

Correlation of Structural Changes in Li Rich Cathode Materials to Their Electrochemical Performance



S. Aryal[#], E. V. Timofeeva and C. U. Segre

Illinois Institute of Technology, Chicago, Illinois, USA

[#]saryal@hawk.iit.edu

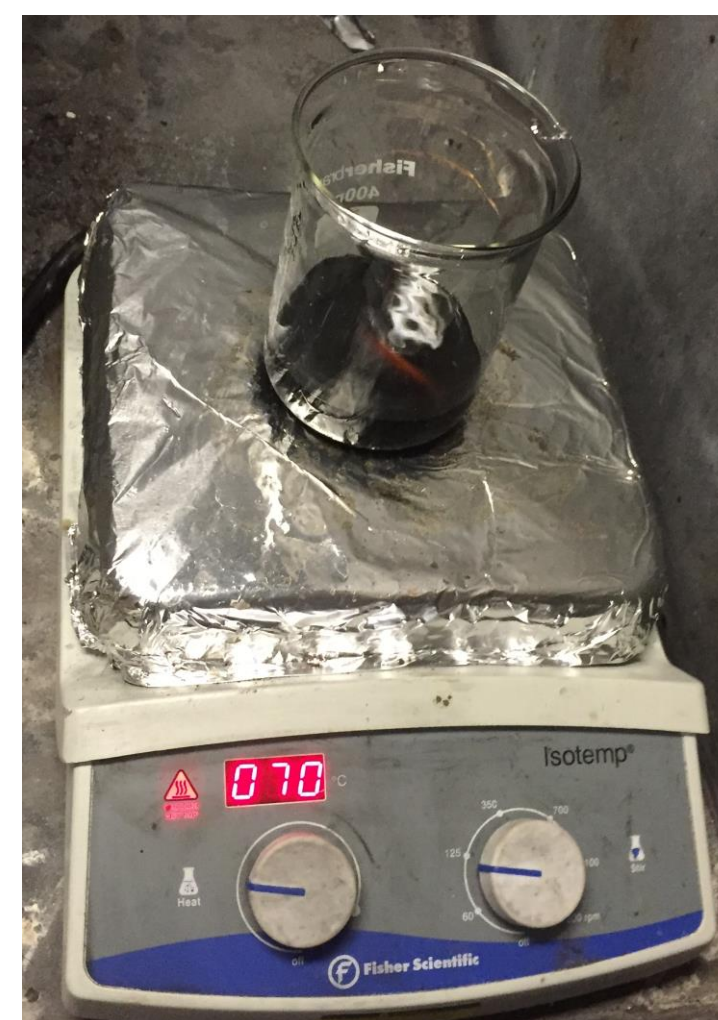
Li rich cathodes, why?

Li rich oxides $x\text{Li}_2\text{MnO}_3(1-x)\text{LiMO}_2$, (M = Ni, Co, Fe, Al, Cr etc.) are structurally integrated composites of two phases: monoclinic C2/m Li_2MnO_3 phase and trigonal R-3m LiMO_2 phase[1]. The reported performance of $\text{Li}[\text{Li}_{1/6}\text{Fe}_{1/6}\text{Ni}_{1/3}\text{Mn}_{1/2}]\text{O}_2$ cathode is 282 mAh/g at first discharge [2], which is double the capacity of LiCoO_2 cathode currently utilized in commercial Li ion batteries. However, before those cathodes could replace traditional materials, two issues with Li-rich cathodes need to be resolved: gradual capacity loss (71% of capacity after 50 cycles [2]), and drop off in discharge voltage upon cycling (3.57 V of midpoint voltage at the 4th discharge decreases to 3.38 V at the 100th discharge [3]). Both degradation phenomena are closely related to structural changes within the cathode materials during cycling. In this poster we will report on the experimental study of evolution of structure as the function of cycle number, charge modes and composition in low cost, Li rich, Co free $\text{Li}_{1+x}(\text{Mn}_{5/8}\text{Ni}_{2/8}\text{Fe}_{1/8})_{1-x}\text{O}_2$, $0.1 < x < 0.3$ layered-layered oxide cathodes by using XRD, SEM and XAS techniques.

Synthesis & Characterization of $\text{Li}_{1.2}(\text{Mn}_{0.5}\text{Ni}_{0.2}\text{Fe}_{0.1})\text{O}_2$

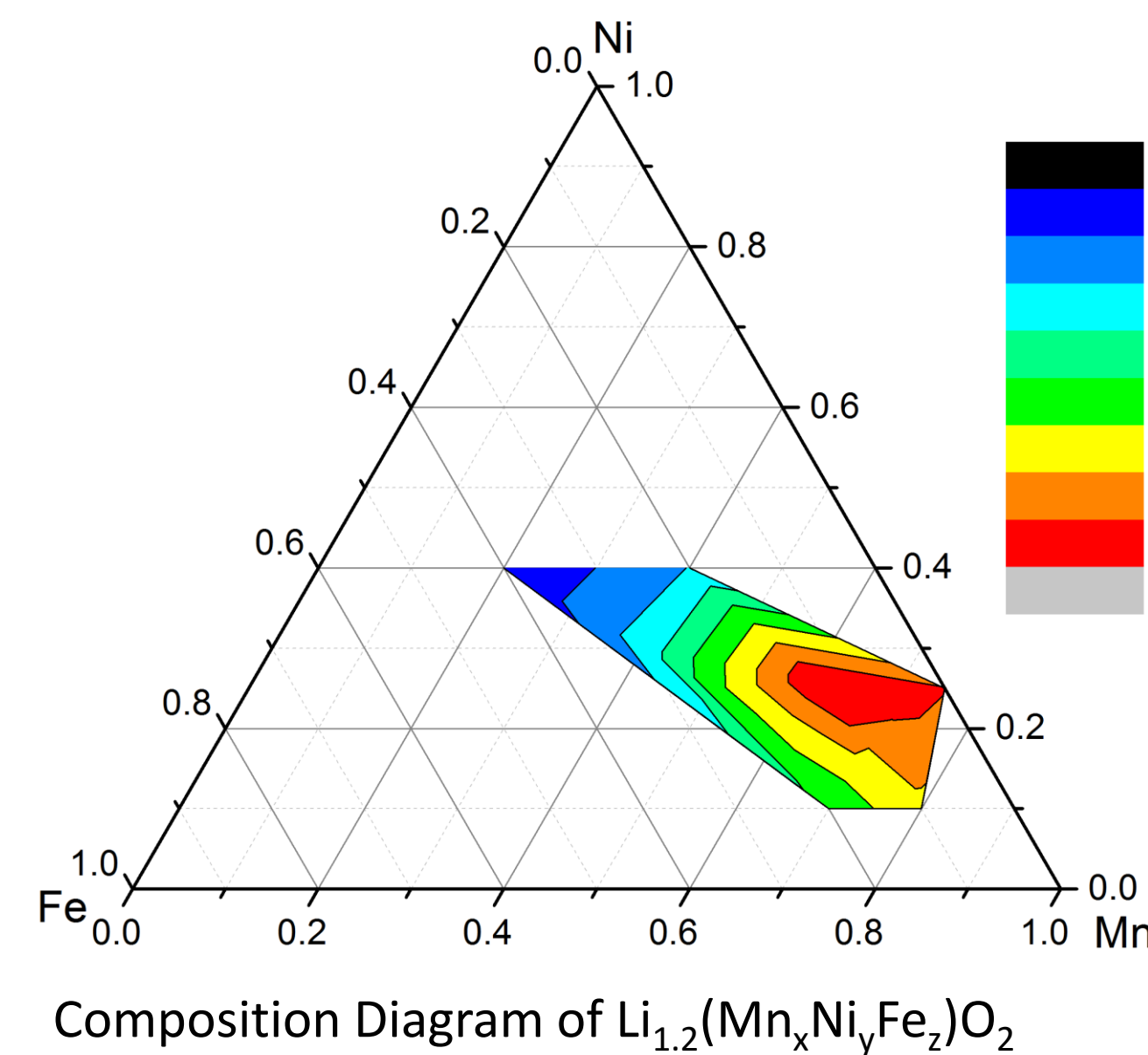
Sol gel synthesis: easy & efficient

- Dissolving precursors
- Gel & dry foam forming
- Decomposition and annealing



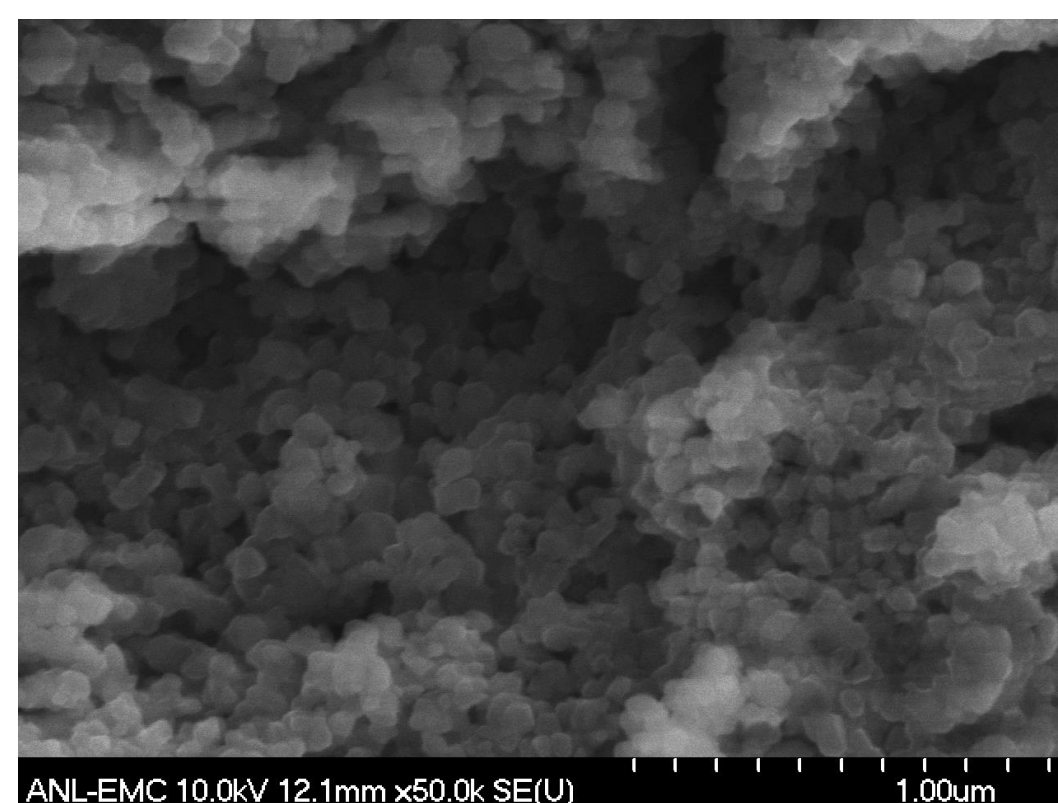
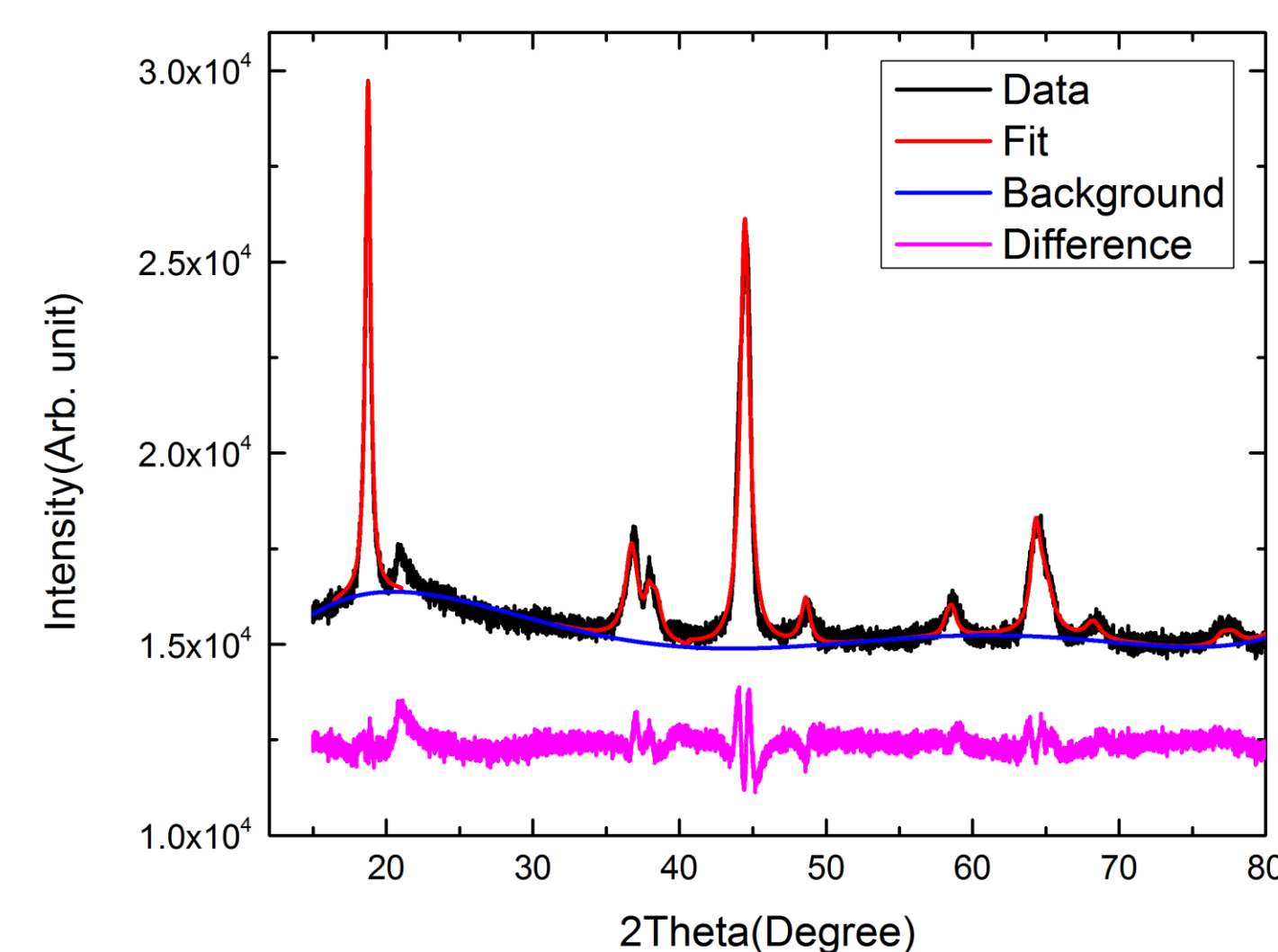
Best values of x, y, & z
 $0.45 < x < 0.55$
 $0.15 < y < 0.25$
 $0.05 < z < 0.15$

Best sample:
 $\text{Li}_{1.2}(\text{Mn}_{0.5}\text{Ni}_{0.2}\text{Fe}_{0.1})\text{O}_2$

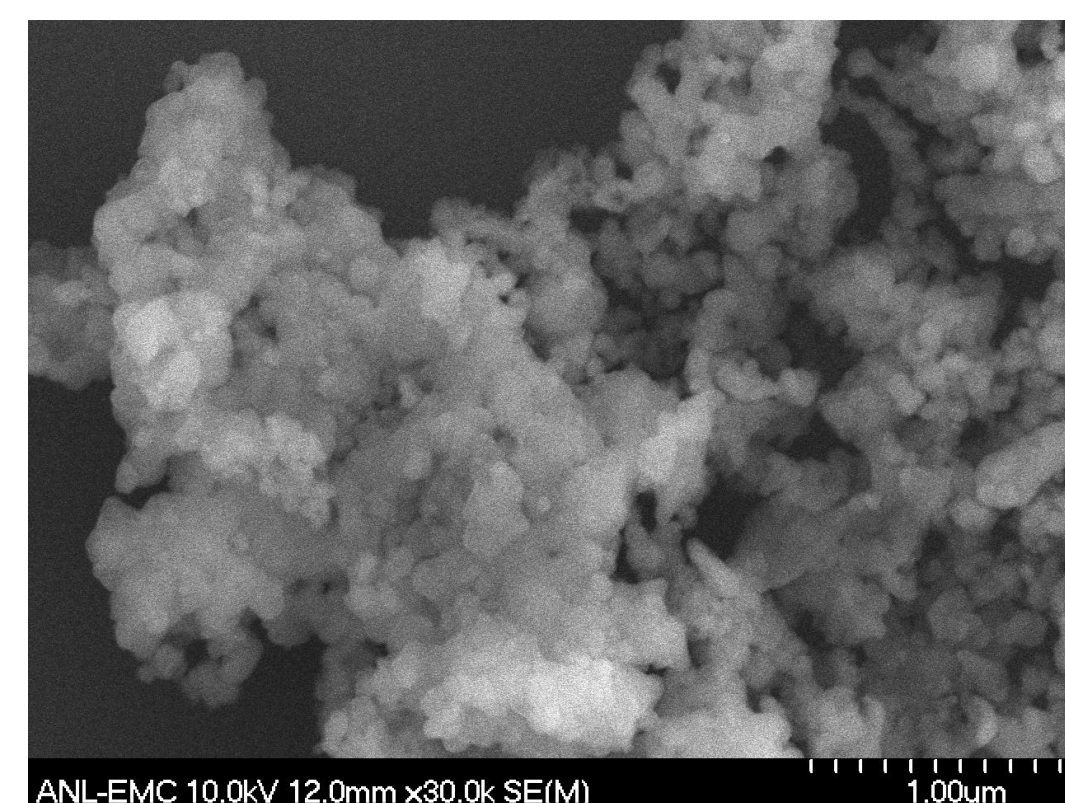


Rhombohedral phase, except the small peak around 20 degree of 2θ

Rhombohedral R-3m Rietveld refinement
 $a = b = 2.8738 \text{ \AA}$ $c = 14.2712 \text{ \AA}$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$
 Reduced $\chi^2 = 3.908$, $wR_p = 0.0157$, $R_p = 0.0114$



$\text{Li}_{1.2}(\text{Mn}_{0.4}\text{Ni}_{0.2}\text{Fe}_{0.2})\text{O}_2$
 50 to 200 nm uniform spherical like particles



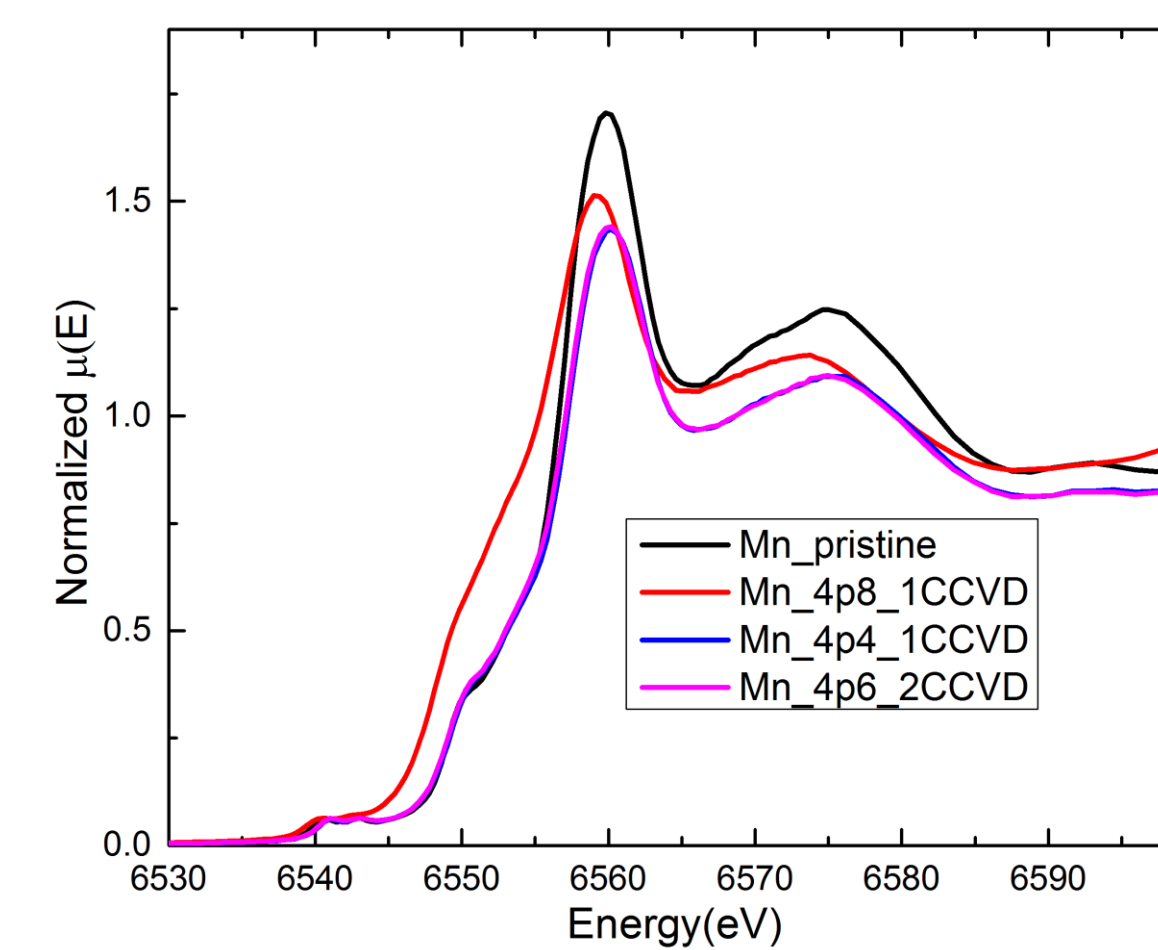
$\text{Li}_{1.2}(\text{Mn}_{0.5}\text{Ni}_{0.2}\text{Fe}_{0.1})\text{O}_2$

Acknowledgement

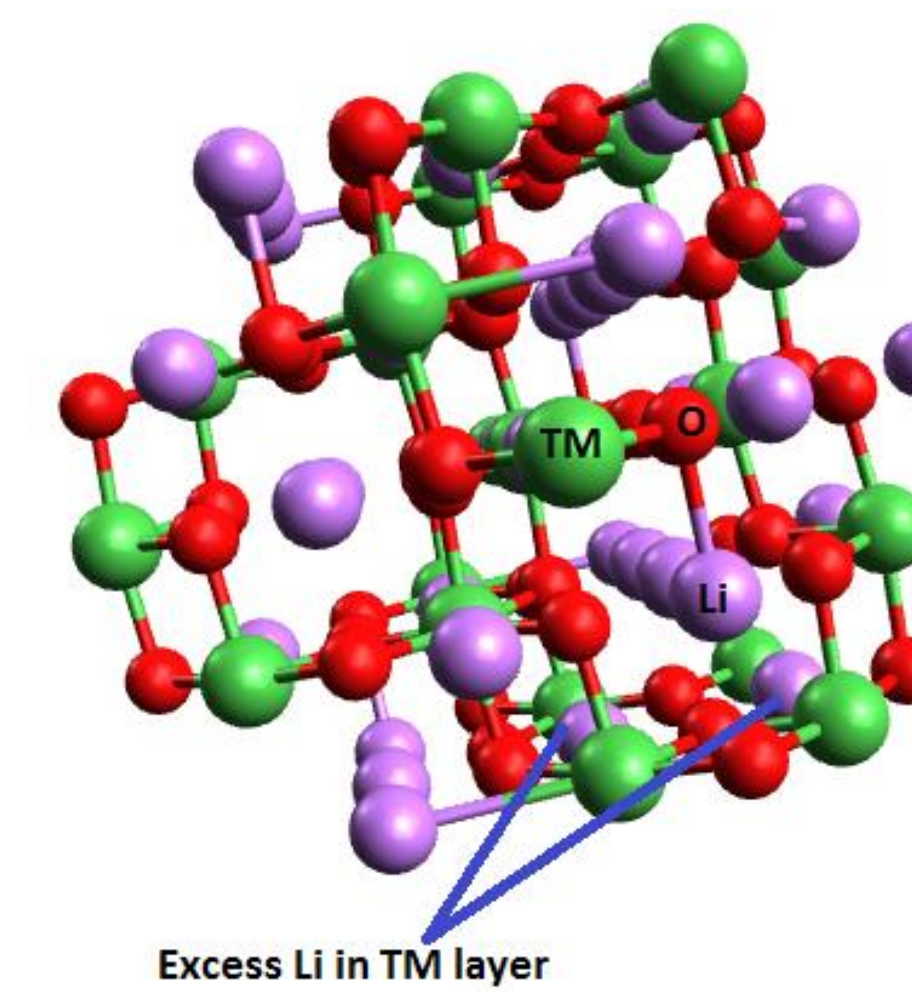
SEM is conducted at electron microscopic center at Argonne National Laboratory. XAS data are collected in MRCAT facility of Advanced Photon Source, sector 10 BM beamline at the Argonne National Laboratory. Argonne National Laboratory is operated by the U. S. Department of Energy, Office of Sciences, Office of Basic Energy Sciences.

Objective

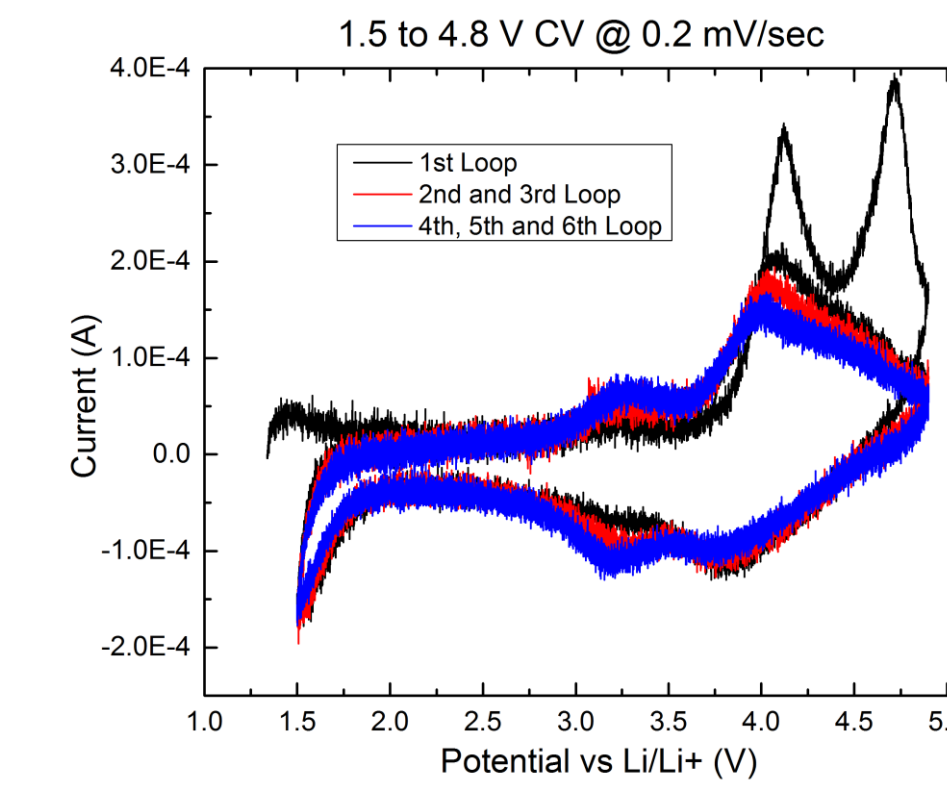
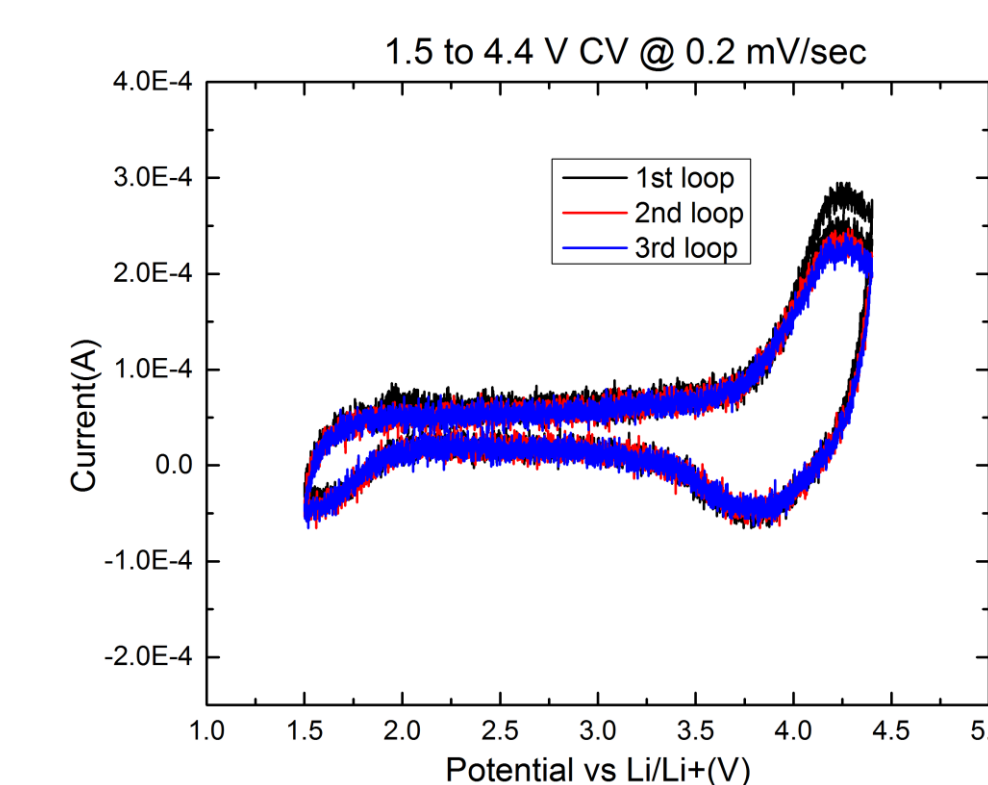
This study estimates and verifies the optimized fractional composition of Mn, Ni, & Fe in Li rich composite oxide cathode for better electrochemical performance from similar previous works. The excess Li is the main cause of formation of extra monoclinic phase, which is electrochemically inactive alone but if it is complexed with the rhombohedral phase & charged to > 4.5 V, it gets activated to add up the electrochemical output. So, this research aims to vary the content of excess Li to check the contribution of monoclinic phase and correlate the structural evolution with electrochemistry.



XANES at Mn edge:
 No change on charging up to 4.6 V but significant reduction at Mn edge on charging to 4.8 V

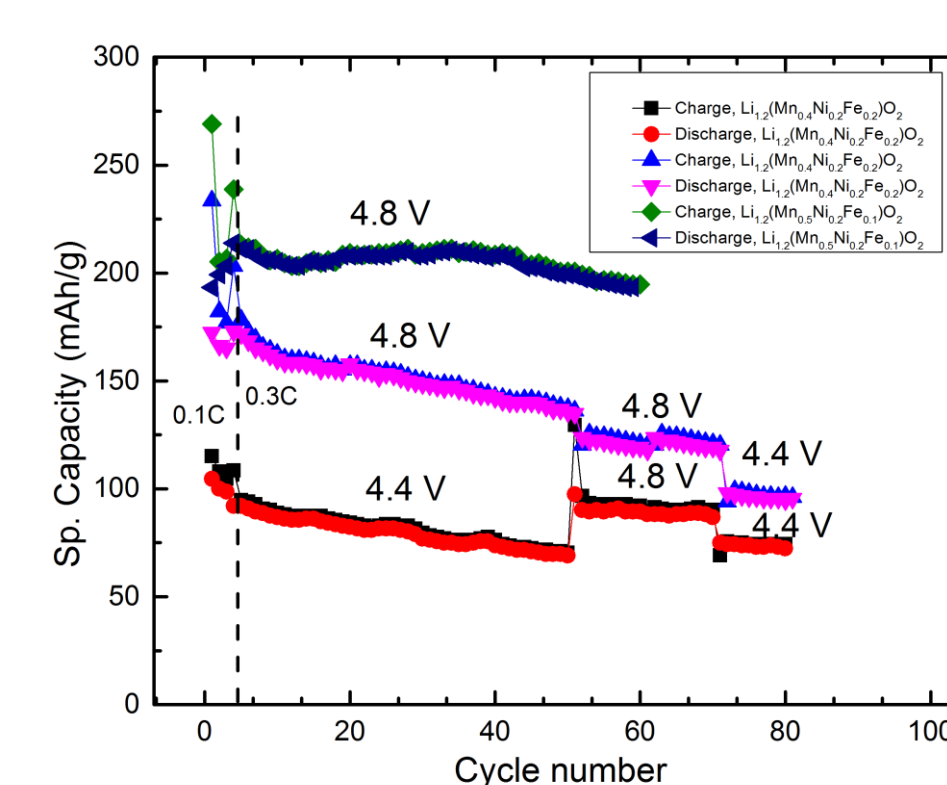
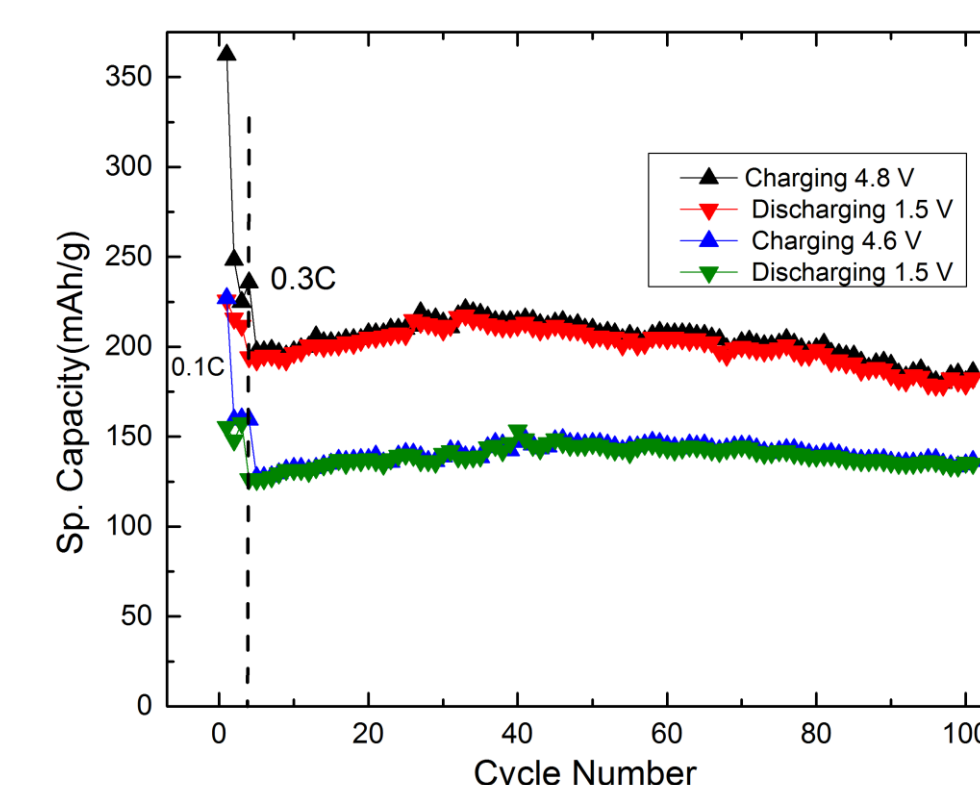


Electrochemistry



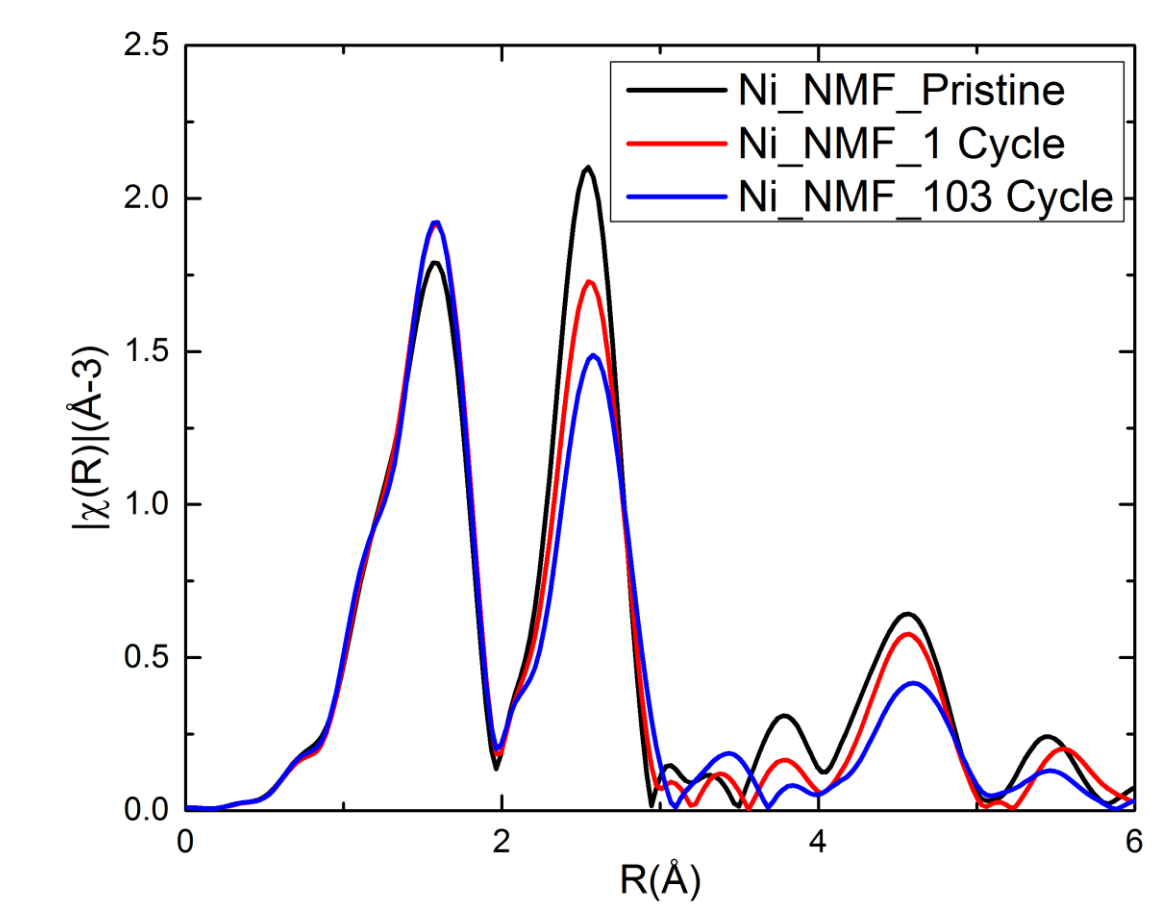
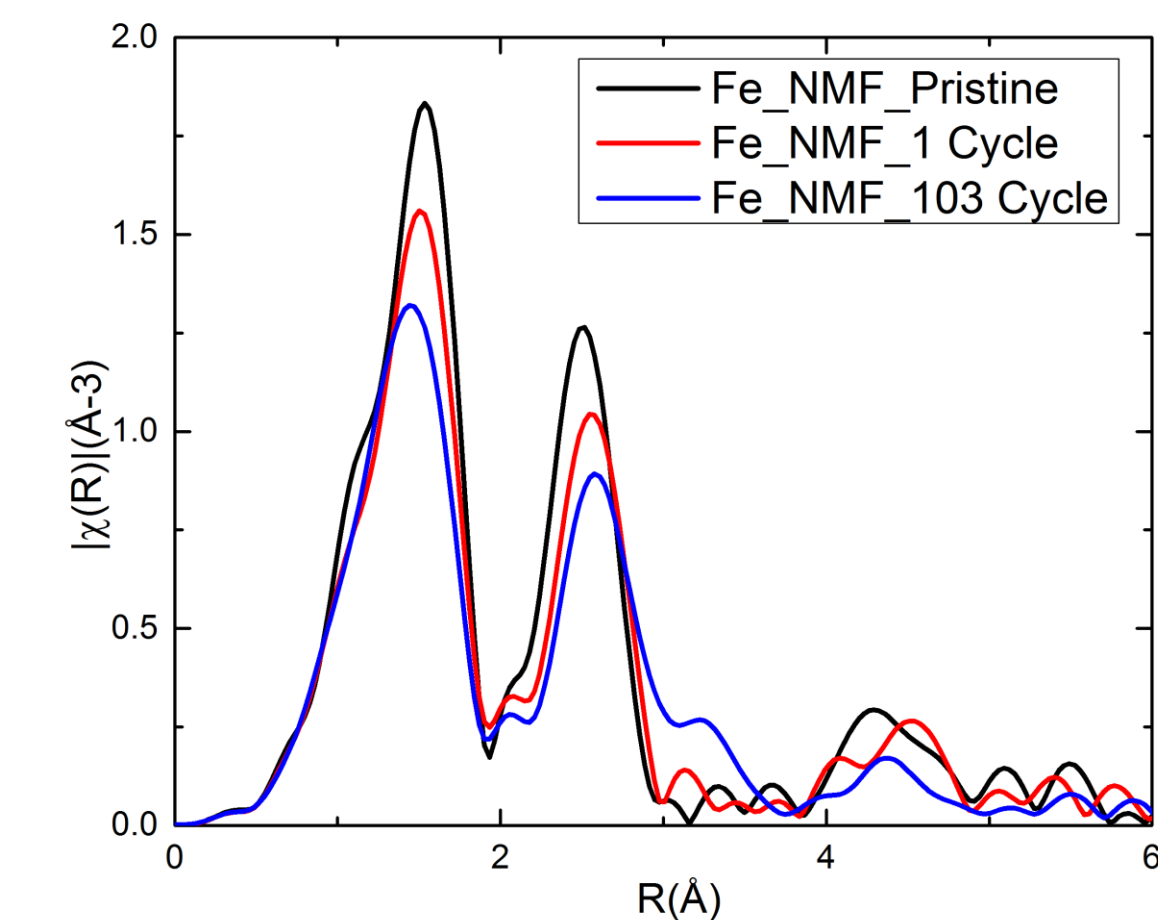
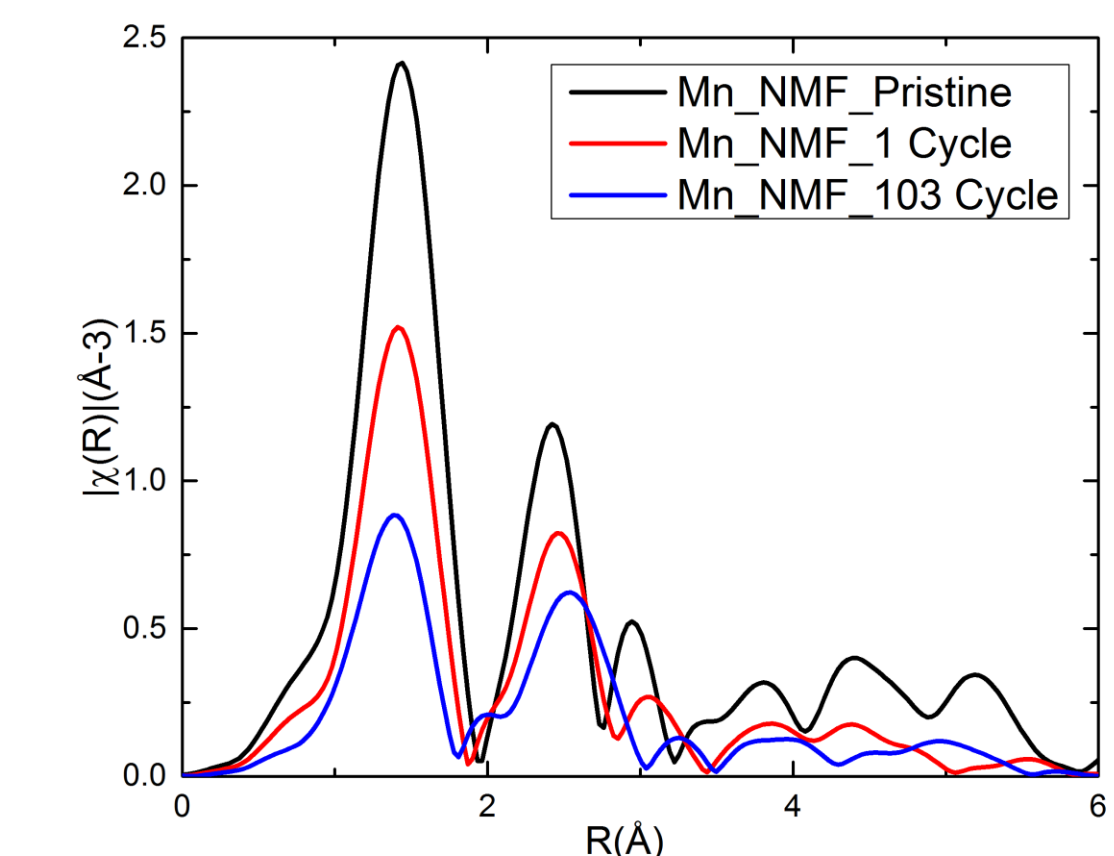
Activating Li_2MnO_3 : Li_2MnO_3 ($>4.6 \text{ V charging}$) = $\text{Li}_2\text{O} + \text{MnO}_2$

- At ~ 3 V: Mn^{3+} oxidation & reduction, So NMF is superior than NMC
- At ~ 4 V: $\text{Ni}^{2+}/\text{Fe}^{3+}$ oxidation & reduction



- 226 mAh/g highest discharge capacity 80% retention after 101 cycles
- Stable specific capacities
- Competitive with published results[2]
- >4.6 V charging to activate Li_2MnO_3 for higher capacity
- Fractional composition of Mn, Ni & Fe is justified

X-ray absorption spectroscopy measurement



Noticeable changes in the XAFS spectra at Mn and Fe edges are the direct evidences of structural changes upon cycling.

Summary

The qualitative & quantitative measurement of the structural change can be estimated from XRD & XAS data analysis & fitting. The XAS data of the electrodes charged to 4.4, 4.6 & 4.8 V are especially important To study the contribution of monoclinic phase in tis complex oxide cathode.

References

1. Thackeray, Michael M., et al. *Journal of Materials Chemistry* 17.30 (2007): 3112-3125.
2. Zhao, Taolin, et al. *ACS applied materials & interfaces* 6.24 (2014): 22305-22315.
3. Zheng, Jianming, et al. *Nano letters* 13.8 (2013): 3824-3830