Electronic Supplementary Information

A novel high-entropy layered cathode with robust structure and fast dynamics at high rate for Na-ion batteries

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Table S1. Stoichiometry from inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) results of NMLTMACZ.

Elements	W (%)	mol ratio
Na	16.33	0.66(8)
Mn	34.73	0.59(3)
Li	0.83	0.11(3)
Ti	4.93	0.09(7)
Mg	1.19	0.04(7)
Al	1.47	0.05(1)
Cu	3.58	0.05(3)
Zn	3.25	0.04(7)

Table S2. Refined crystallographic parameters of NMLTMACZ with the Rietveld method. S.G. *P63/mmc*, $a = b = 2.88(6)$ Å, $c = 11.16(0)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, R_{wp}=5.45%, $\chi^2 = 0.8360$.

Sample	Atom	Site	x	y	z	Occupancy
NMLTMACZ	Mn	2a	0	0	0	0.589(7)
	Li	2a	0	0	0	0.112(3)
	Ti	2a	0	0	0	0.098(2)
	Mg	2a	0	0	0	0.047(8)
	Al	2a	0	0	0	0.051(3)
	Cu	2a	0	0	0	0.053(2)
	Zn	2a	0	0	0	0.047(6)
	Na1	2b	0	0	0.25	0.328(4)
	Na2	2d	0.3333	0.6667	0.75	0.332(6)
	O	4f	0.3333	0.6667	0.0872	1
P63/mmc : $a = b = 2.8859$ (3) Å c =11.1596(4) Å V= 80.49(2) Å^3						
R_p = 4.24% R_{wp} =5.45% GOF(χ^2) = 0.8360						

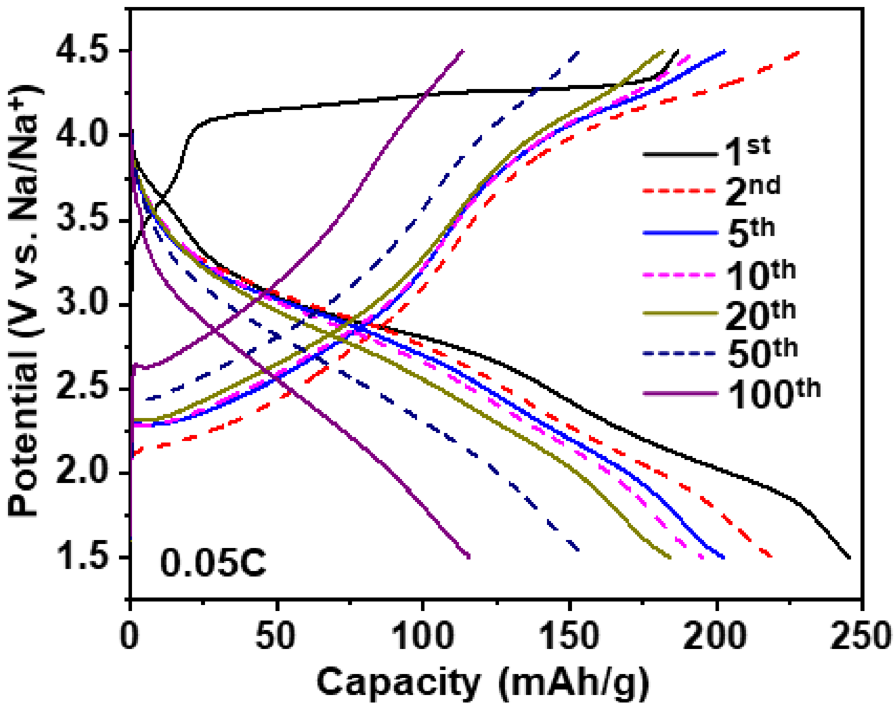

Fig. S1. Typical galvanostatic charge/discharge profiles (1st, 2nd, 5th, 10th, 20th, 50th, 100th) of the NMLTMACZ electrode at 0.05C in the voltage range of 1.5-4.5 V vs. Na^+/Na.

Table S3. Comparison of the electrochemical properties of Na layered cathode materials with O redox reaction.

Electrode materials	**Voltage range (V)**	**Initial reversible capacity (mAh/g)**	**Capacity at high-rate (mAh/g)**	**Capacity retention After cycling**	**Reference**
P2-$Na_{0.72}Li_{0.24}Mn_{0.76}O_2$	1.5-4.5	270 (0.05C)	/	55.5% (0.1C, 30 cycles)	S1
P2-$Na_{0.66}Li_{0.18}Fe_{0.12}Mn_{0.7}O_2$	1.5-4.5	214 (0.05C)	120 (1C)	81.7% (0.1C, 82 cycles)	S2
P2-$Na_{0.6}Li_{0.11}Fe_{0.27}Mn_{0.62}O_2$	1.5-4.5	207.3 (0.1C)	126.2 (1C)	50.3% (0.1C, 80 cycles)	S3
P2-$Na_{0.6}Li_{0.11}Fe_{0.26}Mn_{0.62}Y_{0.01}O_2$	1.5-4.5	215.2 (0.1C)	125.6 (2C)	66.2% (0.1C, 80 cycles)	S4
P2-$Na_{2/3}[Zn_{0.3}Mn_{0.7}]O_2$	1.5-4.6	190 (0.1C)	60 (2C)	80% (26 mA/g , 200 cycles)	S5
P2-$Na_{4/7}[Mn_{6/7}(\square_{Mn})_{1/7}]O_2$	1.5-4.4	220 (0.1C)	/	75% (0.1C , 45 cycles, 2.3-4.2 V)	S6
P2-$Na_{0.6}Mg_{0.3}Mn_{0.7}O_2$	1.5-4.4	210 (0.05C)	52 (2C)	50% (0.05C, 50 cycles)	S7
P3-$Na_{2/3}Mg_{1/3}Mn_{2/3}O_2$.	1.6-4.4	222 (0.05C)	75 (2C)	76.5% (0.1C, 30 cycles)	S8
P2-$Na_{0.67}Mg_{0.2}Mn_{0.8}O_2$	1.8-3.8	158 (0.1C)	107 (5C)	96% (0.1C, 25 cycles)	S9
P2-$Na_{0.7}Mn_{0.6}Ni_{0.2}Mg_{0.2}O_2$	1.5-4.2	130 (0.2C)	72 (2C, 2.5-4.2 V)	79% (1C, 1000 cycles)	S10
P2-$Na_{2/3}[Fe_{1/3}Mg_{1/12}Mn_{7/12}]O_2$	1.5-4.5	253 (0.1C)	115.4 (2C)	50.8% (0.1C, 100 cycles)	S11
P2-$Na_{0.773}Mg_{0.03}Li_{0.25}Mn_{0.75}O_2$	2.0-4.5	192 (15 mA/g)	119 (600 mA/g)	59.7% (20 mA/g, 100 cycles, 2.6-4.5 V)	S12
P2-$Na_{0.67}Mg_{0.1}Zn_{0.1}Mn_{0.8}O_2$	1.5-4.5	230 (0.1C)	125 (5C)	71.7% (0.1C, 50 cycles)	S13
P2-$Na_{0.6}Mg_{0.15}Mn_{0.7}Cu_{0.15}O_2$	2.0-4.5	157 (0.1C)	88.5 (2C)	95.8% (1C, 200 cycles)	S14
P2-$Na_{2/3}Mn_{0.72}Cu_{0.22}Mg_{0.06}O_2$	2.0-4.5	107.6 (0.1C)	87.4 (2C)	87.9% (1C, 100 cycles)	S15
P2-$Na_{0.75}Li_{0.2}Mg_{0.05}Al_{0.05}Mn_{0.7}O_2$	1.5-4.5	245 (0.05C)	80 (2C)	54% (0.05C, 50 cycles)	S16
P2-$Na_{0.84}Mn_{0.67}Ni_{0.3-x}Mg_{x}\square_{0.03}O_2$	1.8-4.4	153 (0.1C)	117.3 (2C)	98.3% (0.1C, 50 cycles)	S17
P2-$Na_{0.66}Li_{0.18}Mn_{0.71}Mg_{0.21}Co_{0.08}O_2$	1.5-4.5	166 (0.1C)	110.8 (1C)	82% (0.1C, 100 cycles)	S18
P2-$Na_{0.67}Mn_{0.71}Cu_{0.02}Mg_{0.02}Ni_{0.25}O_2$	1.5-4.5	152 (0.1C)	108 (2C)	86% (0.1C, 100 cycles)	S19
P2-$Na_{0.66}Mn_{0.6}Li_{0.1}Ti_{0.1}(MgAlCuZn)_{0.05}O_2$	**1.5-4.5**	**245.6 (0.05C)**	**147.2 (1C)**	**77.86% (1C, 100 cycles)**	**This work**

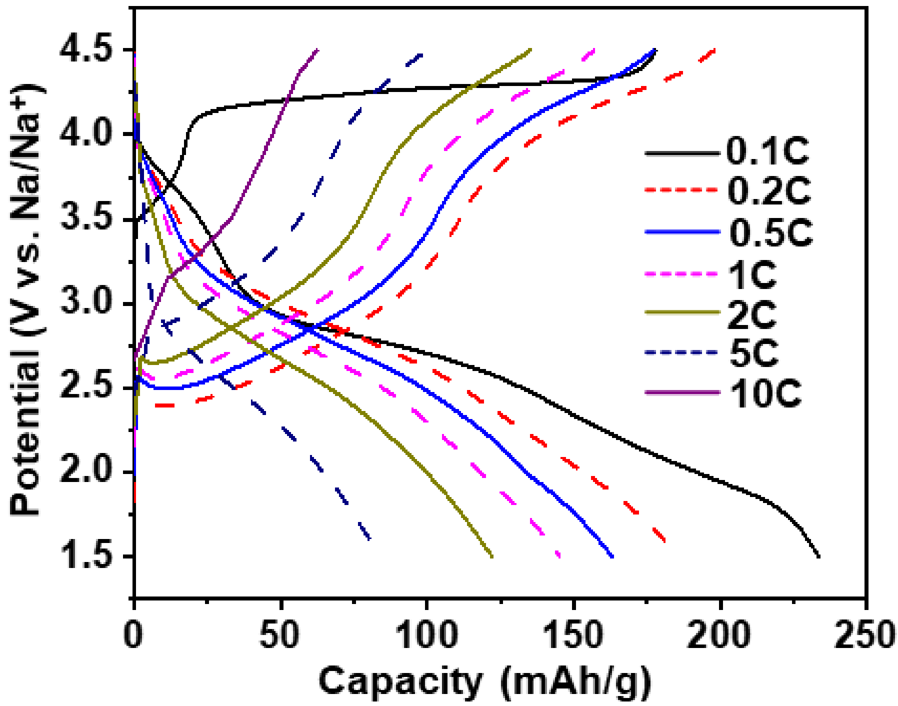

Fig. S2. The charge/discharge profiles at different current rates (0.1C-10C) of the NMLTMACZ electrode in the voltage range of 1.5-4.5 V vs. Na^+/Na.

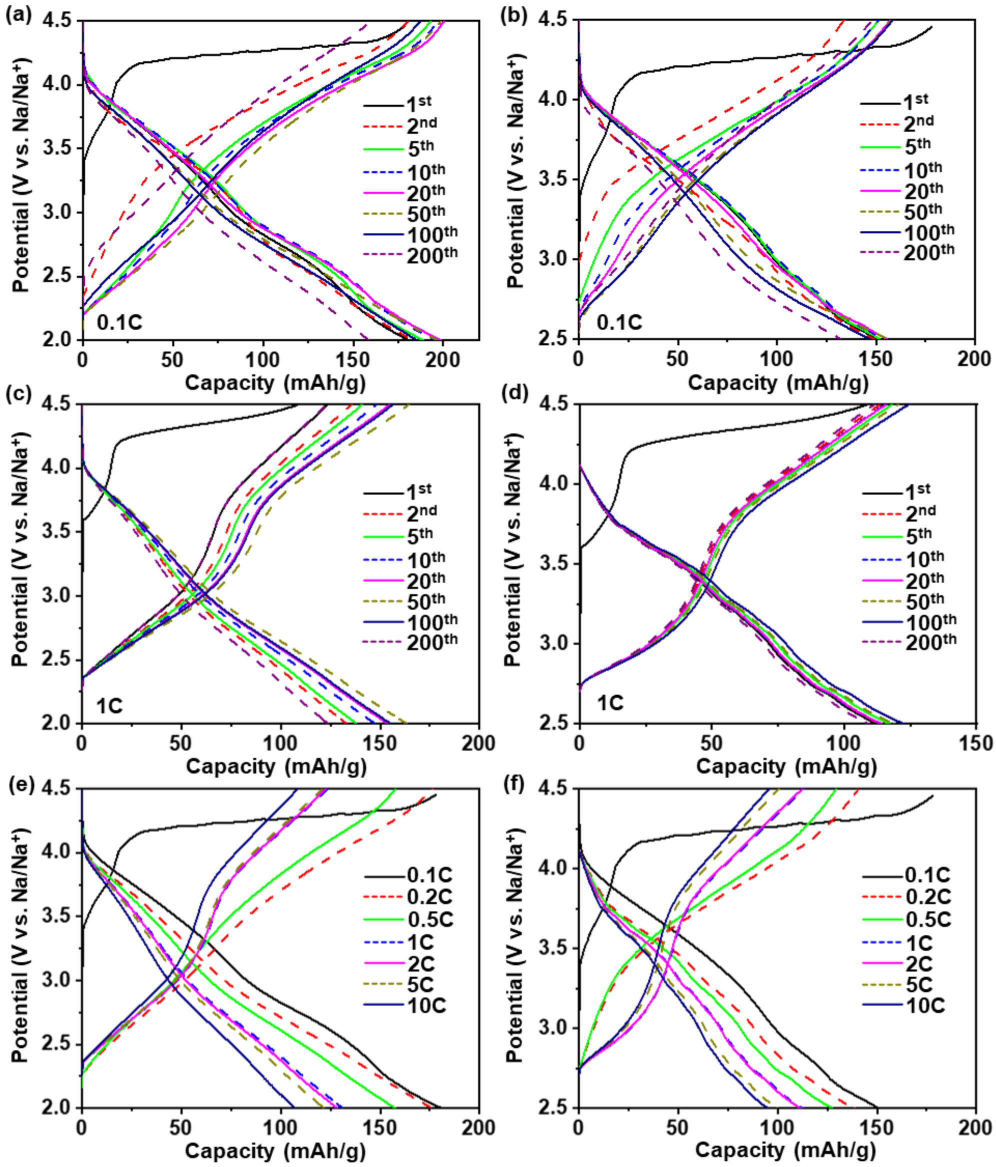

Fig. S3. Typical galvanostatic charge/discharge profiles (1^{st}, 2^{nd}, 5^{th}, 10^{th}, 20^{th}, 50^{th}, 100^{th}, 200^{th}) of the NMLTMACZ electrode within the voltage ranges of (a) 2.0-4.5 V and (b) 2.5-4.5 V vs. Na^+/Na at 0.1C. Typical galvanostatic charge/discharge profiles (1^{st}, 2^{nd}, 5^{th}, 10^{th}, 20^{th}, 50^{th}, 100^{th}, 200^{th}) of the NMLTMACZ electrode within the voltage ranges of (c) 2.0-4.5 V and (d) 2.5-4.5 V vs. Na^+/Na at 1C. The charge/discharge profiles at different current rates (0.1C-10C) of the NMLTMACZ electrode within the voltage ranges of (e) 2.0-4.5 V and (f) 2.5-4.5 V vs. Na^+/Na.

Table S4. Fitting results of the impedance parameters and the corresponding ion conductivities of the NMLTMACZ during 100 cycles at 0.1C and 1C.

Current rate	State	R_e (Ω)	R_{ct} (Ω)	σ (S/cm)	D_{Na^+} (cm^2/s)
0.1C	1st	3.24	452.86	3.13×10^{-6}	1.06×10^{-15}
	2nd	3.06	278.33	5.09×10^{-6}	1.34×10^{-14}
	5th	2.84	94.82	1.49×10^{-5}	1.42×10^{-13}
	10th	2.93	99.62	1.42×10^{-5}	6.48×10^{-14}
	20th	3.03	104.41	1.36×10^{-5}	4.64×10^{-14}
	50th	3.14	152.23	9.30×10^{-6}	2.52×10^{-14}
	100th	3.17	171.34	8.26×10^{-6}	2.27×10^{-14}
1C	1st	3.04	192.01	7.37×10^{-6}	2.12×10^{-15}
	2nd	2.69	131.33	1.08×10^{-5}	2.21×10^{-14}
	5th	3.05	115.98	1.22×10^{-5}	3.01×10^{-14}
	10th	2.96	110.02	1.29×10^{-5}	4.61×10^{-14}
	20th	2.94	105.95	1.34×10^{-5}	4.99×10^{-14}
	50th	2.58	99.96	1.42×10^{-5}	5.29×10^{-14}
	100th	2.43	59.99	2.36×10^{-5}	1.64×10^{-13}

Table S5. Binding energies (eV) and atomic percentages (%) of the main components in the Mn 2p XPS spectra of the NMLTMACZ electrode cycled at 0.1C and 1C, respectively.

0.1C						1C					
Element	State	Species	BE (eV)	%	Average oxidation state	Element	State	Species	BE (eV)	%	Average oxidation state
Mn 2p	Pristine	Mn^{3+}	641.0/652.4	37.2	3.63+	Mn 2p	Pristine	Mn^{3+}	641.1/652.6	36.9	3.63+
		Mn^{4+}	642.1/653.5	62.8				Mn^{4+}	642.1/653.7	63.1	
	1st ch	Mn^{3+}	641.0/652.7	25.7	3.74+		1st ch	Mn^{3+}	641.1/652.1	31.0	3.66+
		Mn^{4+}	642.1/653.7	74.3				Mn^{4+}	642.6/654.0	61.9	
		/	/	/				C-F/Na-F	646.3	7.1	
	1st dis	Mn^{2+}	647.4	2.7	3.21+		1st dis	/	/	/	3.33+
		Mn^{3+}	641.0/652.4	73.8				Mn^{3+}	641.0/652.6	66.8	
		Mn^{4+}	642.4/653.9	23.5				Mn^{4+}	642.3/653.9	33.2	
	2nd ch	Mn^{3+}	641.4/652.4	24.7	3.75+		2nd ch	Mn^{3+}	641.2/652.7	36.5	3.63+

Mn 2p		Mn^{4+}	642.7/654.0	75.3		Mn 2p		Mn^{4+}	642.3/653.8	63.5	
	2^{nd} dis	Mn^{2+}	648.8	2.6	3.21+		2^{nd} dis	/	/	/	3.33+
		Mn^{3+}	641.0/652.5	70.5				Mn^{3+}	641.0/652.4	66.9	
		Mn^{4+}	642.4/653.4	23.3				Mn^{4+}	643.1/653.8	33.1	
		C-F/Na-F	645.6	3.6				/	/	/	
	5^{th} ch	Mn^{2+}	638.1/650.4	4.2	3.69+		5^{th} ch	/	/	/	3.61+
		Mn^{3+}	641.1/652.6	22.1				Mn^{3+}	641.4/652.6	33.0	
		Mn^{4+}	642.2/653.9	72.5				Mn^{4+}	642.5/653.6	52.8	
		C-F/Na-F	647.0	1.2				C-F/Na-F	646.3	14.1	
	5^{th} dis	Mn^{2+}	647.8	13.5	3.17+		5^{th} dis	/	/	/	3.33+
		Mn^{3+}	641.1/652.9	56.3				Mn^{3+}	641.0/652.6	66.7	
		Mn^{4+}	642.7/654.7	30.2				Mn^{4+}	642.7/654.2	33.3	

Table S6. Binding energies (eV) and atomic percentages (%) of the main components in the O 1s XPS spectra of the NMLTMACZ electrode cycled at 0.1C and 1C, respectively.

0.1C					1C				
Element	State	Species	BE (eV)	%	Element	State	Species	BE (eV)	%
O 1s	Pristine	O^{2-}	529.7	62.6	O 1s	Pristine	O^{2-}	530.1	62.7
		$(O_2)^{n-}$	/	/			$(O_2)^{n-}$	/	/
	1st ch	O^{2-}	529.6	9.2		1st ch	O^{2-}	529.6	11.9
		$(O_2)^{n-}$	530.6	14.5			$(O_2)^{n-}$	530.6	8.8
	1st dis	O^{2-}	530.2	50.1		1st dis	O^{2-}	530.1	56.2
		$(O_2)^{n-}$	/	/			$(O_2)^{n-}$	/	/
	2nd ch	O^{2-}	529.9	12.8		2nd ch	O^{2-}	529.6	9.5
		$(O_2)^{n-}$	530.5	12.4			$(O_2)^{n-}$	530.5	8.2
	2nd dis	O^{2-}	530.1	43.0		2nd dis	O^{2-}	530.1	54.6
		$(O_2)^{n-}$	/	/			$(O_2)^{n-}$	/	/
	5th ch	O^{2-}	529.7	11.0		5th ch	O^{2-}	529.2	9.9

		$(O_2)^{n-}$	530.4	11.3			$(O_2)^{n-}$	530.6	8.6
O 1s	5th dis	O^{2-}	530.1	42.2	O 1s	5th dis	O^{2-}	530.0	55.4
		$(O_2)^{n-}$	/	/			$(O_2)^{n-}$	/	/

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