Jahn–Teller Assisted Na Diffusion for High Performance Na Ion Batteries

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ABSTRACT: Na energy storage technology is strategically attractive for large scale applications such as grid energy storage. We show in this paper that there is a clear relation between the Jahn–Teller activity of a transition metal ion at the end of charge and the mobility of Na in a cathode material. This is particularly important as mobility at the end of charge limits the capacity of current materials. Hence, by using this classical piece of physics in the battery world, it is possible to create higher capacity Na-cathode materials. Even more exciting is that the ideal element to impart this effect on cathodes is Fe, which is the least expensive of the transition metal oxides and can therefore enable low cost cathode materials.

1. INTRODUCTION

Sodium (Na) ion batteries have attracted increasing interest recently as an alternative option to lithium (Li) ion batteries. Na resources have a more homogeneous global geographical distribution and are generally less expensive than lithium.1–4 This makes Na energy storage technology strategically attractive, especially for large scale applications such as grid energy storage. Layered NaTMO2 (TM: transition metal) is the most competitive cathode compound in terms of capacity, energy density, and rate capability, with some cathodes already showing energy density well above 500 Wh/kg.5–7 These layered Na-compounds can be synthesized from a broad choice of 3d transition metal elements from Ti to Cu, as well as their combinations,5–27 while the lithium analogs are limited to combinations of Co, Ni, and Mn.28 This broader choice of transition metal elements can reduce the large contribution of materials to the cost of today’s lithium-ion technology.2,4,24 We show in this paper that the ability for Na cathodes to use Fe as an active component is another major advantage over Li-technology. We demonstrate that a unique interplay between the Jahn–Teller physics of Fe4+O6 octahedron and Na diffusion maintains Na mobility up to a very high charge level, thereby endowing Fe-containing cathodes not only with low cost but also with very high capacity. As such, we believe that this is the first and remarkably practical application of this classical physics of TM ions into layered energy storage compounds in the energy field.

The limiting factors for the performance of sodium layered electrodes are the inaccessible capacity in the high voltage range and the significant deterioration of cyclability at high cutoff voltage. The former situation limits the capacity directly,15,17 while the latter leads to a quick decay of the capacity from its high initial value.7 This problem arises from the layer spacing collapse which occurs when most of the alkaline ions in either Na or Li layered cathodes are extracted, leading to reduced alkali mobility.29,30 This fundamental limit to the practical capacity of layered oxides has been difficult to overcome and inhibits cathodes to approach their theoretical energy density. Our work is inspired by the recent discovery of Na-cathode materials with high capacity, all of which contain Fe. For example, compounds such as Na(Mn0.25Fe0.25Co0.25Ni0.25)O2 (MFCN) delivers much higher capacity and better cyclability than others like NaNiO215 or Na(Fe0.5Co0.5)O2 (FC) at high cutoff voltage.6

In this paper, we use layered NaTMO2 compounds as model systems to demonstrate that the unique capability to stabilize the Fe3+O6/Fe4+O6 redox-couple in layered sodium structure is the critical factor to reach optimal battery performance. We identify a new mechanism of Jahn–Teller distortion assisted sodium diffusion which greatly improves the Na diffusivity through a soft-mode buckling of the Jahn–Teller high-spin

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Fe$^{4+}$O$_6$ octahedron. The new mechanism could potentially be applied to any type of sodium intercalation compound whenever the Jahn–Teller active transition metal is face-sharing with the activated site for sodium diffusion, including channeled and zigzag layered structures. A Jahn–Teller (JT) distortion lowers the energy of a system by certain bond length distortions to break the local crystal symmetry and lift the degeneracy of the electronic system. Among the 3d transition metal ions, Mn$^{4+}$, Fe$^{4+}$ and Ni$^{4+}$ in octahedral coordination show the strongest JT effect. The uniqueness of Fe originates from the fact that it is the only 3d transition metal element that becomes JT active at the end of charge in Na$_x$TMO$_2$ when the TM is oxidized to 4+, while Mn$^{3+}$ and Ni$^{4+}$ lose their JT activity in the 4+ state, as illustrated in Figure 1. We will demonstrate through detailed simulation and experimental characterization that it is the JT activity of Fe$^{4+}$O$_6$ that lowers the Na diffusion barrier at the later stage of charge and enables the extraction of more sodium ions.

2. METHODS

2.1. Synthesis and Electrochemical Testing. All the sodium layered compounds were synthesized using solid state reaction by mixing either Na$_2$O or Na$_2$CO$_3$ with the transition metal oxides precursors, following the methods in the previous literature. The new compound O$_3$-MFC was synthesized by sintering at 900 °C for 12 h the pellet that was cold pressed from the ball milled mixture of a stoichiometric amount of Na$_2$CO$_3$, Mn$_2$O$_3$, Fe$_2$O$_3$, and Co$_3$O$_4$ powders. The cathode film was made by mixing as-synthesized powder, Super P carbon black (Timcal), and dry PTFE (DuPont) with the weight ratio of 80:15:5. A Swagelok battery was assembled using glass fiber (Whatman GF/F) as separator, Na$_2$SO$_4$ (Aldrich) in EC/DEC (anhydrous, 1:1 volume ratio) as electrolyte with 1 M Na$_2$CO$_3$ (99%, Sigma-Aldrich) in EC/DEC (anhydrous, 1:1 volume ratio) as electrolyte with the moisture level less than 3 ppm. The galvanostatic cycling was taken on Bruker D8 X-ray diffractometer equipped with a Mo source. In situ XRD spectra were identified by XRD refinement. MFC was cycled between 1.5 and 4.5 V due to its low average voltage. The sodium content after 1 cycle is around Na$_0.5$FeO$_2$ estimated from the dihedral XRD patterns, based on the observation of electron diffraction measurements and the most commonly observed structures reported in prior literature. Specifically, three of these lattices are the spinel (Fd$eta$m), hexagonal-distorted spinel ($R\bar{3}m$), and tetragonal-distorted spinel (I$4$/amd), with the other two being the O3 ($R\bar{3}m$) and O’3 (C$2$/m) lattices. The lattice parameters and figure-of-merit for the fits (i.e., $R_p$) are listed in Table 2. Although the best fit was achieved with the use of a monoclinic lattice (O’3, C$2$/m), the fitting error based on the tetragonal distorted spinel is only marginally higher (8.13 vs 8.08). Considering the much higher symmetry of the tetragonal lattice and the much fewer parameters needed in the refinement (2 vs 4) compared to the monoclinic C$2$/m lattice, we conclude this pattern can be most appropriately indexed with a tetragonal-distorted spinel lattice. This finding is consistent with the electron diffraction measurements where a distorted spinel-like structure was observed.

2.5. Computational. First-principles calculations were performed using density functional theory implemented in the plane-wave-basis-set Vienna ab initio simulation package (VASP). Projector augmented wave potentials with kinetic energy cutoff of 520 eV were employed in all simulations. All calculations were spin-polarized starting from a high-spin ferromagnetic configuration. Exchange and correlation functions were described within Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA). With the GGA+U extension of the standard Dudarev implementation, the on-site Coulomb interaction for localized orbitals in the transition metal is parametrized by $U_{eff} = U - J$. We apply the optimized effective interaction parameter $U_{eff}$ for the transition metals ($U_{eff} = 4.0, 3.9, 5.7$, and $6.1$ eV for Mn, Fe, Co, and Ni, respectively) following Ong et al. GGA+U calculations yield correct transition metal ion spin configurations (e.g., high spin configuration for Fe$^{4+}$O$_6$), though simply applying PBE-GGA results in low spin electronic configurations (e.g., low spin configuration for Fe$^{4+}$O$_6$). Minimum energy pathways and the activation energies were calculated by using the nudged elastic band method.

Table 1. Initial Discharge Capacity and Energy Density of Different Layered O3-NaTMO$_2$ Compounds Cycled between 2 and 4.5 V at C/10 Rate

<table>
<thead>
<tr>
<th>compound</th>
<th>1st discharge capacity (mAh/g)</th>
<th>energy density (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$<em>2$(Mn$</em>{1/4}$Fe$<em>{1/4}$Co$</em>{1/4}$Ni$_{1/4}$)O$_2$ (MFCN)</td>
<td>185</td>
<td>596</td>
</tr>
<tr>
<td>Na$<em>2$(Mn$</em>{1/2}$Fe$<em>{1/2}$Co$</em>{1/2}$)O$_2$ (MFC)</td>
<td>180</td>
<td>533</td>
</tr>
<tr>
<td>Na$<em>2$(Mn$</em>{1/2}$Ni$_{1/2}$)O$_2$ (MFIN)</td>
<td>185</td>
<td>592</td>
</tr>
<tr>
<td>Na$<em>2$(Mn$</em>{1/2}$Fe$_{1/2}$)O$_2$ (MF)</td>
<td>153</td>
<td>424</td>
</tr>
<tr>
<td>Na$<em>2$(Co$</em>{1/2}$Ni$_{1/2}$)O$_2$ (NC)</td>
<td>135</td>
<td>414</td>
</tr>
<tr>
<td>Na$<em>2$(Fe$</em>{1/2}$Ni$_{1/2}$)O$_2$ (FN)</td>
<td>140</td>
<td>430</td>
</tr>
<tr>
<td>Na$<em>2$(Fe$</em>{1/2}$Co$_{1/2}$)O$_2$ (FC)</td>
<td>159</td>
<td>498</td>
</tr>
<tr>
<td>Na$_2$NiO$_2$ (Ni)</td>
<td>147</td>
<td>454</td>
</tr>
<tr>
<td>Na$_2$CoO$_2$ (Co)</td>
<td>127</td>
<td>398</td>
</tr>
<tr>
<td>Na$_2$FeO$_2$ (Fe)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*MFC is cycled between 1.5 and 4.5 V due to its low average voltage. Energy density is calculated by multiplying initial discharge capacity and average voltage for each compound. All listed values are from this work.
sampling were used in all simulations. To model compounds at high voltage with dilute Na concentrations, only one Na atom was kept in the supercell. The lattice parameters in the $ab$ plane of fully sodiated phase were fully optimized by DFT and then fixed for NEB calculations. Na diffusion modeling was performed with various interlayer distances, corresponding to the experimental lattice parameters obtained from in situ XRD.

3. RESULTS AND DISCUSSION

O3 and P3 are two typical stacking types of the oxygen atomic layers in layered NaTMO$_2$. In all structures with O3 stacking, Na diffuses between neighboring octahedral sites through the activated tetrahedral site, while in P3 stacking Na diffuses between neighboring prismatic sites through the transient prismatic site. Oxygen ions are colored in red; transition metal cations are in gray; sodium ions are in yellow. The stable sites (octahedral for O3 and O2; prismatic for P3 and P2) are colored as yellow, and the transition or activated sites (tetrahedral for O3 and O2; prismatic for P3 and P2) are colored in orange.

![Figure 2. Na diffusion path in layered NaTMO$_2$ (TM = Fe, Co, Ni, ...) with four typical oxygen stackings of (a) O3, (b) P3, (c) O2, and (d) P2. Oxygen ions are colored in red; transition metal cations are in gray; sodium ions are in yellow. The stable sites (octahedral for O3 and O2; prismatic for P3 and P2) are colored as yellow, and the transition or activated sites (tetrahedral for O3 and O2; prismatic for P3 and P2) are colored in orange.](image)

Na diffuses between neighboring octahedral sites through the activated tetrahedral site, while in P3 stacking Na diffuses between neighboring prismatic sites through the transient prismatic site, as shown in Figure 2a,b. All O3-type NaTMO$_2$ compounds show a clear O3–P3 transition at around 25% Na-ion extraction. A transition back to the O3 stacking at the later stage of charge has been observed in several in situ X-ray diffraction (XRD) measurements. In the quaternary transition metal layered compound MFCN, the new O3 phase that forms at high voltage shows a significant amount of reversible capacity of 25 mAh/g even though the interlayer distance decreases dramatically at the end of charge. This extra capacity coming from the reversibility of the high-voltage O3 phase leads to high total capacities for several Fe-containing materials. The high initial discharge capacity and energy density of MFCN motivated us to study a series of transition metal combinations picked from Mn, Fe, Co, and Ni, as listed in Table 1. By plotting the initial discharge capacity of various NaTMO$_2$ compounds from Table 1 versus their Fe composition (Figure 3), one can observe that the maximum capacity is obtained when ~30% Fe composition is present in the TM layer. The simple dome-shaped relationship in Figure 3.

![Figure 3. Initial discharge capacity of layered NaTMO$_2$ compounds with different transition metal combinations plotted as a function of Fe composition. Co (Ni) stands for NaCoO$_2$ (NaNiO$_2$). Compounds are listed by their TM content with $M = Mn, F = Fe, C = Co, and N = Ni$, and all compounds contain their TM in equal proportions (e.g., MFCN stands for Na(Mn$_{1/4}$Fe$_{1/4}$Co$_{1/4}$Ni$_{1/4}$)O$_2$). More details can be found in Table 1. All cells were cycled at C/10 rate with 4.5 V high cutoff voltage.](image)
indicates that two competing mechanisms related to Fe may be playing a role: one assists the compound to reach higher capacity and the other to decrease the capacity. We use a combination of experimental and theoretical approaches to investigate this underlying physics.

Using in situ XRD, we observed P3−O3 transitions at the later stage of charge for all the compounds listed in Table 1. For example, the in situ XRD result of MFC (Figure 4) shows a highly reversible structure evolution upon charge and discharge, including a clear P3−O3 transition together with a broad sodium composition range for the high-voltage O3 phase, distinguished by XRD refinement. The evolution of the interslab distances with level of desodiation for all the ternary and quaternary systems is summarized in Figure 5. The interslab distance can shrink from 5.7 Å at the beginning of the high-voltage O3 phase to as low as 4.8 Å at the end of charge. This process is largely reversible, and the interslab distance expands back upon discharge, indicating good Na diffusion even at very low Na slab thicknesses. The reversible capacity of the high-voltage O3 phase and good reversibility upon discharge result in the high initial discharge capacities in these compounds. The structure evolution in the single and binary transition metal systems is different from the ternary and quaternary systems, as shown in Figure 6. The composition ranges of the high voltage O3 phases formed in the initial charge are significantly shrunk upon discharge, associated with unsymmetrical charge−discharge structural evolutions. This leads to reduced initial discharge capacities for single and binary transition metal systems. The asymmetry in structural evolution between charge and discharge indicates structural irreversibility associated with the emergence of high voltage O3 phases, and the Na diffusion can be very sluggish.

We now show that it is exactly the difference in Na mobility at the end of charge that distinguishes the compounds that perform well from those that do not. The Na migration energy as calculated with Density Functional Theory (DFT) in the O3 structures at different interslab distances (see Methods) is shown in Figure 7. The high Na diffusion barrier (beyond 600 meV) associated with small interslab distance below 5 Å

![Figure 5. Interplanar distance of layered NaTMO₂ compounds with different ternary and quaternary transition metal combinations upon charge and discharge measured by in situ XRD. O3 phases at the beginning of charge and end of discharge are marked in blue. P3 phases in the middle range of charge and discharge are marked by green. O3 phases at the end of charge and early stage of discharge are marked by red. The labels of compounds follow the same rule as Figure 3 and Table 1. All in situ XRD batteries were cycled at C/50 rate with 4.5 V high cutoff voltage.](image1)

![Figure 6. Interplanar distance of layered NaTMO₂ compounds with different binary and single transition metal combinations upon charge and discharge measured by in situ XRD. O3 phases are represented by dots, and P3 are represented by empty triangles. Compounds are differentiated by colors with their labels in the legend following the same rule as Figure 3 and Table 1. All in situ cells were cycled between 2 and 4.5 V at C/50 rate.](image2)

![Figure 7. DFT calculated Na activation energies in layered NaTMO₂ with different transition metal combinations at various interslab distances. The labels of Mn, Fe, Co, and Ni in the legend stand for the transition metal cations TM in the NaTMO₂. Ni_in Mn stands for an isolated Ni (adjacent to the Na migration path) embedded in the Mn surroundings, etc. For Fe in Mn, both high spin and low spin electronic configurations of Fe are calculated. The upper right inset shows the calculated Na diffusion path for NaTMO₂ with a single type of transition metal (gray). The lower right inset shows the Na diffusion path when Fe (purple octahedra) embedded in Mn surroundings (gray) is face-sharing with the activated state. Obvious buckling of Fe can be observed. The lower left inset shows the calculated profiles for Na migration at the interslab distance of 5.1 Å.](image3)
suggests poor Na diffusivity in many of the layered NaTMO$_2$ compounds. Only for the metal oxides that embed Fe in high spin configuration, such as Fe$_{HS\text{-in\_MnO}_2}$ in Figure 7, is the Na migration energy considerably lower. In such system, Na$^+$ passes through the tetrahedral site (Na$_{tet}$) face sharing with the high-spin Fe$^{4+}$O$_6$ embedded in an MnO$_2$ host. In contrast to the other systems, when Fe$^{4+}$O$_6$ is near the activated state, the calculation shows a significant buckling of the Fe−O bonds along the direction from Na$_{tet}$ to Fe, as illustrated in the Figure 7 insets. The buckling increases the distance of Fe to the Na-ion as it passes through the face-sharing tetrahedral site. This effect significantly lowers the Na diffusion barrier, improving Na mobility at the top of charge. This mechanism is consistent with the calculated energy profile of Na along the migration path (Figure 7 inset) that dips considerably lower at the tetrahedral site when Fe is embedded in other transition metal surroundings, compared with other non-Fe systems. The shape of the migration energy at the tetrahedral site indicates a local energy minimum caused by the dynamic buckling of Fe.

It is worth noting that such Fe assisted Na migration only occurs when Fe$^{4+}$O$_6$ is in the JT-active high spin electronic configuration (Figure 1). If we force Fe to be in the low spin configuration in the DFT calculation (see Methods), the

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**Figure 8.** (A) Electron diffraction and HRTEM of NaFeO$_2$ after 1 cycle between 2 and 4.5 V at C/10 rate. Red dots label the transition metal columns; green dots label the migrated Fe to the tetrahedral sites; blue dots are migrated to the octahedral sites. (B) Electron diffraction and HRTEM of Na(Fe$_{1/2}$Mn$_{1/2}$)O$_2$ after 1 cycle between 2 and 4.5 V at C/10 rate.

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**Figure 9.** Pawley fit of the diffraction data corresponding to cycled NaFeO$_2$ with 4.5 V high cutoff voltage, with a space group of $I4_1/amd$ (tetragonal-distorted spinel) and lattice parameters of $a = b = 5.9291$ Å and $c = 8.449$ Å. The observed, calculated, and difference patterns are shown in blue, red, and dark gray, respectively. Tick marks for the tetragonal lattice are shown in magenta. The results for all the possible space groups are shown in Table 2.
Figure 10. (A) Comparison of in situ XRD patterns obtained for pristine FC and after one cycle at several different cutoff voltages at C/50 rate. The insets highlight the marked 003 peak region. (B) Comparison of XRD patterns of pristine layered compound and the one after 1 cycle from in situ XRD measurement for MFC, FCN, MFN, and MFCN. The insets show the marked 003 peak region. All in situ batteries were cycled at C/10 rate with 4.5 V high cutoff voltage.
migration barrier becomes as high as those in non-Fe containing systems as illustrated in Figure 7 (Fe in Mn Low Spin). This computational experiment clearly demonstrates that it is the JT activity of high spin Fe⁴⁺O₆ that provides the buckling capability to lower the Na migration barrier. The JT distortion of the Fe⁴⁺O₆ octahedron in layered NaTMO₂ is of the Q3-mode type with two long Fe–O bonds and four short Fe–O bonds, lowering the local octahedron symmetry from O₆ to D₃h. This JT distortion assisted Na diffusion explains the capacity increase with increasing Fe composition up to around 30% shown in Figure 3. The capacity drop beyond 30% Fe composition is caused by the JT distortion assisted Fe migration to the Na layer, as we will discuss below.

NaFeO₂ becomes electrochemically inactive when charged beyond 3.3 V corresponding to 30% Na extraction as shown in Table 1. Fe migration into the Na layer in NaFeO₂ can be directly observed by high resolution transmission electron microscopy (HRTEM) as shown in Figure 8A. The electron diffraction pattern suggests the formation of a spinel-like structure after Fe migration, consistent with our HRTEM result showing some ordered occupancy of Fe in both the tetrahedral and octahedral sites of the Na layer. The spinel-like structure suggested by TEM is also consistent with our synchrotron XRD refinement in Figure 9. These migrated Fe ions will largely impede the Na diffusion and make the compound electrochemically inactive.

For the binary transition metal systems with 50% Fe, including FM, FC, and FN, the structure is not completely reversible after the first electrochemical cycle once the initial charge goes beyond a certain level of Na extraction. In these binary transition metal compounds, TEM still shows a certain degree of local transition metal migration but less serious than in NaFeO₂ as illustrated in Figure 8B using FM as an example. As shown in Figure 10A using FC as an example, the interlayer distance after the first discharge shinks below the value of the pristine structure when charged above 4 V, suggesting the migration of transition metal into the sodium layer. This is consistent with our DFT simulation indicating that, if transition metal ions are located in the tetrahedral sites of the Na layer with sodium vacancies around the migrated TM ion in the sodiated structure, the interlayer distance shrinks below the pristine value.

In the ternary and quaternary transition metal systems, the structure evolution is largely reversible, as shown in Figure 4 for MFC and reported in previous literature for MFCN. After the first cycle, the structure transforms back to the pristine structure even these compounds were charged to 4.5 V, as shown in Figure 10B. No obvious transition metal migration in these ternary and quaternary transition metal systems is observed by HRTEM. We also confirmed with HRTEM the absence of migrated transition metal ions after an electrochemical cycle in the Fe-free systems such as in NaNiO₂, NaCoO₂, and NC. All the above experimental results combined suggest that Fe migrates less with decreasing Fe composition and that below around 30% Fe composition the Fe migration is fully suppressed.

We further validate the idea of composition-dependent Fe migration with DFT calculations. Figure 11 shows that an isolated Fe has a relatively high energy penalty above 700 meV to prevent its migration. On the other hand, the calculated energy penalty for Fe migration from the TM layer into the Na layer drops significantly when Fe starts to form local clusters. The inset in Figure 11 clearly shows that, when Fe clusters together, the distortion of a neighboring JT active Fe ion in the TM layer can accommodate the shortening of the Fe–O bonds in the tetrahedron associated with a migrating Fe. This cooperative local distortion significantly lowers the energy of tetrahedral Fe in the Na layer and thus greatly enhances the probability of the Fe migration. We notice that in the triangular lattice statistically the Fe ions start to form local clusters with edge-sharing FeO₆ octahedra beyond around 33% Fe composition. This Jahn–Teller related Fe migration explains the optimal Fe composition to be around 33% in Figure 3, beyond which the increasing probability of local Fe migration gradually deteriorates the electrochemical activity of the compound.

We expect the mechanisms of JT distortion assisted Na diffusion and Fe migration found in O₃-NaTMO₂ to be transferable to other sodium structures. In P2 layered compounds (Figure 2d), the possible evolution of P2 (Figure 2d) to O₂ (Figure 2c) or OP4 structures at a later stage of charge could potentially lead to similar issues of Fe migration into the Na layer. Our simulation demonstrates that the JT distortion assisted Fe migration into the tetrahedral site in the O₂ structure leads to a lower energy penalty when Fe cluster forms. Furthermore, for many other structures like beta-NaMnO₃ or channel structures, the JT distortion assisted Na diffusion mechanism will be active as long as the Na diffusion path involves an active site face-shared with a JT active transition metal octahedron (e.g., Fe⁴⁺O₆).

4. CONCLUSION

In conclusion, we uncovered a remarkable synergy between an esoteric piece of physics and practical aspects of Na mobility to create high capacity Na-cathode materials. The JT activity of Fe⁴⁺O₆ creates two competitive mechanisms which when carefully balanced can create compounds with high Na-storage capacity. On one hand, its ability, through the electronic
degeneracy of the $d_{1s}$ state, to buckle and distort Fe–O bonds facilitates the Na diffusion when the space along the diffusion pathway is limited, a critically limiting factor in the layered structure at the end of charge. The structural flexibility provided by the JT active transition metal oxygen octahedra effectively assists the Na to squeeze through the bottleneck in the diffusion pathway. On the other hand, the soft-mode behavior of Fe$^{4+}$O$_6$ can also assist Fe migration into the Na layer when too much Fe is present, an effect which is detrimental to the capacity. Our understanding here provides new guidelines to design high capacity and energy density Na intercalation cathode and anode compounds. It is truly exciting that JT-deformation finding its origin in symmetry rules that describe orbital energy degeneracy may find practical application in large-scale electricity storage devices.

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Notes

The authors declare no competing financial interest.

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