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## Understanding the Redox Behaviour of Na<sup>+</sup>/Li<sup>+</sup> Exchanged T<sub>2</sub>/O<sub>2</sub>-Li<sub>0.67+x</sub>Ni<sub>0.33</sub>Mn<sub>0.67</sub>O<sub>2</sub> using soft-XAS

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With the growing need to further enhance the sustainability of lithium-ion batteries (LIBs), the substitution of critical raw materials like cobalt in common positive electrode materials, i.e., layered oxides, by more abundant elements such as nickel and manganese is considered essential [1]. To address the challenging structural instability of such compositions, tuning the stacking order of these layered oxides towards the T<sub>2</sub>/O<sub>2</sub>-type structure is known as an effective approach [2]. However, the inherent Li<sup>+</sup> deficiency and limited first charge capacity remains a major obstacle for any practical application [2,3].

Within this study, we introduce a new synthesis concept to overcome this limitation by exemplarily increasing the Li<sup>+</sup> content in T<sub>2</sub>-Li<sub>0.67</sub>Ni<sub>0.33</sub>Mn<sub>0.67</sub>O<sub>2</sub> obtained by a Na<sup>+</sup>/Li<sup>+</sup> ion-exchange process. Based on a reductive treatment this approach is shown to be capable of significantly enhancing the first charge capacity of such materials and, thus, compensate the Li<sup>+</sup> deficiency. Surprisingly, different synthesis environments appear to strongly influence the shape of the first charge voltage profile with a significant impact on the cycling stability. To understand the mechanism of the lithiation process and the nature of additionally incorporated Li<sup>+</sup>, we performed an in-depth investigation to differentiate between structural and morphological effects, as well as surface and bulk contributions.

In particular, we highlight the capability of ex situ soft-XAS to address such questions regarding the evolution of oxidation states, the composition of surface layers, and the resolution of depth-dependent gradients in the material. Consequently, we present detailed insights into the distinct origin of the increased capacity during the first charge, revealing different underlying redox processes depending on the synthesis conditions.

[1] M. Armand et al., J. Power Sources, 2020, 479, 228708.

[2] D. Eum et al., Nat. Mater., 2020, 19, 419-427.

[3] B. M. de Boisse, J. Electrochem. Soc., 2018, 165, A3630-A3633.

**Primary author:** BOEHLER, Timo (Helmholtz Institute Ulm (HIU))

**Co-authors:** Dr KUENZEL, Matthias (Helmholtz Institute Ulm (HIU)); Dr EISENMANN, Tobias (Helmholtz Institute Ulm (HIU)); Dr ASENBAUER, Jakob (Helmholtz Institute Ulm (HIU)); REZVANI, Javid (University of Camerino); Dr ZARRABEITIA, Maider (Helmholtz Institute Ulm (HIU)); Dr INDRIS, Sylvio (Karlsruhe Institute of Technology (KIT)); Dr JUSYS, Zenonas (Helmholtz Institute Ulm (HIU)); Prof. BEHM, R. Juergen (Ulm University); Prof. PASSERINI, Stefano (Sapienza University Rome); BRESSER, Dominic (Karlsruhe Institute of Technology (KIT))

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