

Aqueous processing of nickel-rich NMC – Li-Ion performance as a function of binder pH value

Lukas Ibing^a, Tobias Gallasch^a, Falko Schappacher^a, Andreas Hintennach^c, Martin Winter^{a,b}

^a MEET Battery Research Center, University of Münster, Corrensstraße 46, D-48149 Münster

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

^c Daimler AG, HPC G012, D-71059 Sindelfingen

E-mail: Lukas.ibing@uni-muenster.de

Although aqueous processing of lithium ion battery anode materials is already well established, a detailed study of the impact of water as solvent on the active material (here: Lithium-Nickel-Cobalt-Manganese-Oxide, NMC) is still missing [1,2].

Especially nickel rich NMC materials suffer from structural instabilities, resulting in poor safety features or phase changes in case of electrochemical (over) delithiation [3]. A well-known process is the exchange of lithium (from NMC) with protons (from aqueous solutions)[4] which might lead to structural changes of the surface resulting in increased charge transfer resistivities and therefore poor C-rate performance.

To reveal the dependence of the applied pH (binder solution) on the cathode performance, NMC532 was picked as active material. The binder pH has been adjusted using lithium hydroxide and set to values of 7, 11.5 and 13. The prepared cathode slurries were casted on carbon coated aluminum current collectors and dried at 60 °C over night. For all tests coin cells (type: CR2032) were used with an electrolyte containing 1 molar LiPF₆ in EC:EMC 3:7. As separator Celgard 2320 was chosen in all cases. Graphite based anodes (in case of long term cycling) and pure lithium metal (in case of the C-rate test) were used as counter electrodes. Impedance studies were carried out in the lithium ion set up using a potentiostatic excitation of 5 mV in a frequency range between 1 Hz and 1 MHz.

The C-rate tests show a significant influence by the preset pH value. Especially at higher C-rates, electrodes produced with higher pH values show increased capacities. Also long term cycling shows increased capacities for higher pH values.

In case of impedance measurements it can be concluded that higher pH values lead to lower charge transfer resistance. One possible explanation could be the higher degree of chemical delithiation by lower pH values (higher proton concentration). It is known from literature that delithiated NMC material tends to form spinel structures instead of the typical layered crystal structure[3]. These spinel structures are less ion conductive and therefore lead to an increased charge transfer resistance of the material. With higher charge transfer resistance the material shows higher overpotentials, especially at high currents resulting in lower capacities.

References:

- [1] Loeffler, Nicholas et al. Journal of Power Sources (2014), 248915–922.
- [2] Lee, Jin-Hyon et al. Journal of Power Sources (2005), 147 (1-2) 249–255.
- [3] Jung, Sung-Kyun et al. Advanced Energy Materials (2014), 4 (1) 1300787.
- [4] Ma, Miaomiao et al. Journal of Power Sources (2007), 165 (2) 517–534.