# Structure, Stability, and Charge/Discharge Behavior of Li(Ni,Mn)O$_2$

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Layered oxides are particularly attractive for us as cathodes in rechargeable lithium batteries. $LiCoO_2$ and $LiNiO_2$ based materials have been explored extensively, but both suffer from instability towards oxygen loss in the charged state. Layered $LiMnO_2$ irreversibly transforms to a spinel structure due to the high mobility of the Mn^{3+} ion [1]. First principles calculations have indicated that the Mn^{4+} ion is not mobile [1]. Hence, the remarkable stability of layered $Li(Ni_{0.5}Mn_{0.5})O_2$ [2] is due to the stable +4 valence of Mn in this material. We have computationally investigated this material and have found electron density and bond length changes to be consistent with an oxidation of Ni^{2+} to Ni^{4+} upon Li removal. The Mn ion is +4 at all times and therefore immobile [3]. The figure below shows the electron spin density change upon lithiation of $(Ni_{0.5}Mn_{0.5})O_2$. The white regions around Ni show a strong electron gain upon Li insertion while Mn is mostly unchanged. The double redox process on Ni, offers interesting materials engineering prospects as it may make it possible to substitute other inactive materials for Mn^{4+}
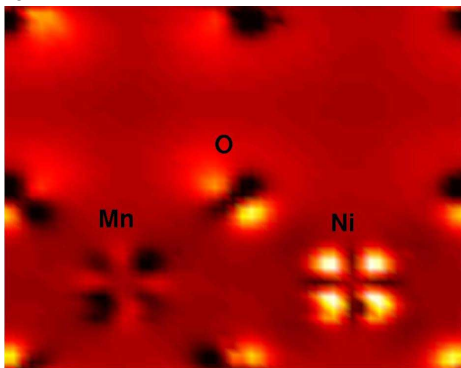
Electron density change when Li is inserted into $(Ni_{0.5}Mn_{0.5})O_2$. Ni^{4+} is reduced to Ni^{2+}

The figure shows the electron spin density change upon lithiation of $(Ni_{0.5}Mn_{0.5})O_2$. The white regions around Ni show a strong electron gain upon Li insertion while Mn is mostly unchanged. The double redox process on Ni, offers interesting materials engineering prospects as it may make it possible to substitute other inactive materials for Mn^{4+}

Using first principles calculations, coupled to the ternary cluster expansion methods, we will present a detailed analysis of the structure of the stoichiometric $Li(Ni_{0.5}Mn_{0.5})O_2$ and Li excess material. The Li_2MnO_3 regions that may form when Li excess is present in the transition metal layer have been pointed at to explain the high cycling stability of this material. We will discuss the origin and stable size of these regions.

By combining calculations of the site energy for Li in the Li-layer and transition metal layer with NMR results [4], we will discuss whether it is possible to remove the Li from the transition metal layer.

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2. Z. Lu, D. D. MacNeil, J. R. Dahn, *Electrochem. and Sol. St. Lett* **4**, (2001) A191-A194.
3. Reed, G. Ceder, *Electrochemical and Solid State Letters* **5**, (2002) A145-A148.
4. C. Grey, unpublished work.