Electronic Supplementary Information

Advances in Sodium Secondary Batteries Utilizing Ionic Liquid Electrolytes

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Table S1 Selected properties, electrochemical characteristics, abundance and cost information of potential charge carriers for secondary battery applications.[1]

	Li	Na	K	Mg	Ca	Al	Zn
Atomic weight (g mol^{-1})	6.94	22.99	39.10	24.31	40.08	26.98	65.38
Shannon's ionic radius (Å)[a]	0.76	1.02	1.38	0.72	1.00	0.54	0.74
Molar volume of metal (cm^3 mol^{-1})	13.0	23.8	45.9	14.0	26.2	10.0	9.2
Melting point of metal (°C)	181	98	64	650	842	660	420
E^0 (V vs. SHE)	–3.04	–2.71	–2.93	–1.55	–2.87	–1.66	–0.76
Gravimetric energy density (mAh g^{-1})	3861	1166	685	2205	1337	2980	820
Volumetric energy density (mAh cm^{-3})	2062	1128	591	3832	2073	8046	5854
Abundance in crust (ppm)	20	24000	21000	23000	41000	82000	70
Abundance in seawater (ppm)	0.17	10500	380	1350	400	0.01	0.01
Price (USD T^{-1})[1]	17000[b]	150[c]	740[d]	4740[e]	120[f]	2535[g]	3197[h]

[a] Coordination number of six

[b–h] Average price of Li_2CO_3, Na_2CO_3, K_2O, Mg metal, CaO, Al metal, or Zn metal

Table S2 Molar concentration (M.C.), ionic conductivity, and viscosity of selected ILs for Na secondary batteries as summarized in Fig. 6.

IL	M.C. / mol dm^{-3}	Ionic conductivity / mS cm^{-1}	Viscosity / mPa s	Ref.
Na[TFSA]	0	9	33	2
-[C$_2$C$_1$im][TFSA]	0.4	5.3	47	
at 25 °C	0.7	3.9	72	
	0	16.6	20.3	3
-[C$_2$C$_1$im][FSA]	0.523	12.2	28.9	
at 25 °C	1.11	8.5	43.4	
	1.769	5.4	78.0	
	2.52	2.9	157.8	
	3.384	1.2	343.7	
Na[BF$_4$]	0	15.3		4
-[C$_2$C$_1$im][BF$_4$]	0.1	14.3		
at 30 °C	0.25	13		
	0.5	12.8		
	0.75	11.8		
Na[FSA]	0	2.4	100	5
-[N$_{1144}$][FSA]	0.361	1.6	141	
at 25 °C	0.784	1.1	209	
	1.28	0.69	356	
Na[FSA]	1.61	1.3	171	5
-[AS(4.5)][FSA]	2.305	0.64	379	
at 25 °C	3.129	0.31	709	
	4.087	0.12	2400	
	5.216	0.036	7570	
Na[TFSA]	0	4.6	19	[6,7]
-[N$_{2(2O2O1)3}$][TFSA]	0.5	1.5	61	
at 60 °C	1.0	0.8	117	
	2.0	0.2	838	
Na[FSA]	0	4.6	19	[6,7]
-[N$_{2(2O2O1)3}$][TFSA]	1.0	1.1	188	
at 60 °C	2.0	0.6	650	
	2.7	0.4	1300	
Na[FSA]	0	8.0	41	8
-[C$_3$C$_1$pyrr][FSA]	0.4459	5.5	60	
at 25 °C	0.983	3.6	95	
	1.584	1.9	163	
	2.275	1.0	303	
	3.084	0.51	779	
Na[FSA]	0	30.8	8.04	8
-[C$_3$C$_1$pyrr][FSA]	0.442	25.1	10.02	
at 90 °C	0.946	19.8	11.84	
	1.524	15.6	15.5	
	2.187	11.5	25.24	
	2.969	8.52	34.22	
Na[TFSA]	0	2.2		9
-C$_4$C$_1$pyrr][TFSA]	0.1	1.9		
at 25 °C	0.25	1.5		
	0.5	1.2		
	0.75	0.8		
	1.0	0.5		

Table S3 Na^+ transport number in ILs for Na secondary batteries shown in Fig. 6.

IL	M.C. / mol dm^{-3}	Na^+ transport number	Ref.
Na[FSA] -[C_2C_1im][FSA] at 90 °C	0.503 1.069 1.704 2.428 3.263	0.13 0.19 0.25 0.27 0.35	3
Na[FSA] -[C_3C_1pyrr][FSA] at 25 °C	0.983 1.584 2.275 3.084	0.01 0.07 0.19 0.32	10
Na[FSA] -[C_3C_1pyrr][FSA] at 90 °C	0.443 0.949 1.529 2.193 2.979	0.08 0.17 0.21 0.28 0.33	8
Na[TFSA] -[C_4C_1pyrr][TFSA] at 25 °C	0.10 0.25 0.50	0.06 0.17 0.19	9
Na[TFSA] -[C_4C_1pyrr][TFSA] at 50 °C	0.10 0.25 0.50	0.10 0.21 0.23	9
Na[TFSA] -[C_4C_1pyrr][TFSA] at 75 °C	0.10 0.25 0.50	0.13 0.24 0.25	9

Table S4 Structural information and electrochemical properties of positive electrode materials tested in Na secondary batteries using IL electrolytes.

Positive electrode	Lattice system	Space group	Redox couple involved	Average potential / V	Theoretical capacity / mAh g^{-1}	Ref.
$Na_2FeP_2O_7$	Triclinic	$P\bar{1}$	Fe^{3+}/Fe^{2+}	2.9	97	11
$Na_{1.56}Fe_{1.22}P_2O_7$	Triclinic	$P\bar{1}$	Fe^{3+}/Fe^{2+}	3.0	118	12-14
$NaFePO_4$ (maricite)	Orthorhombic	$Pnma$	Fe^{4+}/Fe^{3+}	2.6	155	15-17
$NaFePO_4$ (tryphylite)	Orthorhombic	$Pnma$	Fe^{4+}/Fe^{3+}	2.7	155	17
$NaVOPO_4$	Monoclinic	$P2_1/c$	V^{5+}/V^{4+}	3.6	145	18
$Na_3V_2(PO_4)_3$	Rhombohedral	$R\bar{3}c$	V^{3+}/V^{2+}	3.4	117	19
$Na_4Ni_3(PO_4)_2(P_2O_7)$	Orthorhombic	$Pn2_1a$	Ni^{3+}/Ni^{2+}	4.8	127	20
Na_2MnSiO_4	Monoclinic	Pn	Mn^{4+}/Mn^{2+}	3.3	278 (two-electron) 125 (one-electron)	21,22
$Na_{0.44}MnO_2$	Orthorhombic	$Pbam$	Mn^{4+}/Mn^{3+}	3.0	127	23,24
O3-$NaCrO_2$	Monoclinic	$R\bar{3}m$	Cr^{4+}/Cr^{3}	2.9	125	25
O3-$Na_{2/3}Fe_{2/3}Mn_{1/3}O_2$	Rhombohedral	$R\bar{3}m$	Me^{3+}/Me^{4+} (Me = $Fe_{2/3}Mn_{1/3}$)	2.7	174	26,27
P2-$Na_{2/3}Fe_{2/3}Mn_{1/3}O_2$	Hexagonal	$P6_3/mmc$	Me^{3+}/Me^{4+} (Me = $Fe_{2/3}Mn_{1/3}$)	2.5	174	26,27
P2-$Na_{0.6}Mn_{0.9}Co_{0.1}O_2$	Hexagonal	$P6_3/mmc$	Me^{3+}/Me^{4+} (Me = $Mn_{0.9}Co_{0.1}$)	2.2	159	28
P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$	Hexagonal	$P6_3/mmc$	Ni^{4+}/Ni^{2+}	3.5	172	29
P2-$Na_{2/3}Fe_{1/3}Mn_{2/3}O_2$	Hexagonal	$P6_3/mmc$	Me^{3+}/Me^{4+} (Me = $Fe_{1/3}Mn_{2/3}$)	2.0	261	30
P2-$Na_{2/3}Ni_{0.30}Co_{0.15}Mn_{0.55}O_2$	Hexagonal	$P6_3/mmc$	Ni^{4+}/Ni^{2+} Mn^{4+}/Mn^{3+} Co^{4+}/Co^{3+}	1.8	120	31,32
P2-$Na_{0.45}Ni_{0.22}Co_{0.11}Mn_{0.66}O_2$	Hexagonal	$P6_3/mmc$	Ni^{4+}/Ni^{2+} Mn^{4+}/Mn^{3+} Co^{4+}/Co^{3+}	2.7	123	33
P2-$Na_{0.45}Ni_{0.22}Co_{0.11}Mn_{0.66}O_2$	Hexagonal	$P6_3/mmc$	Ni^{4+}/Ni^{2+}		~230*	34
P2-$Na_{0.6}Ni_{0.22}Fe_{0.11}Mn_{0.66}O_2$	Hexagonal	$P6_3/mmc$	Mn^{4+}/Mn^{3+} Co^{4+}/Co^{3+} Ni^{4+}/Ni^{2+} Fe^{3+}/Fe^{2+}	3.1	~150*	35,36
P2-$Na_{2/3}Ti_{0.1}Fe_{0.1}Mn_{0.8}O_2$	Hexagonal	$P6_3/mmc$	Mn^{4+}/Mn^{3+}	2.8	176	27,37

* Specific discharge capacity

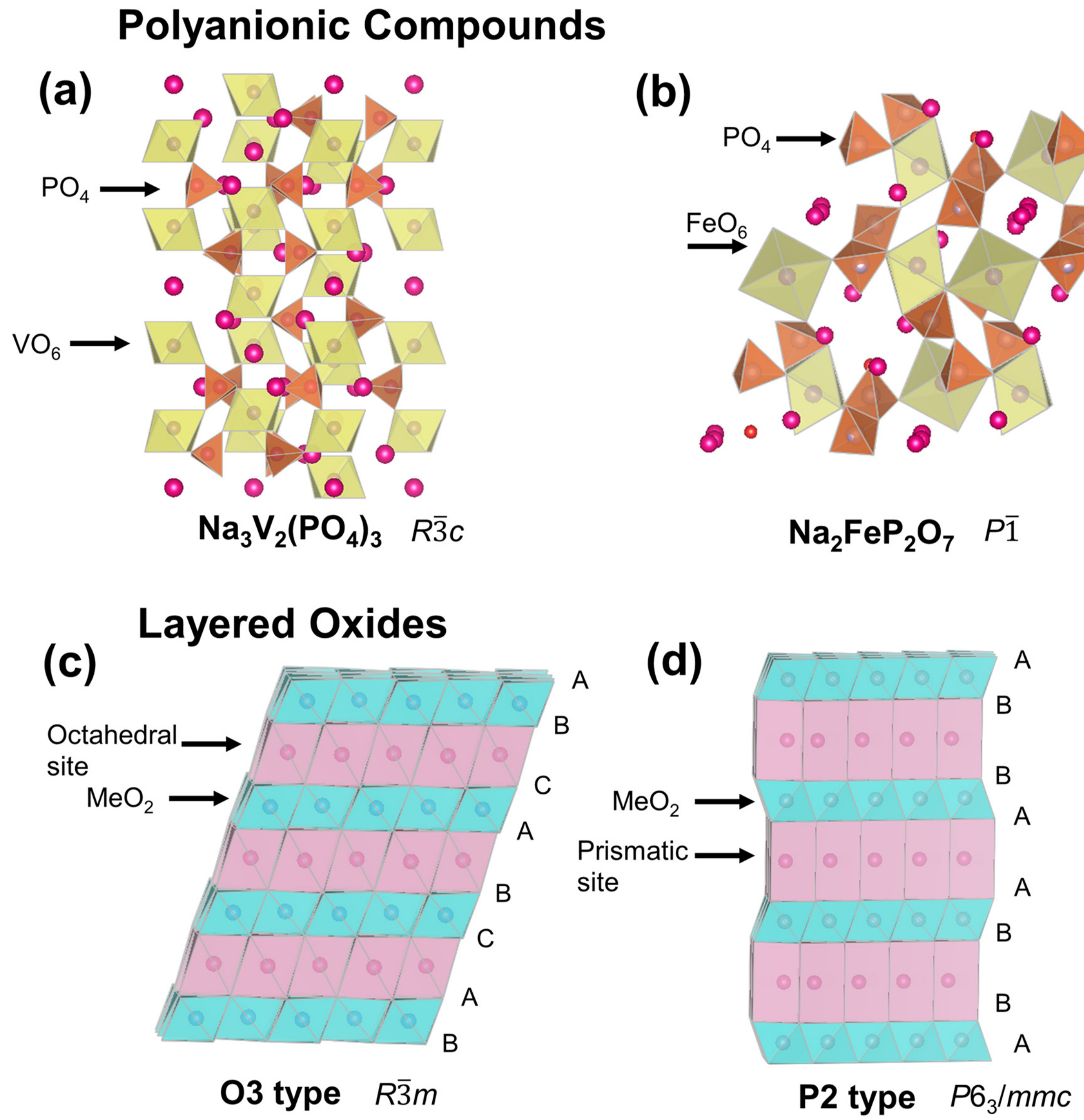

Fig. S1 Crystal structures of selected polyanionic compounds: (a) $Na_3V_2(PO_4)_3$, (b) $Na_2FeP_2O_7$, (c) an O3-type layered oxide, and (d) a P2-type layered oxide (Me = transition metal).

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