

# On the nature of O-O dimer in overcharged lithium/sodium layered oxide cathode

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Layered lithium/sodium transition metal oxides are the dominant commercial cathode materials for rechargeable lithium-ion/sodium-ion batteries. The traditional wisdom tells us that the charge compensation during alkali ion insertion/extraction is realized by the simultaneous reduction/oxidation of transitional metal ions. Therefore, the ultimate capacity of traditional layered oxide cathodes is limited by the amounts of transition metal ions that can be hold in a specific compound. Recently, this rule has been challenged by the fact that lattice oxygen ions can also contribute to the charge compensation in various Li-rich layered oxides where a portion of transition metal ions are replaced by lithium ions (e.g.  $\text{LiLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  or  $\text{LiLi}_{1/3}\text{Ir}_{2/3}\text{O}_2$ ).<sup>1-2</sup> Numerous efforts have been spent on unraveling the chemical nature of the oxygen-related reduction/oxidation. However, no conclusive agreement has been reached so far. The major controversial is on whether  $\text{O}^{2-}$  forms stable localized  $\text{O}^-$  or partially converts to  $(\text{O}-\text{O})^{\text{n-}}$  dimers after large amounts of lithium removal.<sup>3-5</sup> To resolve this controversial, a bulk characterization technique (instead of surface probes such as XPS) that is highly sensitive to both local and average oxygen environments is highly desired.

In this poster, we will report the direct observation of large amounts of short range O-O dimers in the overcharged lithium or sodium layered oxide using neutron pair distribution function. The local and average structure of the O-O dimer containing structure has been successfully resolved using combined X-ray and neutron total scattering. A comprehensive theory has been developed to explain the general behavior of the reversible oxygen redox activity in lithium containing metal oxides. This has also guided us to design and search for the optimized layered oxide structure that can realize the real reversible (both capacity and voltage) cycling of the oxygen redox couple, some successful examples will be presented in the poster.

## References:

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