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Study of Stability and Structural Changes Occurring during High Thermal Load of the High Voltage Cathode Material by *In Situ* Scanning Electron Microscopy

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One of the most progressive battery systems which are used in portable devices, electric vehicles and energy storage systems are Li-Ion batteries. However, currently used cathode materials are close to their limits and in the coming years they are no longer able to meet growing energy demands. Many research groups focus their interest on modifications of existing cathode materials in order to improve their parameters. Some of them search for new types of cathode materials which could replace currently used cathode materials. The result of one of those efforts was the development of the cathode material $LiNi_{0.5}Mn_{1.5}O_4$ [1]. This material is based on the $LiMn_2O_4$ where manganese is partially replaced by nickel, this allows to charge the cathode material up to 5 V. Potential of $LiNi_{0.5}Mn_{1.5}O_4$ against lithium is 4.7 V i.e. 1 – 1.5 V increase in respect to standard cathode materials. With this combination of high potential and theoretical capacity 148 mAh/g, $LiNi_{0.5}Mn_{1.5}O_4$ exhibits high gravimetric energy density approaching 700 Wh/kg which is approximately 20 % more than gravimetric energy density of $LiCoO_2$ and about 30 % more than in the case of the cathode material $LiFePO_4$. Moreover, $LiNi_{0.5}Mn_{1.5}O_4$ is also stable during long term cycling and exhibits good stability at higher current loads because of the spinel structure; however, it still suffers by dissolution of manganese into the electrolyte during cycling at higher temperatures which leads to defects in the structure and capacity decrease [2].

This contribution deals with thermal properties of the $LiNi_{0.5}Mn_{1.5}O_4$ synthesized by a solid-state reaction method. Thermal stability is one of the most important parameters characterizing cathode materials for Li-Ion batteries. Low thermal stability of cathode material can, in the worst case, cause fire of the battery pack like in the case of batteries in Boeing 787 Dreamliner [3]. Precursors based on carbonates and oxides were chosen as basic materials for the synthesis: Li_2CO_3 (Lithium(II) carbonate), $MnCO_3$ (Manganese carbonate), NiO (Nickel oxide) were chosen. The two-step annealing process was selected for the preparation. In the first step, selected precursors were milled in the ball mill FRITSCH Pulverisette 0 for 4 hours, followed by annealing at 600 °C for 10 hours. The second step consists of annealing at 900 °C for 15 hours in oxygen atmosphere. Subsequently, the prepared cathode material was analysed in SEM and TGA (Thermogravimetric analysis) was used to test its thermal stability. The analysis was done in air atmosphere and monitored temperature range was set from room temperature to 900 °C. The heating rate was set to 10 °C/min. The same thermal analysis was performed by using in-situ SEM analysis on Quanta 250 FEG SEM. The experiment was carried out in environmental scanning electron microscopy mode (ESEM) with gaseous secondary electron detector (GSED) and with the 1000°C FEI heating stage. The heating rate was set to 10 °C/min. Pressure in the microscope chamber was set to 200 Pa, water vapor environment was used. The sample surface was imaged from room temperature to 700°C in 100°C steps, the sample was annealed for 15 minutes after reaching 700 °C and finally the specimen was cooled down to room temperature. The structure of the cathode material $LiNi_{0.5}Mn_{1.5}O_4$ after synthesis is shown in Fig. 1 – A). There are aggregates of small crystals in the entire volume. The average size of the crystals is smaller than 5 μm. The TGA analysis (Fig. 1-B) indicates that synthesized $LiNi_{0.5}Mn_{1.5}O_4$ is very stable and there was no significant loss of weight up to

600 °C. The sample also does not contain any water or carbon residuals, which could remain there after the synthesis. The weight decrease above 600 °C is typical for such high-voltage cathode materials; it is caused by losing oxygen and lithium from the cathode structure [4]. Fig. 2 shows development of the cathode structure during heating. There are no sample morphology changes during heating from the room temperature (Fig. 2-A) up to 500 °C (Fig. 2-C). Small cracks and holes are formed on the surface of some crystals below 600 °C. These cracks and holes significantly enlarge after reaching 700 °C and during annealing at 700 °C. These results confirm TGA measurement. *In-situ* SEM provides additional information about the collapse of cathode material caused by release of lithium and oxygen from its structure.

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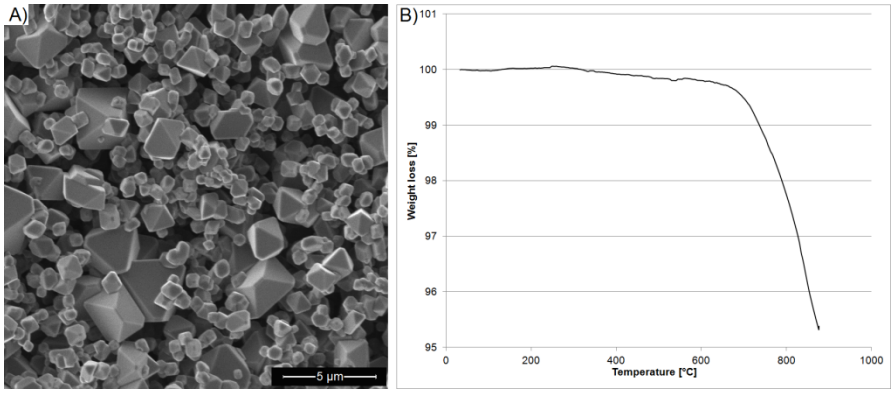

Figure 1. A) SEM picture of the cathode material $LiNi_{0.5}Mn_{1.5}O_4$; horizontal field of view is 20.8 µm, B) TGA analysis of the cathode material $LiNi_{0.5}Mn_{1.5}O_4$.

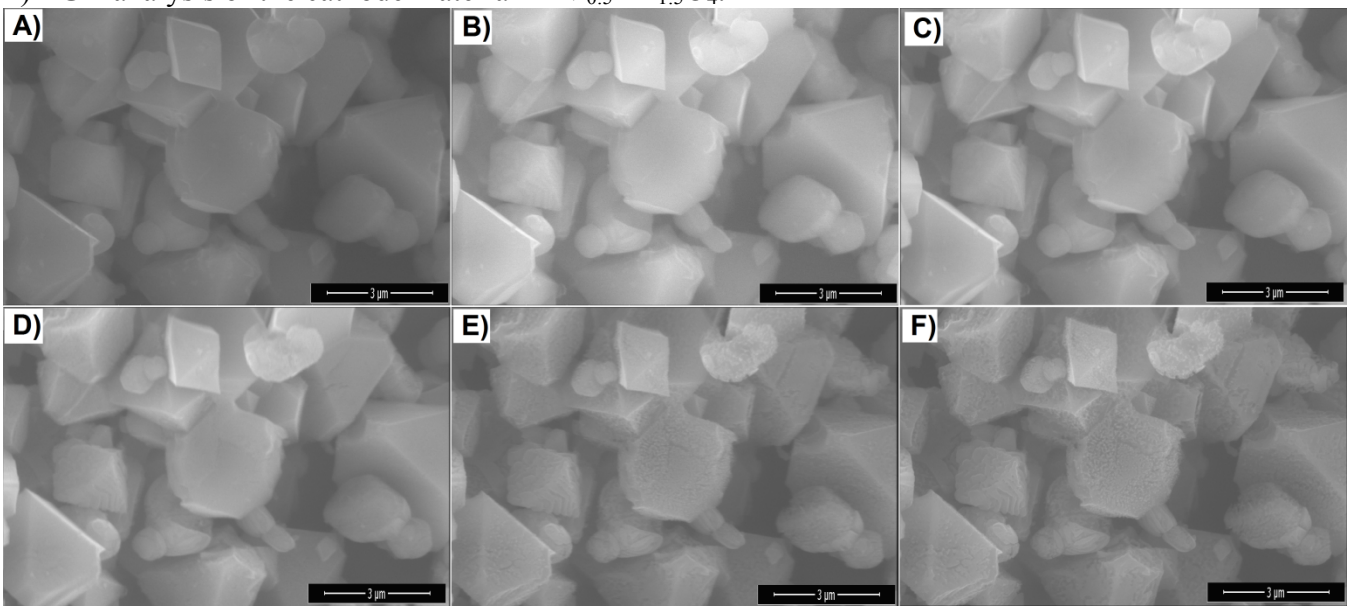

Figure 2. in situ SEM analysis of the cathode material $LiNi_{0.5}Mn_{1.5}O_4$ during heating; A) 25 °C, B) 400 °C, C) 500 °C, D) 600 °C E) 700 °C, F) 700 °C after 15 min, horizontal field width is 12.7 µm.

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