

A New Way of Pre-lithiating High Voltage Spinel $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathodes for Compensation of Active Lithium Loss

Johannes Betz^a, Jan-Paul Brinkmann^a, Laura Nowak^a, Richard Schmuch^a, Martin Winter^{a,b}, Tobias Placke^a

^a University of Münster, MEET Battery Research Center, Institute of Physical Chemistry, Corrensstr. 46, 48149 Münster, Germany

^b Helmholtz Institute Münster, IEK-12, Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster, Germany

E-mail: johannes.betz@uni-muenster.de

The high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) is one of the most promising active materials for future lithium ion battery (LIB) cathodes, as it offers a high specific discharge energy and is free of cobalt. With its theoretical capacity of 147 mAh g^{-1} and a discharge plateau at $\approx 4.7 \text{ V}$ vs. Li/Li^+ , it delivers a specific energy of over 600 Wh kg^{-1} and an energy density of over 2500 Wh L^{-1} on the material level. [1, 2]

Combining LNMO with a high-energy anode material such as silicon in a cell setup without (additional) lithium metal induces the problem of rapid capacity fading due to active lithium loss, especially in the first cycle(s). This problem can be countered following the concept of pre-lithiation.

While electrochemical pre-lithiation of the active material is able to compensate lithium losses, it imposes several problems like *e.g.* the stability in air after pre-lithiation and complexity of the process. Similar reasons oppose the use of lithium metal for lithiation of the anode. These make the process difficult to adapt for industrial purposes. [3]

Chemical lithiation of LNMO with lithium metal in pentanol before preparing the electrode, not only gives the chance of compensating active lithium losses at the anode side during cycling, but also is a simple one-step process. The resulting cathode material is stable in air for several hours and can be processed subsequently without additional equipment (or protective atmosphere).

The lithiation is accomplished by combining LNMO with stoichiometric amounts of metallic lithium ($n_{\text{Li}} / n_{\text{LNMO}} = 0.25$ to 1) in pentanol as solvent and boiling the mixture over night to achieve lithium contents of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($x = 1.1 - 1.8$). The lithium contents are detected by XRD and ICP-OES measurements. During lithiation, the crystal structure of the material is transformed from a cubic to a tetragonal phase, but the morphology of the particles does not change. Once de-lithiated electrochemically, there is nearly no difference between the pre-lithiated and the original material. To investigate the amount of lithium, which can be reversibly de-lithiated in the first cycle, the material is used to prepare cathodes and cycled against lithium metal. Subsequently, the chemically pre-lithiated cathodes are built in cells against different anode materials to evaluate the possible energy increase by pre-lithiation by comparing them to the standard LNMO.

References:

- [1] H. Liu, J. Wang, X. Zhang, D. Zhou, X. Qi, B. Qiu, J. Fang, R. Kloepsch, G. Schumacher, Z. Liu, J. Li, ACS Appl Mater Interfaces, 8 (2016) 4661-4675.
- [2] D. Andre, S.-J. Kim, P. Lamp, S.F. Lux, F. Maglia, O. Paschosa, B. Stiaszny, J. Mater. Chem. A, 3 (2015) 6709-6732.
- [3] V. Aravindan, Y.-S. Lee, S. Madhavi, Adv. Energy Mater, 7 (2017) 1602607, 1-17.