Non-equilibrium phases and cation mixing in Li-rich rock salt derived positive electrode materials

William R. Brant[a]**, Ashok Sreekumar Menon**[a]**, Olof Gustafsson**[a]

[a] Department of Chemistry – Ångström Laboratory, Uppsala University, Sweden
email: william.brant@kemi.uu.se

Often within the domain of inorganic chemistry synthesis, focus is placed on obtaining ideal materials under equilibrium conditions in order to accurately study specific phenomena. However, while extremely valuable, these studies often do not represent the real structures which are formed when materials are utilized in an application or a device. This is particularly true in the case of electrode materials for rechargeable ion batteries where it is notoriously difficult to predict what phases are formed as electrochemical extraction of charged ions proceeds far from the thermodynamically stable configuration of a material. In this contribution I will present results from two different Li-rich rock salt derived oxide systems, $Li_{1+x}TM_{1-x}O_2$ ($0 \leq x \leq ⅓$, *TM*= Mn, Ni and Co) and Li_2VO_2F. Both compounds do not exhibit ideal structures and the properties are intricately tied to the local cation configurations generated via non-equilibrium phase transitions.

The structure of lithium rich layered phases, $Li_{1+x}TM_{1-x}O_2$, is complicated by disorder which manifests over multiple length scales. At the atomic scale Li and TM cations can order forming a superstructure, this superstructure allows for the appearance of stacking faults which extends beyond the unit cell. Finally, phase segregation of different ordered domains can occur on the nano to micron length scale. The disorder present can vary significantly even for a single composition depending upon the specific synthesis conditions. These multiple metastable phases which exhibit near identical average structures has confounded research into these materials, hindering an understanding of their anionic redox properties.

Li_2VO_2F is a metastable disordered rock salt structure which shows promise as a high capacity cathode material. However, significant capacity fade during electrochemical cycling impedes its implementation. Understanding the origin of the capacity fade is challenging due to the reconstructive phase transition that occurs upon lithium extraction. One might expect that over time the structure converts to more thermodynamically stable structures that are less electrochemically active. However, using a combination of X-ray and neutron diffraction, we demonstrate that this is not the case and that other crystalline metastable phases stabilise and grow over successive electrochemical cycles.