Study of the influence of the scandium doping to the properties of high voltage LiNi_{0.5}Mn_{1.5}O₄ cathode

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One of the problems which were always associated with accumulators in general is their low voltage. For powering a more demanding application, there is always the need to stack more cells together to obtain a higher voltage. Conventional Li-ion accumulators are charged to 4.2 V maximum and their nominal voltage is 3.6-3.7 V. There have been attempts to produce an accumulator with higher voltage lately. Its charging voltage should be around 5 V and voltage during discharging over 4.5 V. From the group of high voltage cathode materials, the LiNi_{0.5}Mn_{1.5}O₄ spinel is the most promising material. Solid state reaction method was chosen as the method of synthesis of this material and as the method of stabilizing the structure by doping by other element - in this case by scandium. Doped sample was studied in terms of obtained capacity, cycle life and stability in a high C-rate.

Introduction

The LiNi_{0.5}Mn_{1.5}O₄ material is the basic material considered for high voltage lithium based cells. It is one of the most promising materials due to its high operation voltage close to 4.7 V. It is based on the LiMn₂O₄ material which is often used in standard lithium cells. High voltage cells are often named "5 V" cells because of their charging voltage reaching 5.0 V. Mn in the LiNi_{0.5}Mn_{1.5}O₄ material remains in the +4 oxidation state and thus there are fewer complications during cycling. (1) The theoretical capacity of this material is 147.6 mAh/g. The energy density is 700 Wh/kg that is around 30 % more than LiFePO₄. (2) The cathode material LiNi_{0.5}Mn_{1.5}O₄ reports the high voltage properties with respect to several oxidation steps of manganese cation where Mn³⁺ oxidizes to Mn⁴⁺ at 4 V vs Li and subsequently Ni²⁺ is oxidized to Ni³⁺ at the voltage range of 4.7 - 4.8 V vs Li until it reaches the Ni⁴⁺. (3) This material, however, has a big disadvantage and that is the decrease of capacity during cycling. It is especially noticeable while operating at higher temperatures. This could be solved by doping by the material with other elements and Cr seems to be a good possibility. Chromium is added to this material to form LiCr_{0.1}Ni_{0.4}Mn_{1.5}O₄ modification to reach higher stability. (5)

Experimental

The samples were prepared by the method of reaction in solid state. Precursors based on carbonates and oxides were chosen as basic materials for the production. Li₂CO₃ (Lithium(II) carbonate), MnCO₃ (Manganese carbonate), NiO (Nickel oxide) and Sc₂O₃ (Scandium(III) oxide) were chosen in this case; these materials were mixed in a stechiometric ratio of 0.02 mol/l. Preparation by annealing was done in two steps. Precursors were milled together for 4h for the first step of the process. In the first annealing step, the resultant mixture was annealed at 600 °C for 10h. The second step was annealing at 900 °C for 15h. (4) After this synthesis, a material with face-centered spinel structure was obtained (These materials are also known as disordered materials.). The resulting chemical compound is $LiSc_{0.05}Ni_{0.45}Mn_{1.5}O_4$. The resulting materials were investigated after their creation using by SEM microscopy and EDS analysis. SEM microscope TESCAN VEGA3 XMU and a Bruker EDAX analyser was used for these analyses. The prepared material was then also mixed into a mixture consisting of NMP (N-Methyl-2-pyrrolidon) (solvent), PVDF (Polyvinylidenfluorid) (binder) and carbon Super P. The weight ratio of the materials was the following: 80 % of active material, 10 % of Super P and 10 % of PVDF. The resulting mixture was subsequently deposited on an aluminium foil, dried and pressed by the pressure of 3200 kg/cm2. A disk with a diameter of 18 mm was cut out of the coated aluminium foil and inserted into the electrochemical test cell ECC-STD. The assembly was done in the glove box filled with argon atmosphere. Metal lithium was used as a material for the anode and the electrolyte 1.5 M LiPF₆ EC:DMC 1:2 w/w was soaked in a glass fibre separator. For the comparison of electrochemical properties was used electrode contain by pristine cathode material LiNi_{0.5}Mn_{1.5}O₄. Cyclic voltammetry and galvanostatic cycling were used for electrochemical characterisation. Cyclic voltammetry was done in the potential window from 3.0 to 5.1 V versus lithium and the scan rate was set to 0.5 mV/s. Galvanostatic cycling was carried out with the same potential window from 3.0 to 5.1 V versus lithium. Two charging and discharging cycles were carried out each time during which the used charging and discharging currents were set to 60 mA/g (related to the weight of an active mass). The real value of the capacity of the sample was deducted from these two cycles and the sample was then exposed to long term cycling during which it was cycled ten times by 0.5 C current. It was subsequently cycled five times by 1 C current, then five times by 2 C current and then five times by 5 C current. Next step was cycling again five times by 2 C current, again five times by 1 C current, again five times by 0.5 C



Figure 1: SEM analysis of the samples A) $LiNi_{0.5}Mn_{1.5}O_4$, used view field 41.5 µm and B) $LiSc_{0.05}Ni_{0.45}Mn_{1.5}O_4$, used view field 41.5 µm.

Fig. 1 - A) shows the pure material in greater detail. We can see the orderly crystals which are clean without any cracks or impurities. We can see crystals of the scandium doped material in greater detail in Fig1. – B). The structure is also uniform but it is different than the structure of the pure material. There are visible small particles bonded on the bigger crystals. The crystals look as if there were some impurities but that is caused by the annealing process of sample creation and the scandium itself.



Figure 2: EDS analysis of the sample LiNi_{0.5}Mn_{1.5}O₄.



Figure 3: EDS analysis of the sample LiSc_{0.05}Ni_{0.45}Mn_{1.5}O₄.

Energy-dispersive X-Ray spectroscopy (EDS) was used to figure out the real chemical composition of the samples. The results proved the samples to be properly synthesized. Fig. 2 shows the EDS spectra of the sample LiNi_{0.5}Mn_{1.5}O₄. We can see the ratios of the elements in the sample; the sample contains the demanded elements (Ni, Mn, O) and the ratio Ni:Mn (1:3) is also satisfactory. Fig. 3 shows the EDS spectra of the sample LiSc_{0.05}Ni_{0.45}Mn_{1.5}O₄. Again is evident that all expected elements (Ni, Mn, O, Sc) are present in the synthesized sample.



Figure 4: Comparison of cyclic voltammetry of the samples $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiSc}_{0.05}\text{Ni}_{0.45}\text{Mn}_{1.5}\text{O}_4$, used scan rate 0.5 mV/s.

Fig. 4 shows comparison of cycvlic voltammetry of the samples $LiNi_{0.5}Mn_{1.5}O_4$ and $LiSc_{0.05}Ni_{0.45}Mn_{1.5}O_4$. We can see that the pure material is more electrochemically active the current peaks are higher in both directions. It could mean the performance of the material will be higher during galvanostatic tests. There are smaller subpeaks around 3.7 to 4.1 Volt. These peaks correspond with valence changes of Mn from Mn^{3+} to Mn^{4+} . This peak is greater in the case of doped material it can be assumed that 4 V discharge

plateau will be greater in the case of doped material $LiSc_{0.05}Ni_{0.45}Mn_{1.5}O_4$ and high voltage plateau will be smaller.



Figure 5: Comparison of the capacity during a cycling depends on C-rate of the samples $LiNi_{0.5}Mn_{1.5}O_4$ and $LiSc_{0.05}Ni_{0.45}Mn_{1.5}O_4$.

The difference between doped and non-doped materials is clearly visible in Fig. 5. This chart shows the discharged capacities throughout all the galvanostatic measurements. The capacity of the non-doped sample is higher at all stages and C-rates. The drops of capacity after increasing the current are lower for the pure material as well. The capacity during the first cycle at 0.5 C was 115 mAh/g for the pure sample and 97 mAh/g for the scandium doped sample. The capacity of the pure sample is relatively stable during all 20 cycles at 0.5 C (decrease to 113 mAh/g); the capacity of scandium doped sample decreased from the initial value to 93 mAh/g at the end of 0.5 C cycling. After increasing the load to 1 C, the capacity of the pure sample decreased to 107 mAh/g and remained unchanged throughout this stage. The capacity of the scandium doped sample decreased to a stable value of 85 mAh/g. In the next step, the load was 2 C and the capacity of the pure sample was around 101 mAh/g. At the same load, the capacity of the scandium doped sample was around 78 mAh/g. The highest load, 5 C, brought the most significant drop of capacity. The capacity of the pure sample was 83 mAh/g at the beginning and 86 mAh/g at the end of this stage. It was 56 and 57 mAh/g for the scandium doped sample. Then the load was gradually decreased, first to 2 C (101 for pure and 77 mAh/g for scandium doped sample). Then five cycles at 1C were carried out (106 and 83 mAh/g).And the final stage was another 10 cycles at 0.5 C. The pure sample reached the capacity of 106 mAh/g while the scandium doped sample showed a gradual decrease from 88 to 85 mAh/g. The drop throughout the complete cycling was from 115 to 106 mAh/g for the pure sample and from 97 to 85 mAh/g for the scandium doped one. It represents a drop of 8 % for the pure sample and 9 % for the scandium doped sample.



Figure 6: Comparison of the discharge curve of the samples $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiSc}_{0.05}\text{Ni}_{0.45}\text{Mn}_{1.5}\text{O}_4$.

Comparison of discharge cycles from firs cycle is shown in Fig. 6. We can see that the non-doped sample is significantly better from approximately 60 mAh/g. Scandium doped sample is only better at the beginning of discharging when the voltage is slightly higher. In the case of doped sample we see also longer discharging plateau at 4 V which corresponding with results obtained by cycling voltammetry.

Conclusion

The results from the experimental part show that the material doped with scandium is not the best material for doping the basic cathode materials used in high voltage lithiumbased materials. It can be seen from the charts that the capacity of scandium doped samples is high in the beginning but it decreases quickly during cycling. Also Results from cyclic voltammetry show not very good results for the doped sample. Pictures from the electron microscope show that the structure is crystalline. The basic (non-doped) material is after a few cycles better than the doped material. Scandia doping obviously leads to decrease of capacity and stability and also to changes of the structure which caused to formation of a greater amount of manganese in the valence state Mn³⁺.

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