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A Quinary Layer Transition Metal Oxide of $NaNi_{1/4}Co_{1/4}Fe_{1/4}Mn_{1/8}Ti_{1/8}O_2$ as High Rate Capability and Long Cycle Life Cathode Material for Rechargeable Sodium Ion Batteries

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Electronic Supplementary Information (ESI)

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Experimental Section

Material Synthesis

$NaNi_{1/4}Co_{1/4}Fe_{1/4}$ $Mn_{1/8}Ti_{1/8}O_2$ (NCFMT) was synthesized by a conventional solid state reaction method. Stoichiometric amounts of Na_2CO_3 (99.95% Alfa Aesar), TiO_2 (99.9% Sigma-Aldrich), Fe_2O_3 (99.99% Alfa Aesar), CoO (99.995% Alfa Aesar), Mn_2O_3 (99.99% Alfa Aesar) and NiO (99.99% Sigma-Aldrich) powder were mixed by a mortar and pestle, then the mixture was pressed into a pellet. NCFMT was synthesized by sintering the pellet at 800 °C in an oxygen gas flow for 12 h. The pellet was naturally cooled to room temperature and transferred immediately into an Ar-filled glovebox.

Material Characterization

The morphology of the product was characterized by field mission scanning electron microscopy (SEM, Cambridge S-360). Powder X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer (BrukerD8 Advance, Germany) with Cu-Kα radiation (λ = 0.1540 nm) at 40 kV, 40 mA. Data were obtained over the 2θ range of 10-90° for as-prepared materials and 10-70° for electrodes with a scan rate of 1° min^{-1}. XRD refinement was conducted by using the Rietveld method using GSAS program. High resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) were carried out on a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 200 kV. X-ray absorption spectroscopy (XAS) was performed at beamline 14W of Shanghai Synchrotron Radiation Facility. Ni, Co, Fe, Mn, Ti K-edge XAS was collected in transmission mode. The XAS data was processed using Athena and Artemis software packages.[1,2]

Electrochemistry

The working electrode was prepared by spreading the slurry of 70 wt % NCFMT, 20 wt % carbon black, and 10 wt % polyvinylidenefluoride (PVDF, Sigma-Aldrich) on the aluminum foil. The electrodes were dried at 120°C for 12 h, and punched to small circular pieces with a diameter of 14 mm, the loading of the active material is about 1.8-2.1 g cm^{-2}. Electrochemical cells were assembled in an Ar-filled glovebox (MBraun, Germany). The electrolytes consisted of 1 M $NaClO_4$ (Alfa-Aesar) in a nonaqueous solution of ethylene carbonate (EC, Alfa-Aesar) and propylene carbonate (PC, Alfa-Aesar) with a volume ratio of 1:1, 5wt% fluroethylene carbonate (FEC) were added, according to the literature.[3,4] Galvanostatic charge-discharge measurements were carried out at room temperature on a Land CT 2001A battery test system by using coin cells. The charge-discharge condition for the rate experiment is that galvanostatic charge-discharge at the C-rates of 0.1C, 0.2C, 1C, 2C, 4C, 10C, 20C, 30C, 60C and 120C (1C=130mAh/g) between the potential range of 2.0-4.1V vs. Na^+/Na. The coin cell were assembled with pure sodium foil as the counter electrode, and a glass fiber (Whatman GF/F) as the separator. The current densities and capacities of electrodes were calculated on the basis of the weight of active materials.

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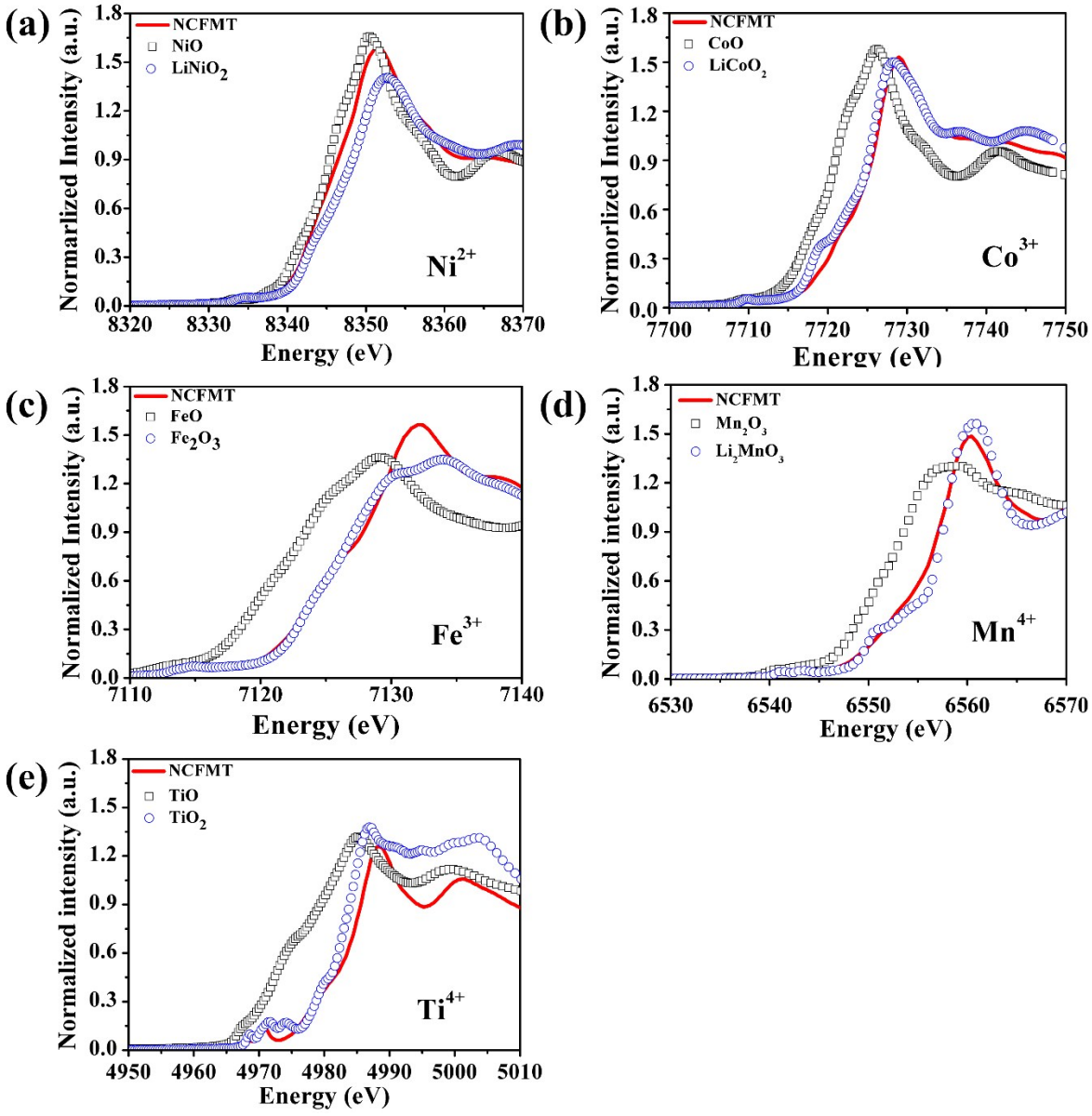

Fig. S1 XANES spectra at the (a) Ni, (b) Co, (c) Fe, (d) Mn and (e) Ti K-edges of pristine NCFMT and corresponding metal oxides references.

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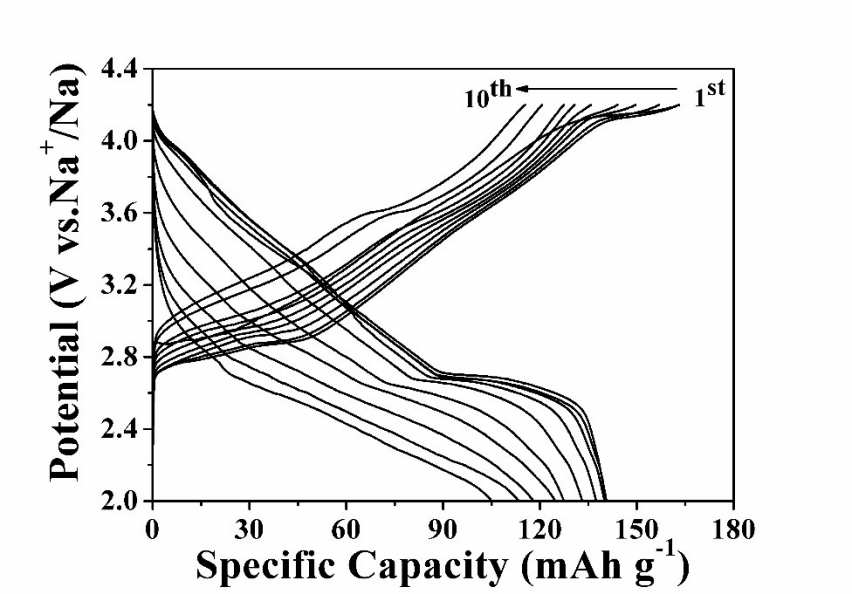

Fig. S2 The charge-discharge curves of NCFMT at a current rate of 0.1C (13 mA g^{-1}) in the potential range of 2.0 – 4.2V versus Na^+/Na.

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Table S1 Comparison of the electrochemical performances of layered cathode materials for sodium ion batteries.

	Electrode materials	Voltage range	Profile shapes	Initial capacity @0.1C (mAh/g)	Cycle retention (rate number retention)	Capacity @ high rate (>1C) (mAh/g)	Ref.
unary	$NaNiO_2$	1.25-3.75	step	125	0.1C 20 93%	No Info.	5
	$NaFeO_2$	1.5-3.6	plateau	82	No Info.	No Info.	6
	$NaTiO_2$	0.6-1.6	step	152	0.1C 60 98%	2C 78	7
	$NaCoO_2$	2.0-3.8	step	116	No Info.	240C 33	8
	α-$NaMnO_2$	2.0-3.8	step	187	0.1C 20 70%	No Info.	9
	β-$NaMnO_2$	2.0-4.2	step	No Info.	0.05C 100 80%	10C 90	10
	$NaCrO_2$	2.0-3.6	smooth	112	0.5C 50 83.3%	20C 15	11
	$NaCrO_2$/C	2.0-3.6	smooth	121	1C 300 90%	105C 100	11
binary	$NaNi_{1/2}Mn_{1/2}O_2$	2.2-3.8	step	No Info.	0.2C 50 70%	1C 105	12
	$NaFe_{1/2}Co_{1/2}O_2$	2.5-4.0	step	160	0.1C 50 85%	30C 90	13
	$NaNi_{1/2}Ti_{1/2}O_2$	2.0-4.0	smooth	102	0.2C 100 93%	10C 20	14
	$NaFe_{1/2}Mn_{1/2}O_2$	1.5-4.2	step	110	0.1C 20 89%	No Info.	15
ternary	$Na_{0.45}Ni_{0.22}Co_{0.11}Mn_{0.66}O_2$	2.0-4.3	step	148	0.1 C 100 82%	5C 45	16
	$Na_{2/3}Ni_{1/3}Mn_{2/3-x}Ti_xO_2$	2.5-4.5	step	127	0.05C 10 94%	2C 90	17
	$Na_{0.5}[Ni_{0.23}Fe_{0.13}Mn_{0.63}]O_2$	1.5-4.6	step	210	0.1C 70 75%	5C 48	18
	$NaNi_{0.25}Fe_{0.5}Mn_{0.25}O_2$	2.1-3.9	smooth	140	0.5C 50 92%	10C 89	19
	$NaNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	2.0-3.75	step	120	0.1C 50 96%	1C 80	20
	$Na[Ni_{1/3}Fe_{1/3}Mn_{1/3}]O_2$	2.0-4.0	smooth	122	0.1C 150 76%	1C 95	21
	$NaNi_{0.4}Fe_{0.2}Mn_{0.4}O_2$	2.0-4.0	smooth	131	0.05C 30 95%	10C 80	22
	$NaNi_{1/3}Co_{1/3}Fe_{1/3}O_2$	2.0-4.2	step	165	0.05C 20 90%	30C 80	23
	$NaFe_{0.2}Ni_{0.4}Ti_{0.4}O_2$	2.6-3.75	smooth	120	0.1C 30 83%	No Info.	24
	$Na_{0.67}[Mn_{0.65}Co_{0.2}Ni_{0.15}]O_2$	2.0-4.4	step	141	0.2C 50 88%	8C 55	25
quaternary	$NaNi_{0.25}Fe_{0.25}Co_{0.25}Mn_{0.25}O_2$	1.9-4.3	step	183	0.1C 20 92%	No Info.	26
	$Na[Ni_{0.4}Fe_{0.2}Mn_{0.2}Ti_{0.2}]O_2$	2.0-4.2	smooth	145	0.1C 200 84%	2C 45	27
quinary	**$NaNi_{1/4}Co_{1/4}Fe_{1/4}Mn_{1/8}Ti_{1/8}O_2$**	**2.0-4.1**	**smooth**	**128**	**4C 300 90%**	**30C 62**	**This work**

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Table S2 Structural parameters of O3-type $NaNi_{1/4}Co_{1/4}Fe_{1/4}Mn_{1/8}Ti_{1/8}O_2$ refined by Rietveld analysis

Space Group = *R*-3*m*					
a = *b* = 2.959 Å and *c* = 15.956 Å					
atom	site	*x*	*y*	*z*	occupancy
Na	3b	0.0	0.0	0.0	1.00
Ni	3a	0.0	0.0	0.5	0.25
Co	3a	0.0	0.0	0.5	0.25
Fe	3a	0.0	0.0	0.5	0.25
Mn	3a	0.0	0.0	0.5	0.125
Ti	3a	0.0	0.0	0.5	0.125
O	6c	0.0	0.0	0.2253	1.00

R_{wp} = 12.10, χ^2 = 7.475

Table S3 EDS report obtained from TEM of the as prepared material

Element	Line Type	*k* Factor	Absorption Correction	*Wt* %	*Wt* % Sigma	Atomic %
O	K series	0.843	1.00	28.39	0.56	51.62
Na	K series	0.501	1.00	15.08	0.35	19.08
Ti	K series	0.459	1.00	6.35	0.23	3.86
Mn	K series	0.490	1.00	6.79	0.26	3.60
Fe	K series	0.490	1.00	14.46	0.35	7.53
Co	K series	0.510	1.00	15.63	0.38	7.72
Ni	K series	0.504	1.00	13.30	0.36	6.59
Total:				100.00		100.00

The ratio (Ni:Co:Fe:Mn:Ti = 6.59:7.72:7.53:3.60:3.86: = 2:2:2:1:1) agrees well with the target component $NaNi_{1/4}Co_{1/4}Fe_{1/4}Mn_{1/8}Ti_{1/8}O_2$.

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