

# Unraveling the Direct Cause of Voltage Decay in Lithium-rich Oxides

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## Abstract

Li-, Mn-rich layered oxides are considered as ones of most promising positive electrode for next-generation Li-ion batteries because of its higher capacity ( $>250 \text{ mAh g}^{-1}$ ) than traditional layered oxides. But their commercialization has been largely retarded by the voltage decay problem upon cycling. Extensive efforts have been devoted to unraveling the true cause of voltage decay in Li, Mn-rich layered oxides. An initial consensus was reached on structural transformation, then leaned towards the lattice oxygen activities. It is challenging to differentiate their explicit roles because these events typically co-occur in most Li-rich layered oxides. Here, we detected the voltage decay in layered Li-rich nickel ruthenium oxide (LNRO), a structurally and electrochemically relevant compound to Li, Mn-rich layered oxide (LMRO), but absent of oxygen activity. Such intriguing characteristics allow us to unambiguously decouple the contribution of transition metal migration and lattice oxygen activity to voltage decay in Li-rich layered oxides. Advanced testing technologies such as in-situ & ex-situ X-ray diffraction (XRD), ex-situ X-ray absorption near edge structure and synchrotron XRD (Figure 1) have been applied to probe the cause of voltage decay observed in LNRO. Our results demonstrate that the microstructural evolution, mainly originating from transition metal migration, is a direct cause of voltage decay, and lattice oxygen activity mostly likely accelerates the decay. Generally, TM migration in the layered oxide follows a similar low-energy hopping pathway: from octahedral TM site to octahedral Li site through an intermediate tetrahedral site. The degree of TM migration is linked to the mobility of TM ions in the close-packed framework of oxygen and depends on the relative stability of TM ions in octahedral and tetrahedral coordination. One relevant factor is the local environment of TM ions. More vacant Li sites at highly charged states can promote TM migration, in contrast, lowering the upper cutoff voltage facilitates stable operating voltage in Li-rich layered oxide. Another important factor that influences the tendency of TM migration, even at a similar delithiation state and/or local environment, is the electronic structure of TM ions. Additional work on manipulating TM cation mobility is important to devise potential strategies for voltage fade suppression.

**Keywords** – Li-ion battery cathodes, Li-rich layered oxide, oxygen activity, transition metal migration, voltage decay.

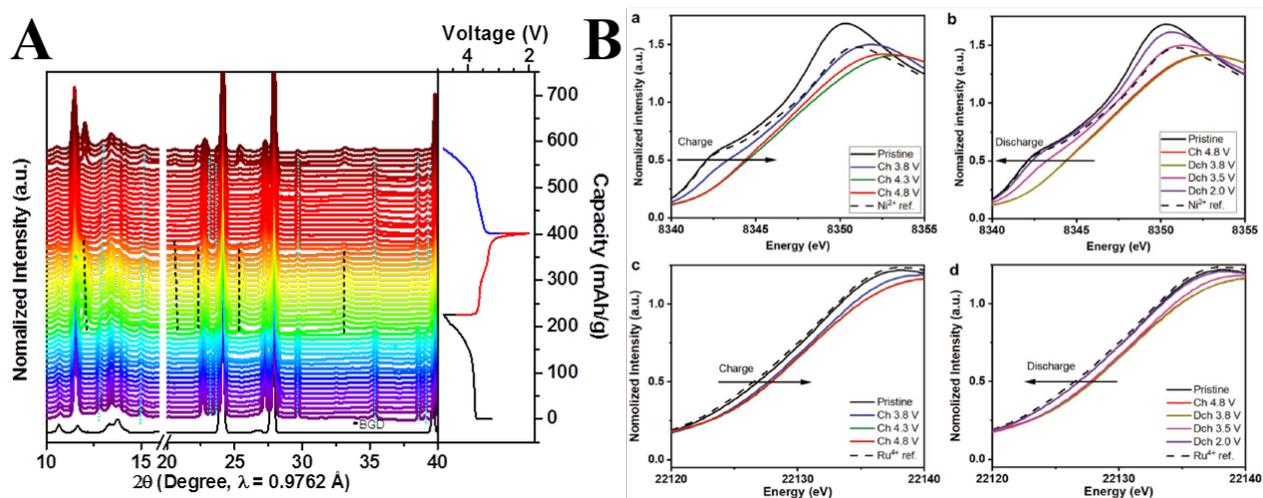


Figure 1. (A) In situ XRD patterns of LNRO during the 1st cycle and 2nd charge, (B) Structural characterization of chemically delithiated and electrochemically cycled LNRO.