

Supporting Information

Synthesis and Physicochemical Characterization of Room Temperature Ionic Liquids and their Application in Sodium Ion Batteries

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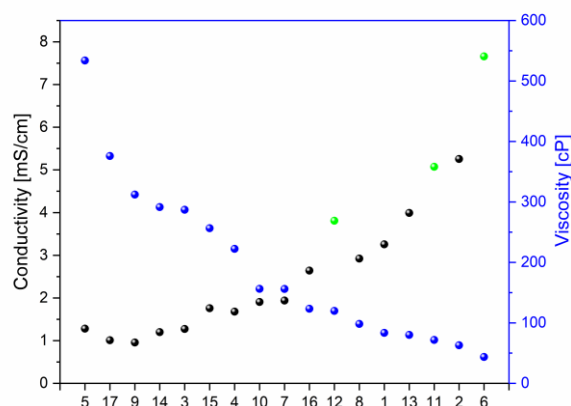


Figure S11: Correlation of conductivity (TFSI ILs: black; FSI ILs: green) and viscosity (blue) of all RTILs included in this study. Numbers on the x-axis mark the respective RTILs.

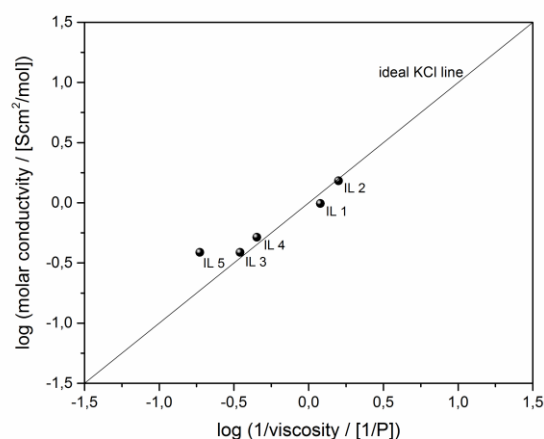


Figure S12: Walden plot for the functionalized pyrrolidinium TFSI ILs.

Figure S12 shows the Walden plot of functionalized pyrrolidinium TFSI ILs. The Walden plot serves to find possible relations between the molar conductivity and the fluidity (reciprocal viscosity).¹ The densities of the ILs, which are required in order to calculate the molar viscosity, were measured by determining the mass of 100 μl of each respective IL (average value of three measurements). Analysis of the Walden plot indicates that the Walden rule is valid for IL 1 to IL 5 because all values lie on or around the so-called "ideal" Walden product line, with the largest deviation being 0.31 for IL 5. Accordingly, these ILs can be described as "good ionic liquids" using the classification diagram by Angell *et al.*,² suggesting a low to vanishing level of ion association.¹⁻⁴

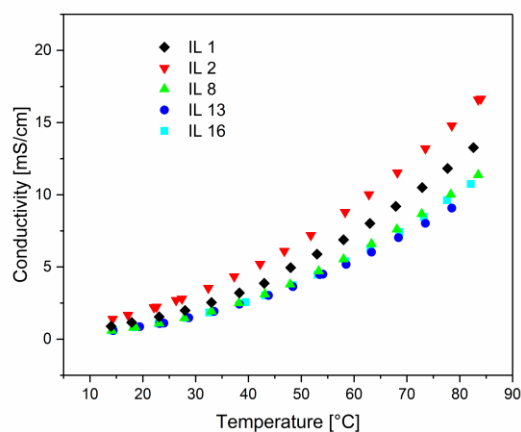


Figure S13: Temperature dependence of the conductivity of selected RTILs with conducting salt (NaFSI 0.5 M).

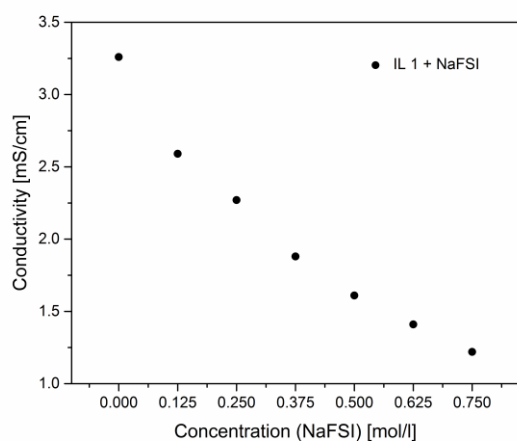


Figure S14: Dependency of the conductivity of IL 1 on the concentration of added conducting salt NaFSI.

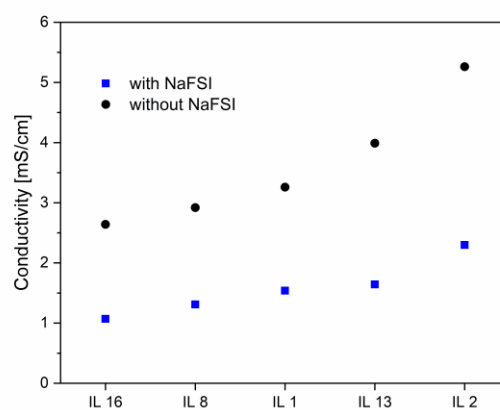


Figure S15: Comparison of conductivities with and without conducting salt (NaFSI 0.5 M) for selected RTILs.

Table S11: Comparison of conductivity and viscosity of IL1 with NaFSI and NaTFSI at RT.

	σ [mS/cm]	η (cp)
IL 1 + NaFSI (0.5 M)	1.61	152
IL 1 + NaTFSI (0.5 M)	1.22	162

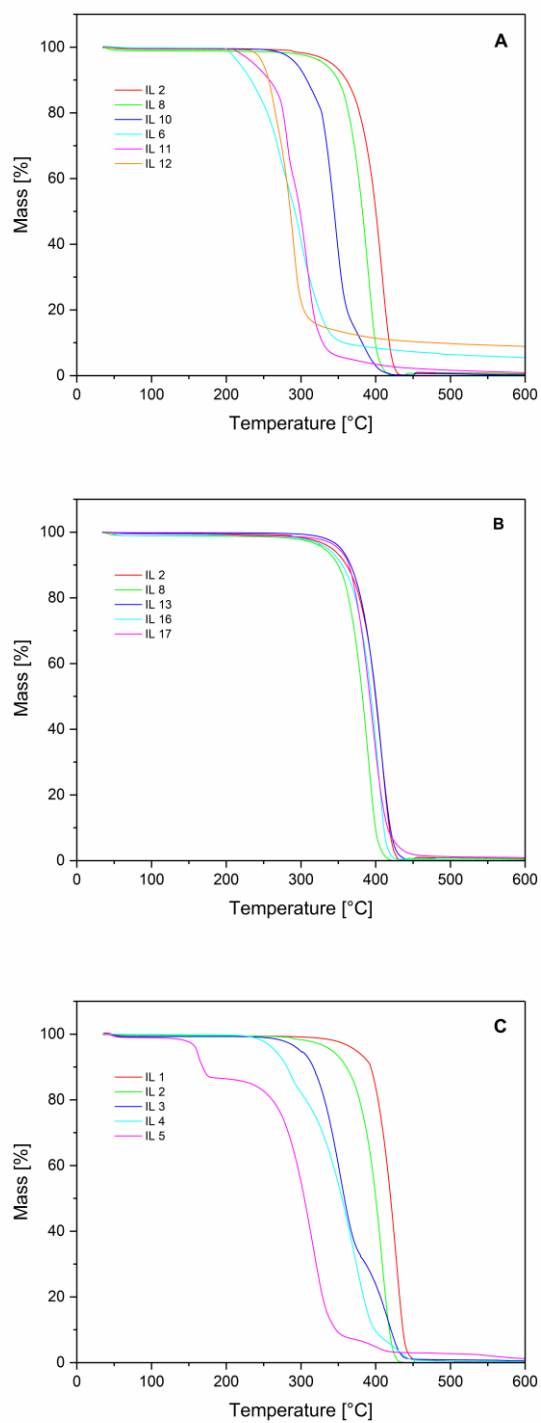


Figure S16: TGA curves for: FSI vs. TFSI RTILs (A), ether functionalized RTILs (B) and pyrrolidinium RTILs (C).

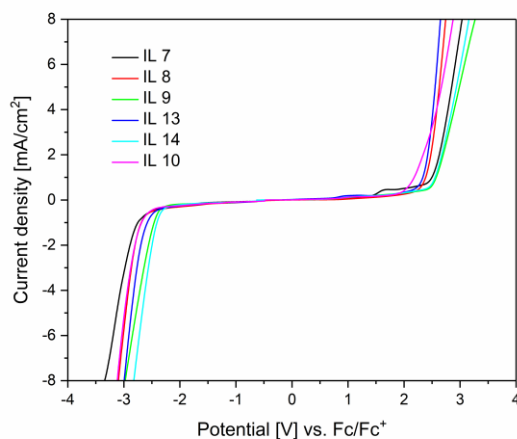


Figure S17: Linear sweep voltammograms of the ammonium based RTILs.

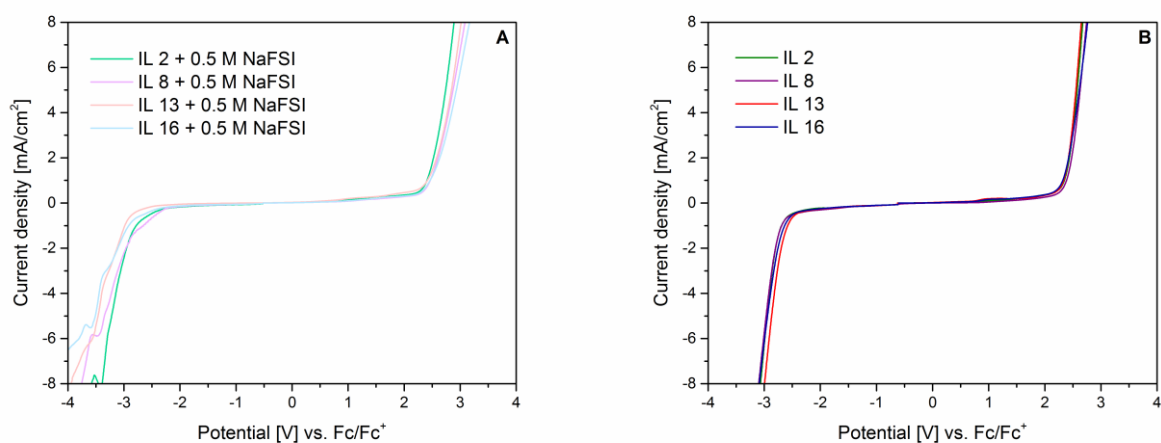


Figure S18: Linear sweep voltammograms of ILs 2, 8, 13 and 16 with (A) and without (B) addition of NaFSI (0.5 M).

Table S12: Electrochemical stabilities vs. Fc/Fc⁺ for ILs 2, 8, 13 and 16 with and without addition of NaFSI (0.5 M).

	E_A [V]	E_C [V]	ESW [V]		E_A [V]	E_C [V]	ESW [V]
IL 2 + NaFSI	2.41	-2.99	5.40	IL 2	2.34	-2.58	4.92
IL 8 + NaFSI	2.41	-2.78	5.19	IL 8	2.35	-2.63	4.98
IL 13 + NaFSI	2.46	-2.91	5.37	IL 13	2.32	-2.64	4.96
IL 16 + NaFSI	2.46	-2.75	5.21	IL 16	2.39	-2.69	5.08

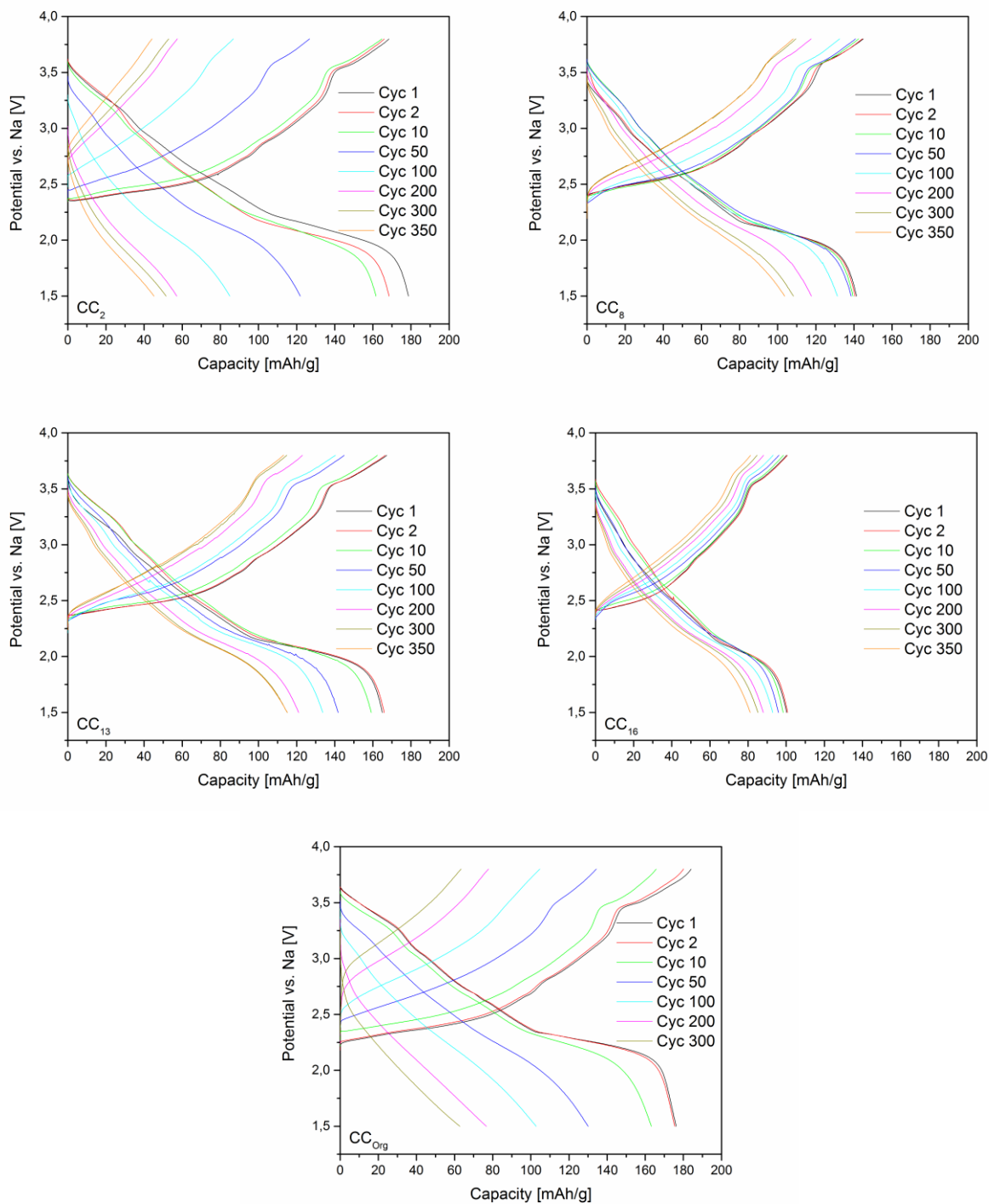


Figure SI 9: Galvanostatic charge-discharge curves for the evaluated coin cells CC_2 , CC_8 , CC_{13} , CC_{16} and CC_{Org} .

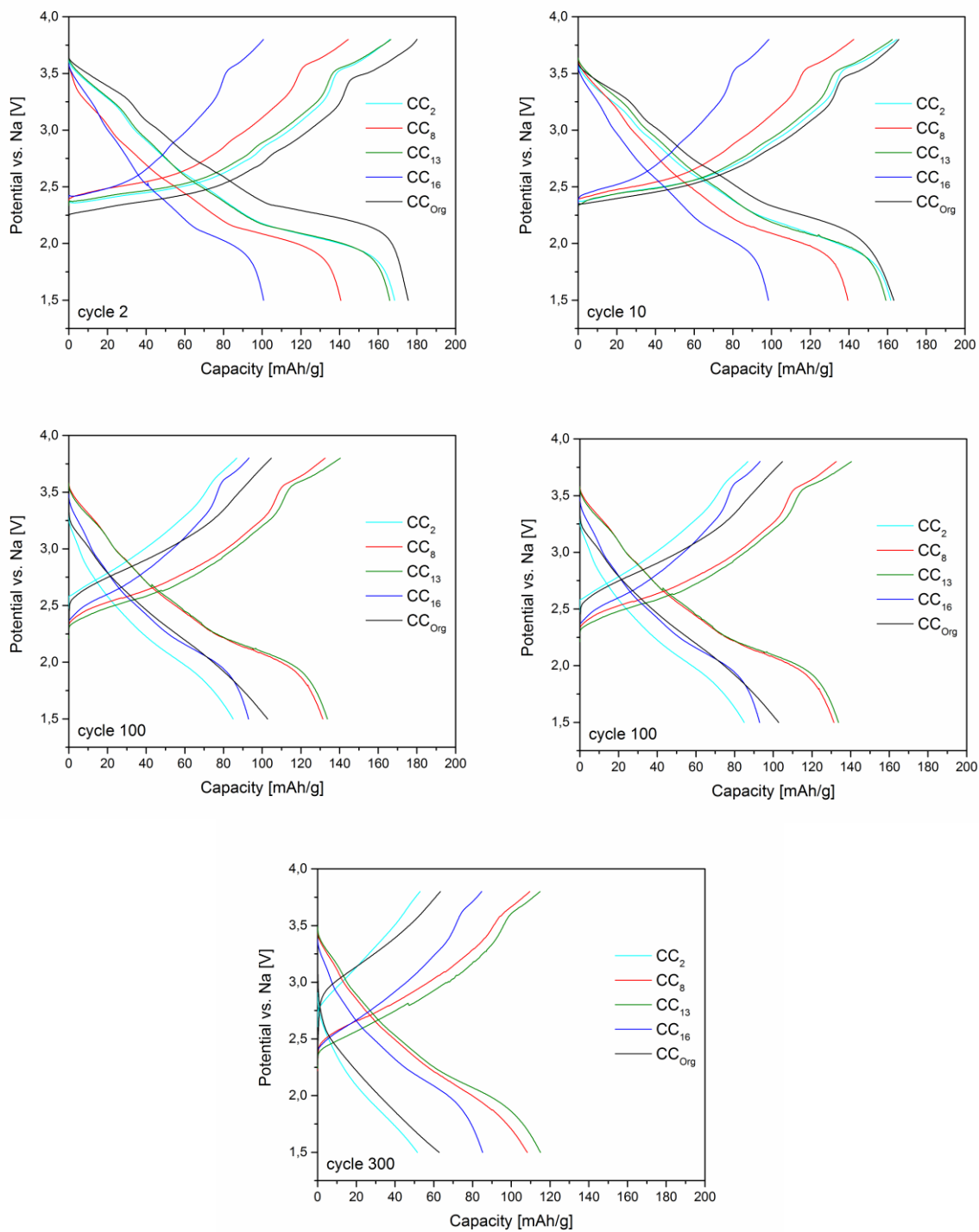


Figure S110: Overview of the galvanostatic charge-discharge curves for different cycles for the evaluated coin cells CC_2 , CC_8 , CC_{13} , CC_{16} and CC_{org} .

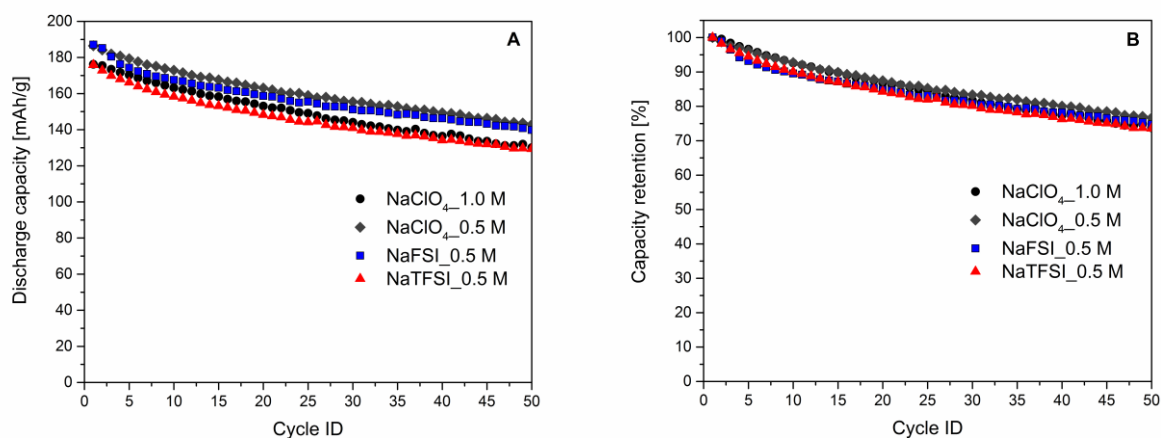


Figure SI11: Galvanostatic cycling of NMO half-cells with EC/PC and different conducting salts: discharge capacities (A) and cycling retention (B).

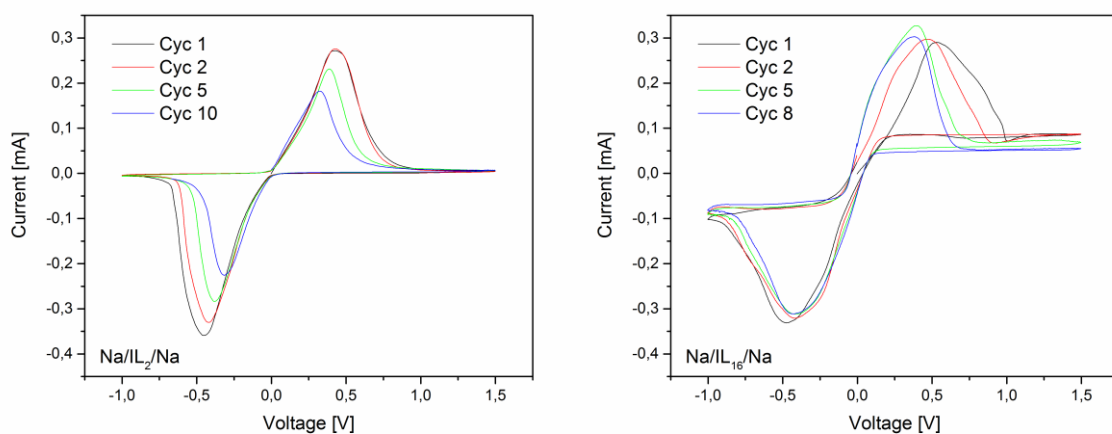


Figure SI12: Cyclic voltammograms of symmetric Na-cells with IL 2 (left) and IL 16 (right).

To investigate the sodium stripping behaviour of the applied electrolytes preliminary studies with the electrolytes based on IL 2 and IL 16 were performed in symmetric Na-cells (Figure SI12) with a scan rate of 0.1 mV/s. The CVs of IL 2 and IL 16 show sodium plating-stripping at around 0.5 V with similar current in the first cycle. IL 2, which displays the worst cycling performance among the IL-electrolytes, shows a continuously decreasing current. This suggests a possibly continually growing SEI layer with repeated cycling, which will most likely affect sodium plating-stripping significantly. On the other hand, the current observed for IL 16, which displays the most stable cycling behavior, remains more or less constant with repeated cycling. This indicates the formation of a relatively stable SEI layer, that would exhibit better sodium plating-stripping characteristics.

2) Synthesis and characterization:

General remarks: Unless noted otherwise, all reactions except for the anion exchanges were carried out under argon atmosphere with standard Schlenk techniques. All chemicals were purchased from commercial sources. The amine precursors and all non-dry solvents were purified by distillation prior to use. Dry solvents were dried using an *MBraun* Solvent Purification System. IL 1 and 7 were purchased from Iolitec (99%) and purified and dried according to the general procedure described in the following.

NMR spectroscopy: NMR spectra were acquired on a *Bruker* Advance Ultrashield 400 MHz spectrometer. All ^1H and ^{13}C chemical shifts δ are reported in parts per million (ppm), with the residual solvent peak serving as internal reference.⁵ The abbreviation of the signal multiplets are as followed: s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet. The coupling constant J is stated as average value in Hz.

Mass spectrometry (ESI MS): Mass spectra were acquired on a *Thermo Scientific* LCQ Fleet by *Thermo Fischer Scientific* (injection of 1 μl of a ~ 1 mg/ml sample in acetonitrile) using electron spray ionization (ESI) and a 3D-ion trap as detector.

Elemental analysis (EA): Elemental analysis was performed by the micro analytical laboratory at the Department of Chemistry of the Technische Universität München. The elements C and H and N were determined with a combustion analyzer (EURO EA-CHNS, *HEKAtech*).

Water content: Water content of the RTILs was determined with 2 g of the respective IL by Karl Fischer titration with a *Mettler-Toledo* DL39 with diaphragm and combi coulomat solution.

Synthesis of the IL precursor salts: The precursor salts for all ILs except the precursor for **IL 14 (PC 14)**, were synthesized following literature procedures⁶⁻¹⁴ with slight modifications in the purification procedures in some cases.

In general, for the quaternization reactions the respective functionalized alkylhalide is added dropwise a solution of the respective amine precursor under argon atmosphere. The resulting reaction mixture is stirred at room temperature or under reflux for 24 to 72 h. Afterwards, the crude product is obtained either by removal of the solvent under reduced pressure, or by addition of diethyl ether to the reaction mixture and subsequent filtration. The crude product is washed with diethyl ether/ethyl acetate or toluene three times followed by a further washing step with pentane. After recrystallization, quaternary ammonium halide salts are obtained as white to off white solids.

***N,N*-diethyl-2-methoxy-*N*-methyl-2-oxoethan-1-aminium bis((trifluoromethyl)sulfonyl)amide (PC 14):** Under argon atmosphere 11.10 g (72.56 mmol, 1.00 eq.) bromoacetic acid methyl ester are added dropwise to a solution of 12.53 g (143.82 mmol, 1.98 eq.) *N,N*-diethylmethylamine in dry acetone (45 ml). The resulting suspension is stirred for 24 h at room temperature. After subsequent removal of the solvent under vacuum the obtained orange dispersion is washed with diethyl ether (3 \times 50 ml). The crude product is recrystallized from ethanol (30 ml) and diethyl ether (30 ml) and dried under vacuum at 70 °C for 24 h. Finally, 7.77 g (32.35 mmol, 45%) of compound **PC 14** are obtained as a white solid.

White solid, 45% yield, ^1H -NMR (CDCl_3 , 400 MHz, 298.6 K, ppm): δ = 4.99 (s, 2H, NCH_2CO), 4.06 – 3.82 (m, 4H, NCH_2CH_3), 3.81 (s, 3H, NCH_3), 3.54 (s, 6H, COCH_3), 1.42 (t, 3J = 7.3 Hz, 6H, NCH_2CH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 300.9 K, ppm) δ = 165.40, 58.89, 57.26, 53.32, 48.38, 8.57; MS (ESI, MeCN): m/z = 160.03; 398.72 (calcd. for $[\text{C}_8\text{H}_{18}\text{NO}_2^+]$: 160.13; $[\text{C}_8\text{H}_{18}\text{NO}_2^+ \text{Br}^- \text{C}_8\text{H}_{18}\text{NO}_2^+]$: 399.19).

General procedure for anion exchange and purification of RTILs: A solution of LiTFSI or LiFSI (1.05 eq.) in water is added to a solution of the respective ammonium halide precursor (1.00 eq) in water. The resulting suspension is stirred at room temperature for 24 h. After removal of the aqueous phase the RTILs are washed 8 – 10 times with distilled water to remove LiBr and unreacted starting material. For better phase separation the IL water mixtures are centrifuged for 2 min prior to decantation of the aqueous washing phase. Presence of halides in the products is excluded by addition of AgNO_3 to the washing solution by the end of each washing step. For further purification the ILs are refluxed in dichloromethane with activated charcoal for 3 h followed by filtration. To reduce the water content to under 5 ppm the ILs are dried at 70 °C in high vacuum for two days (first day: 10^{-3} mbar, second day: 10^{-6} mbar).

Analytical data of the synthesized RTILs:

1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethane)sulfonamide (IL 2):⁸ Colourless liquid, 74% yield, ¹H-NMR (CDCl₃, 400 MHz, 296.7 K, ppm): δ = 3.82 – 3.74 (m, 2H, OCH₂), 3.68 – 3.50 (m, 6H, NCH₂), 3.38 (s, 3H, NCH₃), 3.10 (s, 3H, OCH₃), 2.31 – 2.19 (m, 4H, PyrCH₂CH₂); ¹³C-NMR (CDCl₃, 101 MHz, 297.4 K, ppm) δ = 119.96 (q, CF₃), 66.5, 65.8, 63.6, 59.2, 49.0, 21.5; elemental analysis calcd (%) for C₁₀H₁₈F₆N₂O₅S₂: C 28.30 H 4.28 N 6.60 S 15.11; found: C 28.23 H 4.26 N 6.57 S 15.15; MS (ESI, MeCN): m/z = 144.09; 567.18 (calcd. for [C₈H₁₈NO⁺]: 144.14; [C₈H₁₈NO⁺ TFSI⁻ C₈H₁₈NO⁺]: 568.18); η [cP]: 63; T_d [°C]: 408.6; σ [mS/cm]: 5.26; ESW [V]: 4.98.

1-(2-methoxy-2-oxoethyl)-1-methylpyrrolidinium bis(trifluoromethane)sulfonamide (IL 3):⁹ Colourless liquid, 78% yield, ¹H-NMR (CDCl₃, 400 MHz, 296.6 K, ppm): δ = 3.82 – 3.74 (m, 2H, OCH₂), 3.68 – 3.50 (m, 6H, NCH₂), 3.38 (s, 3H, NCH₃), 3.10 (s, 3H, OCH₃), 2.31 – 2.19 (m, 4H, PyrCH₂CH₂); ¹³C-NMR (CDCl₃, 101 MHz, 297.9 K, ppm) δ = 165.12, 119.90, 65.99, 62.21, 53.33, 49.73, 21.58; elemental analysis calcd (%) for C₁₀H₁₆F₆N₂O₆S₂: C 27.40 H 3.68 N 6.39 S 14.63; found: C 27.33 H 3.66 N 6.36 S 14.80; MS (ESI, MeCN): m/z = 158.02; 595.49 (calcd. for [C₈H₁₆NO₂⁺]: 158.12; [C₈H₁₆NO₂⁺ TFSI⁻ C₈H₁₆NO₂⁺]: 596.15); η [cP]: 287.1; T_d [°C]: 351.9; σ [mS/cm]: 1.27; ESW [V]: 5.04.

1-methyl-1-(2-(methylthio)ethyl)pyrrolidinium bis(trifluoromethane)sulfonamide (IL 4):¹² Colourless liquid, 94% yield, ¹H-NMR (CDCl₃, 400 MHz, 299.2 K, ppm): δ = 3.65 – 3.48 (m, 6H, NCH₂), 3.09 (s, 3H, NCH₃), 2.96 – 2.84 (m, 2H, CNCH₂), 2.37 – 2.24 (m, 4H, PyrCH₂CH₂); ¹³C-NMR (CDCl₃, 101 MHz, 298.5 K, ppm) δ = 119.02, 64.69, 63.50, 48.14, 26.98, 21.33, 15.14; elemental analysis calcd (%) for C₁₀H₁₈F₆N₂O₄S₃: C 27.27 H 4.12 N 6.36 S 21.84; found: C 27.08 H 4.13 N 6.35 S 22.18; MS (ESI, MeCN): m/z = 159.98; 599.57 (calcd. for [C₈H₁₈NS⁺]: 160.12; [C₈H₁₈NS⁺ TFSI⁻ C₈H₁₈NS⁺]: 600.15); η [cP]: 222.4; T_d [°C]: 286.0; σ [mS/cm]: 1.68; ESW [V]: 3.95.

1-(2-cyanoethyl)-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)amide (IL 5):⁶ Colourless liquid, 47 % yield, ¹H-NMR (CDCl₃, 400 MHz, 299.2 K, ppm): δ = 3.63 (t, ³J = 7.3 Hz, 2H, NCH₂CH₂CN), 3.59 – 3.38 (m, 4H, NCH₂CH₂), 3.02 (s, 3H, CH₃), 2.98 (d, ³J = 7.3 Hz, 6H), 2.27 – 2.16 (m, 4H, PyrCH₂CH₂); ¹³C-NMR (CDCl₃, 101 MHz, 299.7 K, ppm) δ = 119.89, 116.26, 65.21, 58.84, 48.16, 21.36, 13.42; elemental analysis calcd (%) for C₁₀H₁₅F₆N₃O₄S₂: C 28.64 H 3.61 N 10.02 S 15.29; found: C 28.31 H 3.62 N 9.93 S 15.42; MS (ESI, MeCN): m/z = 139.07; 557.90 (calcd. for [C₈H₁₅N₂⁺]: 139.12; [C₈H₁₅N₂⁺ TFSI⁻ C₈H₁₅N₂⁺]: 558.16); η [cP]: 533.8; T_d [°C]: 163.4; σ [mS/cm]: 1.28; ESW [V]: 4.91.

1-(2-methoxyethyl)-1-methylpyrrolidinium bis(fluorosulfonyl)amide (IL 6):⁸ Light yellow liquid, 57% yield, ¹H-NMR (CDCl₃, 400 MHz, 299.0 K, ppm): δ = 3.89 – 3.78 (m, 2H, OCH₂), 3.73 – 3.51 (m, 6H, NCH₂), 3.43 (s, 3H, NCH₃), 3.16 (s, 3H, OCH₃), 2.39 – 2.21 (m, 4H, PyrCH₂CH₂); ¹³C-NMR (CDCl₃, 101 MHz, 299.7 K, ppm) δ = 66.51, 65.96, 63.78, 59.33, 49.17, 21.64; elemental analysis calcd (%) for C₈H₁₈F₂N₂O₅S₂: C 29.62 H 5.59 N 8.64 S 19.77; found: C 29.40 H 5.68 N 8.59 S 19.72; MS (ESI, MeCN): m/z = 143.97; 467.60 (calcd. for [C₈H₁₈NO⁺]: 144.14; [C₈H₁₈NO⁺ FSI⁻ C₈H₁₈NO⁺]: 468.20); η [cP]: 43.6; T_d [°C]: 271.2; σ [mS/cm]: 7.66; ESW [V]: 4.89.

N,N,N-triethyl-2-methoxyethanamonium bis(trifluoromethane)sulfonamide (IL 8):¹⁵ Colourless liquid, 70% yield, ¹H-NMR (CDCl₃, 400 MHz, 299.2 K, ppm): δ = 3.80 – 3.70 (m, 2H, OCH₂), 3.44 (dt, ^{2,3}J = 7.4, 2.8 Hz, 2H, NCH₂), 3.41 – 3.31 (m, 9H, OCH₃, NCH₂CH₃), 1.33 (t, ³J = 7.2 Hz, 9H, CH₂CH₃); ¹³C-NMR (CDCl₃, 101 MHz, 299.6 K, ppm) δ = 120.03, 65.73, 59.35, 56.93, 54.15, 7.62; elemental analysis calcd (%) for C₁₁H₂₂F₆N₂O₅S₂: C 30.00, H 5.04, N 6.36, S 14.56; found: C 30.01, H 4.94, N 6.42, S 14.37; MS (ESI, MeCN): m/z = 160.15; 599.68 (calcd. for [C₉H₂₂NO⁺]: 160.17; [C₉H₂₂NO⁺ TFSI⁻ C₉H₂₂NO⁺]: 600.26); η [cP]: 98.2; T_d [°C]: 390.3; σ [mS/cm]: 2.92; ESW [V]: 5.08.

N,N,N-triethyl-2-methoxy-2-oxoethanamonium bis(trifluoromethane)sulfonamide (IL 9): Colourless liquid, 90% yield, ¹H-NMR (CDCl₃, 400 MHz, 296.7 K, ppm): δ = 4.08 (s, 2H, NCH₂CO), 3.85 (s, 3H, OCH₃), 3.58 (q, ³J = 7.3 Hz, 6H, NCH₂CH₃), 1.37 (t, ³J = 7.3 Hz, 9H, NCH₂CH₃); ¹³C-NMR (CDCl₃, 101 MHz, 297.3 K, ppm) δ = 164.51, 119.97, 55.34, 54.89, 53.59, 7.67; elemental analysis calcd (%) for C₁₁H₂₀F₆N₂O₆S₂: C 29.08 H 4.44 N 6.17 S 14.11; found: C 29.05 H 4.30 N 6.21 S 13.99; MS (ESI, MeCN): m/z = 174.06 (calcd. for [C₉H₂₀NO₂⁺]: 174.15); η [cP]: 312.2; T_d [°C]: 410.8; σ [mS/cm]: 1.02; ESW [V]: 5.03.

N,N,N-triethylbut-2-enamonium bis(trifluoromethane)sulfonamide (IL 10): Colourless liquid, 88% yield, ¹H-NMR (CDCl₃, 400 MHz, 299.7 K, ppm): δ = trans: 6.22 – 6.06 (m, 1H, CH₃CHCH), 5.52 – 5.41 (m, 1H, CH₃CHCH), 3.68 (d, ³J = 7.5 Hz, 2H, NCH₂CH), 3.20 (q, ³J = 7.3 Hz, 6H, NCH₂CH₃), 1.83 (d, ³J = 6.5 Hz, 3H, CHCH₃), 1.31 (t, ³J = 7.2 Hz, 9H, NCH₂CH₃); cis: 6.22 – 6.06 (m, 1H, CH₃CHCH), 5.52 – 5.41 (m, 1H, CH₃CHCH), 3.80 (d, ³J = 7.6 Hz, 2H, NCH₂CH), 3.25 (q, ³J = 7.3 Hz, 6H, NCH₂CH₃), 1.79 (d, ³J = 6.0 Hz, 3H, CHCH₃), 1.31 (t, ³J = 7.2 Hz, 9H, NCH₂CH₃); ¹³C-NMR (CDCl₃, 101 MHz, 304.2 K, ppm) δ = 141.88, 118.70, 116.06, 59.34, 52.64, 18.36, 7.41; elemental analysis calcd (%) for C₁₂H₂₂F₆N₂O₄S₂: C 33.03 H 5.08 N 6.42 S 14.69; found: C 32.85 H 5.07 N 6.46 S 14.62; MS (ESI, MeCN): m/z = 156.11; 591.96 (calcd. for [C₁₀H₂₂N⁺]: 156.17; [C₁₀H₂₂N⁺ TFSI⁻ C₁₀H₂₂N⁺]: 592.27); η [cP]: 156.2; T_d [°C]: 345.9; σ [mS/cm]: 1.91; ESW [V]: 4.96.

***N,N,N*-triethyl-2-methoxyethanamonium bis(fluorosulfonyl)imide (IL 11):** Light yellow liquid, 65% yield, ^1H -NMR (CDCl_3 , 400 MHz, 299.0 K, ppm): δ = 3.80 – 3.71 (m, 2H, OCH_2), 3.47 – 3.41 (m, 2H, NCH_2), 3.41 – 3.33 (m, 9H, OCH_3 , NCH_2CH_3), 1.34 (t, 3J = 7.2 Hz, 9H, CH_2CH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 299.5 K, ppm) δ = 65.75, 59.44, 56.95, 54.22, 7.72; elemental analysis calcd (%) for $\text{C}_9\text{H}_{22}\text{F}_2\text{N}_2\text{O}_5\text{S}_2$: C 31.76 H 6.51 N 8.23 S 18.84; found: C 31.58 H 6.53 N 8.17 S 18.58; MS (ESI, MeCN): m/z = 160.01; 499.60 (calcd. for $[\text{C}_9\text{H}_{22}\text{NO}^+]$: 160.17; $[\text{C}_9\text{H}_{22}\text{NO}^+ \text{FSI}^- \text{C}_9\text{H}_{22}\text{NO}^+]$: 500.26); η [cP]: 71.8; T_d [$^\circ\text{C}$]: 280.4; σ [mS/cm]: 5.07; ESW [V]: 5.02.

***N,N,N*-triethylbut-2-enamonium bis(fluorosulfonyl)amide (IL 12):** Colourless liquid, 62% yield, ^1H -NMR (CDCl_3 , 400 MHz, 298.7 K, ppm): δ = trans: 6.29 – 6.09 (m, 1H, CH_3CHCH), 5.58 – 5.41 (m, 1H, CH_3CHCH), 3.71 (d, 3J = 7.5 Hz, 2H, NCH_2CH), 3.24 (q, 3J = 7.3 Hz, 6H, NCH_2CH_3), 1.86 (d, 3J = 6.5 Hz, 3H, CHCH_3), 1.36 (t, 3J = 7.2 Hz, 9H, NCH_2CH_3); cis: 6.29 – 6.09 (m, 1H, CH_3CHCH), 5.58 – 5.41 (m, 1H, CH_3CHCH), 3.83 (d, 3J = 7.6 Hz, 2H, NCH_2CH), 3.32 – 3.27 (6H, NCH_2CH_3), 1.82 (d, 3J = 7.2 Hz, 3H, CHCH_3), 1.36 (t, 3J = 7.2 Hz, 9H, NCH_2CH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 299.3 K, ppm) δ = 142.20, 115.97, 59.46, 52.76, 18.53, 7.57; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{22}\text{F}_2\text{N}_2\text{O}_4\text{S}_2$: C 35.70 H 6.59 N 8.33 S 19.06; found: C 35.76 H 6.66 N 8.31 S 19.08; MS (ESI, MeCN): m/z = 156.00; 491.56 (calcd. for $[\text{C}_{10}\text{H}_{22}\text{N}^+]$: 156.17; $[\text{C}_{10}\text{H}_{22}\text{N}^+ \text{FSI}^- \text{C}_{10}\text{H}_{22}\text{N}^+]$: 492.27); η [cP]: 119.7; T_d : 261.2 [$^\circ\text{C}$]; σ [mS/cm]: 3.81; ESW [V]: 4.82.

***N,N*-diethyl-2-methoxy-*N*-methylethanamonium bis(trifluoromethane)sulfonimide (IL 13):**¹⁶ Light yellow liquid, 89% yield, ^1H -NMR (CDCl_3 , 400 MHz, 298.0 K, ppm): δ = 3.66 (td, $^2,^3J$ = 4.5, 2.3 Hz, 2H, OCH_2), 3.43 – 3.23 (m, 9H, NCH_2CH_3 , NCH_2 , NCH_3), 2.91 (s, 3H, OCH_3), 1.26 (t, 3J = 7.3 Hz, 6H, NCH_2CH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 297.9 K, ppm) δ = 119.7, 65.55, 60.07, 58.84, 57.69, 47.83, 7.60; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{20}\text{F}_6\text{N}_2\text{O}_5\text{S}_2$: C 28.17, H 4.73, N 6.57, S 15.07; found: C 28.03, H 4.74, N 6.58, S 14.90; MS (ESI, MeCN): m/z = 146.02; 571.49 (calcd. for $[\text{C}_8\text{H}_{20}\text{NO}^+]$: 146.15; $[\text{C}_8\text{H}_{20}\text{NO}^+ \text{TFSI}^- \text{C}_8\text{H}_{20}\text{NO}^+]$: 572.23); η [cP]: 80.1; T_d [$^\circ\text{C}$]: 406.5; σ [mS/cm]: 3.99; ESW [V]: 4.92.

***N,N*-diethyl-2-methoxy-*N*-methyl-2-oxoethanaminium bis((trifluoromethyl)sulfonyl)amide (IL 14):** Colourless liquid, 80% yield, ^1H -NMR (CDCl_3 , 400 MHz, 298.52 K, ppm): δ = 4.13 (s, 2H, NCH_2CO), 3.84 (s, 3H, OCH_3), 3.64 (q, 3J = 7.4 Hz, 4H, NCH_2CH_3), 3.21 (s, 3H, NCH_3), 1.39 (t, 3J = 7.4 Hz, 6H, NCH_2CH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 301.0 K, ppm) δ = 164.57, 118.36, 58.29, 58.21, 53.56, 48.34, 8.05; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_6\text{S}_2$: C 27.27 H 4.12 N 6.36 S 14.56; found: C 27.17 H 4.15 N 6.41 S 14.69; MS (ESI, MeCN): m/z = 160.02, 599.43 (calcd. for $[\text{C}_8\text{H}_{18}\text{NO}_2^+]$: 160.13; $[\text{C}_8\text{H}_{18}\text{NO}_2^+ \text{TFSI}^- \text{C}_8\text{H}_{18}\text{NO}_2^+]$: 600.18); η [cP]: 291.5; T_d [$^\circ\text{C}$]: 346.1; σ [mS/cm]: 1.20; ESW [V]: 4.96.

2-acetoxy-*N,N,N*-trimethylethanamonium bis(trifluoromethane)sulfonamide (IL 15):¹⁴ Colourless liquid, 87% yield, ^1H -NMR (CD_3CN , 400 MHz, 297.8 K, ppm): δ = 4.40 (dq, $^2,^3J$ = 7.6, 2.5 Hz, 2H, OCH_2), 3.54 (dt, $^2,^3J$ = 4.9, 2.5 Hz, 2H, NCH_2), 3.09 (s, 3H, NCH_3), 2.05 (s, 3H, CH_3); ^{13}C -NMR (CD_3CN , 101 MHz, 298.5 K, ppm) δ = 170.88, 120.85, 65.69, 58.44, 54.67, 20.83; elemental analysis calcd (%) for $\text{C}_9\text{H}_{16}\text{F}_6\text{N}_2\text{O}_6\text{S}_2$: C 25.35 H 3.78 N 6.57 S 15.04; found: C 25.17 H 3.78 N 6.51 S 15.01; MS (ESI, MeCN): m/z = 145.94; 571.54 (calcd. for $[\text{C}_7\text{H}_{16}\text{NO}_2^+]$: 146.12; $[\text{C}_7\text{H}_{16}\text{NO}_2^+ \text{TFSI}^- \text{C}_7\text{H}_{16}\text{NO}_2^+]$: 572.15); η [cP]: 256.5; T_d [$^\circ\text{C}$]: 367.7; σ [mS/cm]: 1.76; ESW [V]: 5.17.

1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethane)sulfonamide (IL 16):⁸ Colourless liquid, 80% yield, ^1H -NMR (CDCl_3 , 400 MHz, 299. K, ppm): δ = 3.78 (t, 3J = 4.6 Hz, 2H, OCH_2), 3.53 (t, 3J = 4.6 Hz, 2H, NCH_2), 3.50 – 3.30 (m, 7H, NCH_3 , NCH_2), 3.11 (s, 3H, OCH_3), 1.89 (p, J = 6.0 Hz, 4H, PipCH_2), 1.76 – 1.64 (m, 2H, PipCH_2); ^{13}C -NMR (CDCl_3 , 101 MHz, 307.7 K, ppm) δ = 121.60, 65.75, 62.97, 62.72, 59.15, 49.31, 20.70, 20.13; elemental analysis calcd (%) for $\text{C}_{11}\text{H}_{20}\text{F}_6\text{N}_2\text{O}_5\text{S}_2$: C 30.14 H 4.60 N 6.39 S 14.63; found: C 29.98 H 4.63 N 6.41 S 14.51; MS (ESI, MeCN): m/z = 158.13; 595.84 (calcd. for $[\text{C}_9\text{H}_{20}\text{NO}^+]$: 158.15; $[\text{C}_9\text{H}_{20}\text{NO}^+ \text{TFSI}^- \text{C}_9\text{H}_{20}\text{NO}^+]$: 596.23); η [cP]: 123.4; T_d [$^\circ\text{C}$]: 403.7; σ [mS/cm]: 2.64; ESW [V]: 4.96.

4-(2-methoxyethyl)-4-methylmorpholinium bis((trifluoromethyl)sulfonyl)amide (IL 17):¹¹ Colourless liquid, 75% yield, ^1H -NMR (CDCl_3 , 400 MHz, 297.8 K, ppm): δ = 4.01 (t, 3J = 4.4 Hz, 4H, PipOCH_2), 3.90 – 3.84 (m, 2H, OCH_2), 3.78 – 3.72 (m, 2H, PipNCH_2), 3.68 – 3.60 (m, 2H, PipNCH_2), 3.53 – 3.43 (m, 2H, NCH_2), 3.39 (s, 3H, NCH_3), 3.30 (s, 3H, OCH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 298.9 K, ppm) δ = 118.33, 65.66, 64.05, 61.50, 60.75, 59.34, 48.87; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_6\text{S}_2$: C 27.27 H 4.12 N 6.36 S 14.56; found: C 27.36 H 4.17 N 6.35 S 14.32; MS (ESI, MeCN): m/z = 160.03; 599.47 (calcd. for $[\text{C}_8\text{H}_{18}\text{NO}_2^+]$: 160.13; $[\text{C}_8\text{H}_{18}\text{NO}_2^+ \text{TFSI}^- \text{C}_8\text{H}_{18}\text{NO}_2^+]$: 600.18); η [cP]: 375.8; T_d [$^\circ\text{C}$]: 395.1; σ [mS/cm]: 1.01; ESW [V]: 4.96.

NMO material for coin cell preparation

$\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ (NMO) was synthesized following a reported protocol.¹⁷ XRD of the NMO powder used for the coin cell preparation is depicted in Figure SI6. The material is moisture sensitive and known to convert to birnessite under exposure to water or strong moisture.¹⁸

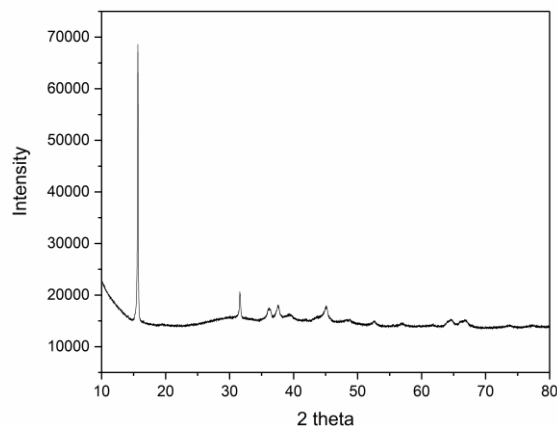


Figure SI13: XRD of the NMO material used for coin cell preparation.

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