O3-type Layered Transition Metal Oxide $Na(NiCoFeTi)_{1/4}O_2$ as a High Rate and Long Cycle Life Cathode Material for Sodium Ion Batteries

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Electronic Supplementary Information (ESI)

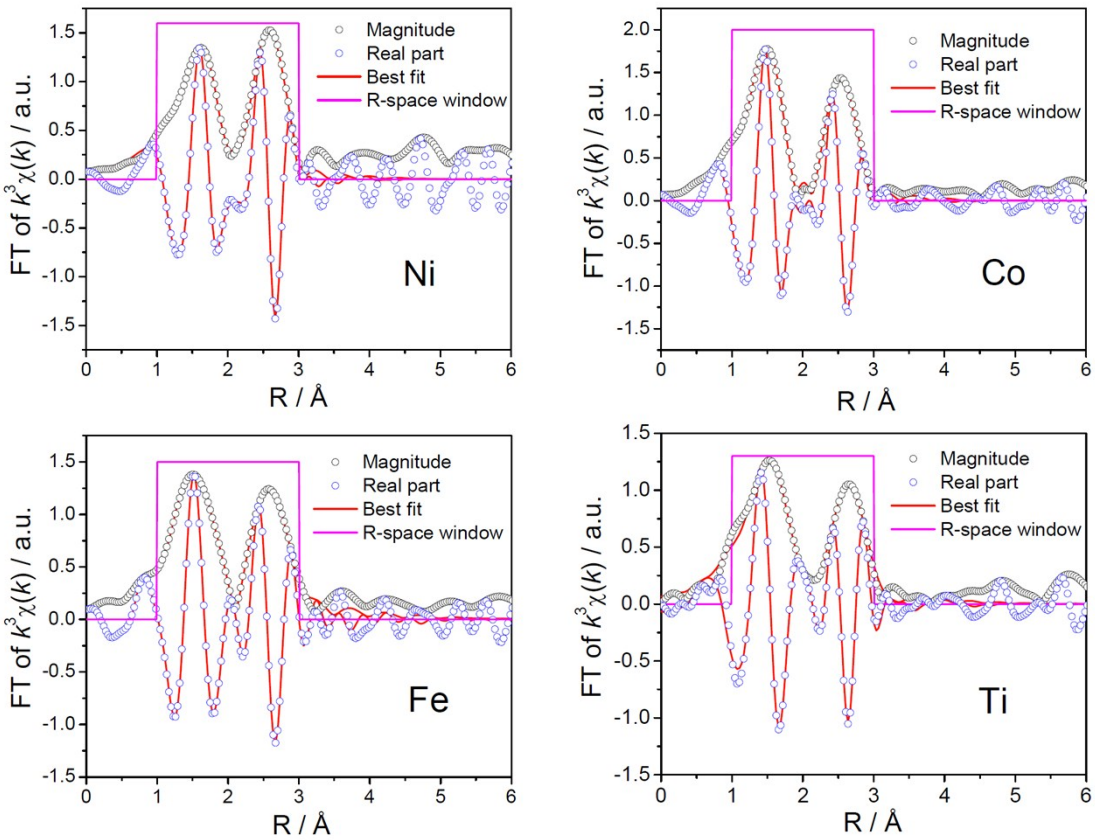

Fig. S1 Least-square fits of the calculated FT-EXAFS phase and amplitude functions (solid red lines) to the experimental EXAFS spectra (open circles) for pristine $NaNi_{1/4}Co_{1/4}Fe_{1/4}Ti_{1/4}O_2$.Phase shift was not corrected in the FT magnitude of EXAFS spectra.

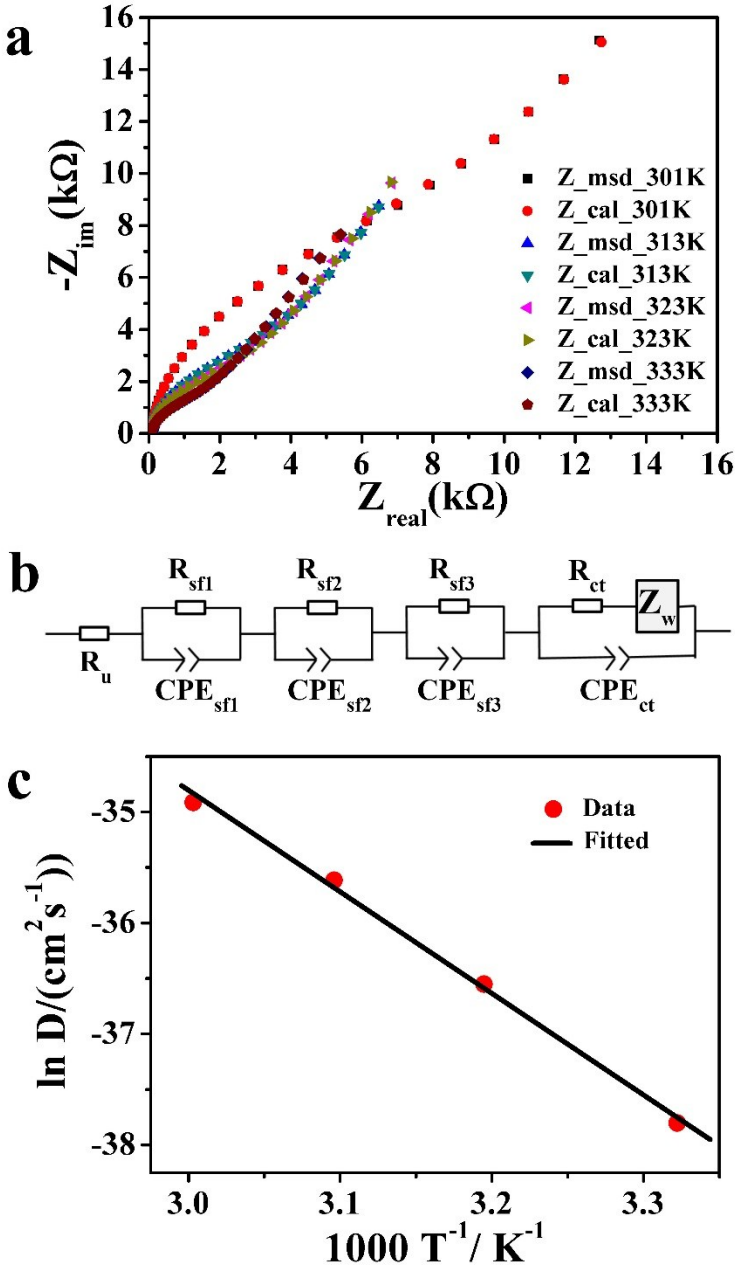

Fig. S2 (a) Nyquist plots of measured electrochemical impedance spectroscopy (EIS) results and calculated results from (b) equivalent circuit model of the $NaNi_{1/4}Co_{1/4}Fe_{1/4}Ti_{1/4}O_2$ electrode at various temperatures. (c) ln(D) as a function of inverse temperature obtain from EIS.

Fig. S2a shows the Nyquist plots of measured electrochemical impedance spectroscopy (EIS) results. The impedance curves of electrochemical cells are analysed using an equivalent circuit model (Fig. S2b) according to previous literature [R. Shanmugam and W. Lai *J. Electrochem. Soc.*, 2015, **162**, A8-A14], the fitted results (Z_msd) are well accord with the measured results (Z_cal). In Fig. S2b Z_W is so-called semi-infinite Warburg diffusion impedance. After fitting the EIS data, one can obtain parameter Y_0, and *D* can be calculated by equation S1:

$$D=\frac{R^2T^2{Y_0}^2}{n^4F^4A^2C^2} \quad (S1)$$

where,*R* is ideal gas constant, *T* is absolute temperature (K), *n* is electron transfer number, F is Faraday constant, *A* is electrode area, *C* isthe concentration of Na^+ in the lattice.

The relationship between diffusion coefficient (*D*) and *T* can be expressed by equation S2:

$$D=D_0e^{(-\frac{E_a}{kT})} \quad (S2)$$

where,*k* is Boltzmann constant, E_a is activation energy. Then,

$$ln^D=-\frac{E_a}{k}\cdot\frac{1}{K}+ln^{D_0} \quad (S3)$$

After linear fitting *D* as a function of inverse temperature, one can get the slope, then,

$E_{a=}-k\cdot slope$=0.786 eV

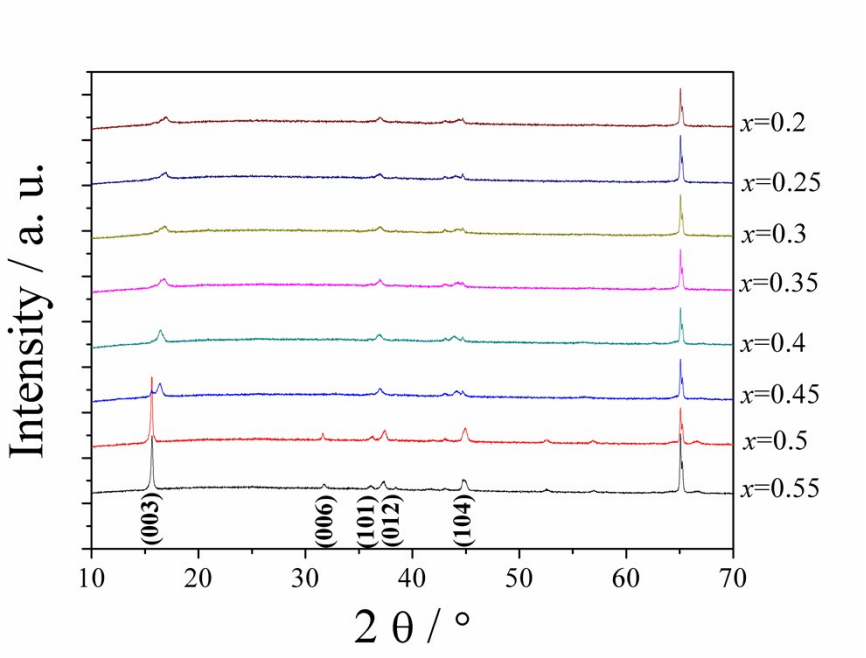

Fig. S3 XRD patterns of O3-$Na_xNi_{1/4}Co_{1/4}Fe_{1/4}Ti_{1/4}O_2$electrode at lower Na content.

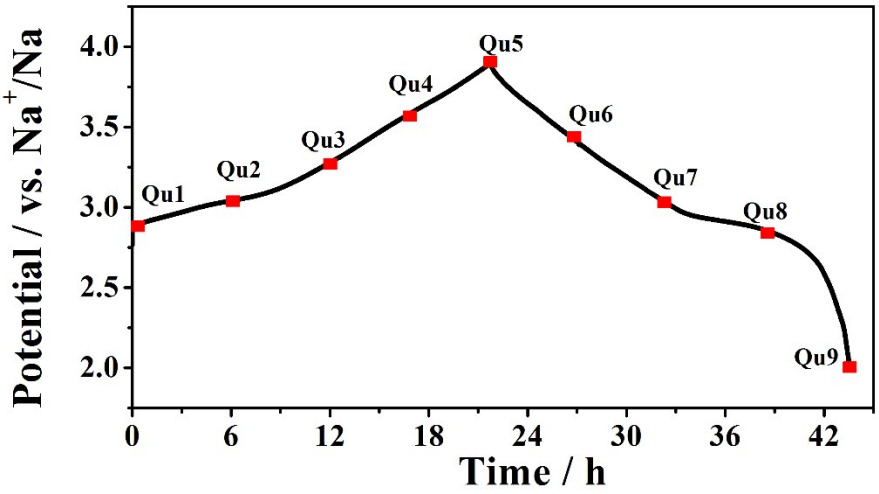

Fig. S4 Charge and discharge curve of O3-type $NaNi_{1/4}Co_{1/4}Fe_{1/4}Ti_{1/4}O_2$ electrode for *ex* XAFS, red solid squares on the curve stand for the state where XAS data were obtained.

Table S1. Structural parameters of O3-type $NaNi_{1/4}Co_{1/4}Fe_{1/4}Ti_{1/4}O_2$ refined by Rietveld analysis

$NaNi_{1/4}Co_{1/4}Fe_{1/4}Ti_{1/4}O_2$					
Space Group=*R*-3*m*					
a = *b* = 2.976 Å and *c* = 16.076 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
Ti	3a	0.0	0.0	0.5	0.25
O	6c	0.0	0.0	0.2325	1.00

R_{wp} = 17.5, χ^2 = 2.377

Table S2. Ni, Co, Fe and Ti K-edge EXAFS structure parameters of pristine NCFT.

TM in NCFT	Path	*r*/Å	σ^2 /10^{-3}Å^2	*ΔE*/eV	*R*
Ni	Ni-O	2.07(4) ± 0.007	8.57 ± 1.24	-0.89 ± 0.93	0.001
	Ni-TM	2.94(6) ± 0.006	8.11 ± 0.71		
	Ni-Na	3.32(9) ± 0.059	27.84 ± 10.17		
Co	Co-O	1.92(4) ± 0.010	3.80 ± 1.55	-3.30 ± 1.39	0.002
	Co-TM	2.89(1) ± 0.008	6.69 ± 1.06		
	Co-Na	3.26(3) ± 0.095	29.99 ± 17.77		
Fe	Fe-O	1.99(7) ± 0.027	6.75 ± 4.00	-1.58 ± 3.96	0.001
	Fe-TM	2.93(4) ± 0.019	6.93 ± 2.53		
	Fe-Na	3.16(4) ± 0.118	28.77 ± 33.21		
Ti	Ti-O	1.92(2) ± 0.029	7.67 ± 3.86	4.66 ± 4.04	0.006
	Ti-TM	2.94(5) ± 0.021	7.29 ± 2.22		
	Ti-Na	3.00(6) ± 0.091	24.29 ± 21.12		

r: bond length; σ^2: Debye-Waller factor (disorder); *ΔE*: inner shell potential shift; *R*: R-factor.