Atomic Re-arrangements and Energetics of Selected TM-oxides Caused by an Na-vacancy

Masoud Aryanpour and Hyo Sug Lee
Advanced Energy Lab, Samsung Electronics
1st Cambridge Center, Cambridge, MA-02142

The high cost and limited capacity of lithium-ion batteries have driven efforts to focus on or re-consider non-lithium cells. Lower prices could be achieved by replacing lithium, as the charge carrier in the electrodes, with other earth abundant elements, such as sodium [1]. However, since the chemistry of sodium is different from lithium, replacing Li with Na is not simple, but requires batteries to be redesigned and optimized to reach similar or better performances.

Layered sodium transition metal oxides (NaMO2) constitute an important class of materials among the categories of viable compounds. Although these compounds have been the topic of research for a few decades, their rich chemistry and range of tunable properties are not yet satisfactorily understood.

One common constraint in using the layered materials for intercalation chemistry is their possible irreversible structural deformations or phase transitions once deintercalation proceeds beyond a certain amount. For instance, the maximum reversible Na-deintercalation in NaVO2 occurs near 0.5 [2], and in NaMnO2 between 0.2-0.75 [3].The irreversible phase transitions impose a strong barrier preventing the extraction of the full theoretical capacity of the electrode material, thus reducing the battery performance.

Phase transitions caused by deintercalation are attributed to factors such as the gliding of oxygen layers, and moving of Na atoms between octahedral and tetrahedral sites. Here, we approach this problem by performing detailed computations on the fully and partially sodiated models of the first few transition metal compounds NaMO2 (M=Sc, Ti, V, Cr, Mn). Our analysis of the structure and energetics reveals both the similarities and the differences among those compounds. Patterns of re-ordering in the sodium layer and the bonding environment of the metal ions are determined and discussed.
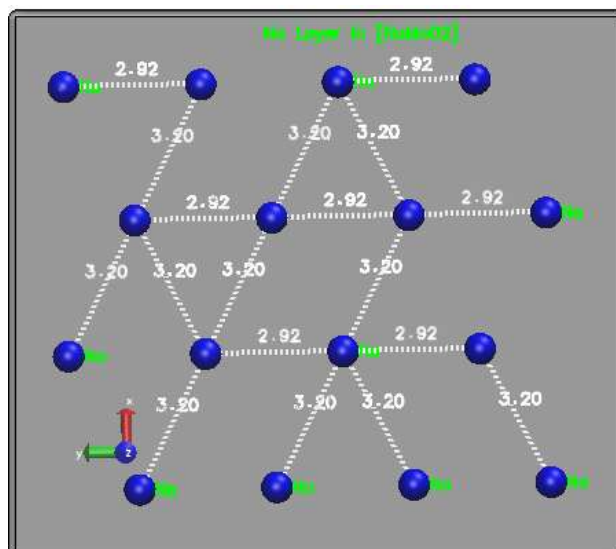

Figure 1 Long and short distances in the Na layer of NaMnO2

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