

In-operando X-ray Diffraction based study of Lithium rich layered oxides, $\text{Li}_2\text{Ru}_{1-x}\text{TM}_x\text{O}_3$, at high-rate charging conditions

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Lithium rich layered compounds have recently garnered attention as a probable cathode material for Electric vehicles. This is mainly due to the fact that these materials exhibit capacities exceeding 250 mAh g^{-1} . Which can be attributed to the ability of this class of compounds to exploit both the traditional transition metal based cationic redox and an oxygen based anionic redox reaction. Despite their exceptional energy storage capacities early studies have indicated that these materials suffer from drawbacks such as voltage decay on cycling, and rapid degradation at high current rates [1]. Previous results have mainly focussed on studying these compounds in an idealised state with cycling rates less than $C/10$, but in order for these materials to be useful for realistic applications it is necessary that the high current performance be understood and improved drastically[2, 3]. In this work, our main focus is to synthesize variants of the compound Li_2RuO_3 by systematically substituting Ru with a range of 3d and 4d Transition metals and conduct *in-operando* X-ray diffraction measurements at incremental charging rates to study the exact nature of structural change occurring in these systems.

$\text{Li}_2\text{Ru}_{1-x}\text{TM}_x\text{O}_3$ was synthesized using a high temperature solid state route. Field Emission scanning microscopy was used to confirm the absence of any morphological effects that might affect the total capacity or high rate performance. X-ray diffraction patterns were collected for the pristine and substituted powders to confirm substitution and phase purity. *In-operando* cells were constructed using modified CR2016 coin cells and the X-ray diffraction measurements were carried out at the High Energy Diffraction beamline (28 ID) at the National Synchrotron Lightsource II at Brookhaven National Lab.

The results of our experiments indicate that the choice of the transition metal has an effect on both the capacity (mAh g^{-1}) and the anionic redox potential. As the material undergoes the first charge process a significant phase change or permanent distortion was observed at low current rates. This distortion is expected to be the trigger mechanism to couple the transition metal and oxygen based redox reaction[4]. At higher rates, it was noted that the phase change did not take place effectively thus leading to oxygen evolution instead of a stable anionic redox reaction. The results obtained contribute significantly towards a better understanding of Lithium rich layered oxides. Such tests are extremely valuable to realistically apply High capacity cathodes such as Lithium rich layered compounds for meeting energy storage needs of an electric vehicle based transport system.

References:

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