

Structural Origins of the Reversible Anionic Redox Activity in Na Layered Oxide Cathode

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Anionic redox reaction (ARR) in lithium- and sodium-ion batteries is under hot discussion, mainly regarding how oxygen anion participates and to what extent oxygen can be reversibly oxidized and reduced. Here, a P3-type $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ with reversible capacity from pure ARR was studied. The interlayer O-O distance (peroxo-like O-O dimer, 2.506(3) Å), associated with oxidation of oxygen anions, was directly detected by using a neutron total scattering technique. Different from Li_2RuO_3 or Li_2IrO_3 with strong metal-oxygen (M-O) bonding, for P3-type $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ with relatively weak Mn-O covalent bonding, crystal structure factors might play an even more important role in stabilizing the oxidized species, as both Li and Mn ions are immobile in the structure and thus may inhibit the irreversible transformation of the oxidized species to O_2 gas.

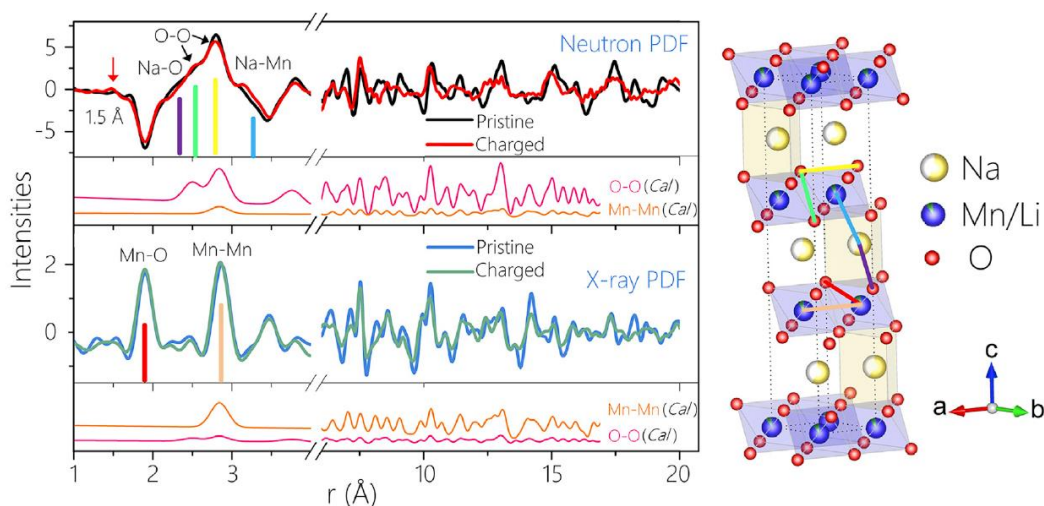


Figure 1. Detection of Local Structural Changes upon Desodiation Comparison of X-ray and neutron PDF of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ collected at pristine and charged state (4.5 V). The representative peaks corresponding to such as the first coordinating O-O, Mn-O, and Mn-Mn bonding are labeled. Due to the relatively larger neutron scattering length of oxygen compared with that of manganese, the changes in the oxygen network associated with oxidation of oxygen anions are able to be detected by neutron PDF.

References:

[1] Rong, Xiaohui, Xiqian Yu and Yong-Sheng Hu et al., *Joule* 2 (2017) 125-140.