Supporting Information


Reversible Flat to Rippling Phase Transition in Fe Containing Layered Battery Electrode Materials

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Reversible flat to rippling phase transition in Fe containing layered battery electrode materials

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**Figure S1 a**, TM position (12 Fe and 36 Mn) of the three layers of the 2x8x3 supercell used for calculation of O3-Fe$_{0.25}$TM$_{0.75}$ (TM=Mn) in Figure 1 of the Main Text. **b**, TM position (16 Fe and 32 Mn) of the three layers of the 2x8x3 supercell used for calculation of O3-Fe$_{1/3}$TM$_{2/3}$ (TM=Mn).
Figure S2 Calculation of rippling for O3-Fe$_{0.5}$TM$_{0.5}$ (TM=Mn and Co). a, TM position (24 Fe and 24 Mn) of the three layers of the 2x8x3 supercell. This particular TM ordering is used for all both TMs. b, c, DFT relaxed rippled Fe$_{0.5}$TM$_{0.5}$ (TM=Mn and Co) from flat structures. Here the c parameter of this three-layer supercell is 15.6Å, but the results are qualitatively the same when we increase c to 16.5Å.
Figure S3 Comparison between the rippled structure of Fe_{0.5}Mn_{0.5} and pure Fe. They share similar rippling geometry, while the amplitude of rippling is larger for pure Fe case.
Figure S4 a, b, The energy of 5 structures with different TM orderings of Na empty Fe$_{0.5}$Mn$_{0.5}$ (FM) and Fe$_{0.5}$Co$_{0.5}$ (FC), respectively, using D2 method. The supercell size is the same as described in Figure S5. Squares are flat structures and circles are rippled structures. Two circles for the same case means the flat structure cannot be stabilized and is relaxed to a rippled one. c, d, Same calculation as in a, b but using D3 method. These two methods provide close quantitative description and the same qualitative description of either having a energy benefit of around 10 meV, or the rippled structure is the only stable structure. e, f, Distortion of FeO$_6$ in Fe$_{0.5}$Mn$_{0.5}$ (FM) and Fe$_{0.5}$Co$_{0.5}$ (FC), respectively. In both cases FeO$_6$ octahedrons in the rippled structure have both larger distortion index and bond angle variance, indicating that structural distortion is strengthened by rippling. This result agrees well with the result in Figure 1 of the Main Text.
Figure S5 DFT calculation of rippling in Fe$_{0.5}$TM$_{0.5}$ with different ordering and different geometry showing the glass phase character. **a**, the 2 layers of an 2x8x2 supercell showing the position of Fe and Mn ions. Such supercell is also used for calculation in Figure S3. **b-d**, three possible rippled structures obtained by DFT relaxation with same TM ordering but different rippling geometry. **e**, the energy of 5 rippled structures with different bending geometries compared with the energy of the
flat structure. All structures have the same TM ordering. The $c$ parameter of this two-layer supercell is 11Å.

**Figure S6 a**, DFT calculation of rippling in Na$_{1/9}$Fe$_{0.5}$TM$_{0.5}$O$_2$ (6x6x3 supercell) with 5 different TM orderings. All energy benefits are larger than 10 meV per Fe for the Na clustered and TM rippling phase compared with the Na evenly distributed and TM flat phase, showing a stronger preference for the rippling to couple with Na ions than without their presence. The calculated structure is as described in Figure 1 of the Main Text. **b**, The energy benefit of ordering #5 using D2, D3BJ method and without van der Waals correction. All three methods show very close value, indicating that the van der Waals correction play a minor role in the case of TM layers coupling to Na ions **c, d**, The existence of rippled structure in this supercell predicted by both D2 and D3BJ methods. The $c$ parameter is 16.5Å, the same as in Figure 1 of the Main Text.
Figure S7 (003) peak evolution of FM (a), FN (b), FMN (c) and FCN (d) from in-situ XRD measurement at C/50 along with the corresponding voltage curves.
Figure S8 a, STEM image of MFCN charged to 4.35V corresponding to Figure 2e. TM layer rippling is found in the entire image. b-d, HRTEM image of pristine (b), charged to 4.35V (c) and 1cycle (d) MFCN samples. The TM layers are flat at pristine (b), rippled at 4.35V (c) and flat again after 1 cycle (d), which agrees well with the features of STEM images.
Figure S9 DFT calculation showing the suppression of TM rippling by Fe migration.

a. Position of Mn and Fe in the two layers of the 2x8x2 supercell used in the calculation. The tetrahedron Fe in layer 2 is migrated in calculation in c. b. Relaxed rippled structure without migration. c. Relaxed structure with one migrated Fe showing reduced rippling.
Figure S10 NEB calculation showing high migration barrier of Fe from the octahedron site inside TMO$_2$ layers to a tetrahedral site in the Na layer. a, schematic of the calculation without Na in the layer that Fe migrates to. Three cases of isolated Fe, 2 neighboring Fe and 3 neighboring Fe are calculated with the result showing in b. The interlayer distance is 5.5Å in every calculation. TM matrix is Mn.
Figure S11 Neutron diffraction measurement showing no long-range TM ordering, magnetic ordering, and very limited short-range ordering down to 5K. 

a. Na(Mn\textsubscript{0.25}Fe\textsubscript{0.25}Co\textsubscript{0.25}Ni\textsubscript{0.25})O\textsubscript{2} (MFCN) b. Na(Fe\textsubscript{0.5}Co\textsubscript{0.5})O\textsubscript{2} (FC). c. Low-angle part of b. A broad peak centered around 12° originates at 5K, which can be a result of short-range magnetic ordering within 1\textsuperscript{st} nearest neighbor. No short range ordering is observed in MFCN.
Figure S12 Battery test voltage curves of the 1st, 2nd and 10th cycles of Na[Fe_{0.5}Co_{0.5}]O_2 (FC), the same test as shown in Figure 4d of the Main Text. Here, instead of showing the hysteresis loop property as in the Main Text, the plot clearly shows that all the plateau features are largely preserved in the charge curves up to the 10th charge, but are disappeared in all the discharge curves.

Figure S13 Average voltage of charge (marked by disks) and discharge (marked by circles) for NaCoO_2 (black) and Na[Fe_{0.5}Co_{0.5}]O_2 (FC) cycled from 2V to 4V (NaCoO_2) and 2.5V to 4V (FC). For NaCoO_2 the average voltage for charge and discharge are 3.100V and 2.936V, respectively, with a difference of 0.164V. For FC,
they are 3.250V and 3.148V, with a difference of 0.102V. The hysteresis FC has both higher average voltage and lower over potential than NaCoO$_2$. 