

The Reversibility of Anionic Redox

Marie-Liesse Doublet,^{a,b} Matthieu Saubanère,^{a,b} Rebekka Gocht^a

^a Institut Charles Gerhardt – CNRS & Université Montpellier, Place Eugène Bataillon, 34095 Montpellier, FRANCE

^b RS2E, CNRS FR3459, 80003 Amiens, FRANCE

E-mail: Marie-Liesse.Doublet@umontpellier.fr

The discovery of anionic redox in Li-rich layered transition metal oxides (LLOs) has generated great hopes in the scientific community that this new phenomenon could enable the next generation of high-energy density Li-ion batteries. Taking advantage of the $O^{2-}/(O_2)^{n-}$ transformation underlying the anionic redox mechanism, new materials with exacerbated capacities have been uncovered with either $3d$, $4d$, or $5d$ metals or combinations of them.^[1-3] Recently, the use of d^0 or non-transition metals or the partial substitution of oxygen for more electronegative anions were also proposed as viable strategies to address the question of structural stability that often comes along with anionic redox.^[4,5] First-principles DFT methods were extensively exploited to bring complementary information on the tricky mechanism underlying the anionic redox activity of Li-rich materials. While the origin of the anionic redox is consensually attributed to the occurrence of oxygen lone-pairs in the electronic structure of LLOs,^[6-7] fundamental questions still remain on the mechanism that makes the $O^{2-}/(O_2)^{n-}$ transformation reversible on long-term cycling and on the directions to follow to prevent electrode degradation. For a large part, this unsolved issue is linked to the difficulty of DFT to accurately reproduce the relative energy of the metallic d -band w.r.t. to the anionic p -band, and therefore to uniquely determine the electronic regime^[7b] (U/Δ with U the on-site electronic repulsion and Δ the charge transfer) that characterizes a given material (i.e. a given mixture of transition metals). Using model systems, we show that conceptual approaches to the electronic band structures can be combined with computational approaches to draw a unified picture of the tricky problem of anionic redox reversibility.

References:

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