

## Supplementary Information

### Comprehensive study of the role of transition metals in O3-type layered $\text{Na}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ ( $x=1/3, 0.5, 0.6$ , and $0.8$ ) cathodes for sodium-ion batteries

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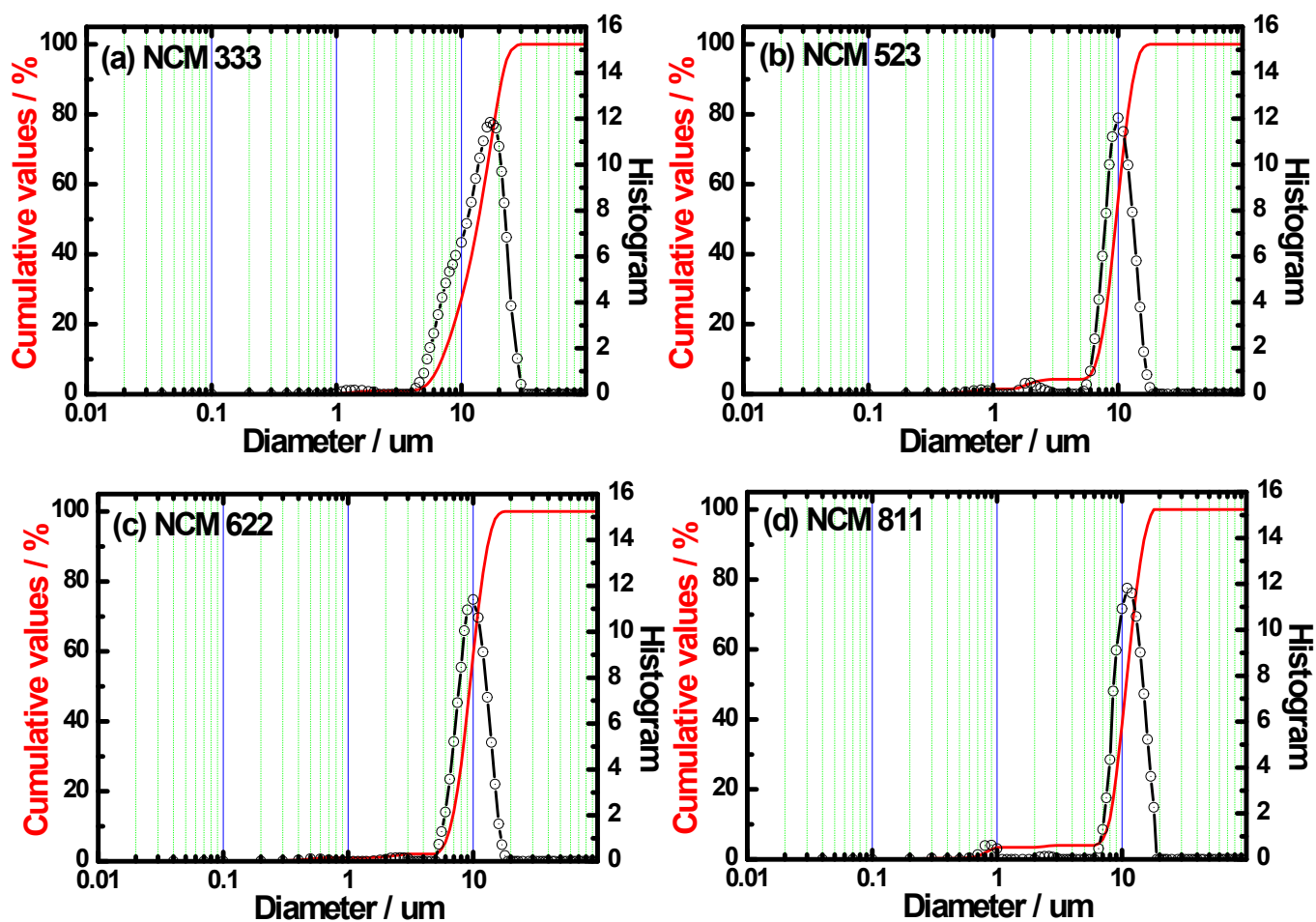
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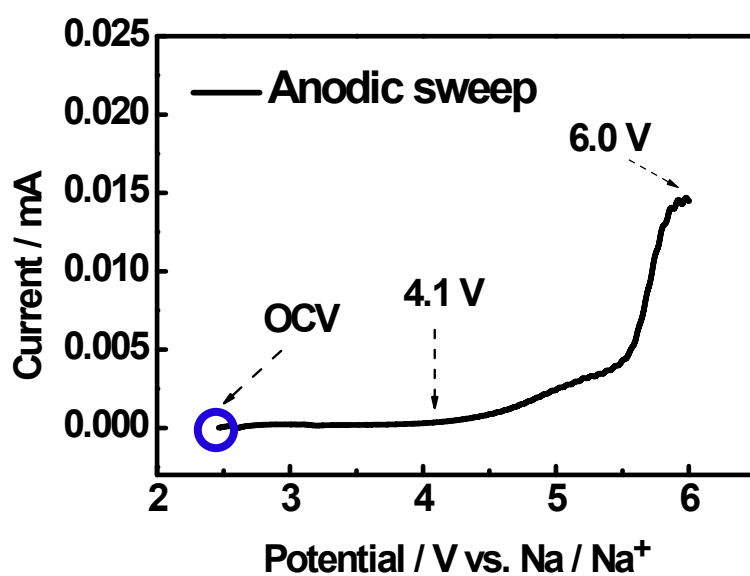
**Fig. S1** Particle size analysis results of the  $[\text{Ni}_x\text{Co}_y\text{Mn}_z](\text{OH})_2$  ( $x=1/3, 0.5, 0.6$ , and  $0.8$ ) precursors.

**Table S1** Chemical compositions of the prepared  $[\text{Ni}_x\text{Co}_y\text{Mn}_z](\text{OH})_2$  ( $x=1/3, 0.5, 0.6$ , and  $0.8$ ) powders determined by ICP-AES.

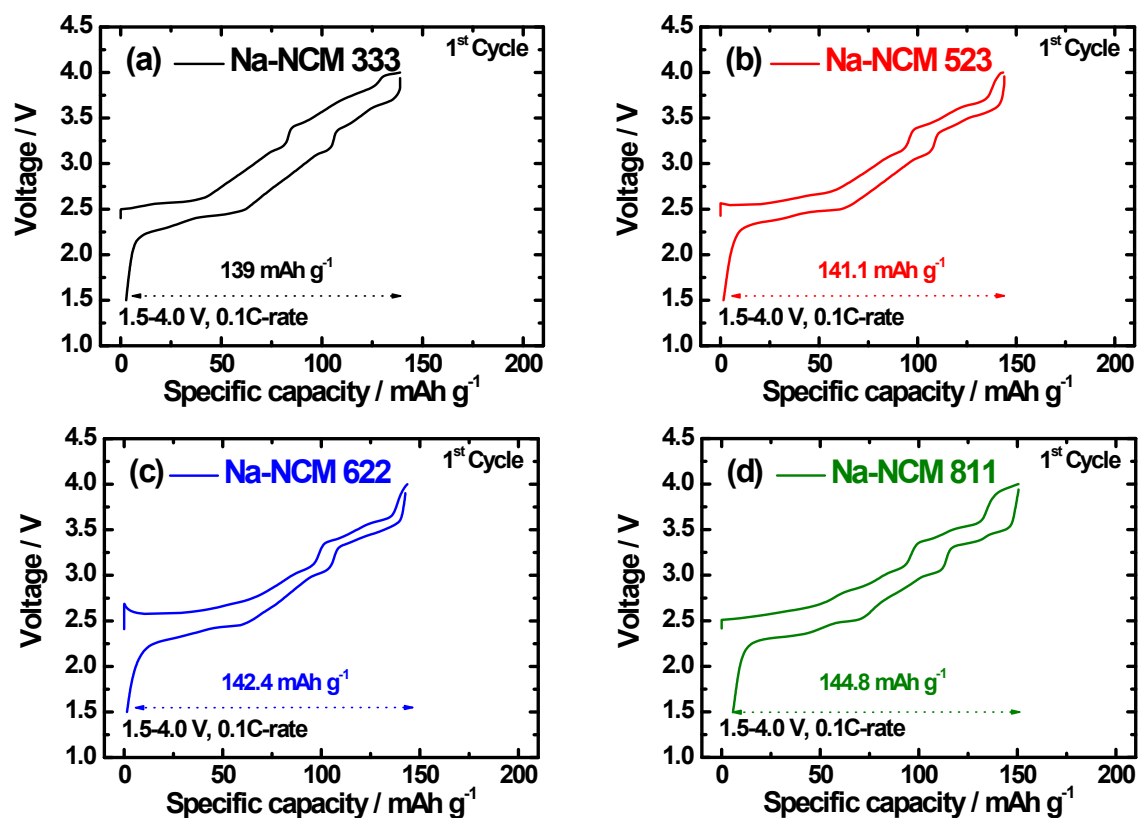
| Metal stoichiometry determined by ICP-AES |                                                                |        |        |        |                                                                         |
|-------------------------------------------|----------------------------------------------------------------|--------|--------|--------|-------------------------------------------------------------------------|
| x                                         | Formula                                                        | Ni     | Co     | Mn     | Prepared Precursor                                                      |
| 1/3                                       | $[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}](\text{OH})_2$ | 0.3244 | 0.3319 | 0.3437 | $[\text{Ni}_{0.3244}\text{Co}_{0.3319}\text{Mn}_{0.3437}](\text{OH})_2$ |
| 0.5                                       | $[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}](\text{OH})_2$ | 0.5062 | 0.1998 | 0.2940 | $[\text{Ni}_{0.5062}\text{Co}_{0.1998}\text{Mn}_{0.2940}](\text{OH})_2$ |
| 0.6                                       | $[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}](\text{OH})_2$ | 0.6086 | 0.1977 | 0.1937 | $[\text{Ni}_{0.6086}\text{Co}_{0.1977}\text{Mn}_{0.1937}](\text{OH})_2$ |
| 0.8                                       | $[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}](\text{OH})_2$ | 0.7913 | 0.1055 | 0.1032 | $[\text{Ni}_{0.7913}\text{Co}_{0.1055}\text{Mn}_{0.1032}](\text{OH})_2$ |

**Table S2** Lattice parameters of the Na[Ni<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>]O<sub>2</sub> (x=1/3, 0.5, 0.6, and 0.8) cathodes.

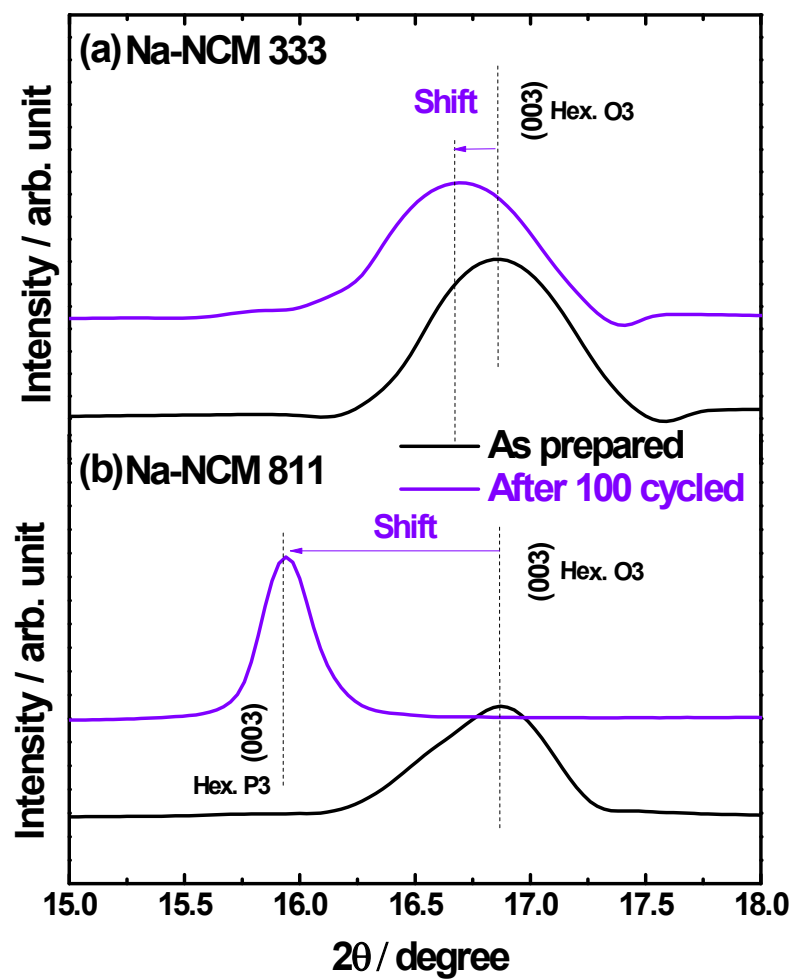
| Cathodes                                                                              | a-axis / Å | c-axis / Å | volume / Å <sup>3</sup> |
|---------------------------------------------------------------------------------------|------------|------------|-------------------------|
| Na[Ni <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> ]O <sub>2</sub> (Na-NCM 333) | 2.9384(2)  | 15.994(1)  | 119.59(4)               |
| Na[Ni <sub>0.5</sub> Co <sub>0.2</sub> Mn <sub>0.3</sub> ]O <sub>2</sub> (Na-NCM 523) | 2.9356(5)  | 15.847(7)  | 118.19(6)               |
| Na[Ni <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> ]O <sub>2</sub> (Na-NCM 622) | 2.9345(2)  | 15.808(2)  | 117.88(2)               |
| Na[Ni <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> ]O <sub>2</sub> (Na-NCM 811) | 2.9309(1)  | 15.776(8)  | 117.36(7)               |



**Fig. S2** Linear sweep voltammetry (LSV) results of a sodium cell using a 0.5 mol dm<sup>-3</sup> NaPF<sub>6</sub> solution in propylene carbonate (PC) and fluoroethylene carbonate (98:2 by volume) electrolyte.



**Fig. S3** The initial charge-discharge profiles of the Na[Ni<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>]O<sub>2</sub> (x=1/3, 0.5, 0.6, and 0.8) electrodes in the voltage range of 1.5-4.0 V.



**Fig. S4** XRD patterns of Na-NCM 333 and Na-NCM 811 electrodes between before and after cycling at 75 mA g<sup>-1</sup> in the voltage range of 1.5 – 4.1 V.