

## Electronic Supplementary Information (ESI)

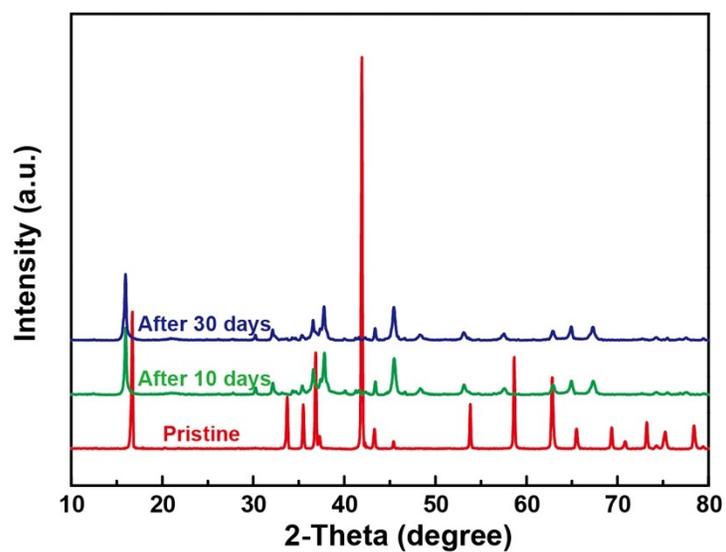
# An O3-type $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode for sodium-ion batteries with improved rate performance and cycling stability

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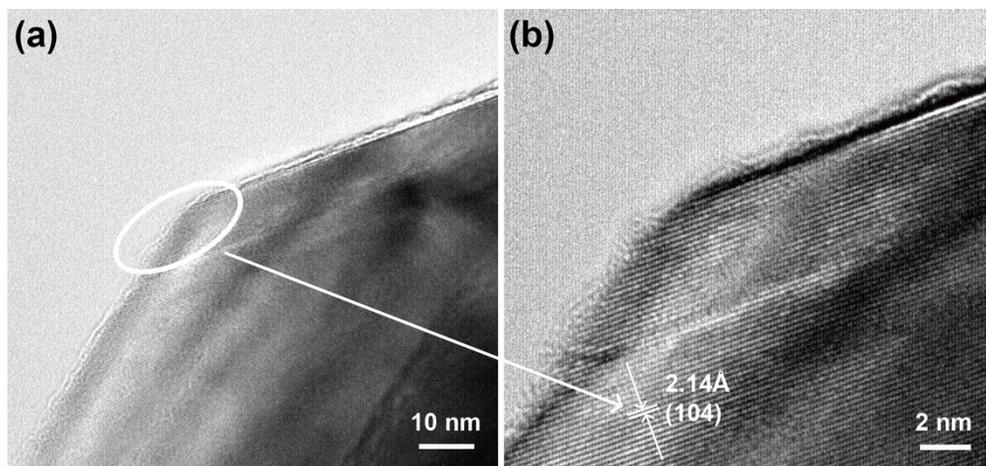
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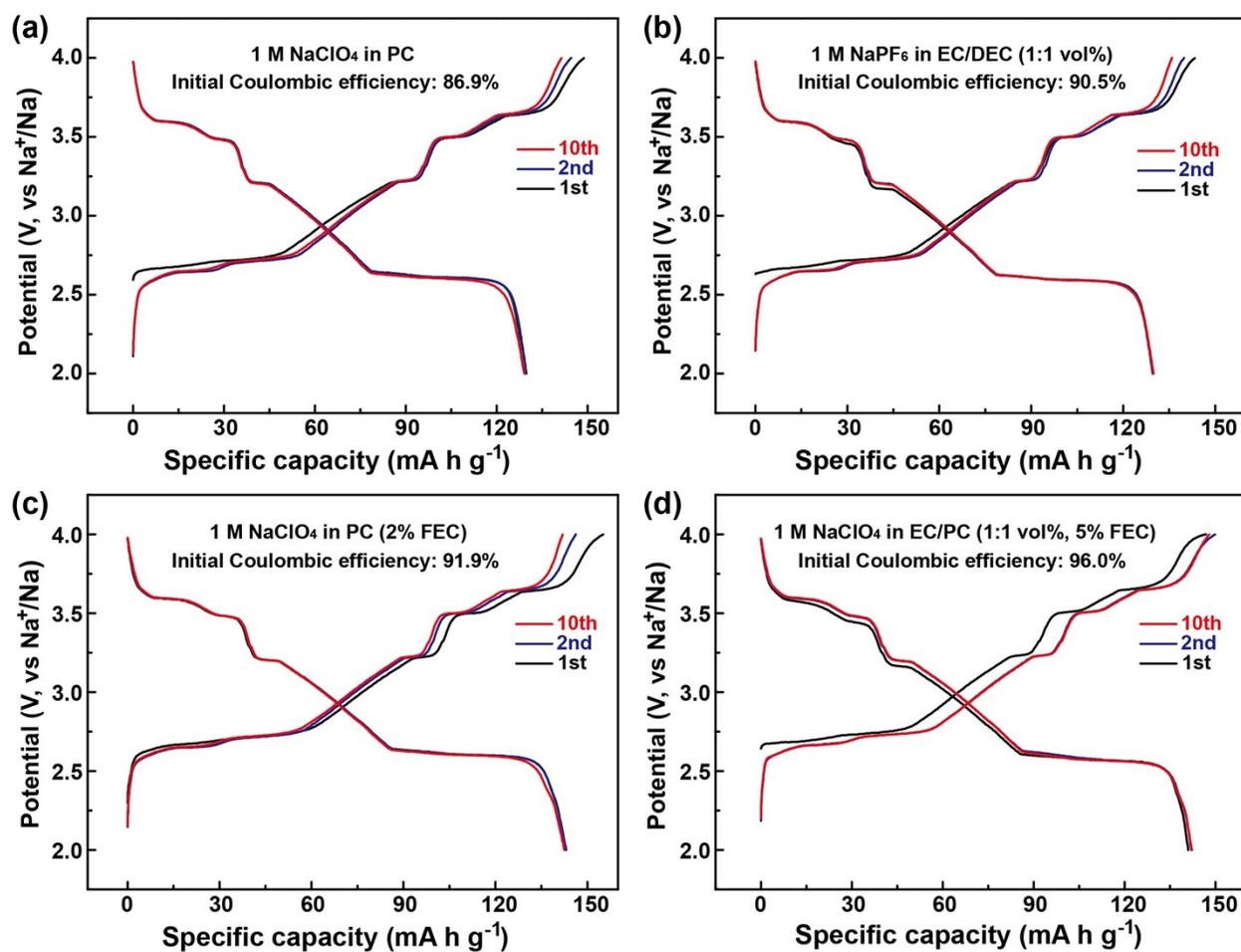
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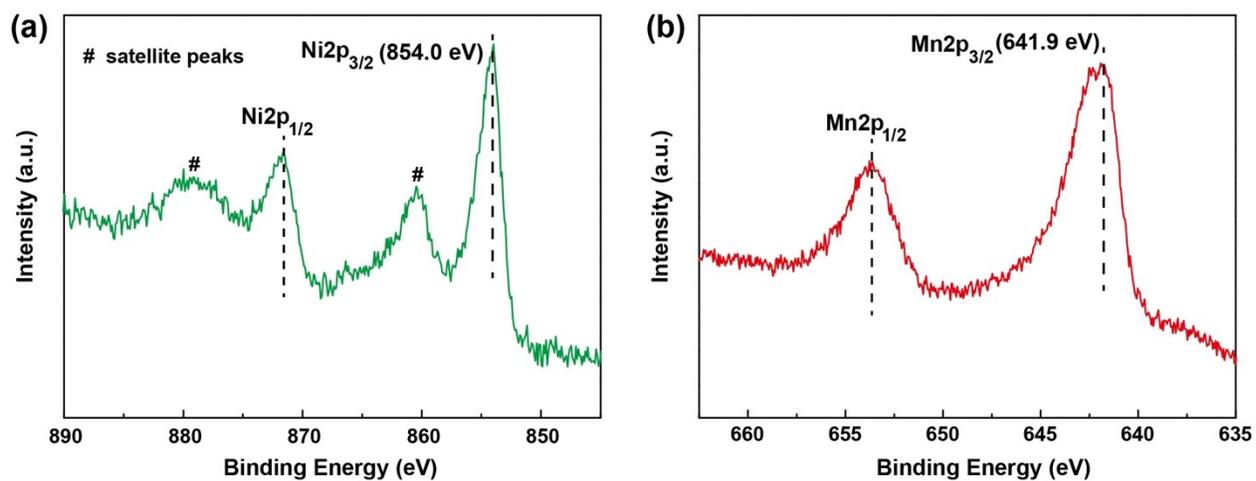
**Fig. S1** Powder X-ray diffraction pattern demonstrating structural stability of  $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  after different days on exposure to air.



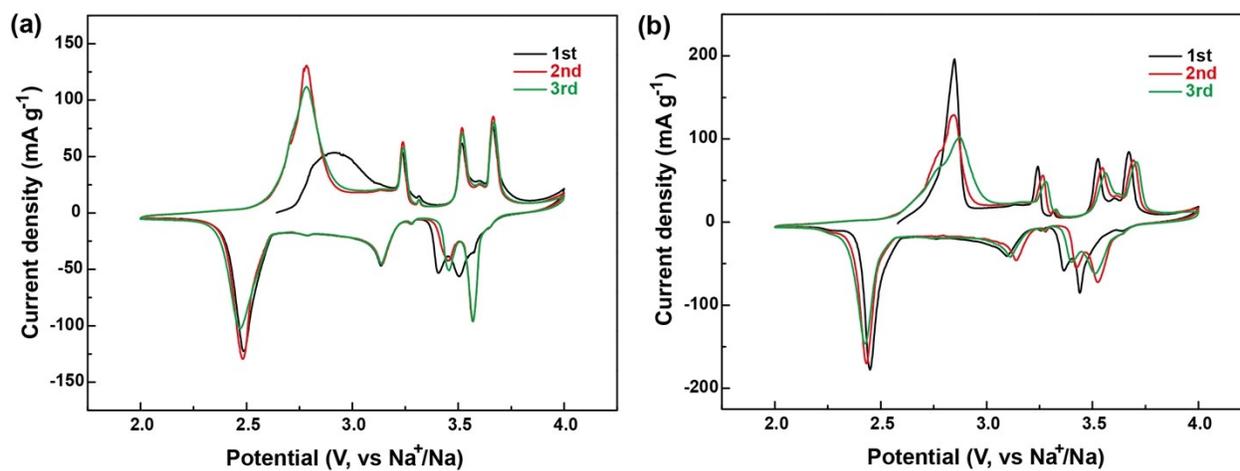
**Fig. S2** (a) TEM and (b) HRTEM images of O3-NaNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> sample.



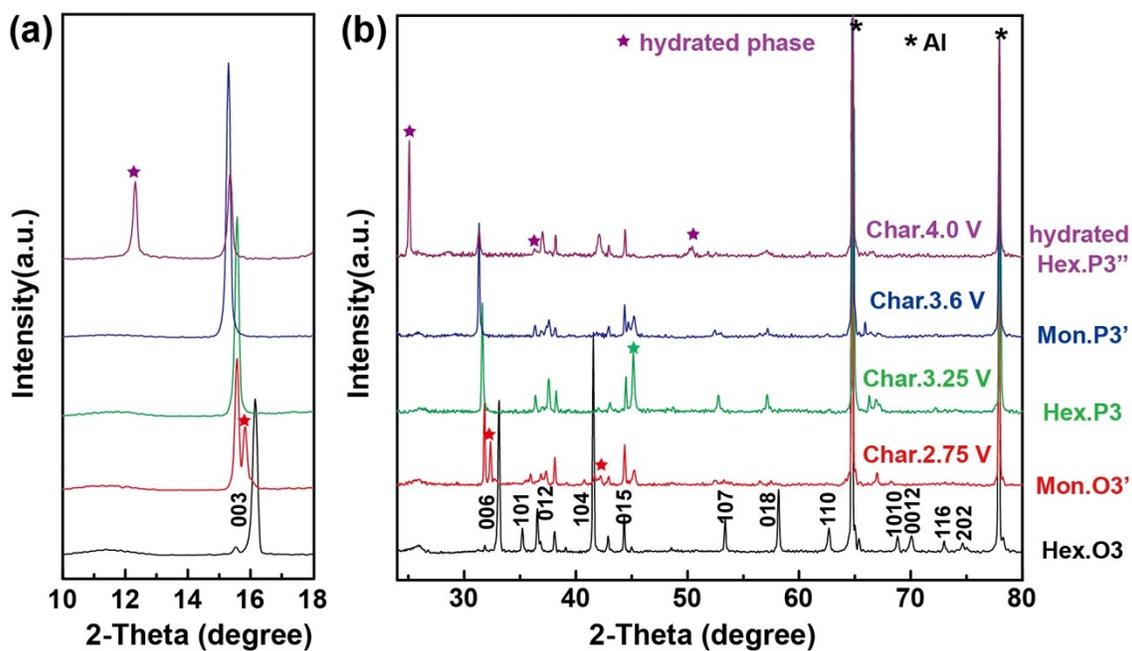
**Fig. S3** The typical charge/discharge profiles of O3-NaNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>/CNT electrodes working in different electrolyte solutions a) 1 M NaClO<sub>4</sub> in PC; b) 1 M NaPF<sub>6</sub> in EC and DEC (1:1 in volume); c) 1 M NaClO<sub>4</sub> in PC (2% FEC); d) 1 M NaClO<sub>4</sub> in EC and PC (1:1 in volume, 5% FEC) between 2 and 4 V at a rate of 0.05 C (1C = 240 mA g<sup>-1</sup>).



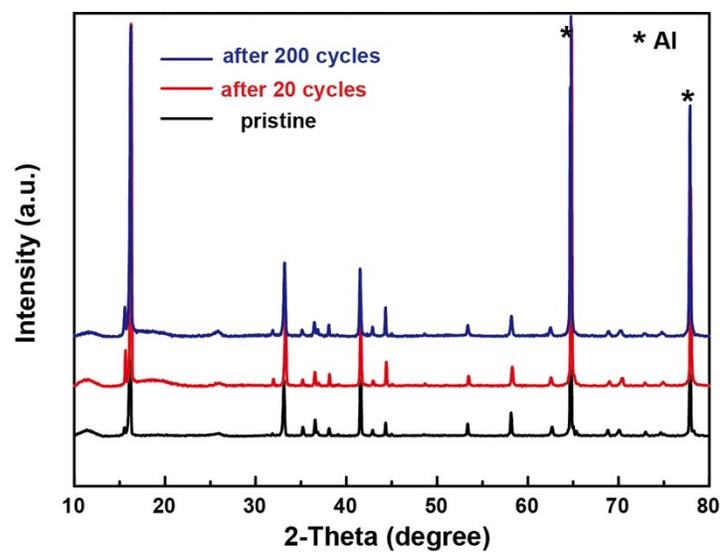
**Fig. S4** XPS spectra of O<sub>3</sub>-NaNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> for (a) Ni2p, (b) Mn2p regions, indicating nickel, manganese elements are in a valence state of +2 and +4, respectively.



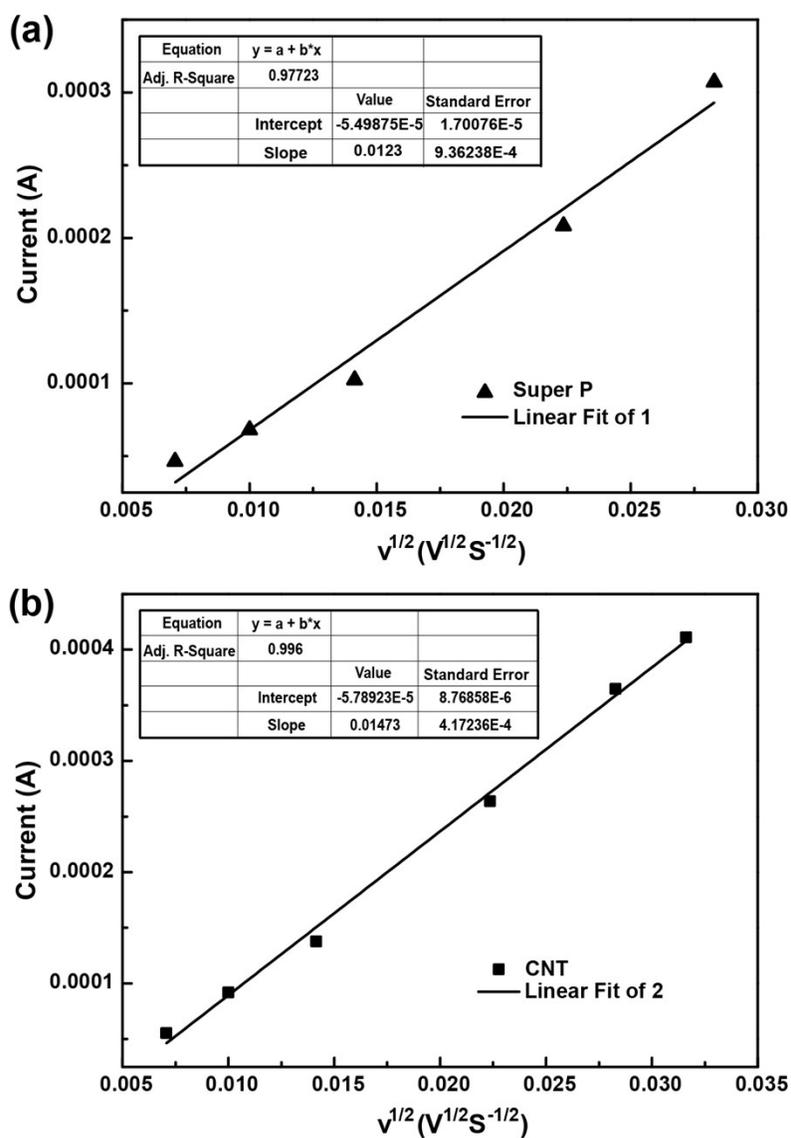
**Fig. S5** Cyclic voltammograms of O3-NaNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> with (a) Super P, (b) CNT as conductive additives, measured at a scan rate of 0.1 mV s<sup>-1</sup> in the voltage range of 2.0-4.0 V.



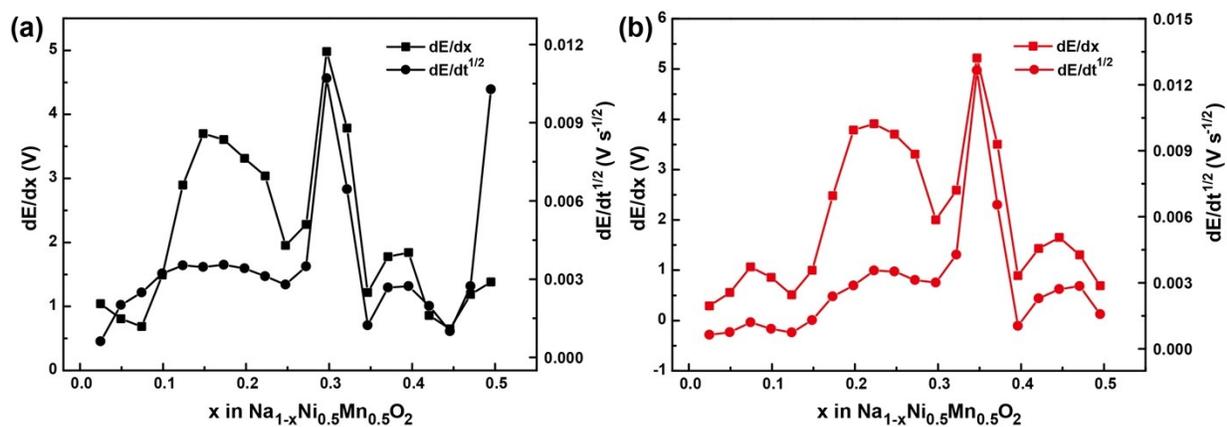
**Fig. S6** (a) The enlarged and (b) highlighted *ex-situ* XRD patterns of O<sub>3</sub>-NaNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> electrodes at different charge states.



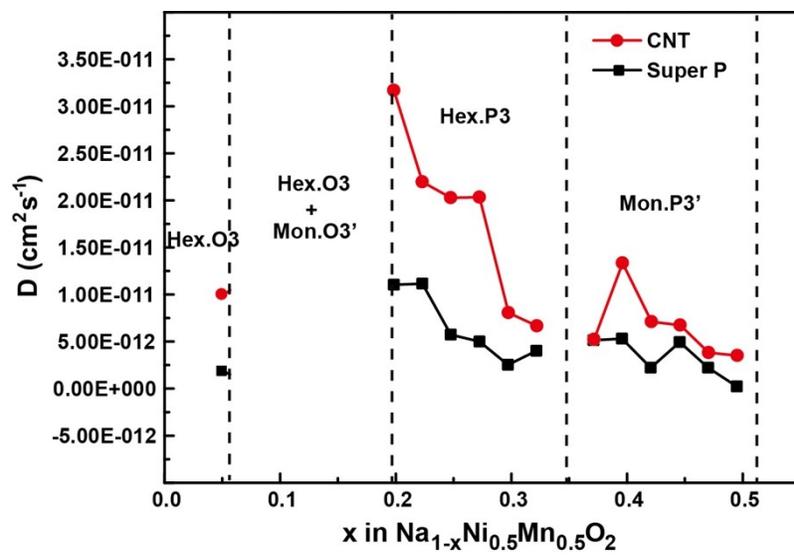
**Fig. S7** XRD patterns of O<sub>3</sub>-NaNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> electrodes after different cycles.



**Fig. S8** Peak current  $I_p$  as a function of square root of scan rate  $v^{1/2}$  for O3- $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  electrodes with (a) Super P, (b) CNT as conductive additives, respectively.



**Fig. S9** The calculated values of  $dE/dx$  and  $dE/dt^{1/2}$  of the O3-NaNm cathode as a function of stoichiometry. The results are calculated from GITT curves of the O3- $NaNi_{0.5}Mn_{0.5}O_2$  cathode with (a) Super P, (b) CNT as conductive additives.



**Fig. S10** Na<sup>+</sup> apparent chemical diffusion coefficients in the single-phase regions as a function of stoichiometry from GITT.

**Table S1** Comparison of cycling stability of O3-NaNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> cathodes for sodium-ion batteries.

Materials	Particle size (μm)	Electrolyte	Practical capacity (mA h g <sup>-1</sup> )	Cycling stability	Reference
NaNi <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>2</sub> /AB	10-20	1 M NaClO <sub>4</sub> in PC	125 (0.2 C, 2.2-3.8 V)	75% (50 cycles)	25
NaNi <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>2</sub> /Super S	3-5	1 M NaClO <sub>4</sub> in PC	125 (0.05 C, 2.0-3.8 V)	-----	34
NaNi <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>2</sub> /AB	10-20	1 M NaClO <sub>4</sub> in PC (2% FEC)	140 (0.05 C, 2.0-3.8 V)	85% (40 cycles)	26
NaNi <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>2</sub> /Super P	30	1 M NaPF <sub>6</sub> in PC	185 (0.1 C, 2.0-4.3V)	54% (20 cycles)	29
NaNi <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>2</sub> /AB	0.1-1.5	1 M NaPF <sub>6</sub> in EC/DEC (1:1 vol %)	124 (0.05 C, 2.0-4.0 V)	87% (30 cycles)	33
NaNi <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>2</sub> /CNT	3-5	1 M NaClO <sub>4</sub> in EC/PC (1:1 vol %, 5% FEC)	141 (0.05 C, 2.0-4.0 V)	90% (100 cycles)	This work

\* AB: acetylene black; CNT: carbon nanotubes; PC: propylene carbonate; FEC: fluoroethylene carbonate; EC: ethylene carbonate; DEC: diethylcarbonate.