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## How do the synthesis conditions impact the microstructure of Mn-rich layered oxides $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$ (M=Mn, Ni) and their carbonate or oxide precursors?

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Nowadays, it is necessary to meet the needs of efficient electric vehicles by increasing the energy density of Li-ion batteries, now about 200 Wh/kg for a full cell. In this scope, Li-rich layered oxides  $\text{Li}_{1+x}(\text{Ni},\text{Mn})_{1-x}\text{O}_2$  are highly promising (1). Actually, cationic redox reactions occur, but also anionic ones with redox activation of oxygen at high potential ( $\sim 4.5\text{V}$  vs  $\text{Li}^+/\text{Li}$ )(2). It allows to get really interesting theoretical energy density higher than 900 Wh/kg (at the material level), 50% higher than current NMC positive electrode materials. Nevertheless, oxygen redox activation leads to irreversible loss of oxygen within the material, inducing a cationic rearrangement at the surface (3), and degrading electrochemical performances. Mechanical strain caused in the primary particles impacts the secondary ones, depending on their initial microstructure (mainly porosity and tortuosity) (4). Understanding these phenomena goes through linking the microstructure of the precursors to those of their associated lithiated phases and their electrochemical performance. This knowledge is critical to control the synthesis for the optimization of the electrochemical performances of these materials.

Two different precursors made by our partner Umicore have been used for the Li-rich layered oxides syntheses. The first one is a Mn/Ni carbonate (65 :35 at.% respectively) made by coprecipitation, and the second one is the corresponding mixed Mn/Ni oxide obtained by roasting the carbonate. Li-rich layered oxides can thus be produced by 2 different synthesis paths: a one-step synthesis by mixing the Mn/Ni carbonate with lithium carbonate, or a two-step synthesis by first degrading the Mn/Ni carbonate and mixing in a second step the as-obtained mixed oxide with  $\text{Li}_2\text{CO}_3$ . Lithiation occurs during a heat treatment at high temperature in air.

To better understand the impact of the synthesis process on the final material microstructure, it is needed to study first the precursors microstructure. The Mn/Ni carbonate has been thermally degraded in different conditions of temperature (350°C to 600°C), heating rate (1.5K/min;5K/min) and duration (5h;10h). Thermogravimetric analysis showed that the carbonate starts decomposing at 300°C before being completely turned into the mixed oxide at about 580°C. 12 different materials have been obtained and characterized by usual laboratory methods as well as by X-ray nano-computed tomography (nanoXCT) coupled to XANES (5) in order to study their microstructure and the chemical distribution within the secondary particles. Some of these precursors have been used to synthesize series of lithiated phases to determine the impact of precursors, synthesis parameters, mostly Li/M ratio, on the structure and the microstructure of as-obtained powders.

### References

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