Supplementary Information

Advanced cathode for Na-ion batteries with high rate and excellent structural stability

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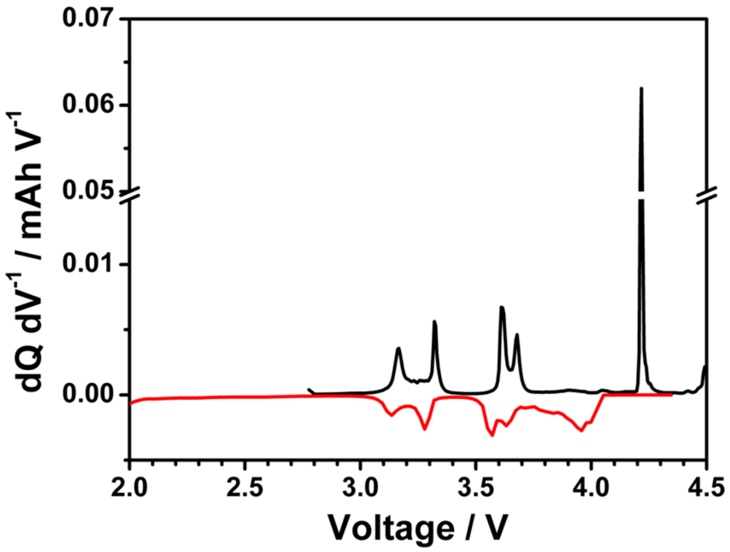
Figure S1. The dQ/dV profiles of P2 - $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ between 2.0 and 4.5V at C/100 rate.



Two major intermediate phases at 3.5 and 4.0 V upon the charge were clearly observed, which correspond to the Na content of 1/2 and 1/3, respectively. Very sharp anodic reaction was observed at 4.22 V indicating that long voltage plateau is occurring. Large polarization was detected especially for the reaction above 4.0 V corresponding to P2-O2 phase transformation.

Table S1. Rietveld refinement results (lattice parameters, Na sites, and R-factors)

Pristine $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ Space group: P 63/m m c						Charged to 3.5 V $Na_{1/2}[Ni_{1/3}Mn_{2/3}]O_2$ Space group: P 63/m m c					
Atom	Site	x	y	Z	Occ.	Atom	Site	x	y	z	Occ.
Ni	2a	0	0	0	1/3	Ni	2a	0	0	0	1/3
Mn	2a	0	0	0	2/3	Mn	2a	0	0	0	2/3
Na_f	2b	0	0	0.25	0.25	Na_f	2b	0	0	0.25	0.21
Na_e	2d	2/3	1/3	0.25	0.43	Na_e	2d	2/3	1/3	0.25	0.27
O	4f	1/3	2/3	0.08	2	O	4f	1/3	2/3	0.08	2
a = b = 2.889 Å , c = 11.149 Å						a = b = 2.874 Å , c = 11.208 Å					
R_{wp} = 0.73%, R_B = 4.42%						R_{wp} = 0.57%, R_B = 6.24%					

Charged to 4.0 V P2 - $Na_{1/3}[Ni_{1/3}Mn_{2/3}]O_2$ Space group: P 63/m m c						Charged to 4.5 V $Na_0[Ni_{1/3}Mn_{2/3}]O_2$ Space group: P 63 m c					
Atom	Site	x	y	Z	Occ.	Atom	Site	x	y	z	Occ.
Ni	2a	0	0	0	1/3						
Mn	2a	0	0	0	2/3						
Na_f	2b	0	0	0.25	0.17	Profile matching					
Na_e	2d	2/3	1/3	0.25	0.17						
O	4f	1/3	2/3	0.08	2						
a = b = 2.861 Å , c = 11.227 Å						a = b = 2.860 Å , c = 9.081 Å					
R_{wp} = 1.11%, R_B = 5.75%						R_{wp} = 0.64%, R_B = 0.29%					

Discharged to 3.75 V $Na_{1/6}[Ni_{1/3}Mn_{2/3}]O_2$
Space group: P 63/m m c

Atom	Site	x	y	Z	Occ.
Ni	2a	0	0	0	1/3
Mn	2a	0	0	0	2/3
Na_f	2b	0	0	0.25	0.10
Na_e	2d	2/3	1/3	0.25	0.11
O	4f	1/3	2/3	0.08	2

a = b = 2.863 Å , c = 11.260 Å

R_{wp} = 1.34%, R_B = 10.33%

Discharged to 3.4 V $Na_{1/3}[Ni_{1/3}Mn_{2/3}]O_2$
Space group: P 63/m m c

Atom	Site	x	y	z	Occ.
Ni	2a	0	0	0	1/3
Mn	2a	0	0	0	2/3
Na_f	2b	0	0	0.25	0.18
Na_e	2d	2/3	1/3	0.25	0.17
O	4f	1/3	2/3	0.08	2

a = b = 2.868 Å , c = 11.235 Å

R_{wp} = 0.76%, R_B = 7.98%

Discharged to 2.5 V $Na_{1/2}[Ni_{1/3}Mn_{2/3}]O_2$
Space group: P 63/m m c

Atom	Site	X	y	Z	Occ.
Ni	2a	0	0	0	1/3
Mn	2a	0	0	0	2/3
Na_f	2b	0	0	0.25	0.25
Na_e	2d	2/3	1/3	0.25	0.35
O	4f	1/3	2/3	0.08	2

a = b = 2.889 Å , c = 11.147 Å

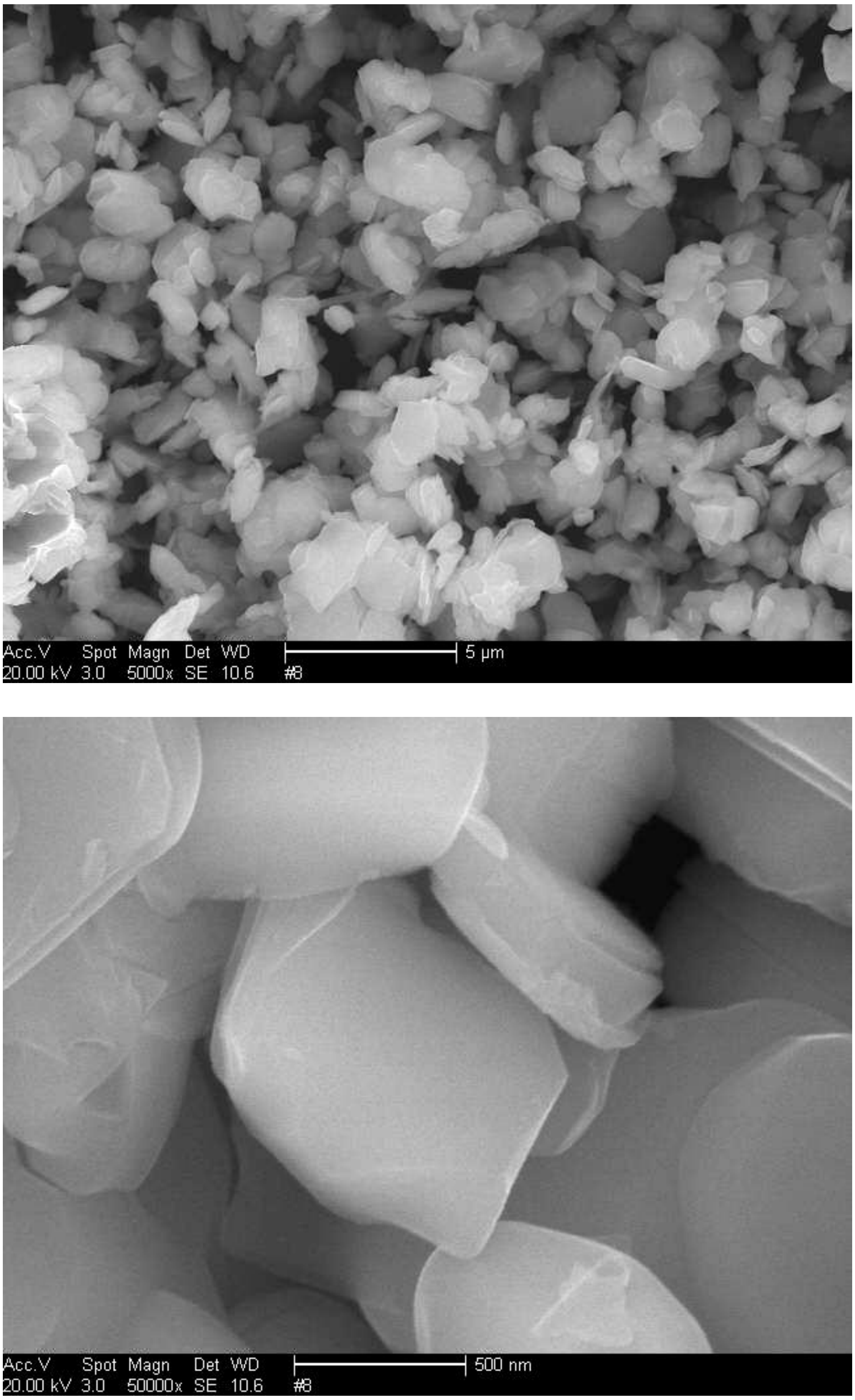
R_{wp} = 1.14%, R_B = 6.69%

Equation S1. GITT calculation

$$\tilde{D}_{Na} = \frac{4}{\pi}\left(I_0 \frac{V_m}{z_A FS}\right)^2 \left(\frac{dE/dx}{dE/dt^{1/2}}\right)^2 \qquad (1)$$

where I_0 is the applied current (1.7 x 10^{-5} A), V_m is the molar volume (21.12 cm^3 mol^{-1}), z_A is the charge number of electroactive species (for a Na-ion battery, $z_A = 1$), F is the Faraday constant (96485.34 C mol^{-1}), and S is the contact area between electrode and electrolyte (0.495 cm^2). The value of $dE/dt^{1/2}$ can be obtained from a plot of the voltage versus the square root of the time during constant current pulse, and dE/dx can be measured by plotting the equilibrium electrode voltage against the electroactive material composition after each current pulse.

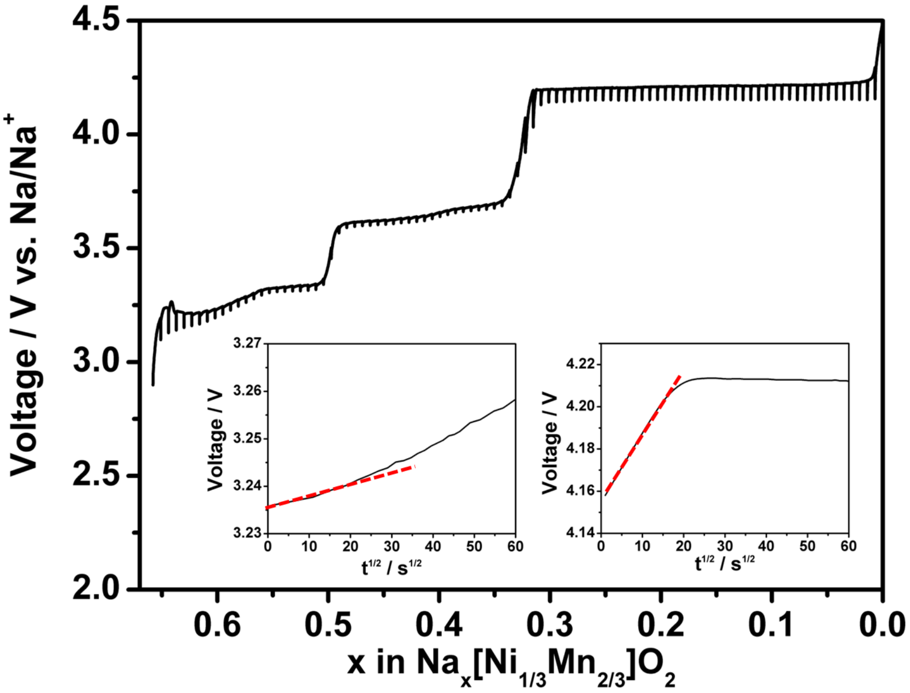
Figure S2. SEM images of as-prepared P2 - $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ powder.



The particle size is 500 nm ~ 1 μm, which is larger than typical O3 structured Li compounds.

No nanosize synthesis is required.

Figure S3. GITT profiles as a function of the Na concentration upon the 1st charge including voltage vs $t^{1/2}$ curves (insets).



To measure the chemical diffusion coefficient, the galvanostatic intermittent titration technique (GITT) was applied at a pulse of 17 μA (C/100) for 1 h and with 2 h relaxation time between each pulse. The voltage vs $t^{1/2}$ curves, which were utilized to calculate the D_{Na}, were provided as insets. Inset (left) presents the slope at the solid solution region around 3.25V and the slope at the phase transformation region at 4.2V is shown in inset (right). Note that potentiostatic intermittent titration technique was also used and consistent trend was observed.

Figure S4. Cycling profiles of P2 – $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ in the voltage ranges of (a) 2.3 ~ 4.5 V at C/100 and (b) 2.3 ~ 4.1 V at C/20.

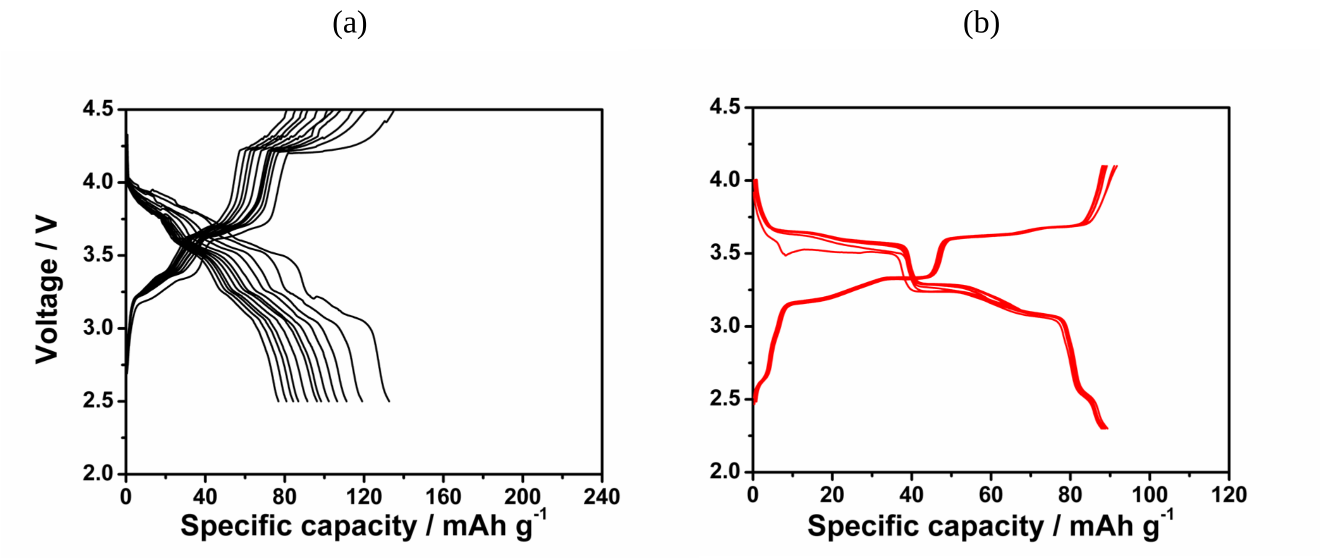


Figure S5. Rate capability between 2.3 to 4.5 V including the phase transformation at C/100, C/50, C/20, C/10, and C/5.