Supporting Information

P2-Type Layered High-Entropy Oxides as Sodium-Ion Cathode Materials

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The configurational entropy, *S*config, is based entirely on the number of different elements in the single-phase structure. *S*config can be increased by increasing the number of elements, which are randomly distributed on the same lattice site(s). The molar configurational entropy can be calculated according to a Boltzmann-entropy-derived equation:

where *R* represent the ideal gas constant, and *x*i and *x*j are the molar fraction of cations or anions on the respective sublattices [DOI: 10.1002/adma.201806236, DOI: 10.1039/d1ee00505g, DOI: 10.1038/s41467-018-05774-5, DOI: 10.1038/ncomms9485].

**Table S1.** Structural parameters from Rietveld refinement analysis.

|  |  |  |  |
| --- | --- | --- | --- |
|  | 3-NTMO2 | 5-NTMO2 | 7-NTMO2 |
| *a* = *b* / Å | 2.8607(1) | 2.8729(1) | 2.8781(1) |
| *c* / Å | 11.1343(4) | 11.1443(6) | 11.1542(5) |
| *V* / Å3 | 78.910(4) | 79.587(5) | 79.876(4) |
| *R*p / % | 1.19 | 1.35 | 1.26 |
| *R*wp / % | 1.56 | 1.99 | 1.73 |

**Table S2.** ICP-OES results for the synthesized materials.

|  |  |
| --- | --- |
| Targeted composition | Experimentally determined composition |
| Na0.67(Mn0.55Ni0.21Co0.24)O2 | Na0.6510(Mn0.5336Ni0.2058Co0.2293)O2 |
| Na0.67(Mn0.45Ni0.18Co0.24Ti0.1Mg0.03)O2 | Na0.6666(Mn0.4467Ni0.1817Co0.2340Ti0.0933Mg0.0254)O2 |
| Na0.67(Mn0.45Ni0.18Co0.18Ti0.1Mg0.03Al0.04Fe0.02)O2 | Na0.6649(Mn0.4433Ni0.1806Co0.1763Ti0.0947Mg0.026Al0.037Fe0.016)O2 |

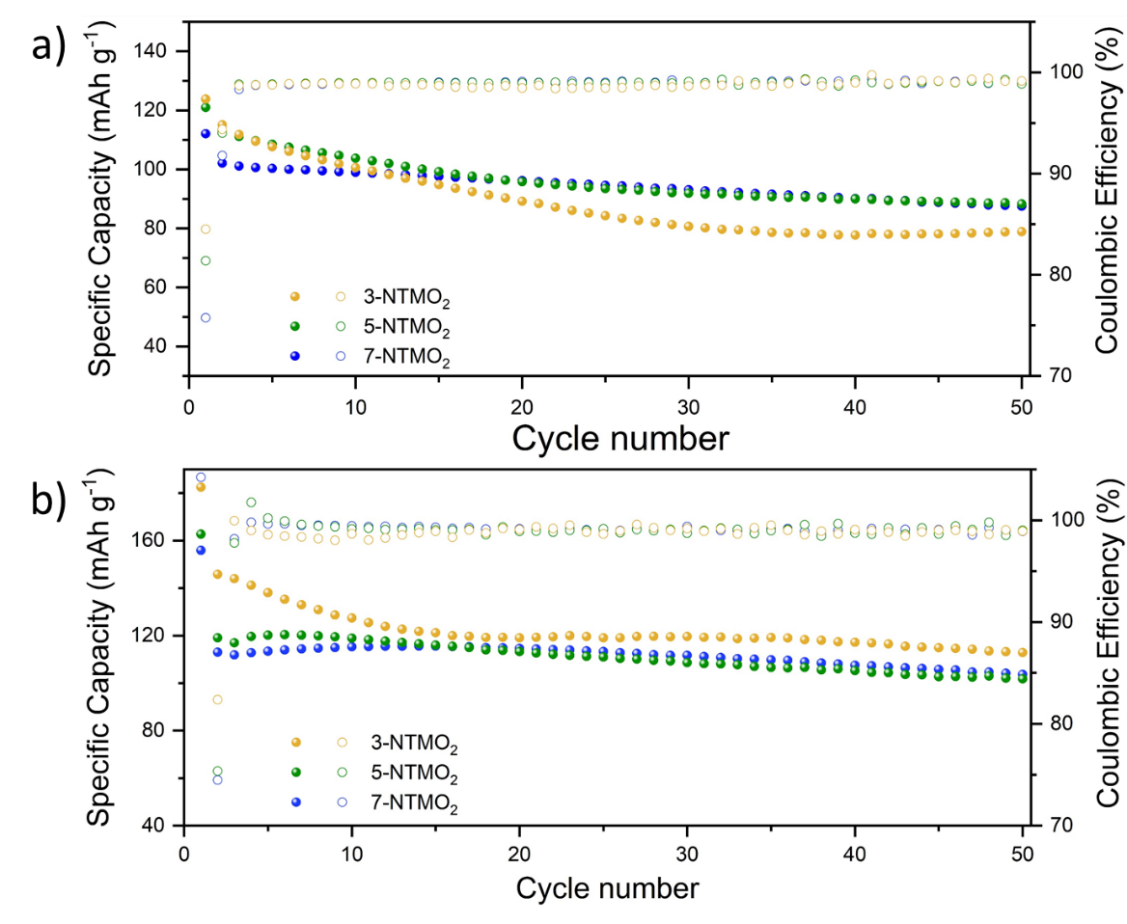
**Table S3.** Summary of the DEMS results.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Material | 1st cycle charge capacity (mAh g-1) | 1st cycle discharge capacity (mAh g-1) | 2nd cycle charge capacity (mAh g-1) | 2nd cycle discharge capacity (mAh g-1) | 2nd cycle Coulombic efficiency (%) | 1st cycle total H2 (µmol g-1) | 1st cycle total CO2 (µmol g-1) | 2nd cycle total H2 (µmol g-1) | 2nd cycle total CO2 (µmol g-1) |
| 3-NTMO2 | 160 | 191 | 197 | 189 | 95.9 | 60 | 315 | 20 | 57 |
| 5-NTMO2 | 156 | 177 | 183 | 178 | 97.3 | 76 | 380 | 27 | 45 |
| 7-NTMO2 | 146 | 172 | 178 | 177 | 99.4 | 54 | 300 | 26 | 36 |

Timeline

Description automatically generated

**Figure S1.** a, b) SEM images, c, d) SAED patterns along [] and [] and e, f) HAADF-STEM image and corresponding high-resolution EDX maps for 3-NTMO2 and 5-NTMO2, respectively.



**Figure S2.** Cycling performance of 3-NTMO2, 5-NTMO2 and 7-NTMO2 in the voltage range of a) 2.6-4.6 V and b) 1.5-4.6 V. Electrochemical testing was carried out at room temperature and 0.5C rate over 50 cycles.

**Figure S2a** shows the cycling performance of the materials in the voltage range 2.6-4.6 V at 0.5C rate. Despite higher initial specific capacities, the 3-NTMO2 and 5-NTMO2 electrodes show obvious decay in the first 15 cycles. After that, the trend towards lower specific capacity is not alleviated for 3-NTMO2, while it tends to be moderate for 5-NTMO2. In contrast, the 7-NTMO2 electrode exhibits superior cycling stability. The cycling performance of the materials in the voltage range 1.5-4.6 V at 0.5C rate is shown in **Figure S2b**. A similar trend in capacity degradation is observed as that found in the range of 2.6-4.6 V. However, the cell with the 3-NTMO2 delivers a higher specific capacity (113 mA h g-1) after 50 cycles than 5-NTMO2 and 7-NTMO2. The higher discharge capacities are due to the Mn4+/Mn3+ redox couple, leading to fast working voltage decay and low capacity retention. In contrast, the 5-NTMO2 and 7-NTMO2 electrodes display slower fading, with remaining specific capacities of 102 and 104 mA h g-1 after 50 cycles, corresponding to 63 % and 67 % capacity retention, respectively.

Diagram

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**Figure S3**. *Operando* XRD data between 6 and 26 h, where desodiation and resodiation proceed at high voltages (> 4.2 V vs. Na+/Na).

A picture containing chart

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**Figure S4.** Carbon dioxide and hydrogen evolution rates from DEMS in the first cycle for the 3-NTMO2, 5-NTMO2 and 7-NTMO2 electrodes.

Diagram

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**Figure S5.** FT-IR spectra of the as-prepared 3-NTMO2, 5-NTMO2 and 7-NTMO2 powders.

Chart

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**Figure S6.** Differential capacity plots (d*q*/d*V*) of the first two cycles at 0.05C rate and 25 °C for the a) 3-NTMO2, b) 5-NTMO2 and c) 7-NTMO2 electrodes.

Chart

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**Figure S7.** Carbon dioxide and hydrogen evolution rates from DEMS in the first discharge cycle for the 3-NTMO2, 5-NTMO2 and 7-NTMO2 electrodes.

Chart, histogram

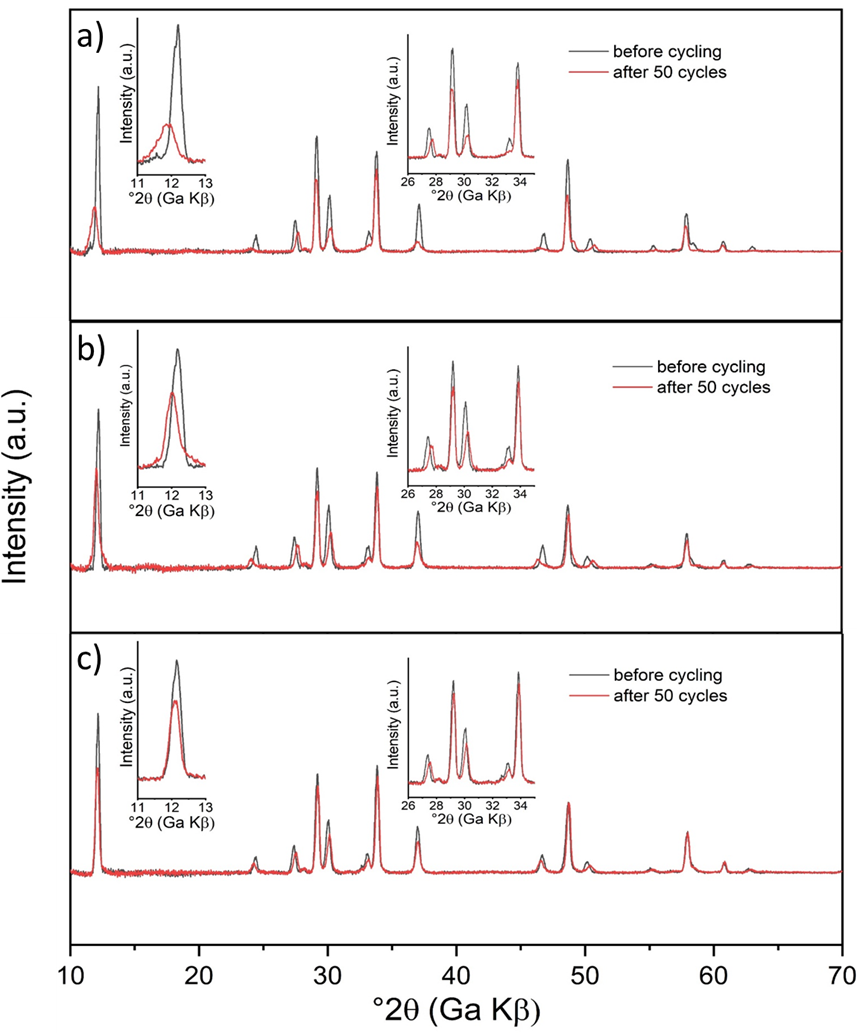
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**Figure S8.** Carbon dioxide evolution rates and voltage as a function of specific charge capacity in the 2nd cycle.

Chart, histogram

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**Figure S9.** Carbon dioxide evolution rates as a function of voltage in the 2nd cycle.



**Figure S10.** *Ex situ* XRD patterns for a) 3-NTMO2, b) 5-NTMO2 and c) 7-NTMO2 in the pristine state and after discharge in the 50th cycle.

Chart, histogram

Description automatically generated

**Figure S11.** XPS spectra of the Mn 2p region for the 3-NTMO2, 5-NTMO2 and 7-NTMO2 electrodes prior to cycling.