Electronic supporting information (ESI)

Exploring a high capacity O3-type cathode for sodium-ion batteries and its structural evolution during electrochemical process

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Experiments

Material synthesis

$NaFe_{0.25}Mn_{0.25}Ni_{0.25}Ti_{0.25}O_2$ (NFMNT) was prepared by a traditional solid state reaction. Stoichiometric amounts of Fe_2O_3, Mn_2O_3, NiO, TiO_2 with 5% excess Na_2CO_3, were mixed by ball milling at 300 rmp for 5 h and the resulting mixture were pressed pellets, and then pellets were heated 900 ºC for 15 h under flowing O_2 at a heating rate of 5 ºC/min. After quenching down to room temperature, the sample was stored into an Ar filled glove box.

Material characterization

All the XRD patterns were collected on a D8 Advance diffractometer (Bruker) with Cu Kα radiation (λ = 1.5418 Å). Rietveld refinement of the XRD data were performed with general structural analysis system (GSAS).[1] The morphology of powder was observed by scanning electron microscopy (SEM, Hitachi SU8010) and high-resolution transmission electron microscopy (HRTEM, FEI TECNAI F20).The distribution of each element was tested by the energy dispersive spectroscopy (EDS) mapping. The accurate elementary composition of the sample was measured by inductively coupled plasma-absorption emission spectrometry (ICP-AES). X-ray photoelectron spectroscopy (XPS) were conducted on a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer.

Electrochemical measurements

The cathode consists of NFMNT: acetylene black: polyvinylidene fluoride (PVDF) with the ratio of 60: 35: 5 onto a clean Al foil coating carbon. And then the electrode was placed in a vacuum oven at 120 ºC for 5h. Sodium half-cells were assembled in an Ar-filled glove box with a solution of 1 M $NaPF_6$ in propylene carbonate (PC, with 2% fluoroethylene carbonate (FEC) as an additive) as electrolyte. The electrochemical properties were carried out on a Land BT2000 battery tester in Na half-cells at the galvanostatic mode. The operando XRD data was collected by a "relaxed" in situ test. The cell was tested at 0.4 C for 5 min, then a relaxation process was equal to 1 h.

Tab. S1. Cell parameters and other results of NFMNT sample

Sample	NFMNT	
Phase	O3-type	
Space Group	$R\bar{3}m$	
Cell Parameters	a (Å)	2.97390(5)
	b (Å)	2.97390(5)
	c (Å)	16.22774(3)
	α (°)	90.000
	β (°)	90.000
	γ (°)	120.000
	Volume (Å^3)	124.29(2)
Agreement Factors	R_{wp} (%)	5.42
	R_p (%)	3.16
	CHI	7.062

Tab. S2. Atomic positions from XRD for each element of NFMNT sample

Position	x	y	z	*U*iso	*Occ*.
Na	0	0	0.5	0.0470(9)	0.937(5)
Fe	0	0	0	0.0298(3)	0.267(1)
Mn	0	0	0	0.0310(4)	0.240(3)
Ni	0	0	0	0.0311(5)	0.250(3)
Ti	0	0	0	0.0625(6)	0.237(0)
O	0	0	0.2694	0.0362(0)	0.972(2)

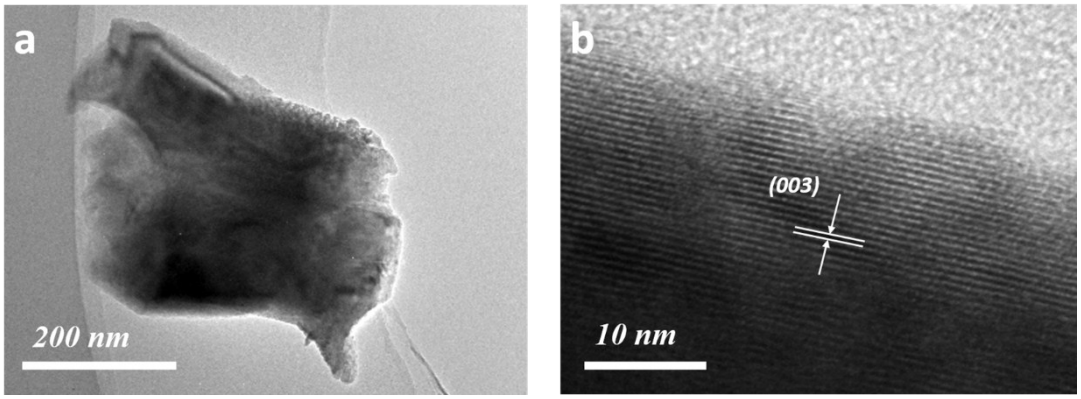

Fig. S1. (a) TEM and (b) HRTEM image of NFMNT.

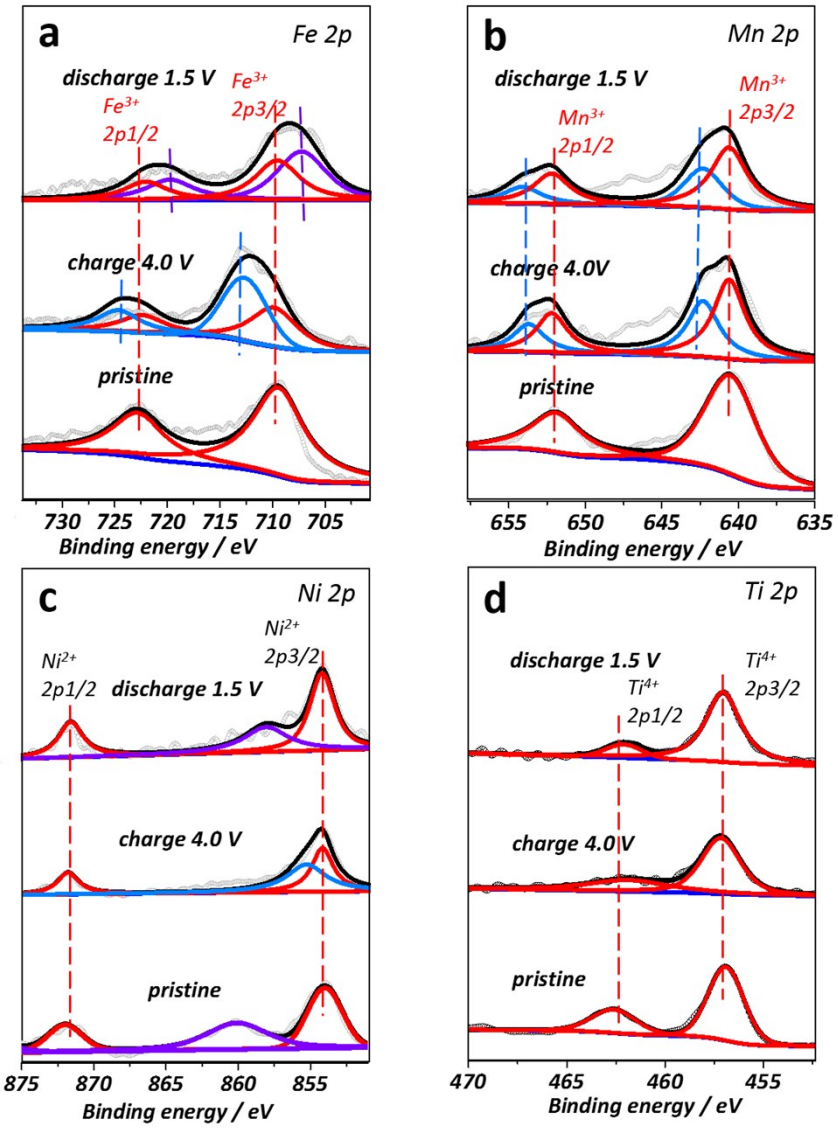

Fig S2. XPS patterns of (a) Fe 2p, (b) Mn 2p, (c) Ni 2p and (d) Ti 2p for the pristine, charged and discharged electrodes, respectively. The satellite peak of ~460 eV in Ni 2p spectra also was presented.

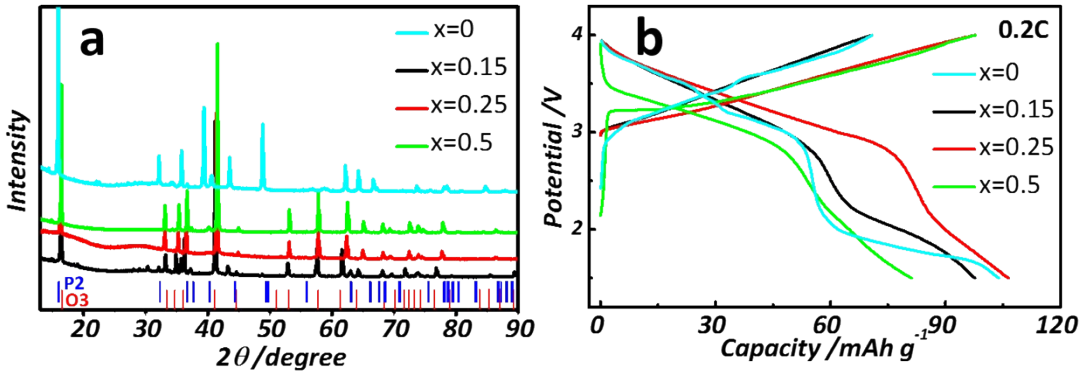

Fig S3. (a)The XRD data and (b) charge-discharge curves of $NaFe_xMn_{0.5-x}Ni_{0.25}Ti_{0.25}O_2$

References

1. Larson, A. C. and Von Dreele, R. B. GSAS: General Structure Analysis System (LANSCE, MS-H805, Los Alamos, NM, 1994).