Contribution ID: **100** Type: **Poster**

First Principles Study on the Effect of Lithiation on the Spinel LixMn2O4 Structure using CASTEP and ONETEP Codes.

Despite the poor performance demonstrated by layered and spinel cathode materials during cycling, their composite cathode material exhibits enhanced performance. Such distinction qualifies the composite electrode material as one of the promising cathode material to potentially accelerate the rate performance of lithium ion batteries and meet the high energy needs posed by the exponential growth in technology. A vast number of studies have focused on improving the specific capacity of these layered-spinel composites. However, the internal structural changes responsible for the noted enhanced performance of these materials during the discharge (lithiation) process are not yet fully understood. As such, we perform the spin polarised density functional theory DFT calculations using the CASTEP and the ONETEP (linear-scaling DFT) codes embedded in Material Studio to elucidate the effect of lithiation on the electronic structure of spinel LixMn2O4. The electronic structure of spinel LiMn2O4, the delithiated-Mn2O4 and the lithiated-Li2Mn2O4 spinel were investigated the generalized gradient approximation (GGA). The electronic structure analysis depicted semiconducting properties for delithiated-Mn2O4 with a band gap of ~0.65 eV whilst LiMn2O4 and lithiated-LiMn2O4 were found to be conductors. Furthermore, it was found that less amount of energy is required for electrons to occupy the eg orbitals of LiMn2O4 than of the eg orbitals of the delithiated-Mn2O4. This indicates that lithiation favours Mn3+ which is in line with what was observed experimentally. The LiMn2O4 DOS calculated with ONETEP clearly distinguish dx2-y2 and dz2 orbitals. The dx2-y2 orbital is filled and dz2 orbital is empty which is consistent with the dual-existence of Mn4+ and Mn3+. We also performed a scaling test with ONETEP on supercells of LiMn2O4 spinel structure and the best performance was achieved by ensuring that the product of MPI processes and OMPI_THREADS are equivalent to the requested number of cores in the Lengau cluster. Our current findings forms a basis for moving from traditional DFT to linear-scaling DFT which will enable the study of the electronic properties of Li-Mn-O layered-spinel nanoarchitectures at larger scales.

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Session Classification: SIG Poster

Track Classification: SIG Seminar: Chemistry, Material Science and Health Science