Influence of synthesis parameters on electrochemical performance of $LiCo_{2x}Ni_{0.5-x}Mn_{0.5-x}O_2$

M. Wohlfahrt-Mehrens, P. Axmann, H. Dittrich, M. Kasper, W. Weirather, S. Ströbele, J. Garche

[1]ZSW – Center for Solar Energy and Hydrogen Research, Helmholtzstr. 8, D-89081 Ulm, Germany
* margret.wohlfahrt-mehrens@zsw-bw.de

Recently, growing interest has been focussed on layerd $LiCo_{2x}Ni_{0.5-x}Mn_{0.5-x}O_2$ compounds as promising cathode materials for Lithium-Ion batteries due to their low cost, high capacity and high thermal stability.[1] [2] The electrochemical performance seems to be strongly dependent on preparation conditions. For the present contribution the influence of preparation conditions on electrochemical performance has been studied in more detail.

In the present work $LiCo_{2x}Ni_{0.5-x}Mn_{0.5-x}O_2$ materials with different cobalt content were prepared by two different synthesis routes. In the first one we coprecipitated mixed nickel cobalt manganese hydroxides from metal salts. After washing and drying these precursors were mixed with LiOH and subsequently heat treated for several hours at temperatures between 600°C and 1000°C. An alternative route started from coprecipitated mixed carbonates. These precursors were also mixed with LiOH and heat treated at temperatures between 600°C and 1000° C.

The obtained powders were characterized by X-ray powder diffraction measurements. The X-ray diffraction patterns of the obtained materials could be indexed based on the α-$NaFeO_2$ structure. Some samples of $LiNi_{0.5}Mn_{0.5}O_2$ obtained impurities of Li_2MnO_3. At temperatures above 1000°C a spinel phase was observed. The Li/Me ratio was determined by ICP analysis and the. average oxidation state of the transition metals was analyzed by redox titration techniques. It is assumed that nickel is in the divalent, cobalt in the trivalent and manganese in the tetravalent state. Hydroxide precursors form plate like primary crystallites whereas carbonate precursors lead to a more compact morphology. The primary crystallites grow with increasing heat treatment temperature Beside the morphology the heat treatment temperature also influences the structural parameters of the end product. The c lattice parameter increases slightly with increasing temperature.

Figures 1 shows the charge/discharge cycles of the 1st and 2nd to 5th cycles of materials with different cobalt content from the hydroxide precursor route. The reversible capacity was slightly increased with increasing cobalt content. The reversible capacity for the cobalt free $LiNi_{0.5}Mn_{0.5}O_2$ was only about 140 mAh/g and this material also shows the highest polarization.

Polarization and cycling stability are influenced by precursor chemistry and heat treatment temperature. The samples heat treated at 1000°C give the best electrochemical performance regarding maximum discharge capacity, polarization and cycling stability. However the first charge/discharge curve shows an additional voltage plateau and exhibits higher irreversible capacity compared to lower temperature products.

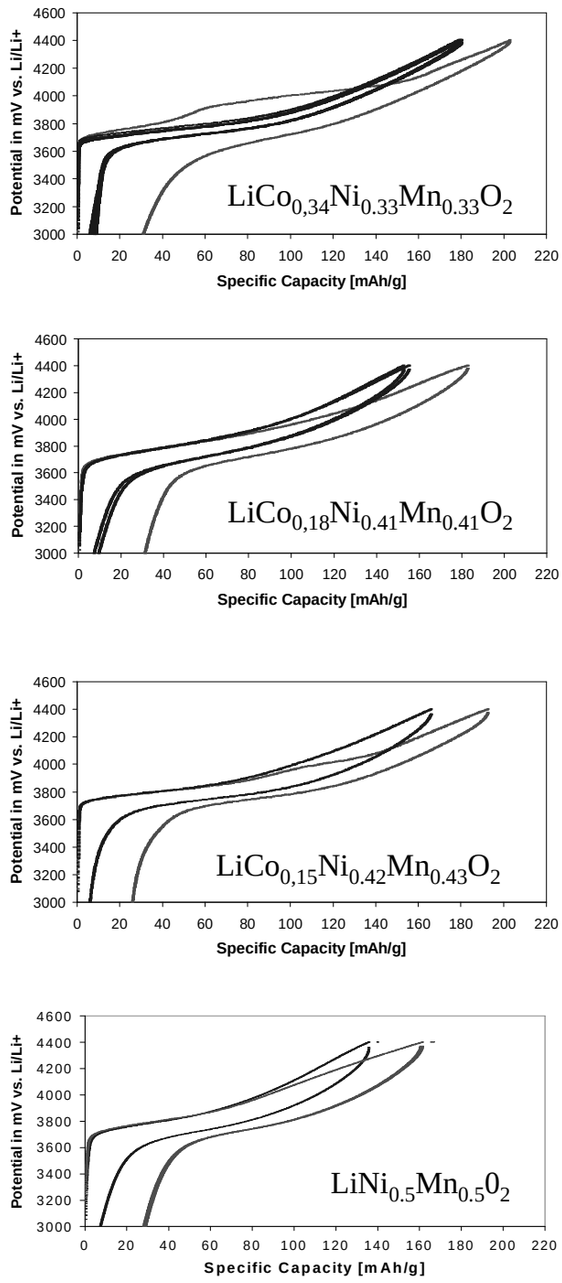

Fig. 1: Charge/discharge of 1st and 2nd to 5th cycles of $LiCo_{2x}Ni_{0.5-x}Mn_{0.5-x}O_2$ with different cobalt content prepared by mixed hydroxide route, constant C/20 rate

[1] T. Ohzuku, Y. Makimura, Chemistry Letters (2001) A191
[2] Z. Lu, D. D. MacNeil, J. R. Dahn, Electrochem. Solid State Lett. 4 (2001) A191