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Effects of Delithiation on Lithium Manganese Oxides: A Combined DFT and NMR Based Study

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Lithium manganese oxide ($LiMnO_2$) has generated significant interest as a low cost and low toxicity alternative cathode material to the widely used $LiCoO_2$ (1-4). It can be produced in two polymorphic forms, the thermodynamically stable orthorhombic phase *o*-$LiMnO_2$ (*Pmmn*) and the monoclinic phase *m*-$LiMnO_2$ (*C/2m*) first synthesized by Armstrong *et al* (5,6). It is known that on initial delithiation both phases undergo an irreversible phase transformation resulting in significant capacity loss on first discharge (2,3). The exact transformation mechanism differs between the polymorphs, but relies on the large scale rearrangement of Mn ions within the structures. After extended cycling, a 'spinel like' phase is observed in both materials (2,3)

Solid state NMR has previously been shown to be an effective tool in the determination of local structure in cathode materials (6,7). However the interpretation of the spectra so obtained is often challenging, as electron-nuclear interactions within these transition metal containing paramagnetic solids can result in significant peak broadening and loss of resolution. Solid-state density functional theory calculations have proved to be a useful aid to the interpretation of these complex spectra (8,9). The present study applies periodic hybrid density functional theory calculations to assess the magnetic structures and couplings, and the hyperfine shifts of the stoichiometric and partially delithiated *o*-$LiMnO_2$ and *m*-$LiMnO_2$ phases. A detailed knowledge of the magnetic couplings in these materials is a prerequisite of the theory scaling the computed hyperfine parameters into the paramagnetic regime at which the NMR spectra were recorded. Using a recently published bond decomposition method (10), the individual Li-O-Mn bond pathway contributions were calculated, permitting for a detailed interpretation of the ^{6}Li and ^{7}Li NMR spectra in terms of local coordination environments.

The following topics are addressed:

- How do the magnetic structures of *o*-$LiMnO_2$ and *m*-$LiMnO_2$ phases vary?
- How does delithiation affect the magnetic structure of $LiMnO_2$?
- Do hybrid DFT calculations provide a sufficiently accurate model of the solid state NMR spectra of lithiated and delithiated $LiMnO_2$?

The experimental magnetic susceptibilities of both stoichiometric *o*-$LiMnO_2$ and *m*-$LiMnO_2$ phases were found to deviate from ideal Curie-Weiss behavior in the experimental temperature regime T~320K. The nature of the magnetic ordering was found to vary between the structures displaying strong 2D antiferromagnetic correlations (*o*-$LiMnO_2$) and 1D antiferromagnetic correlations (*m*-$LiMnO_2$). The introduction of Mn^{4+} electronic defects into the structure was found to disturb the local antiferromagnetic correlations and to significantly alter the equilibrium magnetizations of neighboring Mn^{3+} sites. Having calculated the relevant magnetic couplings, the hyperfine scaling factors and individual M^{3+}-O-Li and M^{4+}-O-Li bond pathway contributions were determined, as shown for Mn^{3+} in Fig 1. These shifts may then be directly compared to NMR spectra of cycled $LiMnO_2$ to assess the local environments present upon first delithiation.

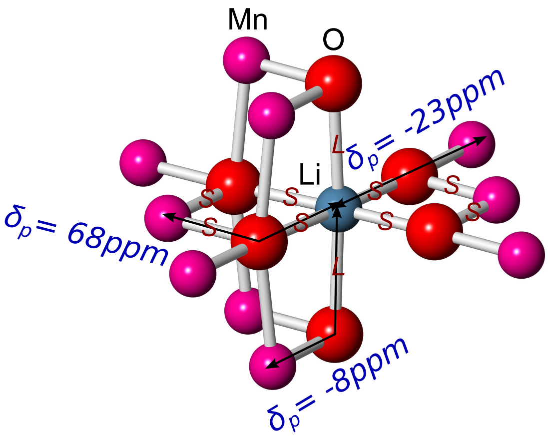

Fig. 1. ^{6}Li Li-O-Mn bond pathway Fermi Contact shift contributions in stoichiometric *o*-$LiMnO_2$ using the B3LYP hybrid functional. L and S represent long and short metal-oxygen bond distances respectively.

References

1. J. N. Reimers, E. W. Fuller, E. Rossen and J. R. Dahn, *J. Electrochem. Soc.,* **140**, 3396 (1993).
2. R. J. Gummow, D. C. Liles and M. M. Thackeray, *Materials Research Bulletin,* **28**, 1249 (1993).
3. G. Vitins and K. West, *J. Electrochem. Soc.,* **144**, 2587 (1997).
4. R. A. Armstrong and P. G. Bruce, *Nature,* **381**, 499 (1996).
5. R. Hoppe, G. Brachtel and M. Jansen, *Z. Anorg. Allg. Chemie.,* **417**, 1 (1975).
6. C. P. Grey and N. Dupre, *Chemical Reviews-Columbus* **104**, 4493 (2004).
7. C. P. Grey and Y. J. Lee, *Solid State Sciences,* **5**, 883 (2003).
8. J. Kim, D. S. Middlemiss, N. A. Chernova, B. Y. X. Zhu, C. Masquelier and C. P. Grey, *J. Am. Ceram. Soc.,* **132**, 16825 (2010).
9. R. J. Clément, A. J. Pell, D. S. Middlemiss, F. C. Strobridge, J. K. Miller, M. Whittingham, L. Emsley, C. P. Grey and G. Pintacuda, *J. Am. Ceram. Soc.,* **134**, 17178 (2012).
10. D. S. Middlemiss, A. J. Ilott, R. J. Clément, F. C. Strobridge and C. P. Grey, *Chemistry of Materials* **25**, 11794 (2013).