

A comparative study of anionic redox chemistry in 3d and 5d transition metal-based Li-rich cathode materials by synchrotron X-ray techniques

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Lithium-rich layered oxides, $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ ($M = \text{Ni}, \text{Co}, \text{Mn}$) have attracted significant attention as cathode materials for lithium-ion batteries in recent decades because of their promising electrochemical capacity, up to 300 mAh/g. However, this class of cathode materials has several critical problems as well including, large irreversible capacity loss in the first cycle mainly due to the oxygen release at the end of charge, insufficient cycling performance, side reactions with electrolyte at high cut-off voltage and, migration of transition metal from transition metal layer to lithium layer that leads to voltage decay during cycling.^[1] In order to eliminate some of these drawbacks, $\text{Li}_2\text{M}_{1-x}\text{Sn}_x\text{O}_3$ ($M = \text{Ru}, \text{Ir}$) type lithium-rich cathode materials have been recently designed by taking advantage of 4d, 5d transition metals.^[2] These materials are structurally related to the 3d transition metal-based traditional lithium-rich cathode materials. Studies on these new materials, using X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) show a cumulative cationic ($\text{M}^{n+} \rightarrow \text{M}^{(n+1)+}$) and anionic ($\text{O}^{2-} \rightarrow \text{O}_2^{2-}$) reversible redox process.^[2,3] However, the structural changes in Li-rich cathode materials during anionic redox process are very complex and still remain a controversial issue that needs further investigation.

In this study, $\text{Li}_{1.167}\text{Mn}_{0.58}\text{Ni}_{0.25}\text{O}_2$ and $\text{Li}_2\text{Ir}_{0.75}\text{Sn}_{0.25}\text{O}_3$ were synthesized and these cathode materials delivered a capacity of 287 mAh/g and 214 mAh/g respectively in the first charge. Synchrotron radiation-based high-resolution X-ray powder diffraction (HRPD) and hard & soft X-ray absorption spectroscopy (XAS) along with several electrochemical characterization techniques were utilized to investigate the redox reaction in $\text{Li}_{1.167}\text{Mn}_{0.58}\text{Ni}_{0.25}\text{O}_2$ and $\text{Li}_2\text{Ir}_{0.75}\text{Sn}_{0.25}\text{O}_3$ cathodes in terms of local and bulk crystal structural changes. XAS data shows that Ni is the only electroactive metal in $\text{Li}_{1.167}\text{Mn}_{0.58}\text{Ni}_{0.25}\text{O}_2$ whereas in $\text{Li}_2\text{Ir}_{0.75}\text{Sn}_{0.25}\text{O}_3$, only Ir is electroactive. Quantitative calculations show that the charge compensated by the transition metals is significantly lower than the actual charge capacity of these cathode materials and the charge is mostly compensated by the anionic redox chemistry involving oxygen. O K-edge soft XAS spectra were measured to understand the mechanism and quantify the charge compensation by oxygen. These spectra reveal the formation of $\sigma^*(\text{O}-\text{O})$ bond indicating the formation of peroxide in $\text{Li}_2\text{Ir}_{0.75}\text{Sn}_{0.25}\text{O}_3$, however in $\text{Li}_{1.167}\text{Mn}_{0.58}\text{Ni}_{0.25}\text{O}_2$ only holes formation in O 2p bands was observed and Rietveld refinement of the HRPD patterns show reversible formation of oxygen vacancies in $\text{Li}_{1.167}\text{Mn}_{0.58}\text{Ni}_{0.25}\text{O}_2$ only. DFT-based theoretical calculations were performed to understand the origin of different redox mechanism in these 3d and 5d transition metal-based lithium-rich cathode materials. Detailed findings will be presented at the time of the meeting.

References:

- [1] J. Wang et al. *Advanced Energy Materials* 6 (2016) 1600906
- [2] M. Sathiya et al. *Nature Materials* 12 (2013) 827–835
- [3] E. McCalla et al. *Science* 350 (2015) 1516–1521