

## Anion Redox Reactions in Layered Oxides and Sulfides: Structural Effects

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Li-rich layered oxide ( $\text{Li}[\text{Li}_x\text{M}_{1-x}]\text{O}_2$ , ( $\text{M} = \text{Mn}, \text{Ni}, \text{Co}, \dots$ )) positive electrode materials are considered as a key component for next generation lithium ion batteries, as they display outstanding specific energy originating from a combination of additional lithium de-intercalation and the unusual oxidation of oxygen anions.

Recently we have extended these studies to the homologous titanium sulfides belonging to the  $\text{LiTiS}_2 - \text{Li}_2\text{TiS}_3$  system. Layered  $\text{Li}_2\text{TiS}_3$  was obtained for the first time by direct reaction of  $\text{Li}_2\text{S}$  on  $\text{TiS}_2$ . Overlithiated compositions ( $\text{Li}[\text{Li}_t\text{Ti}_{1-t}]\text{S}_2$ , ( $0 < t \leq 0.33$ )) were synthesized and structurally characterized.

The electrochemical studies shows that up to 1.1 Li per  $\text{Li}[\text{Li}_t\text{Ti}_{1-t}]\text{S}_2$  can be reversibly cycled with a negligible irreversibility. The high capacity ( $\approx 240$  mAh/g) and the shape of the charge curves suggest that  $\text{Ti}^{3+}$  ions are oxidized in a first step and the  $\text{S}^{2-}$  ions in a second step to form  $\text{S}_2^{2-}$  ions. The very small irreversibility results from the easy oxidation of  $\text{S}^{2-}$  ions which does not induce any sulfur release from the particle surface and subsequent structural densification.

Contrary to oxides, there is a very small fading and voltage decay upon cycling. This behavior suggests that there is no significant structure modification as it is observed in lithium-rich oxides.

The experimental characterizations of lithium rich phases and the theoretical calculations made by Ceder *et al.* show that the oxygen involvement in the redox process is directly related to the amount of lithium within the  $\text{MO}_2$  ( $\text{MS}_2$ ) slabs. In fact, it is the presence of no-bonded oxygen orbitals which make easier the oxygen oxidation.

This behavior was recently extended to some  $\text{P2-Na}_x(\text{L},\text{M})\text{O}_2$  ( $\text{L} = \text{Li}, \text{Mg}$ ) phases which present a very high electrochemical activity in Na-batteries.

A general overview of these properties will be discussed in this conference.