Supporting information

P2-type $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ as cathode materials with high-rate and long-life for sodium ion storage

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Table S1. Values of structure parameters obtained from XRD refinement of NNMO.

			x	y	z	Occupation	Site
1	Na	Na2	0.66667	0.33333	0.25000	0.340	2d
2	Na	Na1	0.00000	0.00000	0.25000	0.322	2b
3	Mn	Mn1	0.00000	0.00000	0.00000	0.665	2a
4	O	O1	0.66667	0.33333	0.08388	0.980	4f
5	Ni	Ni1	0.00000	0.00000	0.00000	0.361	2a

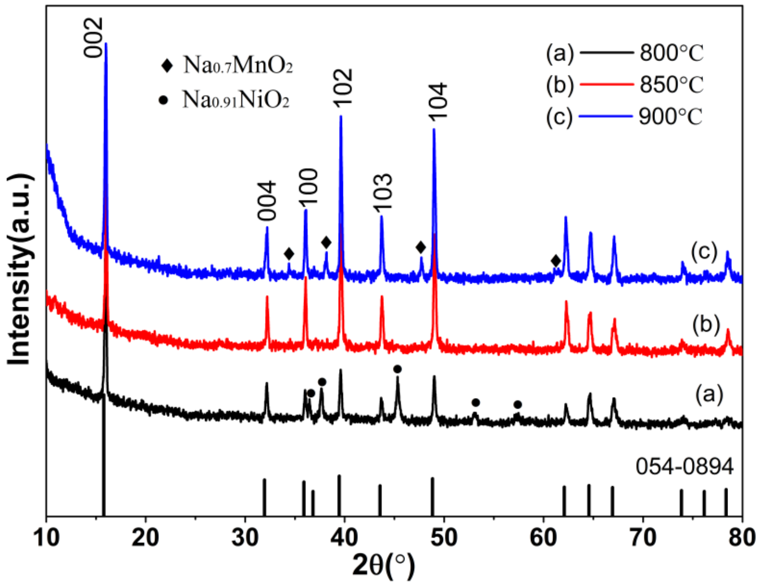

Figure S1. XRD patterns of NNMO prepared at different temperatures.

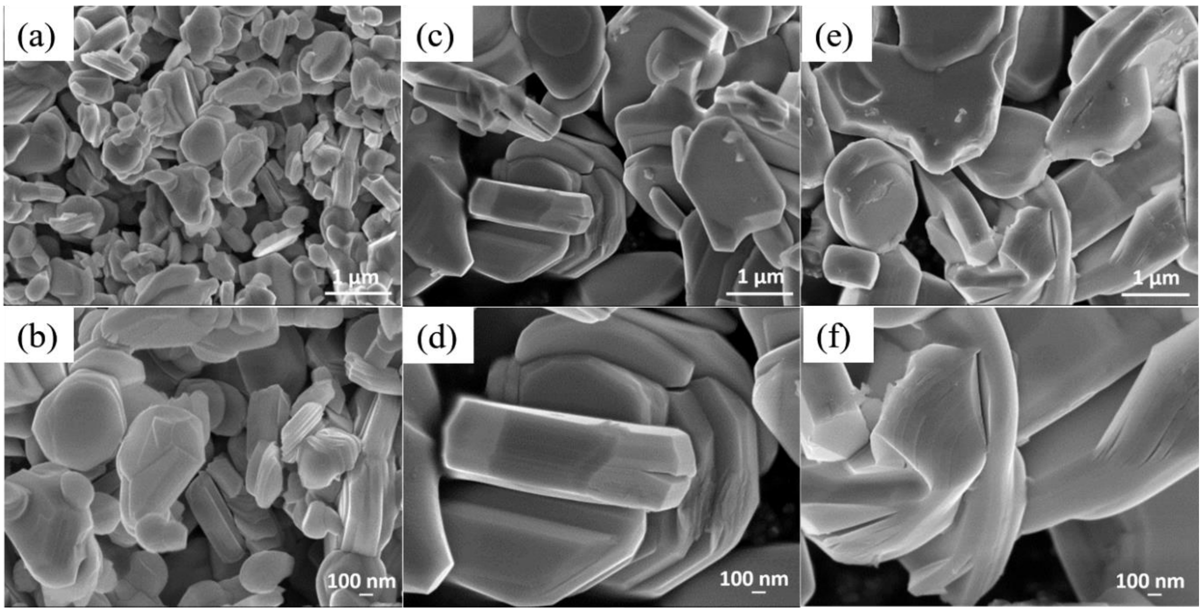

Figure S2. SEM morphologies of NNMO powders calcined at different temperatures: (a, b) 800; (c, d) 850; and (e, f) 900°C.

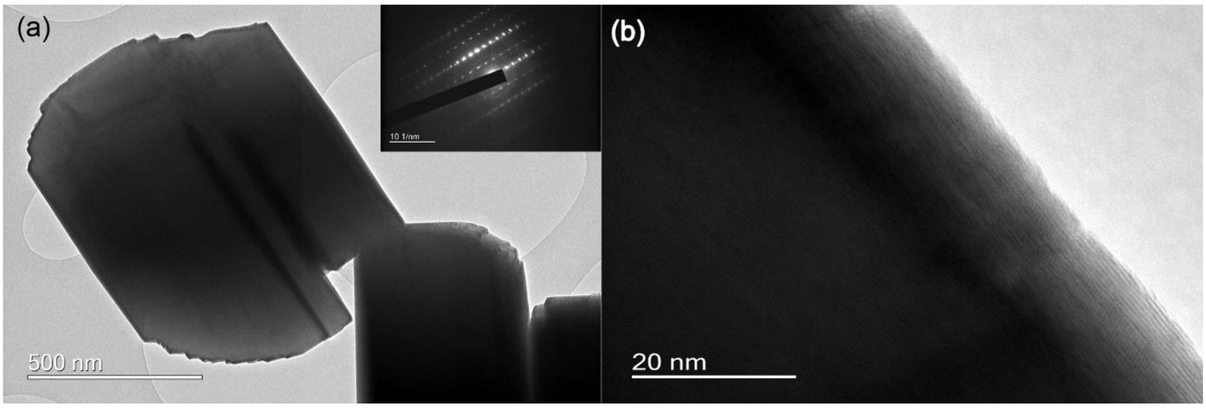

Figure S3. (a) TEM image and (b) high resolution TEM image showing lattice fringes of NNMO prepared at 850°C (inset: SADE pattern).

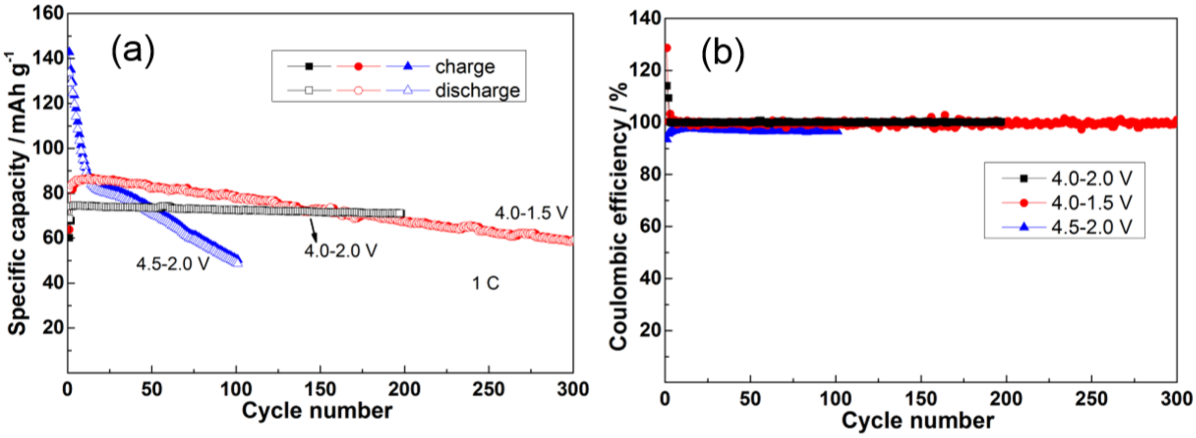

Figure S4. (a) Cycling performance and (b) corresponding CE of prepared NNMO with different cut-off voltages at 1 C.

Table S2. Comparison among electrochemical performances of selected reported P2-type $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ materials.

Ref.	Electrolyte	Voltage range (V)	Discharge capacity (mAh g^{-1})/current density (mA g^{-1})/cycle number	Rate capacity (mAh g^{-1}) /current density (mA g^{-1})
[S1]	1 M $NaPF_6$ in EC:DEC (3:7, v/v)	4.5-2.0	104.5/10/30th	-
[S2]	1 M $NaClO_4$ in PC:FEC (95:5, v/v)	4.0-2.0	80/17/200th	81/173
[S3]	1 M $NaClO_4$ in PC:FEC (98:2, v/v)	3.75-1.5	123.5/17/50th	98.9/173
[S4]	1 M $NaPF_6$ in PC	4.5-2.0	134/13/50th	~125/260
[S5]	1 M $NaPF_6$ in PC	4.5-2.3	52/8.6/100th	78.5/86.5

Our work	1 M $NaClO_4$ in EC:DEC:FEC (48.5:48.5:3, v/v/v)	4.0-2.0	89/17/100th	60.7/1730

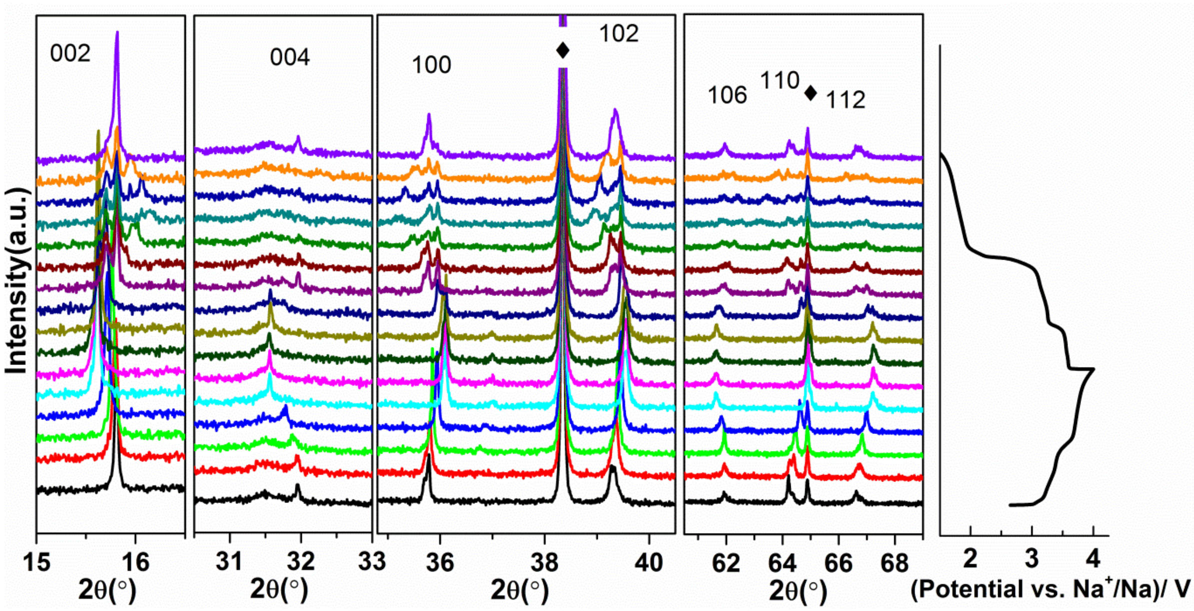

Figure S5. *In-suit* synchrotron XRD patterns of NNMO cycling between 4.0 and 1.5 V, the 2θ has been converted based on the Cu wavelength for convenience.

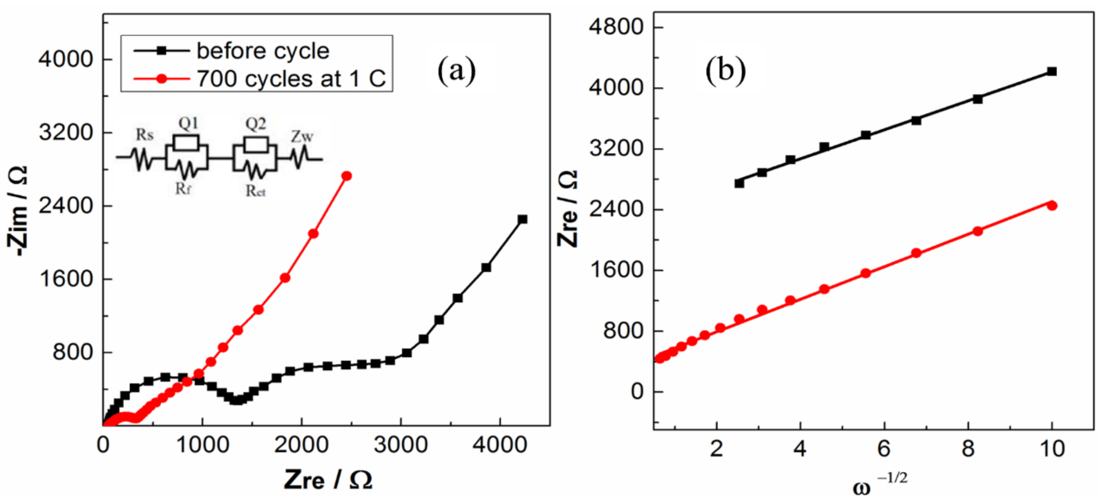

Figure S6. (a) Nyquist plots of prepared NNMO at 850℃ before and after 700 cycles at 1 C (inset: equivalent circuit); and (b) corresponding Z_{re} vs. $\omega^{-1/2}$ plots in the low frequency region.

Table S3. Values of fitted parameters obtained from EIS.

	R_s (Ω)	R_f (Ω)	R_{ct} (Ω)	D_{Na+} ($cm^2\ s^{-1}$)
Before cycle	53.32	882.9	1161	9.02×10^{-12}
After 700 cycles at 1 C	52.99	41.44	178.5	7.15×10^{-12}

Figure S6a shows the EIS Nyquist plots of prepared NNMO before and after 700 cycles at 1 C between 4.0-2.0 V with the equivalent circuit inset at the open circuit potential (OCP). The Nyquist plot consists of two semicircles at high frequency area corresponding to the film resistance (R_f) and charge transfer resistance (R_{ct}), respectively. The inclined line at low frequency region is related to the Warburg impedance (Z_w) associated with Na^+ diffusion. The values of different parameters obtained from EIS plots are shown in Table S3. The value of R_f and R_{ct} both decreased after 700 cycles at 1 C, resulting from the enhanced contact between the electrolyte and cathode material and the stabilized layers of cathode material. The low R_{ct} at the electrode/electrolyte interface is favourable for the transfer of Na^+ ions and electrons at the surface and the diffusion of liquid electrolyte. The apparent Na^+ diffusion coefficient (D_{Na+}) can be calculated by the Z_{re} vs. $\omega^{-1/2}$ plots in the low frequency region (Fig. S6b). The D_{Na+} calculated for electrode before and after 700 cycles at 1 C at OCP are 9.02×10^{-12} and 7.15×10^{-12} $cm^2\ s^{-1}$, respectively.

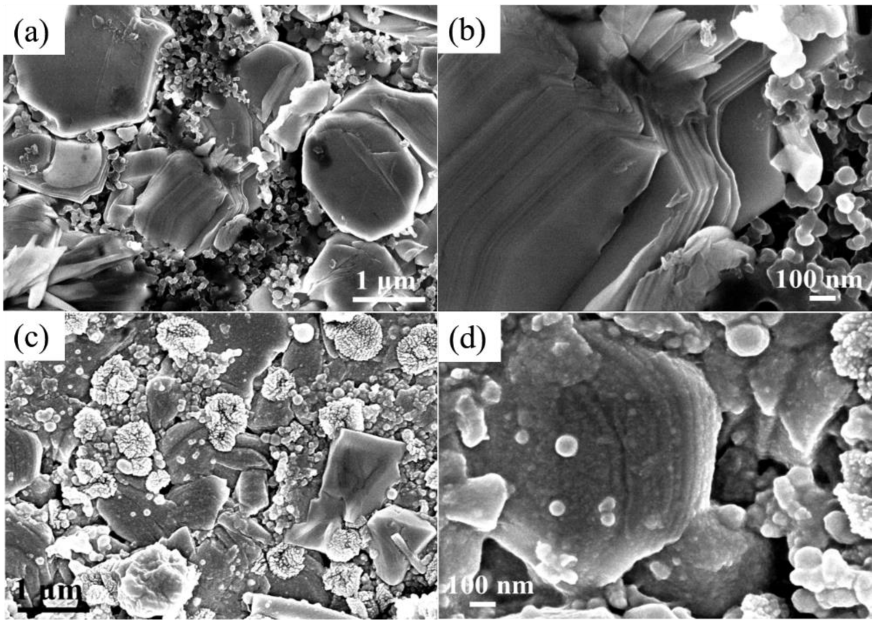

Figure S7. Electrodes before (a, b) and after (c, d) 1000 cycles at 1 C with super P and PVDF binder around.

References

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