -84.2, -119.6 (t, J = 15.9 Hz).

3.2. 1-Methyl-1-(2,2,3,3,3-pentafluoropropyl)pyrrolidinium bis(fluorosulfonyl)imide (P_fMpyr-FSI)

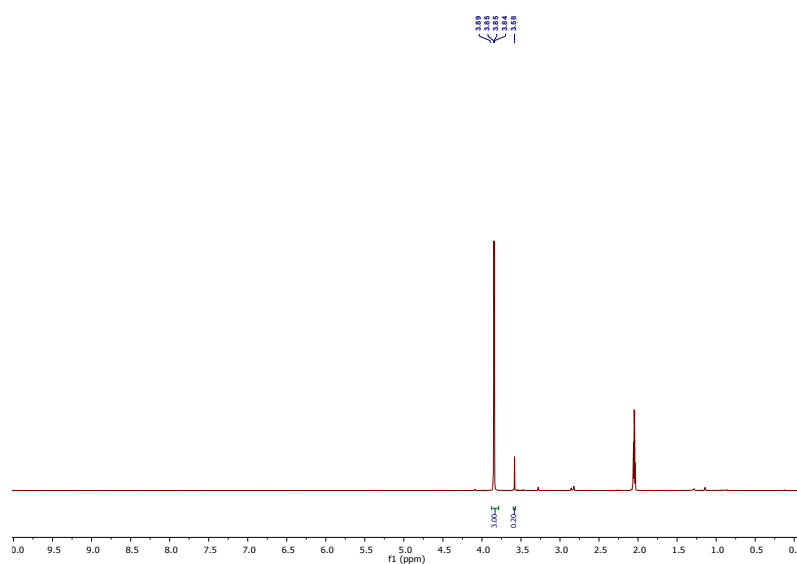
A flask was charged with 1-(2,2,3,3,3-pentafluoropropyl)pyrrolidine (20.3 g, 100 mmol) and ethyl acetate (200 mL), CH₃FSI (19.5 g, 14 mmol) was added slowly and the mixture was stirred at room temperature for 2 h. Then activate charcoal (20 g) was added and the mixture was stirred overnight. The activate charcoal was removed by filtration and the volatiles were removed under vacuum to yield colorless oil (33.2 g, 83%). The resulted IL was dried in lyophilizer for at least 2 days, then stored over 4 Å molecular sieves and filtered before use. ¹H NMR (300 MHz,

Acetone- d_6) δ 4.84 (t, $J = 16.7$ Hz, 2H), 4.26 – 3.90 (m, 4H), 3.58 (s, 3H), 2.62 – 2.33 (m, 4H).
 ^{19}F NMR (282 MHz, Acetone- d_6) δ 51.4, -85.75, -116.87 (t, $J = 16.7$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Acetone- d_6) δ 120.6 (qt, $J = 382.0, 33.9$ Hz), 115.6 (tq, $J = 389.2, 38.4$ Hz), 68.7, 60.3 (t, $J = 17.9$ Hz), 50.6, 22.0.

4. Multi-NMR Spectra

Figure S1. NMR spectra of CH_3FSI in acetone- d_6 . ($\delta = 3.58$, 1,4- dioxane, 2 %)

(a) ^1H NMR



(b) ^{19}F NMR

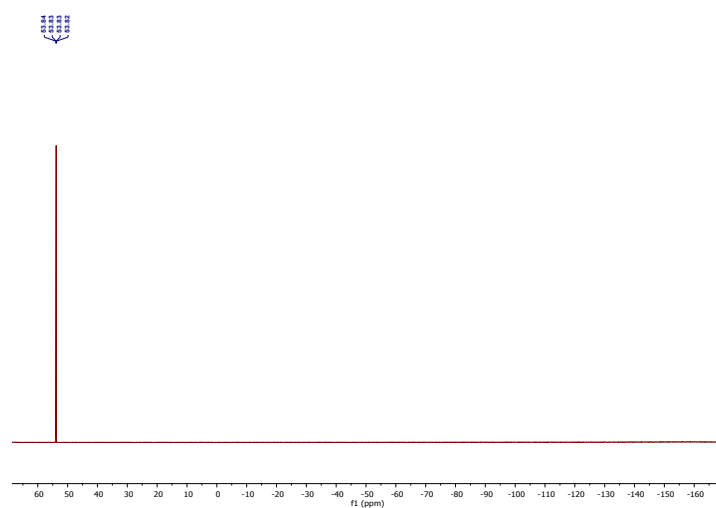
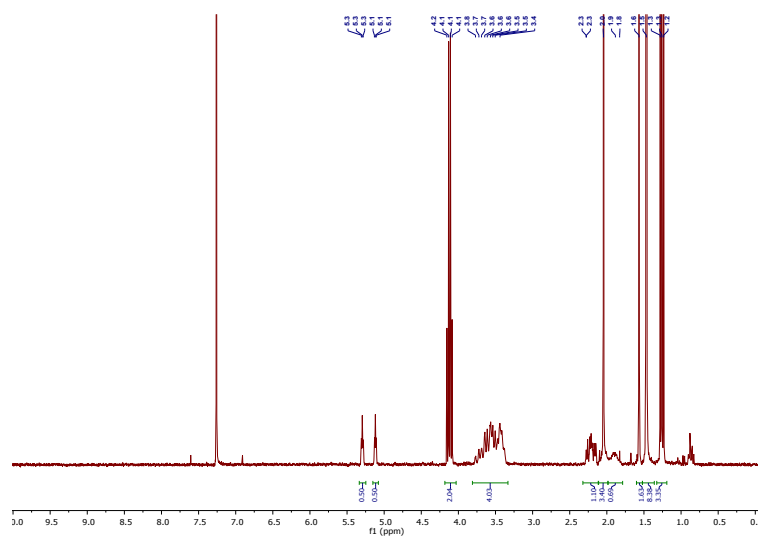


Figure S2. NMR spectra of 1-boc-3-fluoropyrrolidine in CDCl₃.

(a) ¹H NMR



(b) ¹⁹F {¹H } NMR

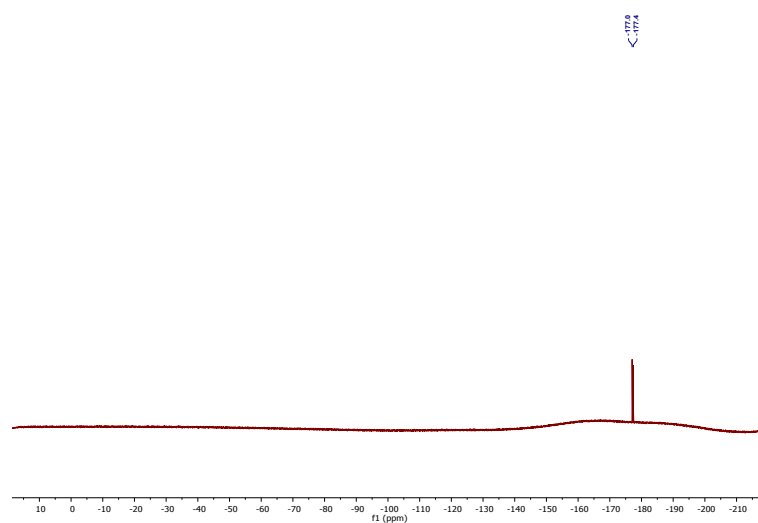
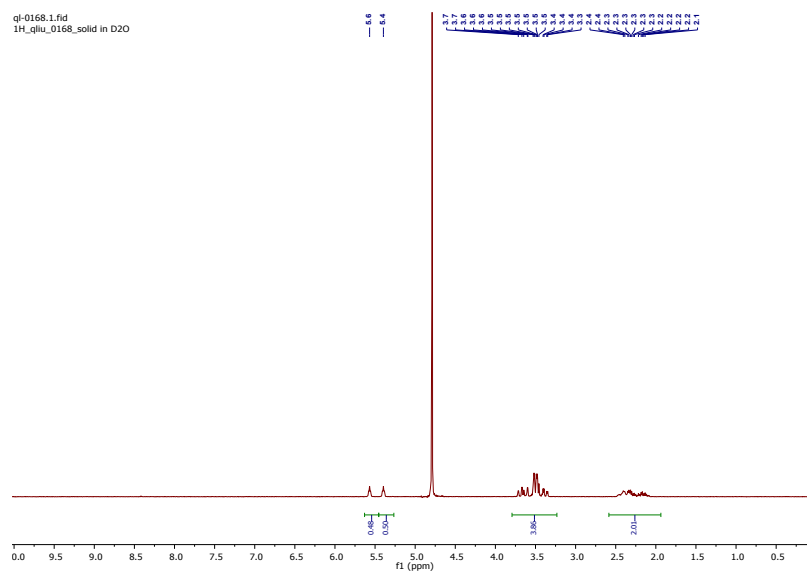


Figure S3. NMR spectra of 3-fluoropyrrolidine hydrochloride in D₂O.

(a) ¹H NMR



(b) ¹⁹F{¹H} NMR

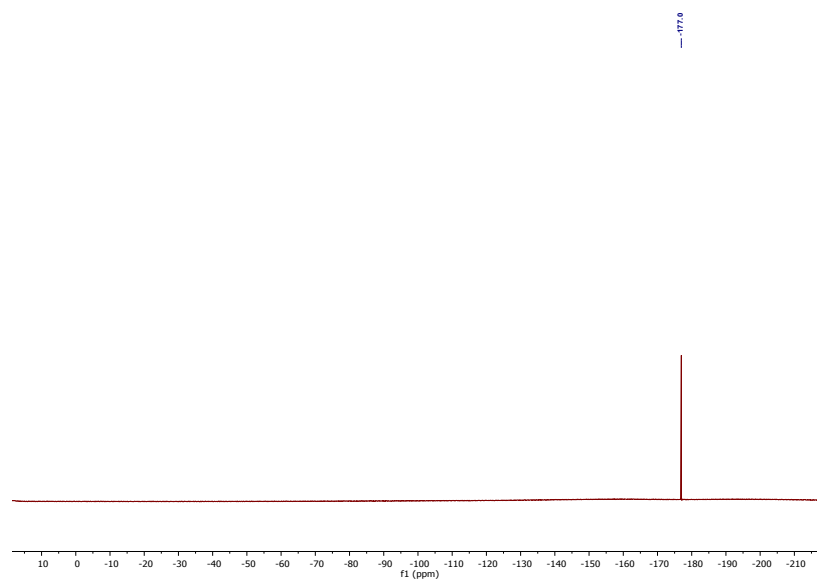
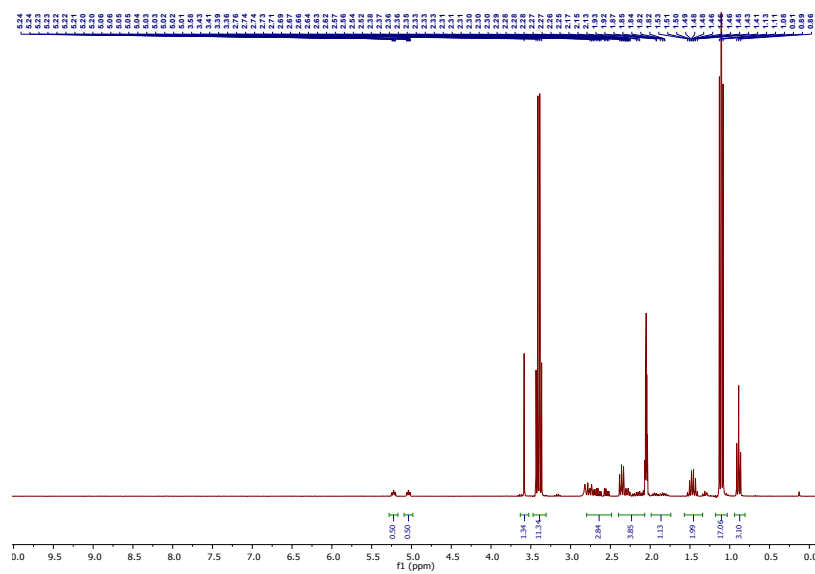


Figure S4. NMR spectra of 1-propyl-3-fluoropyrrolidine in acetone- d_6 .

(a) ^1H NMR



(b) $^{19}\text{F}\{^1\text{H}\}$ NMR

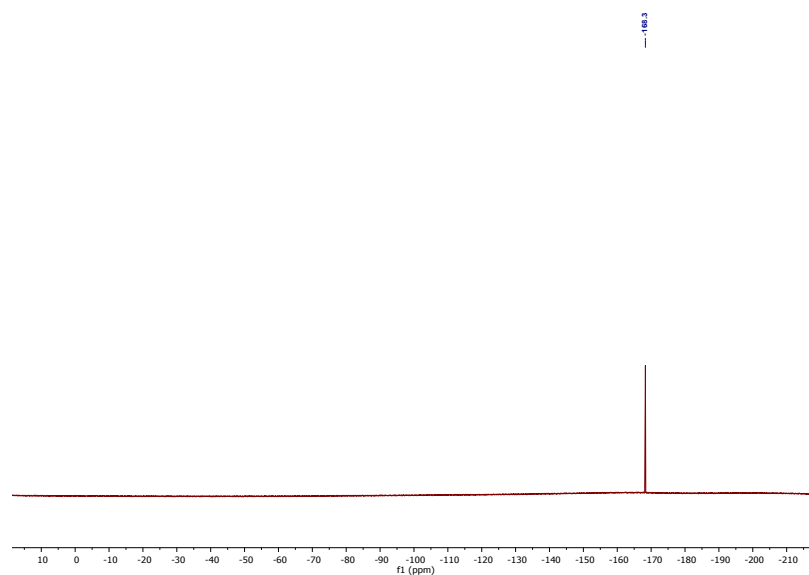
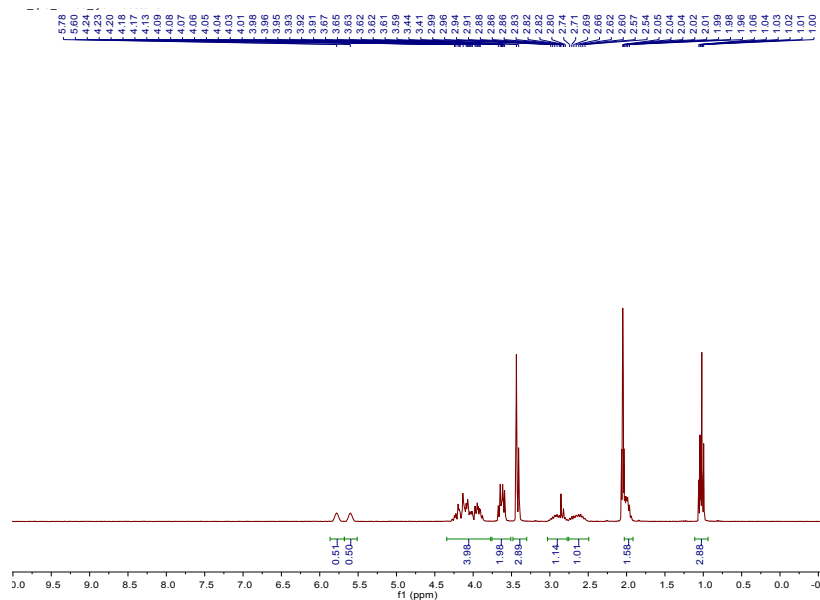
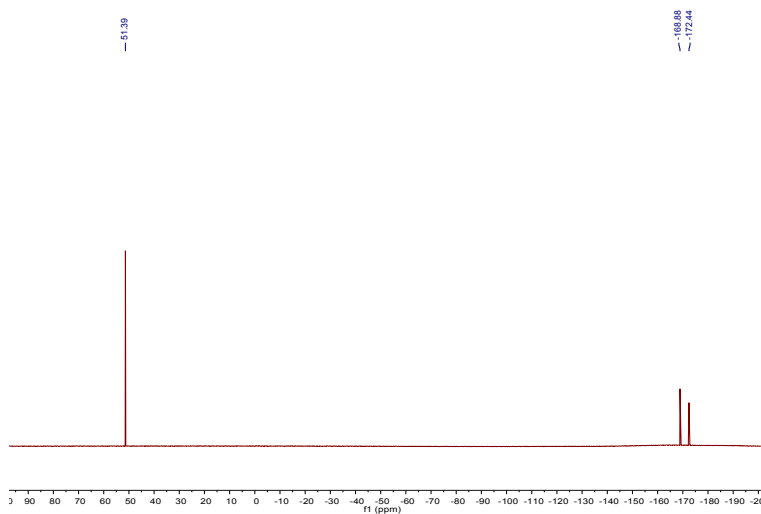


Figure S5. NMR spectra of 1-methyl-1-propyl-3-fluoropyrrolidinium bis(fluorosulfonyl)imide (PMpyr_F-FSI) in acetone-*d*₆.

(a) ¹H NMR



(b) ¹⁹F{¹H} NMR



(c) $^{13}\text{C}\{^1\text{H}\}$ NMR

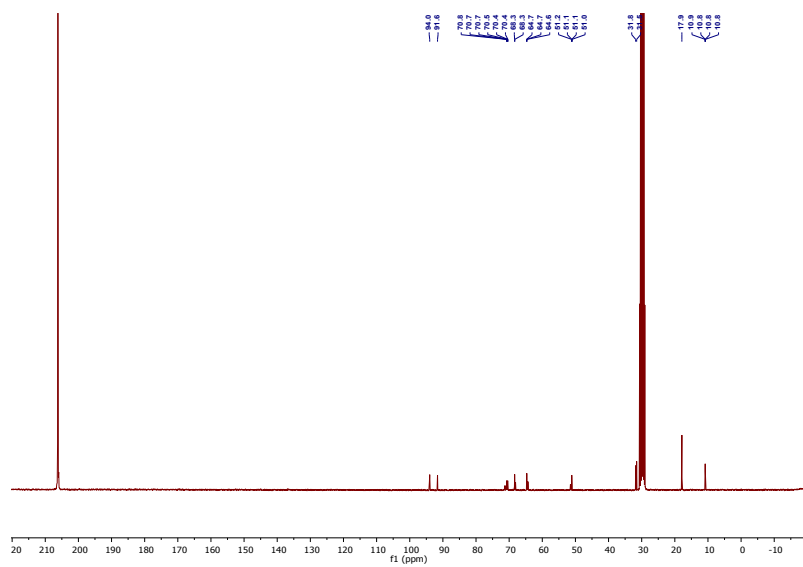
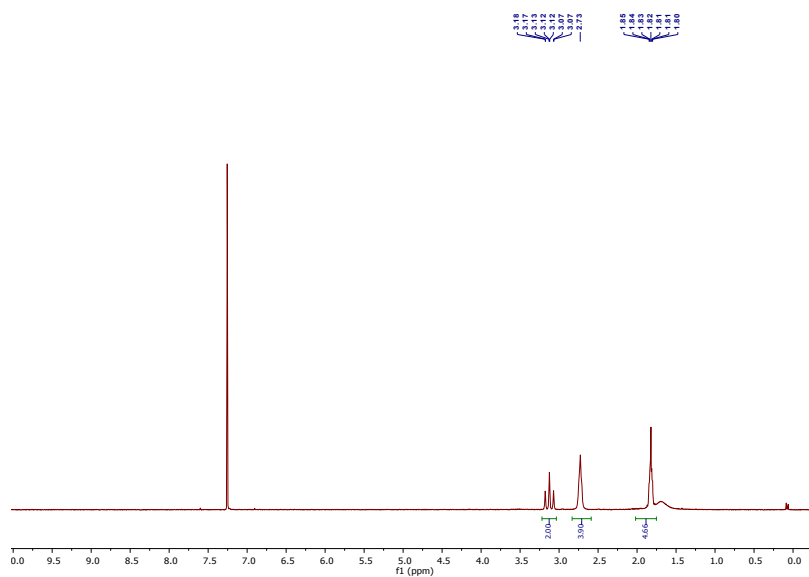


Figure S6. NMR spectra of 1-(2,2,3,3,3-pentafluoropropyl)pyrrolidine in CDCl_3 .

(a) ^1H NMR



(b) ^{19}F NMR

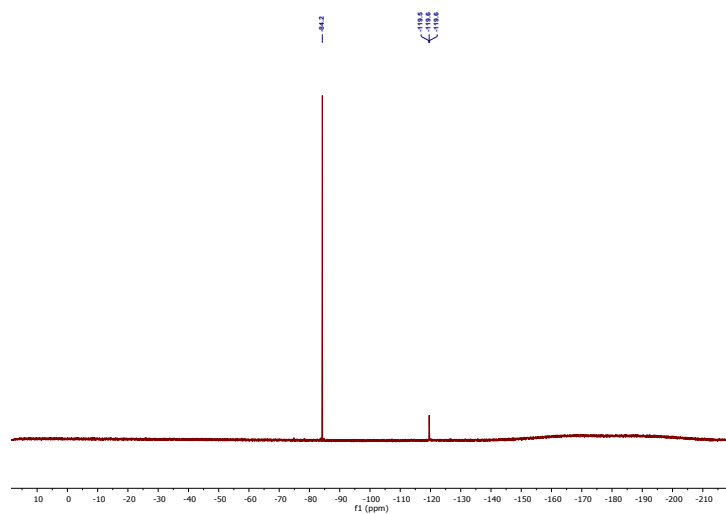
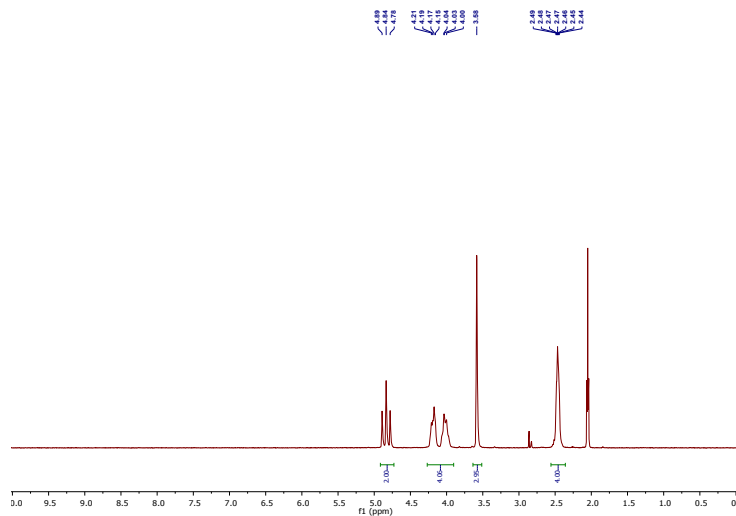
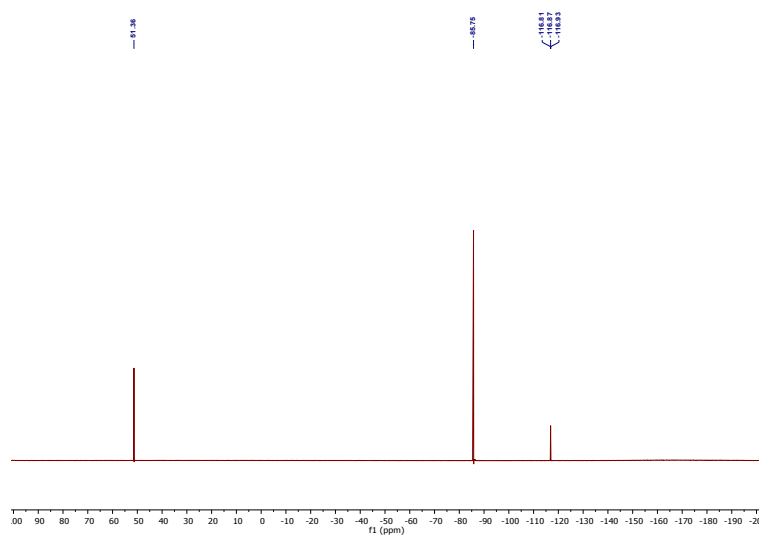


Figure S7. NMR spectra of 1-methyl-1-(2,2,3,3,3-pentafluoropropyl)pyrrolidinium bis(fluorosulfonyl)imide ($\text{P}_f\text{Mpyr-FSI}$) in acetone- d_6 .

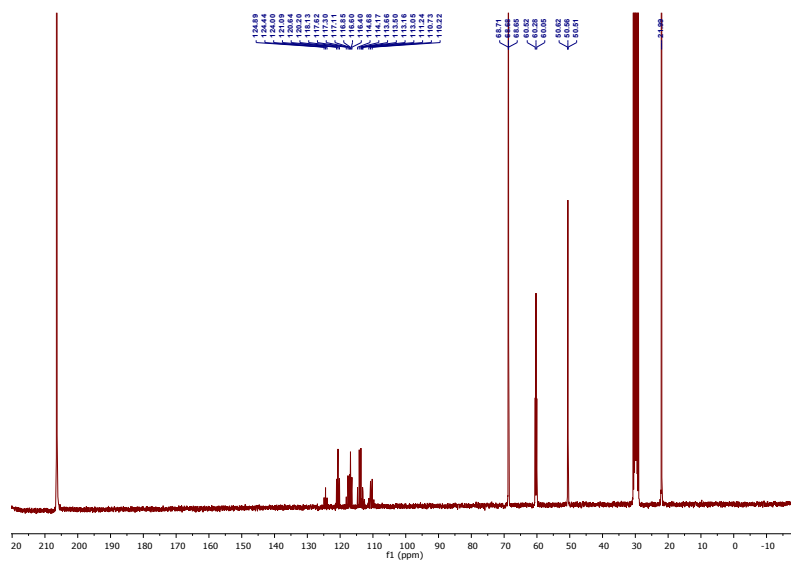
(a) ^1H NMR



(b) $^{19}\text{F}\{^1\text{H}\}$ NMR



(c) $^{13}\text{C}\{^1\text{H}\}$ NMR



5. Supplemental electrochemical data

Table S1. Viscosity and Ionic Conductivity of Pristine Ionic Liquids and Electrolytes.

| | Viscosity (cP @ 25°C) | Ionic Conductivity (mScm ⁻¹ @ 25°C) |
|--|--------------------------|---|
| PMpyr-FSI | 40 | 9.32 |
| PMpyr _r -FSI | 83 | 4.25 |
| PMpyr _r -FSI + 1 M LiFSI ^a | 150 | 2.57 |
| PMpyr _r -FSI + 4 M LiFSI ^a | 528 | 0.55 |
| P _f Mpyr-FSI | 261 | 1.68 |
| P _f Mpyr-FSI + 1 M LiFSI ^a | 364 | 1.18 |
| P _f Mpyr-FSI + 4 M LiFSI ^a | 1127 | 0.36 |

^aDenoted concentration of LiFSI is determined by the X millimoles of LiFSI dissolved in 1 mL of IL.

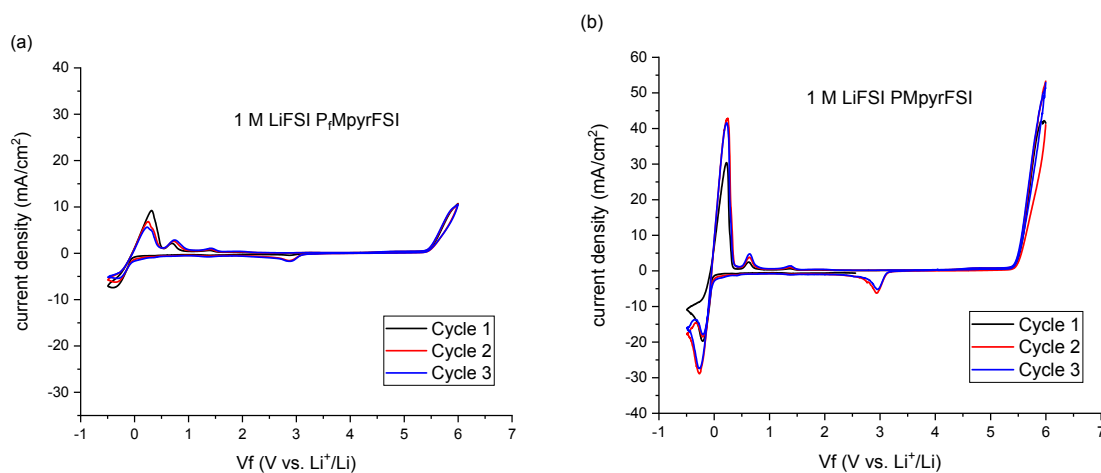


Figure S8. Cyclic voltammetry profiles of (a) 1 M LiFSI P_fMpyr-FSI and (b) 1 M LiFSI PMpyr-FSI. Scan potential vs Li⁺/Li from -0.5 to 6 V.

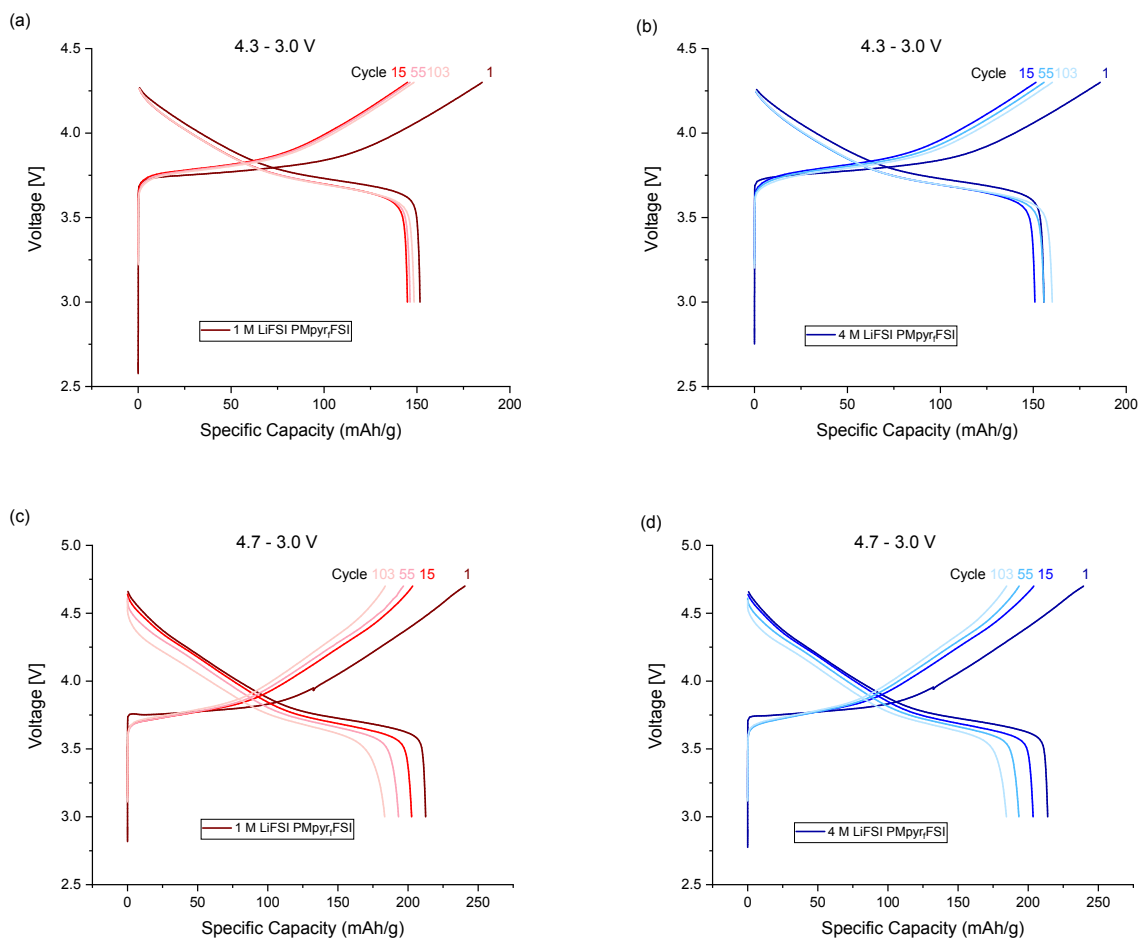


Figure S9. Voltage profiles of NMC532/Li cells using 1 M LiFSI PMpyr₇-FSI (a and c) and 4 M LiFSI PMpyr₇-FSI (b and d). Cutoff voltage: 4.3 – 3.0 V (a and b); 4.7 – 3.0 V (c and d).

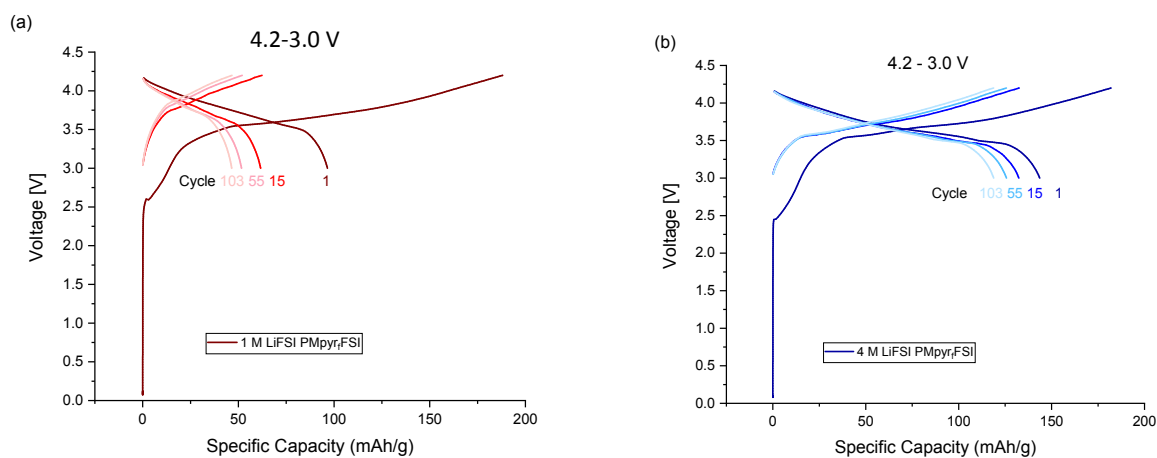


Figure S10. Voltage profiles of NMC532/graphite cells using 1 M LiFSI PMpyr₄-FSI (a) and 4 M LiFSI PMpyr₄-FSI (b). Cutoff voltage: 4.2 – 3.0 V.

Reference

1. T. Mantani, K. Shiomi, T. Konno, T. Ishihara and H. Yamanaka, A Convenient Preparation of 3,3,3-Trifluoro-1-propynylamines and Their Lewis Acid Catalyzed Reaction with Carbonyl Compounds Leading to (Z)- α -(Trifluoromethyl)- α,β -unsaturated Amides. *J. Org. Chem.* 2001, **66** (10), 3442.