First Principles Investigation of the Electronic and Structure Changes for Ti-substituted Lithium Nickel Manganese Cobalt Oxide Cathodes

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Layered materials $Li_{1+z}(Ni_xMn_xCo_{1-2x})O_2$ or NMCs are attractive cathode materials for Li-ion batteries due to fast rate capability, high capacity and reduced Co content compared to $LiCoO_2$. Recently NMCs have been reported to have superior performance when Ti substitutes Co by 2-4%[1]. Among the improvements are better first cycle reversibility, increased capacity, and decreased capacity fading.

Using density functional theory (DFT) we investigated the electronic and structural changes resulting from the addition of Ti, in order to explain the performance enhancement.

The crystal structure is approximated to have local order belonging to the $P3_112$ space group, with results being compared to four structures that have the transition metals arranged randomly.

Structural results indicate that Ti substitution decreases the volume change upon deintercalation as observed from experimental results. Furthermore, there is an increase in the spacing of the O-Li-O layer before and after delithiation, which facilitates lithium deintercalation, allowing more material to become electro-active.

Analysis of the electronic structure suggest that in order to charge compensate for the aliovelant Ti substitution a nearby Mn localizes a polaron as can be seen in Fig. 1.

We will also investigate how the electronic structure changes upon delithiation and the change in energy barrier for lithium removal.

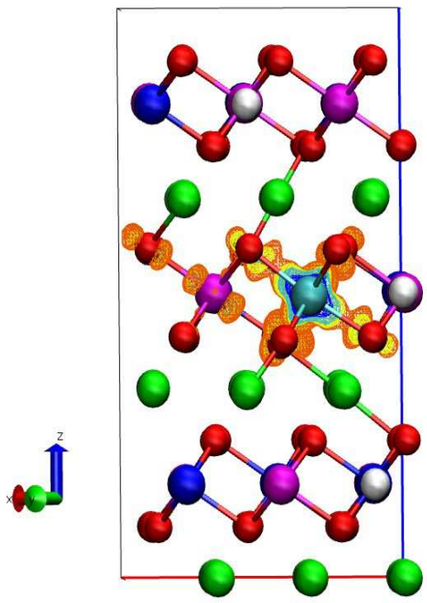

Fig. 1 Charge density difference map between the Ti substituted and unsubstituted structures.

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References

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