Fluoroborate ionic liquids as sodium battery electrolytes

Dale T. Duncan¹, Samantha L. Piper¹, Maria Forsyth², Douglas R. MacFarlane¹ and Mega Kar^{*2}

*corresponding authors

Mega Kar: <u>m.kar@deakin.edu.au</u>

¹School of Chemistry, Monash University, Wellington Road, Clayton, VIC 3800, Australia

²Institute of Frontier Materials, Deakin University, 221, Burwood Highway, Burwood, VIC 3125, Australia

Table S1: List of abbreviations used in the main manuscript and supplementary information.

Abbreviation	Definition
[B(hfip) ₄] ⁻	(tetrakis)hexafluoroisopropoxy borate
[B(tfe) ₄] ⁻	(tetrakis)trifluoroethoxy borate
[C₃mpyr]⁺	N-methyl-N-propylpyrrolidinium
$[closo-CB_{11}H_{12}]^{-}$	mono-closoborane
[DFOB] ⁻	difluoro(oxolato)borate
[FSI] ⁻	bis(fluorosulfonyl)imide
[N ₂₍₂₀₂₀₁₎₃] ⁺	N-ethyl-N,N,N-tris(2-(2-methoxyethoxy)ethyl) ammonium
[P _{122i4}]+	iso-butyl(diethyl)methyl phosphonium
[PF ₆] ⁻	hexafluorophosphate
[TFSI] ⁻	bis(trifluoromethanesulfonyl)imide
[TOS] ⁻	tosylate
1a	[N ₂₍₂₀₂₀₁₎₃][B(tfe) ₄]
1b	[N ₂₍₂₀₂₀₁₎₃][B(hfip) ₄]
2a	[P _{122i4}][B(tfe) ₄]
2b	[P _{122i4}][B(hfip) ₄]
За	[C₃mpyr][B(tfe)₄]
3b	[C₃mpyr][B(hfip)₄]
CA	Chronoamperometry
CE	counter electrode
DCM	dichloromethane
DMC	dimethyl carbonate
DME	1,2-dimethoxyethane
DSC	Differential scanning calorimetry
E	Potential
EC	ethylene carbonate
ECW	electrochemical window
EDX	Energy dispersive x-ray spectroscopy
EIS	Electrical impedance spectroscopy
Fc	Ferrocene
FWHM	Full-width half-maximum
GC	glassy carbon
h	hour
ICP-OES	Inductively coupled plasma optical emision spectrosocpy

IL	ionic liquid
J	Current density
J _{max}	Maximum current density
k _η	Pseudo-activation energy (viscosity)
k_{σ}	Pseudo-activation energy (conductivity)
LIB	Lithium-ion battery
LP30	1 M Li[PF ₆] in EC:DMC (1:1 vol.)
MeCN	Acetonitrile
MS	Mass spectroscopy
Na[FSI]:1b	Na[FSI] in [N ₂₍₂₀₂₀₁₎₃][B(hfip) ₄] at 50 mol% NaFSI (equimolar)
NMC	Nickel manganese cobalt oxide
NMR	Nuclear magnetic resonance
OCV	Open circuit potenial
OIPC	Organic ionic plastic crystal
PET	Poly(ethylene terephthalate)
PTFE	Poly(tetrafluoroethylene)
RE	reference electrode
RT	Room temperature
SC-XRD	Single crystal x-ray diffraction
SEM	Scanning electron microscopy
TFSI	bis(trifluoromethanesulfonyl)imide
TGA	Thermal gravimetric analysis
t	time
T _d	Temperature of decomposition
T _g	Glass transition temperature
T _m	Melting point temperature
T _{ss}	Solid-solid transition temperature
Τ _η	Ideal glass transition temperature (viscosity)
T _σ	Ideal glass transition temperature (conductivity)
VTF	Vogel-Tammann-Fulcher
WCA	Weakly coordinating anion
WE	working electrode
wt	weight
vol	Volume
ΔH	Change in enthalpy
ΔH_{f}	Enthalpy of fusion
ΔS	Change in entropy
ΔS_{f}	Entropy of fusion
σ	Ionic conductivity
ρ	Density
η	Viscosity
Λ _m	molar conductivity

Table S2: Elemental analysis by inductively coupled plasma optical emission spectroscopy of sodium (Na⁺), lithium (Li⁺), potassium (K⁺) and bromide (Br⁻) of purified materials synthesised in this study.

		Concentration /ppm				
		Na ⁺	Li+	K+	Br⁻	
1a	[N ₂₍₂₀₂₀₁₎₃][B(tfe) ₄]	3477.2	1.0	40.3	54.8	
1b	[N ₂₍₂₀₂₀₁₎₃][B(hfip) ₄]	626.0	1.0	48.3	0.3	
2a	[P _{122i4}][B(tfe) ₄]	710.2	16.4	63.5	0.7	
2b	[P _{122i4}][B(hfip) ₄]	556.9	1.5	43.2	0.0	
3a	[C₃mpyr][B(tfe)₄]	1225.1	5.8	81.0	56.6	
3b	[C ₃ mpyr][B(hfip) ₄]	642.7	1.1	63.6	0.2	



Figure S1: ¹H-NMR of $[N_{2(20201)3}][B(tfe)_4]$ (**1a**) (DMSO 2.5 ppm). Peak integration is calibrated to the six proton -CH₂- environment of $[N_{2(20201)3}]^+$ at 3.80 ppm.



Figure S2: ¹H-NMR of $[N_{2(20201)3}][B(hfip)_4]$ (**1b**) in D6-DMSO (DMSO 2.5 ppm). Peak integration is calibrated to the four proton -CH- environment of $[B(hfip)_4]^-$ at 4.65 ppm.



Figure S3: ¹H-NMR of $[P_{122i4}][B(tfe)_4]$ (**2a**) in D6-DMSO (DMSO 2.5 ppm). Peak integration is calibrated to the eight proton -CH₂- environment of $[B(tfe)_4]^-$ at 3.68 ppm.



Figure S4: ¹H-NMR of $[P_{122i4}][B(hfip)_4]$ (**2b**) in D6-DMSO (DMSO 2.5 ppm). Peak integration is calibrated to the four proton -CH- environment of $[B(hfip)_4]^-$ at 4.65 ppm.



Figure S5: ¹H-NMR of $[C_3mpyr][B(tfe)_4]$ (**3a**) in D6-DMSO (DMSO 2.5 ppm). Peak integration is calibrated to the eight proton -CH₂- environment of $[B(tfe)_4]^-$ at 3.68 ppm.



Figure S6: ¹H-NMR of $[C_3mpyr][B(hfip)_4]$ (**3b**) in D6-DMSO (DMSO 2.5 ppm). Peak integration is calibrated to the four proton -CH- environment of $[B(hfip)_4]^-$ at 4.65 ppm.

Identification code	[P _{122i4}][B(tfe) ₄] (2a)	[C ₃ mpyr][B(tfe) ₄] (3a)	[C₃mpyr][B(hfip)₄] (3b)	
CCDC identifier	2246730	2246729	2246728	
Empirical formula	C ₁₇ H ₂₉ BF ₁₂ O ₄ P	1069.87	C ₂₀ H ₂₂ BF ₂₄ NO ₄	
Formula weight	567.18	123.15	807.19	
Temperature/K	123.15	monoclinic	123.15	
Crystal system	triclinic	P2 ₁ /c	triclinic	
Space group	P-1	17.6281(2)	P-1	
a/Å	9.0301(3)	18.6841(2)	8.6128(3)	
b/Å	9.9200(3)	28.3710(3)	11.9192(3)	
c/Å	14.9196(4)	90	14.6382(4)	
α/°	85.444(3)	96.4010(10)	93.623(2)	
β/°	80.521(3)	90	94.957(3)	
γ/°	77.435(3)	9286.16(18)	93.773(2)	
Volume/Å ³	1285.34(7)	8	1490.27(8)	
Z	2	1.531	2	
ρ _{calc} g/cm ³	1.465	1.527	1.799	
µ/mm ⁻¹	1.970	4380.0	2.039	
F(000)	582.0	?×?×?	804.0	
Crystal size/mm ³	; × ; × ;	CuKα (λ = 1.54184)	0.265 × 0.087 × 0.085	
Radiation	CuKα (λ = 1.54184)	7.598 to 162.2	CuKα (λ = 1.54184)	
20 range for data collection/°	9.142 to 160.832	-22 ≤ h ≤ 22, -23 ≤ k ≤ 9, -36 ≤ l ≤ 35	7.45 to 163.75	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 11, -19 ≤ l ≤ 18	100545	$-11 \le h \le 10, -14$ $\le k \le 11, -18 \le l \le$ 18	
Reflections collected	25457	19939 [R _{int} = 0.0656, R _{sigma} = 0.0370]	29888	
Independent reflections	5472 [R _{int} = 0.0689, R _{sigma} = 0.0394]	19939/0/1233	6319 [R _{int} = 0.0566, R _{sigma} = 0.0393]	
Data/restraints/parameters	5472/0/350	1.056	6319/0/454	
Goodness-of-fit on F ²	0.939	$R_1 = 0.1284,$ w $R_2 = 0.3749$	1.097	
Final R indexes [I>=2σ (I)]	$R_1 = 0.0727,$	$R_1 = 0.1420,$	$R_1 = 0.0455,$	
	wR ₂ = 0.1848	wR ₂ = 0.3835	wR ₂ = 0.1268	
Final R indexes [all data]	R ₁ = 0.0846,	1 98/-0 86	$R_1 = 0.0528,$	
	wR ₂ = 0.1931	1.50, 0.00	wR ₂ = 0.1329	
Largest diff. peak/hole / e Å ⁻³	0.58/-0.65	1069.87	0.56/-0.31	

Table S3. Crystal data and refinement details for $[P_{122i4}][B(tfe)_4]$ (**2a**), $[C_3mpyr][B(tfe)_4]$ (**3a**) and $[C_3mpyr][B(hfip)_4]$ (**3b**).

Additional crystal data and refinement details

For the structure of $[P_{122i4}][B(tfe)_4]$, one ethyl group and the methyl group were modelled as disordered over two positions, as to suggest that the position of the methyl and ethyl group alternate throughout the extended structure. The two disorder components had refined occupancies linked through a free variable, with values of 0.49704 and 0.50296. One P-C bond (from P1 to C21) was restrained to a length of 1.8(0.02) Å using the DFIX restraint. The second ethyl group was refined over two positions with relative occupancies of 0.4 and 0.6. One of the CF₃ groups in this structure has large (~ 0.12) equivalent isotropic displacement parameters of the fluorine atoms suggesting that this group may be disordered, however the reported structure was found to be the best fit to the data.

A large number of crystals were screened for $[C_3mpyr][B(tfe)_4]$, each of which proved to have problematic diffraction. The current dataset showed evidence of twinning which affected the overall data quality, however this was the best that could be achieved with the current sample. The structure was modelled with disorder of one of the CF₃ groups over two positions. The two disorder components had fixed occupancies of 0.6667 and 0.3333. The propyl group of one of the cations was refined to be disordered over two positions with fixed component occupancies of 0.6667 and 0.3333. There is some residual electron density in the structure, including a maximum peak of 2 (located 1.244 Å from F5). This may be attributed to disorder of this CF₃ group, however attempts to model this disorder did not improve the quality of the model. This may also be an artefact of unresolved twinning.



Figure S7: Crystallographically determined structure of $[P_{122i4}][B(tfe)_4]$ (**2a**) and extended crystal packing of **2a** down the a (a), b (b) and c (c) axes. Two unit cells are packed along each axis. Boron atoms are shown in pink, carbon atoms in grey, fluorine atoms in green, nitrogen atoms in blue and hydrogen atoms in white.



Figure S8: Crystallographically determined structure of $[C_3mpyr][B(tfe)_4]$ (**3a**) and extended crystal packing of **3a** down the a (a), b (b) and c (c) axes. Two unit cells are packed along each axis. Boron atoms are shown in pink, carbon atoms in grey, fluorine atoms in green, nitrogen atoms in blue and hydrogen atoms in white.





Figure S9: Crystallographically determined structure of $[C_3mpyr][B(hfip)_4]$ (**3b**) and extended crystal packing of **3b** down the a (a), b (b) and c (c) axes. Two unit cells are packed along each axis. Boron atoms are shown in pink, carbon atoms in grey, fluorine atoms in green, nitrogen atoms in blue and hydrogen atoms in white.



Figure S10: Differential scanning calorimetry cooling trace (2nd cooling) of all synthesised materials with phase transitions labelled.



Figure S11: All observed phase transitions of $[N_{2(20201)3}][B(tfe)_4]$ (**1a**) from differential scanning calorimetry analysis.



Figure S12: All observed phase transitions of $[N_{2(20201)3}][B(hfip)_4]$ (**1b**) from differential scanning calorimetry analysis.



Figure S13: All observed phase transitions of $[P_{122i4}][B(tfe)_4]$ (**2a**) from differential scanning calorimetry analysis.



Figure S14: 2b All observed phase transitions of $[P_{122i4}][B(hfip)_4]$ (**2b**) from differential scanning calorimetry analysis.



Figure S15: All observed phase transitions of $[C_3mpyr][B(tfe)_4]$ (**3a**) from differential scanning calorimetry analysis.



Figure S16: All observed phase transitions of $[C_3mpyr][B(hfip)_4]$ (**3b**) from differential scanning calorimetry analysis.



Figure S17: Thermal gravimetric analysis of synthesised ionic liquids $[N_{2(20201)3}][B(tfe)_4]$ (**1a**), $[N_{2(20201)3}][B(hfip)_4]$ (**1b**), $[P_{122i4}][B(tfe)_4]$ (**2a**), $[P_{122i4}][B(hfip)_4]$ (**2b**), $[C_3mpyr][B(tfe)_4]$ (**3a**) and $[C_3mpyr][B(hfip)_4]$ (**3b**).



Figure S18: Still frames taken from the video recording of the flammability test of $[N_{2(20201)3}][B(tfe)_4]$ (**1a**). Images are at specified timepoints.

The flame was applied to the sample at t = -2 s where the sample on contact with the flame. A hole was torn when moving the blow-torch in the experiment. The flame was applied for 2 s until t = 0 s where the sample was still combusting. The sample continued to sustain combustion, seen at t = 5 s, until the sample was consumed at t = 10 s.



Figure S19: Still frames taken from the video recording of the flammability test of $[N_{2(20201)3}][B(hfip)_4]$ (**1b**). Images are at specified timepoints.

The flame was applied to the sample at t = -5 s where the ignited after 3 s. The flame was removed at t = 0 s and the sample rapidly extinguished seen at t = 2 s. Sample was blackened but not entirely consumed.



Figure S20: Still frames taken from the video recording of the flammability test of $[P_{122i4}][B(tfe)_4]$ (**2a**). Images are at specified timepoints.

The flame was applied to the sample at t = -4 s where the sample melted on contact with the flame before ignition after 2 s. Following ignition, the flame was applied for 2 s until t = 0 s where the sample was continued combustion. The sample continued to sustain combustion, seen at t = 3 s, until the sample was mostly consumed at t = 6 s.



Figure S21: Still frames taken from the video recording of the flammability test of $[P_{122i4}][B(hfip)_4]$ (**2b**). Images are at specified timepoints.

The flame was applied to the sample at t = -2 s where the sample rapidly ignited. The flame was removed at t = 0 s and the sample rapidly extinguished seen at t = 2 s. Sample was blackened but not entirely consumed.



Figure S22: Still frames taken from the video recording of the flammability test of $[C_3mpyr][B(tfe)_4]$ (**3a**). Images are at specified timepoints.

The flame was applied to the sample at t = -3 s where the sample melted on contact with the flame before ignition. The flame was applied for 2 s until t = 0 s, the sample continued combustion. The sample continued to sustain combustion, seen at t = 3 s, until the sample was mostly consumed at t = 11 s.



Figure S23: Still frames taken from the video recording of the flammability test of $[C_3mpyr][B(hfip)_4]$ (**3b**). Images are at specified timepoints.

The flame was applied to the sample at t = -5 s where the sample ignited after 3 s. The flame was removed at t = 0 s and the sample rapidly extinguished seen at t = 2 s. Sample was blackened but not entirely consumed.



Figure S24: Still frames taken from the video recording of the flammability test of $[C_3mpyr]$ [FSI]. Images are at specified timepoints.

The flame was applied to the sample at t = -4 s where the sample ignited after 2 s. The flame was removed at t = 0 s and the sample rapidly extinguished seen at t = 2 s. Sample was blackened but not entirely consumed.



Figure S25: Solid-state conductivity of synthesised ionic liquids $[P_{122i4}][B(tfe)_4]$ (**2a**), $[P_{122i4}][B(hfip)_4]$ (**2b**), $[C_3mpyr][B(tfe)_4]$ (**3a**) and $[C_3mpyr][B(hfip)_4]$ (**3b**).

Table S4: Calculated fitting parameters of the experimental cor	nductivity and viscosity values
to the VTF equation of the RTILs studied.	

	Conductivity (Equation 1)			Viscosity (Equation 2)				
	σ_0 /mS cm ⁻¹	<i>k</i> _σ /Κ	<i>Τ</i> _σ /Κ	r ²	η_0 /mPa s	k _η /Κ	<i>Τ</i> η /Κ	r ²
	122	1200	155	0.0000	504	953	181	0 0000
1a	± 1.15	± 47.5	± 3.35	0.9999	± 1.24	± 62.2	± 4.58	0.9998
	183	701	175	0.0000	254	568	195	0 0000
1b	± 1.07	± 21.0	± 2.25	0.9999	± 1.03	± 6.62	± 0.730	0.9999
	910	779	131	0.0096	273	770	144	0 0000
[C₃mpyr][FSI]	± 1.63	± 192	± 24.1	0.9980	± 1.02	± 8.11	± 0.939	0.9999



Figure S26: Conductivity measurements from 25 °C to 90 °C in 5 °C increments of neat ionic liquids $[N_{2(20201)3}][B(tfe)_4]$ (**1a**), $[N_{2(20201)3}][B(hfip)_4]$ (**1b**) and $[C_3mpyr][FSI]$ with the fitted VFT equation overlaid.



Figure S27: Viscosity measurements from 20 °C to 90 °C in 5 °C increments of neat ionic liquids $[N_{2(20201)3}][B(tfe)_4]$ (**1a**), $[N_{2(20201)3}][B(hfip)_4]$ (**1b**) and $[C_3mpyr][FSI]$ with the fitted VFT equation overlaid.



Figure S28: Al||Na coin-cell with $[N_{2(20201)3}][B(hfip)_4]$ (**1b**) at room-temperature in the **a**) cyclic voltammetry, **b**) linear sweep and **c**) chronoamperometry protocols detailed below.

The cell was held at open-circuit voltage (OCV) for 12 hours then commenced a cyclic voltammetry protocol at 1 mV s⁻¹ starting from OCV and sweeping from 2 to 7 V vs Na⁺/Na, currents decreased with each following cycle (all cycles shown). The cell was held at OCV for 1 minute before a sweep to 7 V at 1 mV s⁻¹, after which the 7 V polarisation was held for 12 hr. Currents quickly decreased over the 7 V polarisation.



Figure S29: Al||Na coin-cell in the with $[C_3mpyr][FSI]$ at room-temperature in the **a**) cyclic voltammetry, **b**) linear sweep and **c**) chronoamperometry protocols detailed below.

The cell was held at open-circuit voltage (OCV) for 12 hours then commenced a cyclic voltammetry protocol at 1 mV s⁻¹ starting from OCV and sweeping from 2 to 7 V vs Na⁺/Na, currents decreased with each following cycle (all cycles shown). The cell was held at OCV for 1 minute before a sweep to 7 V at 1 mV s⁻¹, after which the 7 V polarisation was held for 12 hr. Currents quickly decreased over the 7 V polarisation.

	Al	С	0	F	В	S	Na
				Atomic%			
Pristine Al	92.1	6.6	1.1	ND	ND	ND	ND
Na[FSI]: 1b	87.4	10.7	1.4	0.2*	ND	0.1*	ND
1b 50 C	75.9	19.5	1.8	2.4	ND	ND	0.2
1b RT	81.3	10.8	1.8	0.6	5.3*	ND	0.1*

Table S5: Tabulated atomic% of each Al-surface analysed by energy dispersive x-rayspectroscopy.

ND: not detected

*below limit of accurate quantification.



Figure S30: Elemental mapping by energy dispersive x-ray spectroscopy of the pristine Al foil.



Figure S31: Elemental mapping by energy dispersive x-ray spectroscopy of the Al foil anodised with Na[FSI]:**1b** at 50 °C.



Figure S32: Elemental mapping by energy dispersive x-ray spectroscopy of the Al foil anodised with neat **1b** at 50 °C.



Figure S33: Elemental mapping by energy dispersive x-ray spectroscopy of the Al foil anodised with neat **1b** at RT.



Figure S34: X-ray photoelectron spectroscopy of the S 2p chemical environments of the anodised foils at 7 V where **1b** is $[N_{2(20201)3}][B(hfip)_4]$.



Figure S35: Stage-tilted scanning electron microscopy micrograph of the irregular passivation on the anodised foil with neat $[N_{2(20201)3}][B(hfip)_4]$ (**1b**) at 50 °C.



Figure S36: X-ray photoelectron spectroscopy of the C1s chemical environments of the anodised foils at 7 V where **1b** is $[N_{2(20201)3}][B(hfip)_4]$.



Figure S37: X-ray photoelectron spectroscopy of the N 1s chemical environments of the anodised foils at 7 V where **1b** is $[N_{2(20201)3}][B(hfip)_4]$. **1b** RT and **1b** 50 C measurements were reduced for noise-reduction.



Figure S38: X-ray photoelectron spectroscopy of the O 1s chemical environments of the anodised foils at 7 V where **1b** is $[N_{2(20201)3}][B(hfip)_4]$.