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SUPPLEMENTARY INFORMATION

Recent developments of $Na_4M_3(PO_4)_2(P_2O_7)$ as the cathode material for alkaline-ion rechargeable batteries: challenges and outlook

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For the sake of easier comparison, the overview of electrochemical properties of different materials $Na_4M_3(PO_4)_2(P_2O_7)$, where M=Co, Fe, Ni and Mn, was presented in tabular form, Table S1.

Table S1. The literature survey of the mixed-polyanionic compounds of the composition $Na_4M_3(PO_4)_2(P_2O_7)$ in the terms of the synthesis methods, the particles size, the specific capacity, rate and cyclic capability in the half-cell.

The synthesis procedure	~ Particle size	Electrolyte, binder	~ Initial specific discharge capacity /mAh g^{-1}	C-rate mA g^{-1}	~ Cap. retention (No. cycles, C-rate)
Co (~4.5 V vs. Na^+/Na)					
Sol-gel: $(CH_3COO)_2Co$, $Na_4P_2O_7$, $NH_4H_2PO_4$, $C_2H_4O_3$ + VGCF (700 °C, 50 h, Air + 5 h, Ar) $Na_4Co_3(PO_4)_2(P_2O_7)$[68,110]	3 µm polycrystal	1 M $NaPF_6$ / EC+DEC, 5wt%PVdF[NMP]	95 (0.2 C) 90 (10 C) 80 (25 C)	170	No fade (100, 0.2 C)
Sol-gel: $(CH_3COO)_2M$, $Na_4P_2O_7$, $NH_4H_2PO_4$, $C_2H_4O_3$ + VGCF (700 °C, 50 h, Air + 5 h, Ar) $Na_4Co_{2.4}Mn_{0.3}Ni_{0.3}(PO_4)_2(P_2O_7)$/0.5%$NaCoPO_4$[69]	/	1 M $NaPF_6$ / EC+DEC, 5wt%PVdF[NMP]	90 (0.2 C) 106 (2 C) 103 (5 C)	170	93 % (10, 2 C) 88 % (10, 5 C)
Sol-gel: $(CH_3COO)_2Co$, $Na_4P_2O_7$, $NH_4H_2PO_4$, $C_2H_4O_3$ + VGCF (680 °C, 50 h, Air + 5 h, Ar) $Na_4Co_3(PO_4)_2(P_2O_7)$/3wt%$NaCoPO_4$/C + desod. (4.8 V vs. Na), $Na_{1.4}Co_3(PO_4)_2(P_2O_7)$[109]	0,3-3 µm	1 M $LiPF_6$ / EC+DEC 5wt%PVdF[NMP]	100 (0.2 C), 90 (2 C), 80 (5 C)	170	80 % (5 C)
		1 M $NaPF_6$ / EC+DEC 5wt%PVdF[NMP]	99 (0.2 C), 92 (2 C), 89 (5 C)		90 % (5 C)
Sol-gel: $Co(CH_3COO)_2 \cdot 4H_2O$, $(NH_4)_2HPO_4$, $Na_4P_2O_7$ + MWCNTs (650 °C, 24 h, Air + 6 h, Ar) $Na_4Co_3(PO_4)_2(P_2O_7)$/16.7wt%C[67]	200 nm	1 M $NaPF_6$ / EC+DMC, 10wt%CMC	92 (0.1 C), 78 (0.1 C, 55 °C), 48 (2 C), 39 (5 C), 31 (10 C), 20 (20 C)	129	90 % (50, 0.1 C) 85 % (45, 0.1 C, 55 °C)
Spray-drying: $Co(NO_3)_2$, $Al(NO_3)_3$, $NaH_2PO_4 \cdot 2H_2O$, $C_6H_8O_7 \cdot H_2O$, CNTs (700 °C, 10 h, Ar) $Na_{4-x}Co_{3-x}Al_x(PO_4)_2(P_2O_7)$ (x=0, 0.05, 0.1, 0.15, 0.2) Al0.15-NCPP/C[111]	0.5-3 µm (465 nm)	1 M $NaPF_6$ / EC+DEC+5%FEC, 10wt%PVdF[NMP]	99 (0.5 C), 89 (2 C), 86 (5 C), 83 (10 C), 73 (50 C) ♦	170	98 % (800, 5 C) 96 % (900, 10 C) 83 % (8k, 30 C) ♦
Fe (~ 3.2 vs. Na^+/Na)					
Mechanochemically assisted solid-state: $Fe_2C_2O_4 \cdot 2H_2O$, $NH_4H_2PO_4$, $Na_4P_2O_7$, $C_{10}H_6O_8$ (500 °C, 12 h, Ar) - Kim's procedure $Na_4Fe_3(PO_4)_2(P_2O_7)$/4wt%$NaFePO_4$/C[47]	/	1 M $NaClO_4$ / PC, 10wt%PVdF[NMP]	108 (0.025 C) 102 (0.05 C)	129	No fade (15, 0.025 C)

Kim's procedure□: $Na_4Fe_3(PO_4)_2(P_2O_7)$/4wt%$NaFePO_4$[71]	100-200 nm	1 M $NaClO_4$ / PC, 10wt%PVdF^{NMP}	106 (0.05 C), 100 (0.1 C), 97 (0.2 C)	129	99 % (20, 0.05 C)
Kim's procedure + chemical Na-Li exchange: $Li_3NaFe_3(PO_4)_2(P_2O_7)$[47]	100-200 nm	1 M $LiPF_6$ / EC+DMC, 10wt%PVdF^{NMP}	129 (0.05 C), 25 ^{o}C 140 (0.2 C), 60 ^{o}C	~ 140	86 % (100, 0.2 C), 60 ^{o}C
Kim's procedure□: $Na_4Fe_3(PO_4)_2(P_2O_7)$/4wt%$NaFePO_4$[112]	100-200 nm	1 M $NaClO_4$ / PC+EC, 10wt%PVdF	128 (0.05 C)	~ 129	97 % (100, 0.05 C)
Kim's procedure□: $Na_4Fe_3(PO_4)_2(P_2O_7)$/4wt%$NaFePO_4$[141]	/	0.5 M $NaClO_4$/ I/II/III/IV, I/II/III/IV+5%FEC♠ 10wt%PVdF^{NMP}	/	100	/
		EC+PC^{I}	93, 94♠ (0.5 C)		99, 98♠ % (100, 0.5 C)
		EC+PC+DMC^{II}	94, 88♠ (0.5 C)		97, 99♠ % (100, 0.5 C)
		EC+PC+EMC^{III}	91, 94♠ (0.5 C)		No fade, 99♠ % (100, 0.5 C)
		EC+PC+DEC^{IV}	92, 96♠ (0.5 C)		99, 99♠ % (100, 0.5 C) 97♠ % (300, 0.5 C)
Kim's procedure□: $Na_4Fe_3(PO_4)_2(P_2O_7)$/4wt%$NaFePO_4$[140]		5 M NaFSI/DME 10wt%PVdF^{NMP}	116 (0.5 C)	0.56 mA cm^{-2}	94 % (300, 0.5 C)
		1 M $NaPF_6$ / EC+PC 10wt%PVdF^{NMP}	111 (0.5 C)		85 % (300, 0.5 C)
Modified Kim's procedure□: the addition of the conducting carbon (Super C65) + heated in N_2 $Na_{3.97}Fe_3(PO_4)_2(P_2O_7)$/3wt%$NaFePO_4$/7.8wt%C[114]	/	1 M $NaClO_4$ / PC+EC, 5wt%PVdF^{NMP}	99 (1 C)	129	90 % (50, 1 C)
		1 M Na_2SO_4 / H_2O, 5wt%PVdF^{NMP}	84 (1 C)		74 % (50,1 C)
Modified Kim's procedure: 550 ^{o}C[115]	50-200 nm	1 M $NaClO_4$, 10wt%PTFE	100 (1 C)	129	Only for the full-cell
		17 M $NaClO_4$, 10wt%PTFE	90 (1 C)		

Modified Kim's procedure□: the soot as the carbon source (3wt%) + the ball-milling time is shortened to 5 min (400-600 °C, 4 h, Ar), NFPP-450 89.1wt%$Na_4Fe_3(PO_4)_2(P_2O_7)$/10.9wt%$NaFePO_4$/C[97]	100 nm, 2-3 nm C layer	1 M $NaClO_4$ / PC+EC, 5wt%PVdF^{NMP}	104 (0.2 C), 60 (1 C), 5 (10 C)	129	79 % (50, 0.2 C)
		1 M $LiPF_6$ / EC+DMC, 5wt%PVdF^{NMP}	95 (0.2 C), 82 (1 C) 10 (10 C)		82 % (50, 0.2 C)
Modified Kim's procedure□: the soot as the carbon source (3wt%) + shorter ball-milling time to 5min (450 °C, 4 h, Ar), NFPP-450 + desod. in a Li cell: $Na_{2.4}Li_{1.2}Fe_3(PO_4)_2(P_2O_7)$, ed-NFPP/Li-Na[97,113]	100 nm, 2-3 nm C layer	(0.9 M $LiPF_6$ + 0.1 M $NaPF_6$) / EC+DMC, 5wt%PVdF^{NMP}	106 (0.2 C) 91 (1 C) 65 (3 C)	129	91 % (45, 0.2 C)
Solution combustion (NFPP/C powder) + pulsed laser deposition: NaH_2PO_4, $Fe(NO_3)_3{\cdot}9H_2O$, $C_6H_8O_6$ (600 °C, 12 h, Ar), $Na_4Fe_3(PO_4)_2(P_2O_7)$/C NFPP/C film[116,117]	220 nm film	1 M $NaClO_4$ / PC, 10wt%PVdF^{NMP}	126 (0.1 C) for powder	129	96 % (10, 0.1 C) for powder
		1 M $NaClO_4$ / EC+DMC, 10wt%PVdF^{NMP}	125 (2 μA cm^{-2}) 110 (10 μA cm^{-2})		No fade (500, 1 C)
Sol-gel: Fe, $NaH_2PO_4{\cdot}2H_2O$, $C_6H_8O_7$, ethylene glycol (400-600 °C, 10 h, Ar) $Na_4Fe_3(PO_4)_2(P_2O_7)$/8.7wt%C NFPP/C-500[50]	100-150 nm, 7-8 nm C layer	1 M $NaClO_4$ / PC+FEC, 10wt%PVdF^{NMP}	99 (0.2 C), 95 (1 C), 78 (10 C), 25 °C 109 (0.2 C), 103 (1 C), 81 (10 C), 55 °C	129	89 % (300, 0.5 C)
Sol-gel: Fe, $NaH_2PO_4{\cdot}2H_2O$, $C_6H_8O_7$, ethylene glycol, GO (500 °C, 8 h, Ar/5%H_2) $Na_4Fe_3(PO_4)_2(P_2O_7)$/10.8wt%C NFPP@AC/rGO[107]	50-100nm, (1 μm with rGO)	1 M $NaClO_4$ / PC+2%FEC, 10wt%PVdF^{NMP}	99 (1 C), 85 (10 C), 66 (50 C), 30 °C 89 (1 C), 53 (10 C), 29 (50 C), -15 °C	129	83% (300, 20 C), 30 °C 89 % (300, 20 C), -15 °C
Sol-gel: Fe, $C_6H_8O_7$, p-CC, $NaH_2PO_4{\cdot}2H_2O$, ethylene glycol (500 °C, 8 h, Ar/5%H_2) $Na_4Fe_3(PO_4)_2(P_2O_7)$/$NaFePO_4$/7.2wt%C NFPP@NFP@C-CC[119]	80-100 nm	1 M $NaClO_4$ / PC+5%FEC, No binder	136 (0.1 C), 127 (0.5 C), 118 (1 C), 97 (10 C), 75 (50 C) 68 (100 C) ▽	129	No fade (3k, 10 C) ▽
Sol gel: CH_3COONa, $NH_4H_2PO_4$, $C_6H_{12}O_6$, $C_{18}H_{36}O_2$, $(CH_3COO)_2Fe$, EDTA, CTAB (500 °C, 24 h, Ar) $Na_4Fe_3(PO_4)_2(P_2O_7)$/4wt%$NaFePO_4$/3.6wt%C NFPP-E[99]	150 nm, 4 nm C layer	1 M $NaClO_4$ / EC+PC+5%FEC, 10wt%PVdF^{NMP}	108 (0.1 C), 99 (1 C), 84 (10 C), 80 (20 C)	120	100 % (50, 0.05 C) 85 % (250, 0.2 C) 69 % (4.4k, 20 C)
Sol gel: CH_3COONa, $NH_4H_2PO_4$, $C_6H_{12}O_6$, $C_{18}H_{36}O_2$, $(CH_3COO)_2Fe$, $C_6H_8O_7{\cdot}H_2O$ (500 °C, 24 h, Ar) $Na_4Fe_3(PO_4)_2(P_2O_7)$/4wt%$NaFePO_4$/4.1wt%C NFPP-C[99]	2μm, 3 nm C layer		105 (0.1 C), 80 (1 C), 67 (10 C), 62 (20 C)		57 % (4.4k, 20 C)

Template method: Pluronic-F127, $Na_4P_2O_7$, $NH_4H_2PO_4$, $Fe(NO_3)_3 \cdot 9H_2O$, phenolic resol, HCl (500 °C, 12 h, Ar) $Na_4Fe_3(PO_4)_2(P_2O_7)$/14.3wt%C NFPP/HC[63]	29 nm, 3 nm C layer	1 M $NaClO_4$/ EC+DEC+5%FEC, 10wt%PVdF^{NMP}	120 (1 C), 114 (10 C), 79 (100 C) $^{\Delta}$	~129	63 % (4k, 10 C) $^{\Delta}$
Spray pyrolysis: $NaH_2PO_4 \cdot 2H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ $C_6H_8O_7 \cdot H_2O$, GO, (500 °C, 10 h, Ar/10%H_2) $Na_4Fe_3(PO_4)_2(P_2O_7)$/8.3wt%C NFPP@rGO[102]	60 nm, (1-4 µm with rGO)	1 M $NaClO_4$/ EC+DEC+5%FEC, 10wt%PVdF^{NMP}	128 (0.1 C), 114 (1 C), 101 (10 C), 60 (100 C), 35 (200 C) $^{\Delta}$	129	88 % (1.3k, 1 C) 62 % (6k, 10 C) $^{\Delta}$
Spray pyrolysis: $Fe(NO_3)_3 \cdot 9H_2O$, CH_3COONa, NH_4H_2PO4, MCNTs (600 °C, 10 h, Ar/H_2) $Na_4Fe_3(PO_4)_2(P_2O_7)$/3.457wt%MCNTs NFPP@MCNTs[64]	20-50 nm	1 M $NaClO_4$/ EC+DEC+5%FEC, 10wt%PVdF^{NMP}	116 (0.1 C), 99 (1 C), 82 (10 C), 63 (20 C)	129	95 % (1.2k, 2 C)
Ni (4.8 V vs. Na^+/Na)					
Mechanochemically assisted solid-state: $Na_4P_2O_7 \cdot 10H_2O$, $Ni(OCOCH_3)_2 \cdot 4H_2O$, $NH_4H_2PO_4$, $C_6H_8O_7 \cdot H_2O$ (500 °C, 10 h, Ar) $Na_4Ni_3(PO_4)_2(P_2O_7)$/6.3wt%C[96]	500 nm	10 mol % NaTFSI/ $Py_{14}FSI$, 10wt%PVdF^{NMP}	63 (0.08 C)	~ 127	79 % (10, 0.08 C)
		1 M $NaPF_6$/ EC+DEC, 10wt%PVdF^{NMP}	40 (0.08 C)		70 % (10, 0.08 C)
Sol-gel: $Ni(OCOCH_3)_2 \cdot 4H_2O$, $(NH_4)_2HPO_4$, $Na_4P_2O_7$ + $C_{12}H_{22}O_{11}$ (700 °C, 24 h Air + 24 h Ar) $Na_4Ni_3(PO_4)_2(P_2O_7)$/8.45wt%C, NNPP/C[98]	600 nm, 7 nm C layer	1 M $NaPF_6$/ EC+DMC, 10wt%CMC	74 (0.1 C)	127	36 % (50, 0.1C) for both NNPP/C and NNPP/rGO
Sol-gel: $Ni(OCOCH_3)_2 \cdot 4H_2O$, $(NH_4)_2HPO_4$, $Na_4P_2O_7$ + GO (700 °C, 24 h Air + 24 h Ar) $Na_4Ni_3(PO_4)_2(P_2O_7)$/8.90wt%C, NNPP/rGO[98]	550 nm, 7 nm C layer		72 (0.1 C)		
Mn (4.8 V vs. Na^+/Na)					
Mechanochemically-assisted solid-state: $Na_4P_2O_7$, $Mn_2C_2O_4 \cdot 2H_2O$, $NH_4H_2PO_4$ + $C_{10}H_6O_8$, (600 °C, 6 h Air + 2 h Ar) $Na_4Ni_3(PO_4)_2(P_2O_7)$/4wt%$NaMnPO_4$/3wt%C[77]	200-500 nm	1 M $NaBF_4$/ EC+PC, 10wt%PVdF^{NMP}	109 (0.05 C), 90 (1 C), 67 (10 C), 25 °C	~ 130	82% (100, 0.05 C) 86% (100, 0.2 C), 25 °C
			121 (0.05 C), 112 (2 C), 92 (10 C), 60 °C		70% (200, 1C), 60 °C
Spray-drying: $Mn(NO_3)_2$, $Co(NO_3) \cdot 6H_2O$, $C_6H_8O_7$, CNTs (630 °C, 10 h, Ar) $Na_4Mn_2Co(PO_4)_2(P_2O_7)$/C-Xwt%CNTs (X=3, 5, 7) NM_2CPP/C-5wt%CNTs (opt.conc)[108]	150 nm, (2-3 µm with CNTs)	1 M $NaClO_4$/ EC+PC+10%FEC, 10wt%PVdF^{NMP}	96 (0.1 C) 74 (1 C) 41 (10 C)	~ 129	78 (100, 0.5 C) 76 (150, 1 C)

Solution combustion: $Na_4P_2O_7$, $Mn(NO_3)_2·4H_2O$, $Co(NO_3)_2·6H_2O$, $NH_4H_2PO_4$, $C_2H_5NO_2$ + GO (600 °C, 6 h, Air + 2 h, Ar) $Na_4Mn_{2.4}Co_{0.6}(PO_4)_2(P_2O_7)$/less than 2wt%$Mn_2O_3$ and $Na_2MnP_5O_{15}$/6.1wt%C, NMCMP/rGO[121]	100-200 nm	1 M $NaPF_6$ / EC+DEC, 10wt%PVdF	76 (0.1 C) 34 (1 C)	130	77 % (40, 0.1 C)
			47 (0.1 C) for Co-free		60 % (40, 0.1 C) for Co-free

VGCF-Vapor Grown Carbon Fiber, $C_2H_4O_3$-glycolic acid, PVdF[NMP]-polyvinylidene fluoride as binder and N-methyl-2-pyrrolidone as solvent, MWCNTs-multiwalled carbon nanotubes, CMC-carboxymethyl cellulose, $C_6H_8O_7$-citric acid, ♦-it was emphasized that the capacity was based on the Al0.15-NCPP mass, $C_{10}H_6O_8$-pyromellitic acid, □-Kim's procedure without pyromellitic acid, NaFSI/DME-sodium bis (fluorosulfonyl)imide in 1,2 dimethoxyethane, PTFE-polytetrafluoroethylene, $C_6H_8O_6$-ascorbic acid, GO-graphene oxide, p-CC-pretreated carbon cloth, ∇-it was emphasized that the capacity was based on the NFPP@NFP mass, $C_6H_{12}O_6$-glucose, $C_{18}H_{36}O_2$-stearic acid, $C_{12}H_{22}O_{11}$-sucrose, CTAB-cetyltrimethylammonium bromide, ETDA-ethylenediaminetetraacetic, Δ-it was emphasized that the capacity was based on the NFPP mass, $C_2H_5NO_2$-glycine

The survey of some polyanionic-type structures (phosphate, pyrophosphates, fluorophosphates and silicates) in terms of the synthesis and electrochemical performance, is shown in the Table S3.

Table S2. The literature survey of other polyanion-type electrode materials for sodium-ion batteries

The synthesis procedure	**~ Voltage**	**Electrolyte, binder**	**~ Initial specific discharge capacity / mAh g^{-1}**	**C-rate mA g^{-1}**	**~ Cap. retention (No. cycles, rate)**
Phosphates: $NaMPO_4$ (M=Fe, Co) and NASICON $Na_3V_2(PO_4)_3$					
Co-precipitation: $Fe(NO_3)_3·9H_2O$, H_3PO_4, $C_{12}H_{22}O_{11}$, NH_4OH + Li_2CO_3 (500 °C, 10 h, Ar/H_2 + 750 °C, 15 h, Ar/H_2) $LiFePO_4$/3.1wt%C + delith. (4.3 V vs. Li) $FePO_4$/C + sod. (2.2 V vs. Na) Olive, **$NaFePO_4$**/C, 8 µm [72]	2.7 V	1 M $NaClO_4$ / PC+2%FEC, 7.5wt%PVdF[NMP]	125 (0.05 C) 110 (0.1 C) 99 (0.2 C) 85 (0.5 C) ♦	~ 154	90 % (50, 0.05 C) ♦
Solid-state + ball-miling (500 rpm, 24 h): Na_2CO_3, $FeC_2O_4·2H_2O$, $NH_4H_2PO_4$ (350 °C, 5 h, Ar + 600 °C, 10 h, Ar) + dry ball-milling with 20wt% Super P (200 rpm, 12 h) Maricite, **$NaFePO_4$**/20wt%C, 50nm [73]	2.7 V	1 M $NaPF_6$ / EC+PC, 10wt%PVdF[NMP]	142 (0.05 C) 131 (0.2 C) 106 (0.5 C) 64 (2 C)	~ 155	95 % (200, 0.05 C)

Electrospinning: PVP, NaH_2PO_4, $C_6H_8O_7$, $Fe(NO_3)_3 \cdot 9H_2O$ (300 °C, 2 h + 600 °C, 3 h, N_2) Maricite, **$NaFePO_4$**/27wt%C/2.1wt%N_2,115 nm [156]	2.6 V	1 M $NaClO_4$ / PC+5%FEC, No binder	145 (0.2 C), 134 (0.5 C), 129 (1 C), 115 (2 C), 102 (5 C), 84 (10 C), 73 (20 C) 61 (50 C)$^{\nabla}$	150	89 % (6.3k, 5 C)$^{\nabla}$
Microwave-assisted: H_3PO_4, $NaNO_3$, $C_8H_{18}O_5$, $Co(NO_3)_2 \cdot 6H_2O$ (800 rpm, 3 min, 100-300 °C) Red-phase **$NaCoPO_4$**/$CoPO_4$, 0.5-10 µm, [82]	4.2 V	1 M $NaPF_6$ / EC+EMC+2%FEC, 5wt%PTFE^{H2O}	35 (0.02 C)	120	/
Template: CTAB, CH_3COONa, $C_{15}H_{21}O_6V$, $(NH_4)H_2PO_4$ (650 °C, 6 h, Ar/H_2) **$Na_3V_2(PO_4)_3$**/6wt%C, 500-900 nm [75]	3.4 V	1 M $NaClO_4$ / EC+PC, 10wt%PVdF^{NMP}	117 (0.1 C), 114 (1 C), 106 (10 C), 92 (20 C), 63 (40 C)	~ 117	87 % (1k, 1 C) 85 % (1k, 10 C) 90 % (3.5k, 20 C) 50 % (30k, 40 C)
Sol-gel: NaOH, NH_4VO_3, $NH_4H_2PO_4$, $C_6H_8O_7$ (400 °C, 3 h + 700 °C, 8 h, N_2) **$Na_3V_2(PO_4)_3$**/8wt%C NVP/C [132]	3.4 V	1 M $NaClO_4$ / ED+DMC+5%FEC 10wt%PVdF^{NMP}	108 (1 C), 95 (3 C), 81 (10 C), 73 (20 C), 55 (50 C), 19 (100 C)	~ 117	86 % (100, 1 C)
Sol-gel + coating: NaOH, NH_4VO_3, $NH_4H_2PO_4$, $C_6H_8O_7$, CC (400 °C, 3 h + 700 °C, 8 h, N_2) **$Na_3V_2(PO_4)_3$**/8wt%C, NVP/C-CC [132]		1 M $NaClO_4$ / ED+DMC+5%FEC No binder	116 (1 C), 113 (3 C), 112 (10 C), 108 (20 C), 105 (50), 97 (100 C), 70 (200 C)		94 % (100, 1 C) 82 % (2k, 20 C) 78 % (2k, 50 C)
Pyrophosphates: $Na_2MP_2O_7$ (M= Fe, Co, Mn)					
Solution-combustion: NaH_2PO_4, $Fe(NO_3)_3 \cdot 9H_2O$, $C_6H_8O_7$ (600 °C, 6 h, Ar) 90wt%**$Na_2FeP_2O_7$**/7wt%$Na_4P_2O_7$/1.5wt%$NaFePO_4$/ 1.4wt%$Na_4Fe_3(PO_4)_2(P_2O_7)$/C, 300-500 nm / 5 nm C layer [53]	3 V	1 M $NaClO_4$ / PC, 5wt%PTFE	82 (0.05 C), 75 (1 C), 67 (5 C), 48 (10 C)	97	/
Solid-state: Na_2CO_3, $(NH_4)_2HPO_4$, $FeC_2O_4 \cdot 2H_2O$ (350 °C, 3 h, Ar + 600 °C, 6 h, Ar) + dry ball-milling with Super P (24 h, 500 rpm), (600 °C, 10 h, Ar) **$Na_2FeP_2O_7$**/C1-2 µm /15-20 nm C layer [56]	3 V	1 M $NaClO_4$ / PC, 10wt%PVdF^{NMP}	87 (0.05 C), 80 (0.2 C), 68 (0.5 C), 60 (1 C), 47 (2 C)	97	No fade (80, 0.05 C)
Solid-state: Na_2CO_3, $FeC_2O_4 \cdot 2H_2O$, $NH_4H_2PO_4$, $C_6H_{12}O_6$ (650 °C, 6 h, Ar/H_2) **$Na_2FeP_2O_7$**, B-NFP, 20-50 nm [133]	2.5/3 V	1 M $NaClO_4$ / EC+PC, 15wt%PVdF^{NMP}	84 (0.05 C)	97	65 % (100, 0.2 C)
Sol-gel: $Fe(COOCH_3)_2$, $C_6H_8O_7$, $Na(COOCH_3)$, $NH_4H_2PO_4$ (600 °C, 3 h, Ar/H_2) A-NFP-NPs + ball-milling,			95 (0.05 C), 89 (0.5 C), 87 (1 C), 81 (5 C), 77 (10 C), 73		83 % (10k, 10 C) 84 % (10k, 60 C)

M-NFP-NPs/17wt%C, 20-50 nm [133]			(20 C), 55 (60 C)		
Ball-milling: NFP-NPs + ZrO_2 balls, ethanol (600 °C, 3 h, Ar/H_2), NFP-NPs slurry + PCC (600 °C, 3 h, Ar/H_2) NFP-NPs@PCC, 20-50 nm [133]		1 M $NaClO_4$ / EC+PC, No binder	95 (0.1 C), 90 (0.5 C), 87 (1 C), 84 (2 C), 77 (5 C), 68 (10 C)		82 % (2k, 10 C)
Combustion: NaH_2PO_4, $Co(NO_3)_3{\cdot}6H_2O$, $C_6H_8O_7$ (600 °C, 1-6 h), Orthorhombic (blue-phase), **$Na_2CoP_2O_7$**, 0.2-1 µm[83]	3 V	1 M $NaClO_4$ / PC+2%FEC, 10wt%PVdF[NMP]	80 (0.05 C)	~ 96	/
Solid-state + ball-milling (300 rpm, 12 h): Na_2CO_3, excess as much as 10% of CoO, $(NH_4)_2HPO_4$ (650 °C, 2 h, N_2), cooling (-10 °C min^{-1} with holding at 500 °C, 20 min) Triclinic (rose-phase), **$Na_2CoP_2O_7$** [S1]	4.3 V	1 M $NaPF_6$ / EC+DEC, 10wt%PVdF[NMP]	80 (0.05 C)	95	86 % (30, 0.1 C)
Solid-state: Na_2CO_3, $(NH_4)_2HPO_4$, MnO_2 (350 °C, 3 h, Ar + 500 °C, 9 h, Ar) + ball-milling with 20wt% Super P (500 rpm, 24 h + 500 °C, 9 h, Ar) **$Na_2MnP_2O_7$**/C, 1 µm [79]	3.8 V	1 M $NaClO_4$ / PC, 10wt%PVdF[NMP]	90 (0.05 C), 85 (0.1 C), 78 (0.2 C), 69 (0.5 C), 61 (1 C)	~ 97	96 % (30, 0.2 C)
Combustion: NaH_2PO_4, $Mn(CH_3COO)_2{\cdot}4H_2O$ or $Mn(NO_3)_2{\cdot}6H_2O$, $C_6H_8O_7$, (600 °C, 1-6 h, Ar) **$Na_2MnP_2O_7$, 1-2 µm** [S2]	3.6 V	1 M $NaClO_4$ / PC, 10wt%PVdF[NMP]	80 (0.05 C)	~ 97	83 % (15, 0.05 C)
Fluorophosphates: Na_2MPO_4F (M=Fe, Co, Mn) and $Na_3V_2(PO_4)_2O_2F$					
Ionothermal: Na_3PO_4, FeF_2, 1,2-dimethyl-3-butylimidazolium bis trifluoromethanesulfonyl imide (270 °C, 48 h, Ar) + centrifugation: Na_2FePO_4F/NaF + washed with cold water (60 °C, 1 h) Na_2FePO_4F + 20wt%$C_{12}H_{22}O_{11}$ (700 °C, 10 min, Ar) **Na_2FePO_4F**/5wt%C, 25-50 nm [S3]	3 V	1 M $NaClO_4$ / PC,	115 (0.06 C)	124	93 % (10, 0.06 C)
Solid-state + ball-milling: NaF, $NaHCO_3$, $NH_4H_2PO_4$ $FeC_2O_4{\cdot}2H_2O$, $C_6H_8O_6$ (300 °C, 2 h, N_2 + 600/650 °C,10 h, N_2) **Na_2FePO_4F**/1.3wt%C, 30-200 nm [76]	2.91/3.06 V	1 M $NaClO_4$ / PC+ FEC, 10wt%PVdF[NMP]	110 (0.05 C), 109 (0.1 C), 87 (0.2 C), 72 (0.5 C), 58 (1 C), 45 (2 C), 15 (8 C)	124	70 % (20, 0.05 C)
Ultrasonic spray pyrolysis: NaF, $NaNO_3$, $Fe(NO_3)_3{\cdot}9H_2O$, H_3PO_4, $C_{12}H_{22}O_{11}$ + PTFE (500 °C, 3 h, N_2 + 600 °C, 8 h, Ar) **Na_2FePO_4F**/6-8wt%C,500 nm / 10 nm C layer[152].	2.9/3.1 V	1 M $NaClO_4$ / EC+DMC, 10wt%PVdF[NMP]	89 (0.1 C), 75 (1 C)	124	90 % (100, 0.1 C) 80 % (750, 1 C)

Solid-state + ball-milling: NaF, $NaHCO_3$, CoO, $(NH_4)_2HPO_4$, $C_6H_8O_6$, (300 °C, 2 h, Ar + 600/650 °C, 10 h, Ar) **Na_2CoPO_4F**/2wt%$C_6H_8O_6$ [85]	4.3 V	1 M $NaPF_6$ / EC+DEC+2%FEC, 10wt%$PVdF^{NMP}$	100 (6.2 mA g^{-1})	/	/
Spray-drying: $Co(NO_3)_2{\cdot}6H_2O$, $C_6H_8O_7$, NaF, H_3PO_4 (600 °C, 6 h, Ar) **Na_2CoPO_4F**/4wt%C, 20 μm, [S4]	4.3 V	1 M $NaPF_6$ / EC+DMC+2%FEC 10wt%$PVdF^{NMP}$	107 (0.5 C), 98 (1 C), 80 (2 C), 73 (3 C), 65 (5 C)	~ 122	37 % (20, 0.5 C)
Solid-state + ball-milling (500 rpm, 12 h): Na_2CO_3, NaF, $Mn(C_2O_4){\cdot}2H_2O$, $NH_4H_2PO_4$, $C_{10}H_6O_8$ (300 °C, 2 h, Ar + 600 °C, 12 h, Ar) **Na_2MnPO_4F**/6wt%C,100 nm [S5]	3.6,4.6	1 M $NaClO_4$ / PC, 10wt%$PVdF^{NMP}$	120 (10 mA g^{-1})	/	/
Spray drying: $Mn(CH_3COO)_2{\cdot}4H_2O$, $C_6H_8O_7$, NaF, $NH_4H_2PO_4$, (350 °C, 3 h, Ar + 700 °C, 6 h, Ar) **Na_2MnPO_4F**/10.5 wt%C, 100 nm [80]	3.5	1 M NaClO4 / EC+PC, 10wt%$PVdF^{NMP}$	140 (0.05 C), 123 (0.1 C), 101 (0.2 C), 73 (0.5 C), 60 (1 C) 30°C▼	124	54 % (50, 0.05 C) 30°C▼
Hydrothermal: V_2O_5, $H_2C_2O_4$, $NH_4H_2PO_4$, NaF (170 °C, 12 h) **$Na_3V_2(PO_4)_2O_2F$**/$Na_3V_2(PO_4)_2F_3$ [157]	3.6, 4 V	1 M $NaClO_4$ / EC+PC+5%FEC 10wt%CMC^{H2O}	128 (0.1 C), 117 (0.5 C), 113 (2 C), 101 (10 C), 97 (15 C), 93 (20 C), 81 (40 C)	130	94 % (200, 0.2 C) 88 % (1k, 1 C) 81 % (2k, 20 C)
Silicates: Na_2MSiO_4 (M=Fe, Mn, Co)					
Solvotermal: $CH_3COONa{\cdot}3H_2O$, $Si(C_2H_5O)_4$ $FeC_2O_4{\cdot}2H_2O$, $C_6H_8O_6$, $C_2H_6O_2$:ethanol solution (230 °C, 7 days + 300 °C, 2 days) Monoclinic, 85wt%**Na_2FeSiO_4**/15wt%Na_2SiO_3/C, 1-5 μm [S6]	1.66V	1 M $NaPF_6$ / EC+DMC 5wt%PTFE	126 (0.025 C)	138	/
Sol-gel: Fe, $C_6H_8O_7$, $CH_3COONa{\cdot}3H_2O$, $C_2H_6O_2$, $Si(OC_2H_5)_4$, (500 °C, 10 h, Ar) Cubic, **Na_2FeSiO_4**/16wt%C 30-50 nm [74]	1.9 V	1 M $NaClO_4$ / PC, 10wt%$PVdF^{NMP}$	106 (5 mA g^{-1})	/	95 % (20, 10 mA g^{-1})
Sol-gel: $FeC_2O_4{\cdot}2H_2O$, CH_3COONa, $C_6H_8O_7$, $Si(OC_2H_5)_4$, (60 °C, 12 h) + ball-milling with 5wt% $C_{12}H_{22}O_{11}$ (10 h, 100 °C + 600 °C, 8 h, Ar) Triclinic, **Na_2FeSiO_4**/4.63wt%C, 0.5-1 μm [S7]	2 V	10wt%CMC^{NMP}	181 (0.1 C), 140 (0.2 C), 109 (0.5 C), 96 (1 C)	276	88 % (100, 0.1 C)
Solid-state: $Na_2C_2O_4$, $C_6H_{10}O_4$, SiO_2 (700 °C, 12 h, Ar) **Na_2FeSiO_4**/5wt%C,110 nm / 2-3 nm C layer [S8]	2 V	1 M $NaClO_4$ / EC+DEC, 10wt%PTFE	105 (0.25 C), 77 (1 C), 62 (2.5 C), 55 (3.5 C)	140	85 % (200, 0.25 C) 80 % (1k, 3.5 C)
Sol-gel: CH_3COONa, $(CH_3COO)_3Mn{\cdot}2H_2O$,	3 V	Na[FSA]-	70 (0.1 C) 25 °C,	139	80 % (10, 0.1 C)

$Si(OC_2H_5)_4$, CH_3 COOH, $C_{12}H_{22}O_{11}$ (700 °C, 12 h, Ar/5%H_2) **Na_2MnSiO_4**/Na_2SiO_3/MnO/13.5wt%C [S9]		[C3C1pyrr][FSA] IL, 5wt%PTFE	125 (0.1 C), 115 (1 C), 89 (2 C), 56 (5 C),76 (3 C), 34 (10 C) 90 °C		90 °C
Facile sol-gel: GO, $C_6H_{12}O_6$, CH_3COONa, $Si(OC_2H_5)_4$, $(CH_3COO)_2Mn·4H_2O$, C_3H_8O, CH_3 COOH (650 °C, 10 h, Ar) **Na_2MnSiO_4**/MnO/24.9wt%C,30-40 nm [S10]	2 V	1 M $NaClO_4$ / PC+50%FEC, 5wt%PVdF^{NMP}	182 (0.1 C), 130 (0.5 C), 107 (1 C), 80 (2 C), 60 (5 C)$^{•}$	139	65 % (30, 0.5 C) 64 % (30, 1 C) 75 % (30, 2 C) 79 % (30, 5 C)$^{•}$
Two-step process: $(CH_3COO)_2Mn·4H_2O$, $Si(OC_2H_5)_4$, $C_6H_8O_7$, (700 °C, 6 h, Ar) + Na_2CO_3 (500 rpm, 30 min) + $C_6H_8O_7$ (500 rpm, 10 min) (750 °C, 8 h, Ar) + Super P (500 rpm, 4 h + 750 °C, 6 h, Ar) **Na_2MnSiO_4**/24wt%C, 60-90 nm /2-3 nm C layer[81]	3 V	1 M $NaPF_6$ / EC+PC+5%VC, 10wt%PVdF^{NMP}	155 (1^{st}, 0.1 C), 210 (10^{th}, 0.1 C) with VC 129 (1^{st}, 0.1 C), 80 (20^{th}, 0.1 C) without VC	139	90 % (500, 1 C) /
Sol-gel: PS, PF, HCl, $NaNO_3$, $Mn(NO_3)_2$, $Si(OC_2H_5)_4$ (120 °C, 24 h + 700 °C, 12 h, Ar) **Na_2MnSiO_4**/19.9wt%C,40-50 nm thickness, [S11]	2. 5 V	1 M $NaPF_6$ / PC, 10wt%PVdF^{NMP}	205 (0.1 C), 113 (0.5 C), 88 (2 C), 76 (5 C)	139	76 % (345, 2 C)
Co-precipitation: $CoCl_2$, $Si(OC_2H_5)_4$, HNO_3, NaOH, $C_2H_6O_2$ (700 °C, 8 h, N_2) **Na_2CoSiO_4**/C, 300-500 nm, [84]	3.3 V	0.5 M $NaClO_4$ / PC, 10wt%PVdF^{NMP}	121 (0.05 C)	100	86 % (25, 0.05 C)
Solid-state: Na_2SiO_3, $CoCO_3$ (400 rpm, 30 min + 800 °C, 8 h, N_2) **Na_2CoSiO_4,** 0.5-20 µm [84]	3.3 V		107 (0.05 C)		59 % (25, 0.05 C)
Solvothermal: CH_3COONa, $(CH_3CO0)_2Co·4H_2O$, $C_2H_6O_2$, $Si(OC_2H_5)_4$ (200 °C, 24 h + 800 °C, 12 h, Ar_2) + 5wt%MWCNTs (800 °C, 12 h, Ar_2) **Na_2CoSiO_4**/Na_2SiO_3/C, 300 nm [S12]	3.3 V	1 M $NaClO_4$ / EC+DEC, 10wt%PVdF	125 (0.05 C), 87 (1 C), 71 (2 C)$^{\#}$	136	78 % (50, 0.05 C)$^{\#}$

$C_{12}H_{22}O_{11}$- sucrose; PVdF^{NMP}- polyvinylidene fluoride as binder and N-methyl-2-pyrrolidone as solvent; $^{◆}$- the applied current and the resulting capacity were calculated from weight of the pristine $LiFePO_4$ electrode; PVP- polyvinylpyrrolidone; $C_6H_8O_7$- citric acid; $^{\nabla}$- the applied current densities and the specific capacity values were calculated based on the mass of $NaFePO_4$; $C_8H_{18}O_5$- tetraethylene glycol; PTFE^{H2O}- polytetrafluoroethylene as binder and water as solvent; CTAB- hexadecyl(trimethyl)ammonium bromide as cationic surfactant; CC- carbon cloth; $C_{15}H_{21}O_6V$- vanadium(III)acetylacetonate; $C_6H_{12}O_6$- glucose; NFP-NPs -$Na_2FeP_2O_7$ nanoparticles embedded in carbon; A-NFP-NPs- NFP-NPs covered by an unidentified substance; M-NFP-NPs- milled NFP-NPs; PCC- porous carbon cloth; $^{□}$- the active material was coated with graphite but only the mass of as-prepared material was used for calculation of specific capacities; $^{□}$- it was emphasized that the capacity was based on the mass of active material; $C_6H_8O_6$- ascorbic acid; $C_{10}H_6O_8$- pyromellitic acid; $^{▼}$- it was emphasized that the capacity was based on the net mass of Na_2MnPO_4F; $C_2H_6O_2$- ethylene glycol; CMC^{NMP}- carboxymethylcellulose sodium as binder with N-methyl-2-pyrrolidone as solvent; $C_6H_{10}O_4$- diethyl oxalate; GO- graphene oxide; C_3H_8O- propanol; $^{•}$- it was emphasized that the capacity was calculated on the net weight of Na_2MnSiO_4; VC- vinylene carbonate; PS- polystyrene and PF- phenol/formaldehyde were used as template and carbon source; MWCNTs- multi-walled carbon nanotubes; $^{\#}$- it was emphasized that the capacity was based on the mass of active material Na_2CoSiO_4.

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The comparative electrochemical properties of the full-cells containing $Na_4M_3(PO_4)_2P_2O_7$ cathode are shown in Figure S3.

Table S3. Comparison of electrochemical performance of full cells containing $Na_4M_3(PO_4)_2P_2O_7$ cathode

Full cell Anode Electrolyte Cathode	**~ U / V**	**~ Charge capacity^{cycle} / mAh g^{-1}**	**~ Discharge capacity / mAh g^{-1}**	**~ Discharge capacity Retention / % (No. cycles, C-rate)**	**~ Cathode Coulombic /% Effic as Q_c/Q_d (Cell eff. as Q_d/Q_c)**	**~ E / Wh kg^{-1}**
NCPP cathode						
HC 1 M $NaPF_6$ / EC+DEC NCPP-C [68, 110]	4 (0.2 C)	140^{1} , 98^{2} (0.2 C)	93 (0.2 C) $^{\Delta,*}$ 80 (1 C), 65 (5 C), 55 (10 C), 30 (20 C)	93 (50, 0.2 C) 83 (100, 0.2 C)	150 (66)	/
$Li_4Ti_5O_{12}$ 1 M $LiPF_6$ / EC+EMC+DMC NCPP-C [109]	3 (0.2 C)	120^{1}, 98^{2} (0.05 C)	80 (0.05 C) $^{\Delta,*}$ 80 (0.2 C), 65 (2 C) , 50 (5 C)	89 (50, 0.2 C)	150 (66)	/
$NaTi_2(PO_4)_3$-MWCNT 1 M $NaPF_6$ / EC+DMC NCPP-CNT [67]	2.25 (0.2 C)	100^{1}, 91^{2} (0.2 C)	78 (0.2 C) $^{\Diamond}$	50 (40, 0.2 C)	128 (78)	/
HC 1 M $NaPF_6$ / EC+DEC+5%FEC $Al_{0.15}$-NCPP-C [111]	4.36 (0.5 C)	112^{1}, 98^{2} (0.5 C)	88 (0.5 C) $^{\Delta,\blacklozenge}$ 83 (1 C), 70 (30 C)	95 (200, 1 C)	127 (69)	/
NFPP cathode						
$NaTi_2(PO_4)_3$ 17 M $NaClO_{4aq}$ NFPP [115]	0.7-1 (0.2 C)	52^{1}, $45^{2,\blacktriangle}$ (1 C)	83 (1 C) $^{\Diamond,\blacklozenge}$, 46 (0.2 C) $^{\blacktriangle}$, 44 (1 C) $^{\blacktriangle}$, 39 (5 C) $^{\blacktriangle}$, 34 (10 C) $^{\blacktriangle}$	75 (200, 1 C) 70 (500, 5 C)	118 (84)	$36^{\blacktriangle}$
HC 1 M $NaClO_4$ / PC+2%FEC NFPP@AC/rGO$^{\circ}$, [107]	2.4-2.5 (0.2 C)	$110^{1\text{-}3,\circ}$ (0.2 C)	102 (0.2 C) $^{\Diamond,\blacklozenge}$, 95 (0.5 C), 82 (1 C), 84 (1.5 C), 50 (5 C)	94 (132, 1.5 C)	108 (93)	$250^{\blacklozenge}$
HC 1 M $NaClO_4$ / PC+5%FEC NFPP@NFP@C-CC$^{\circ}$, [119]	2.2-3 (50 mA g^{-1} or 0.39 C)	$125^{1\text{-}20,\circ}$ (50 mA g^{-1} or 0.39 C)	114 (50 mA g^{-1} or 0.39 C) $^{\Diamond}$ 78 (200 mA g^{-1} or 1.55 C) 25 (500 mA g^{-1} or 3.88 C)	97 (110, 200 mA g^{-1} or 1.55 C)	110 (91)	/
(PPy)-coated Fe_3O_4 1 M $NaClO_4$ / EC+PC+5%FEC NFPP-E$^{\circ}$, [99]	0.1-4 (100 mA g^{-1} or 0.83 C)	$235^{1\text{-}3,\circ}$ (100 mA g^{-1} or 0.83 C)	225 (100 mA g^{-1} or 0.83 C) $^{\Diamond,\blacktriangledown,\heartsuit}$	76.9 (500, 100 mA g^{-1} or 0.83 C)	107 (93)	/
HC 1 M $NaClO_4$ / EC+PC+5%FEC	2-3.5 (100 mA g^{-1}	178^{1}, 160^{10} (100 mA g^{-1}	170^{1} (100 mA g^{-1} or 0.83 C) $^{\Diamond,\blacktriangledown}$	< 50 (120, 100 mA g^{-1}	105 (95)	/

NFPP-E°, [99]	or 0.83 C)	or 0.83 C)		or 0.83 C)		
CHC 1 M $NaClO_4$ / EC+DEC+5%FEC NFPP@MCNTs [64]	3.04 (0.1 C)	88^{1}, 70^{2-3} (0.1 C)	69 (0.1 C) ◊,▲ 60 (0.5 C), 52 (1 C), 35 (5 C)	85 (100, 1 C)	170 (59)	210▲
NMPP cathode						
HC 1 M $NaClO_4$ / EC+PC+10%FEC NM_2CPP/C-5wt%CNT°, [108]	3.85 (0.1 C)	121^{1}, $101^{2,}$ ° (0.1 C)	89 (0.1 C) ♠, ▲, 82 (0.5 C), 75 (1 C), 57 (5 C)	75 (100, 0.1 C)	131 (77)	249.9 ▲

E- energy density, Q_d - dicharge capacity, Q_c- charge capacity, HC- hard carbon, $^{\Delta}$1 C = 170 mA g^{-1}; $^{◊}$1 C = 129 mA g^{-1} ; $^{♠}$1 C = 128.7 mA g^{-1} ; * -the used mass is not indicated; ♦- calculated per cathode mass,▲ calculated per mass of both anode and cathode; ▼ calculated per anode mass; ° anode was previously cycled in a sodium half-cell to reduce the irreversible capacity loss; /- the specific energy density is not indicated in the paper, but it can estimated by multiplying the average voltage with the specific capacity;♥1C = 120 mA g^{-1}.