ABSTRACT

CORRELATION OF POINT DEFECTS IN LITHIUM-RICH LAYERED CATHODE MATERIALS FOR LITHIUM-ION BATTERY APPLICATIONS

By

Christine James

Adviser: Dr. Yue Qi

The layered excess lithium transition metal oxides of the form: $x\text{Li}_2\text{MnO}_3-(1-x)\text{Li(Ni,Co,Mn)}\text{O}_2$ have shown have promising higher capacities of $>200\text{mAh/g}$ compared to other common cathode materials for lithium-ion batteries (LIBs), such as LiCoO$_2$, LiFePO$_4$ and LiMn$_2$O$_4$. The high capacity is, at least in part, due to the removal of oxygen that activates the material during the first cycle. However, the amount of oxygen released and the role of the oxygen vacancies are still not very well understood. Therefore, this work takes an atomic level computational approach using density functional theory (DFT) calculations to explore the impact of oxygen vacancies and the correlated effects on voltage, capacity, lithium diffusion, chemical strain, dopants and electrolyte decomposition for non-stoichiometric Li$_{2-x}$MnO$_3$. 
It is shown here that the oxygen vacancies can decrease the formation energy of lithium vacancies and thus improve the capacity of Li$_{2-x}$MnO$_{3-δ}$. However, it was also found that the lithium migration energy barrier near oxygen vacancies increases, causing a decreased rate capability of these materials. A model of the chemical expansion in the material was also developed which showed that the oxygen vacancies and lithium vacancies are highly correlated causing the associated chemical expansion to not be a linear sum of the individual vacancy types. Additionally, the impact of Si and Al dopants on the amount of oxygen vacancies and possibly the capacity of the materials was also explored. The silicon was shown to decrease the oxygen vacancy formation energy in neighboring octahedral to the silicon, thus activating the manganese and increasing the capacity of the materials, consistent with experimental observations. Lastly, the presence of oxygen vacancies on the surface was shown to have an impact on the adsorption and decomposition of a commonly used electrolyte solvent, ethylene carbonate (EC). Overall, the oxygen vacancies generated in the lithium-excess layered cathode materials are shown to have a very highly correlated impact on lithium, dopant and electrolyte-surface interactions which therefore can significantly impact battery performance and life.