

The Influence of Solvents and Salts on the Properties of High-Voltage Cathode Materials

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Received: 22 March 2015 / Accepted: 29 May 2015 / Published: 24 June 2015

Lithium - ion batteries play an increasingly important role in the battery industry and they have become the dominant source of energy in the recent years, especially for portable electronic devices due to their high gravimetric energy density. This article examines the influence of mixtures of solvents with different combinations of lithium salts on the stability of two types of high-voltage cathode materials: $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ produced by a solid phase reaction. These materials were combined with several different electrolytes, cycled at various loads and higher temperature. Various combinations of solvents ethylene carbonate (EC), dimethyl carbonate (DMC) and Tetrahydrothiophene 1.1-dioxide (Sulfolane) were used for these measurements. Salts LiPF_6 , LiNO_3 and LiTFSI were used. The influence of solvents and salts on the properties of high-voltage cathode materials was tested by cycling at different current loads and by cycling at high temperature. It was found out, by LSV analysis, that the addition of Sulfolane increases the stability of electrolyte. The addition of chromium to the cathode material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ causes increasing of capacity and stability at high temperature. The combination of the cathode material $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ with the electrolyte 1.5 M LiPF_6 EC:DMC:Sulfolane 1:2:1 w/w/w leads to increased stability in comparison with other electrolytes.

Keywords: Lithium ion battery, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, electrolyte, sulfolane

1. INTRODUCTION

Higher voltage materials are mostly based on material LiMn_2O_4 . It is its spinel structure that makes it more stable than LiCoO_2 . This material is less toxic because of the use of Mn, it has low

exothermic corruption. Its specific capacity is ~ 120 mAh/g and the voltage against lithium is 4 V.[1-3] If one fourth of manganese is substituted by nickel, this material can be charged up to 5 V and the voltage against lithium about 4.7 V. This voltage is therefore about 1 V more than by other commonly used materials today.[1-2] The theoretical capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material is ~ 147 mAh/g. Its energy density is 700Wh/kg due to its capacity and high voltage which is approximately 20% higher than LiCoO_2 and 30% higher than LiFePO_4 . [4] The material remains stable during cycling and handles well by higher current loads thanks to the spinel structure. This cathode material reaches the high voltage using several oxidation steps at which there occurs conversion $\text{LiNi}_{0.5}^{\text{II}}\text{Mn}_{1.5}^{\text{III}}\text{O}_4/\text{Ni}_{0.5}^{\text{IV}}\text{Mn}_{1.5}^{\text{IV}}\text{O}_4$. Mn^{3+} oxidizes to Mn^{4+} at 4 V vs Li and subsequently Ni^{2+} is oxidized to Ni^{3+} at the voltage range 4.7 – 4.8 V vs Li and then to Ni^{4+} . [5,6] The result of these successive changes of valence of nickel is joining two discharge plateaus in one very stable discharge plateau. Two types of cathode materials ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and its modification $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$) were chosen for the experiment in this article thanks to these properties. The Modification of the material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using chromium is used to increase the stability of the cathode material during cycling and higher loads. [1,7-11] Cr is most often a partial replacement for Ni during the process of doping $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by chromium. The ionic radius of Cr^{+3} is 0.615 Å which is close to the ionic radius of Ni^{+2} (0.65 Å). This partial substitution – for example in $\text{LiCr}_{0.05}\text{Ni}_{0.45}\text{Mn}_{1.5}\text{O}_4$ - leads to the improved electrochemical properties due to higher strength of the bond Cr-O than the bond between Ni- and Mn-O. This stronger Cr-O bond leads to an increase in the strength of the structure and maintains its properties during long term cycling even at higher loads. [1,7,8] The modification $\text{LiCr}_{0.05}\text{Ni}_{0.45}\text{Mn}_{1.5}\text{O}_4$ or alternatively $\text{LiCr}_{0.2}\text{Ni}_{0.4}\text{Mn}_{1.4}\text{O}_4$ are most frequently mentioned in scientific articles. [8-11] The modification $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ was chosen for this article to verify whether doping by Cr in a specific ratio can improve the material properties. The main part of this article focuses on investigation of the effect of utilized electrolytes on the electrochemical properties of these two cathode materials. EC (ethylene carbonate), DMC (dimethyl carbonate) and sulfolane were chosen as solvents. EC and DMC are commonly used as solvents and sulfolane was chosen because of its higher thermal stability and it was also expected it would be more stable at higher voltages.[12] LiPF_6 , LiNO_3 and LiTFSI were chosen as salts. The LiNO_3 salt was selected for the assumption that its addition into the mix will increase the stability of the electrolyte. LiTFSI is used as a stable salt for Li-S batteries and it was chosen for the validation of the stability of these cathode types. [13]

2. EXPERIMENTAL

The method of reaction in solid state was chosen for the production of this material. Precursors based on carbonates and oxides were chosen as basic materials for the production. Li_2CO_3 (Lithium(II) carbonate), MnCO_3 (Manganese carbonate), NiO (Nickel oxide) and Cr_2O_3 (Chromium(III) oxide) were chosen in our case; these materials were mixed in a stoichiometric ratio of 0.02 mol/l. The two-step annealing process was selected for the preparation. Selected precursors are milled together for 4h during the first step of this process. In the first annealing step, the resultant mixture is annealed at 600 °C for 10h. The second step is annealing at 900 °C for 15h. [14] After this synthesis we obtain

materials with face-centered spinel structure therefore known as disordered. The prepared material was then mixed into a mixture consisting of NMP (N-Methyl-2-pyrrolidone) (solvent), PVDF (Polyvinylidene fluoride) (binder) and carbon Super P. The weight ratio of the materials was: active material 80%, Super P 10%, PVDF 10%. The resulting mixture was subsequently deposited on an Al foil, dried and pressed by the pressure of 3200 kg/cm^2 . A disk with a diameter of 18 mm was cut out of the coated aluminium foil and inserted into the electrochemical test cell El-Cell© ECC-STD. The assembly was done in a glove box filled with argon atmosphere. Metal Lithium was used as a material for the anode and the electrolyte was soaked in a glass fibre separator. 1 M LiPF_6 EC:DMC 1:1 w/w, 1.5 M LiPF_6 EC:DMC 1:2 w/w, 1.5 M LiPF_6 + 0.1 M LiNO_3 EC:DMC 1:2 w/w, 1.5 M LiPF_6 EC:DMC:Sulfolane 1:2:1 w/w/w, 1.5 M LiPF_6 + 0.1 M LiNO_3 EC:DMC:Sulfolane 1:2:1 w/w/w, 0.75 M LiTFSI + 0.1 M LiNO_3 EC:DMC 1:2 w/w and 0.75 M LiTFSI + 0.1 M LiNO_3 EC:DMC:Sulfolane 1:2:1 w/w/w were used as electrolytes.

Linear Sweep Voltammetry (LSV) was used for testing of the stability of electrolytes in the voltage window from 3.0 to 5.2 V versus lithium. Scan rate was set to 5 mV/s and 1 mV/s. Galvanostatic cycling was used for measuring electrodes with different electrolytes; the potential window was set from 3.0 to 5.1 V versus lithium. Two cycles of charging and discharging have always been carried out during which the used charging and discharging currents were 0.5 C (calculated from the weight of the deposited material provided that the capacity of the material is 120 mAh/g). The real value of 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 current, and finally there were ten cycles by 0.5 C current at the temperature of 50 °C. SEM microscope TESCAN VEGA3 XMU with Bruker EDAX analyzer was used to determine the distribution of the elements in the materials. TGA analysis was used for the comparison of structural stability of the synthesized cathode material.

3. RESULTS AND DISCUSSION

It is evident that the decomposition of electrolytes with salts LiTFSI and LiNO_3 occurs after exceeding of 3.7 V when comparing with the curves in Fig. 1. The electrolyte 1.5 M LiPF_6 EC:DMC 1:2 showed lower stability from the other electrolytes. The stability of the electrolyte was increased after the addition of salt LiNO_3 and it was even better after the addition of Sulfolane. The electrolyte 1.5 M LiPF_6 EC:DMC:Sulfolane 1:2:1 appeared to be the most stable. The LSV at a scan rate of 1 mV/s is shown in Fig. 2. It is evident from these graphs that the lowest stability again exhibit the electrolytes with the salt mixture of LiTFSI and LiNO_3 . Better stability was again discovered, like in the previous measurement, after the addition of LiNO_3 salt into the electrolyte 1.5 M LiPF_6 EC:DMC 1:2. 1.5 M LiPF_6 EC:DMC:Sulfolane 1:2:1 seems to be the most stable electrolyte again. The electrolytes with a mixture of LiTFSI and LiNO_3 salts were discarded for the next measurements of the properties of cathode materials with different electrolytes due to their high instability. A similar instability in the

region above 4 V was shown also by the commonly used electrolyte 1 M LiPF₆ EC: DMC 1:1 which is evident at both scan rates. For this reason, the conventional electrolyte 1 M LiPF₆ EC: DMC 1:1 was excluded from the next measurement.

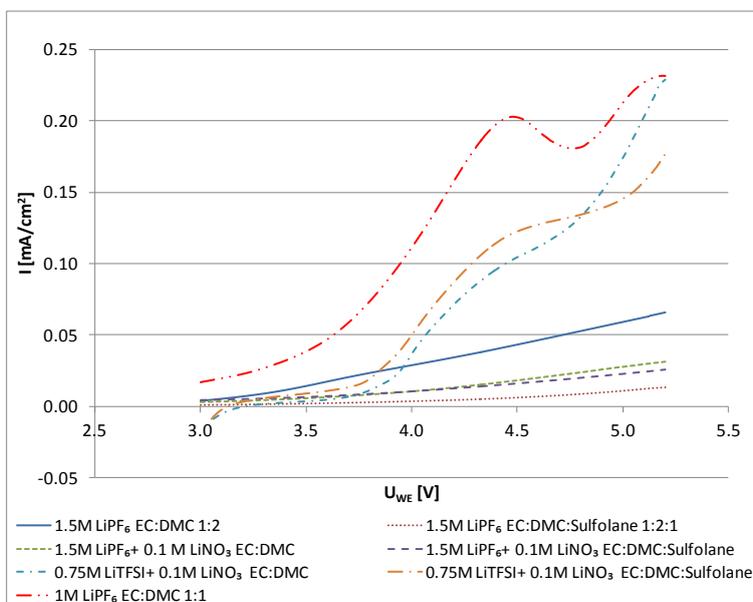


Figure 1. LSV curves of half-cells using different electrolytes at the scan rate of 5 mV/s. The working electrode used in the half-cells is Al

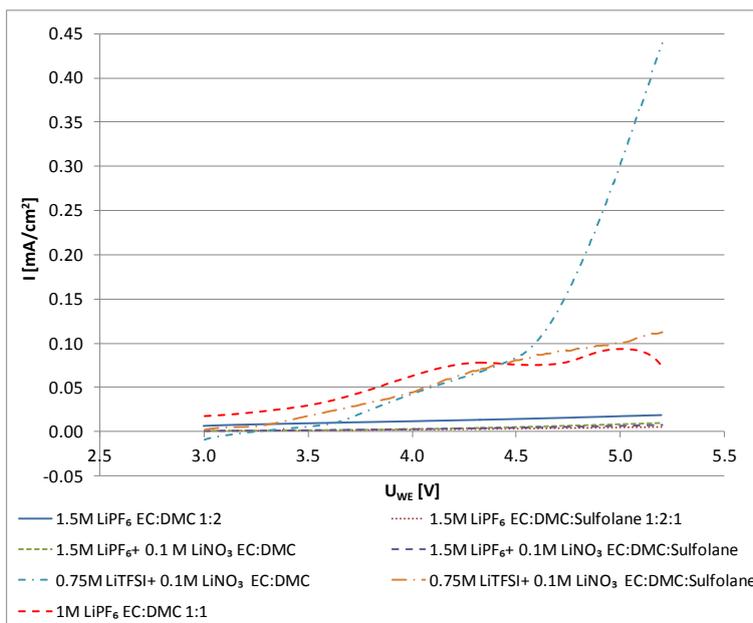


Figure 2. LSV curves of half-cells using different electrolytes at the scan rate of 1 mV/s. The working electrode used in the half-cells is Al

The materials LiNi_{0.5}Mn_{1.5}O₄ and LiCr_{0.1}Ni_{0.4}Mn_{1.5}O₄ were analysed using SEM microscopy. We can see structures of both synthesised materials in Fig. 3, the field of view for both samples is 41.5

µm. It is possible to observe the crystal structure of synthesized samples in both cases. We can see that the crystal size of the material $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ is somewhat smaller than in the material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

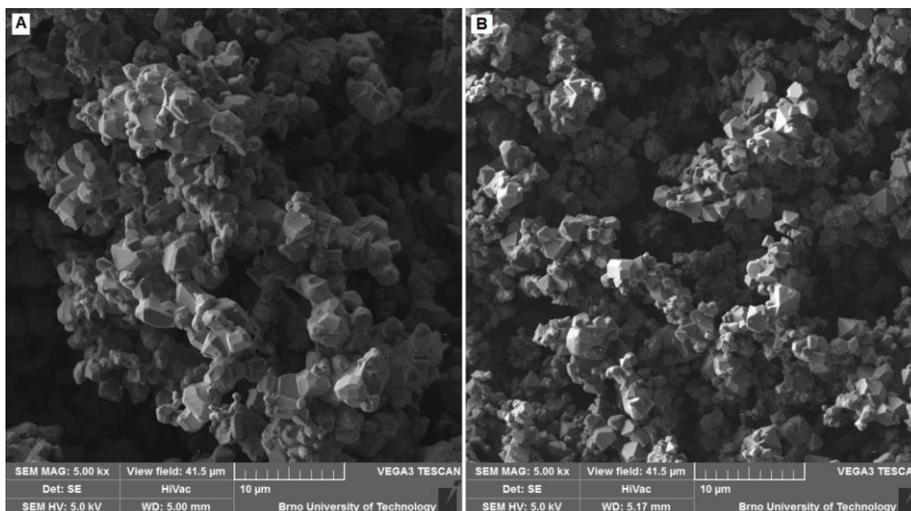


Figure 3. SEM analysis of the samples A) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and B) $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ view field used - 41.5µm

The last analysis carried out on samples $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ was EDX analysis of their composition. Results for both materials are shown in Fig. 4. As shown in Fig. 4-1) the distribution of elements in the material is uniform and the resulting material contains oxygen, nickel and manganese. Fig. 4-2) shows the result of EDX analysis of the sample $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$, it is again evident that, like in the material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, uniform distribution of elements on the surface of the sample was achieved, and there are nickel, oxygen, manganese and chromium.

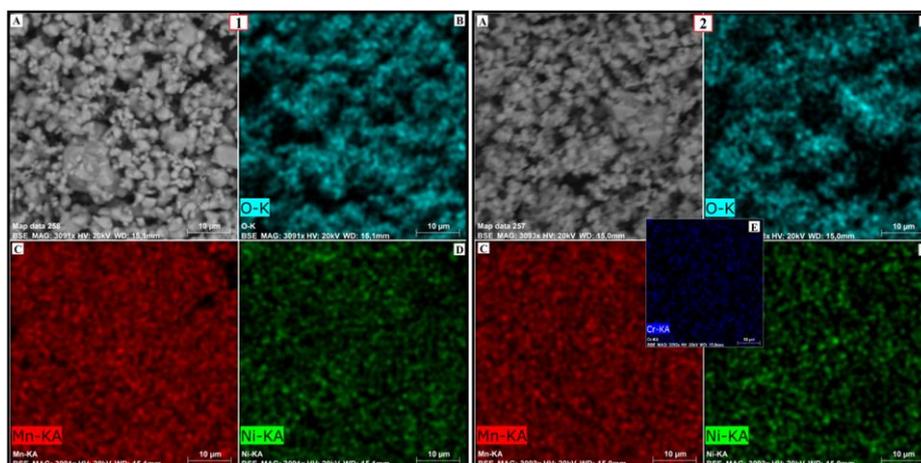


Figure 4. Mapping of the sample of 1) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ A) SEM particles $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ B) distribution of oxygen C) distribution of manganese D) distribution of nickel 2) $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ A) SEM particles $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ B) distribution of oxygen C) distribution of manganese D) distribution of nickel E) distribution of chromium

The structural stability of the cathode materials $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ was investigated by thermal analysis (Fig. 5).

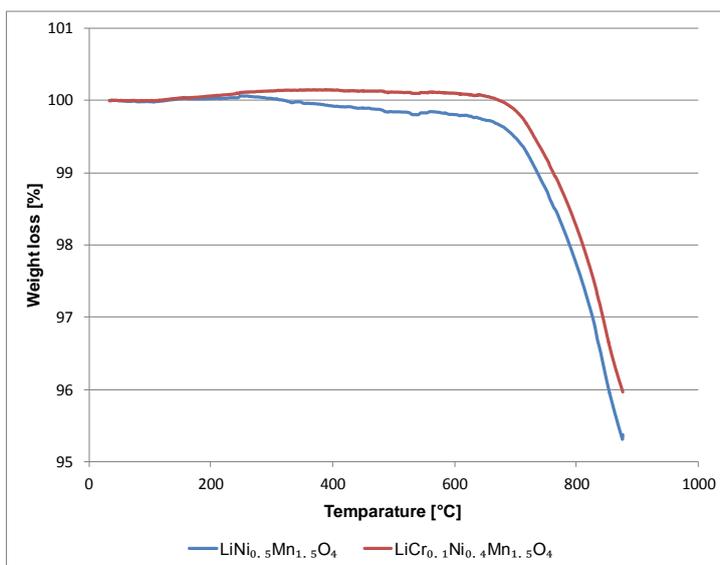


Figure 5. TGA analysis of the samples A) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and B) $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$

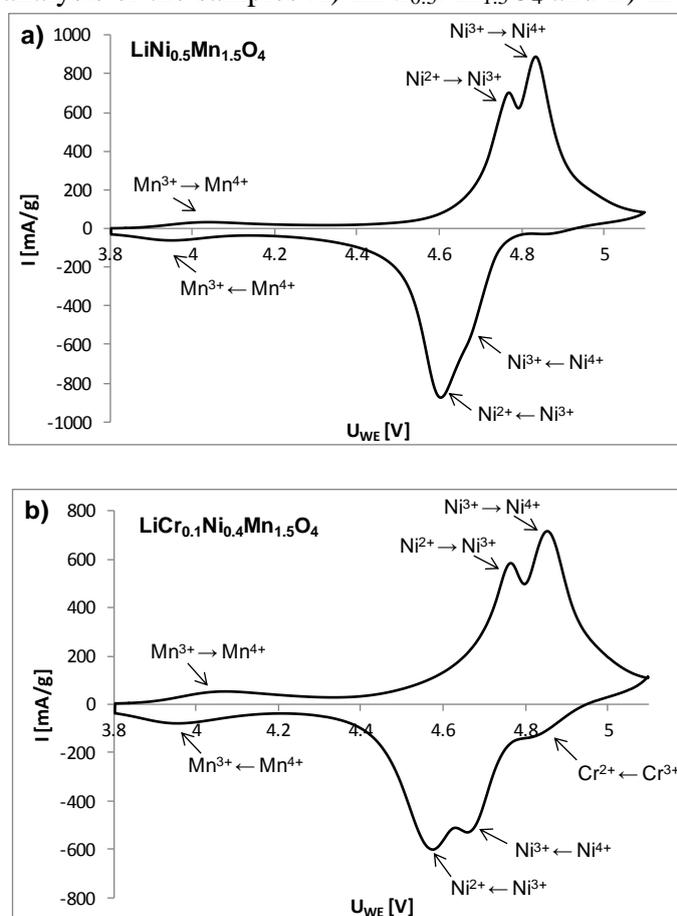


Figure 6. CV of a) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ b) $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ and valence changes ongoing during cycling. Half-cell whit electrolyte 1.5 M LiPF_6 EC:DMC 1:2 at the scan rate of 0.5 mV/s.

TGA analysis was performed in the temperature range from room temperature to 900 °C and the temperature was increased at 10 °C/min rate. It is evident that the largest weight loss was observed in the range between 600 °C to 900 °C. This drop of weight is caused by losing of oxygen and lithium from the cathode material structure. [15] Material with Cr exhibits the highest stability during heating. Adding of chromium caused stabilization of the structure of the cathode material which leads to a significant stabilization of weight in comparison with the pristine material.

We can see CV of both types of high-voltage cathode materials ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$) used in combinations with 1.5 M LiPF_6 EC:DMC 1:2 electrolyte in Fig. 6. The peaks corresponding to the changes of valence ongoing in these materials are visible in the charts. There is an evident redox peak of about 4 V in both cathode materials which is caused by the change in the valence of Mn^{3+} to Mn^{4+} and back. This peak is more significant in the case of the material $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ where it leads to an increase of the 4 V discharge plateau. We can see redox peaks related to the change of the oxidation state of nickel in both cathode materials. In the material $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$, we can another reduction peak corresponding to the change in the valence of chromium at about 4.85 V.

We can see a comparison of the two discharge cycles of the materials $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ in Fig. 7. It is evident from these curves that the material $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ has a slightly higher discharge plateau due to the incorporation of chromium in its structure and its steeper decline due to the larger spacing of changes in the valence of nickel. This material also shows a greater plateau at 4 V. This change is also caused by chromium doping which leads to greater change in the valence of manganese. These changes correspond with the data obtained by using CV.

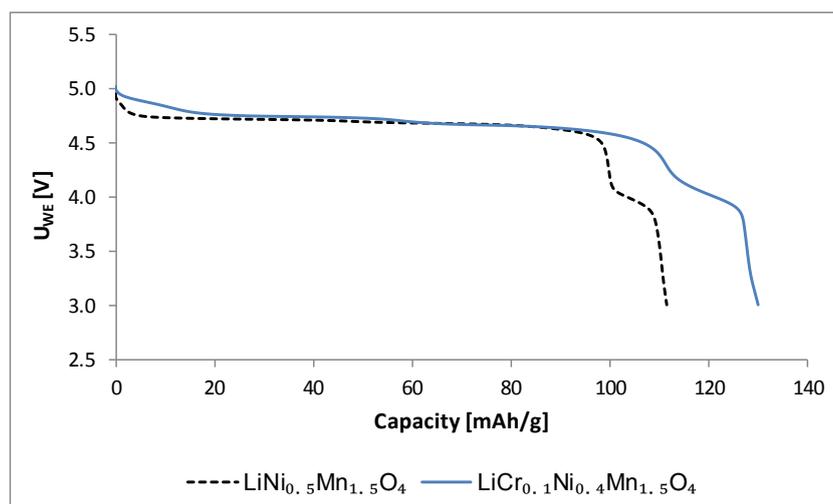


Figure 7. Comparison of first discharge curves of $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (dot-dash line) and $\text{Li}/\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ (blue line) in half-cells at 0.5 C using the 1.5 M LiPF_6 EC:DMC 1:2 electrolyte

Fig. 8 shows the cycling of the material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in combination with different electrolytes at different loads. It is evident that all four samples achieve similar capacities of about 112

mAh / g during the first 10 cycles at 0.5C and the most stable sample seems be the electrolyte 1.5M LiPF₆ EC:DMC 1:2 which reached 100.5 % of the capacity of the first cycle in the tenth cycle. The least stable was the sample with the electrolyte 1.5M LiPF₆ + 0.1M LiNO₃ EC:DMC:Sulfolane 1:2:1 which lost 2.3 % of its capacity in the first cycle after ten cycles. Different declines of capacity can be seen for cathode materials with different electrolytes during next cycling at higher loads up to 5 C. The material LiNi_{0.5}Mn_{1.5}O₄ with the electrolyte 1.5M LiPF₆ EC:DMC 1:2 appears to be the most stable one reaching 89.2 % of the capacity from the first cycle at the end of cycling at 5 C (99.5 mAh/g) followed by the sample with the electrolyte 1.5M LiPF₆ EC:DMC:Sulfolane 1:2:1 which reached 82.2 % capacity thus 92.1 mAh/g. If we compare these results with the results which were reported in the previous article [16] we can see that both the capacity and the stability achieved during cycling in the experiment described in the paper are higher than those in the case of using a standard electrolyte 1M LiPF₆ EC: DMC (1: 1) and the overall results are better than the ones achieved in the case of using salt LiBOB. We can see similar results in comparison with the data from the article [17] in this article the author again reported lower capacities in all tested C-rates in the case of standard electrolyte 1M LiPF₆ EC: DMC (1: 1). In this article there is also reported increase of achieved capacities in the case of use of the electrolyte with addition of Sulfolane but the reached capacity and stability are again lower than the ones achieved in our measurements. The highest decrease was recorded for the material with electrolyte LiPF₆ + 1.5M 0.1M LiNO₃ EC:DMC:Sulfolane 1:2:1 which at the end of cycling at 5 C had 72.8 % of the capacity from the first cycle, thus 81.8 mAh/g. The load was afterwards reduced again to the value of 0.5 C. Five charge and discharge cycles were carried out by this load, followed by cycling at 50 °C.

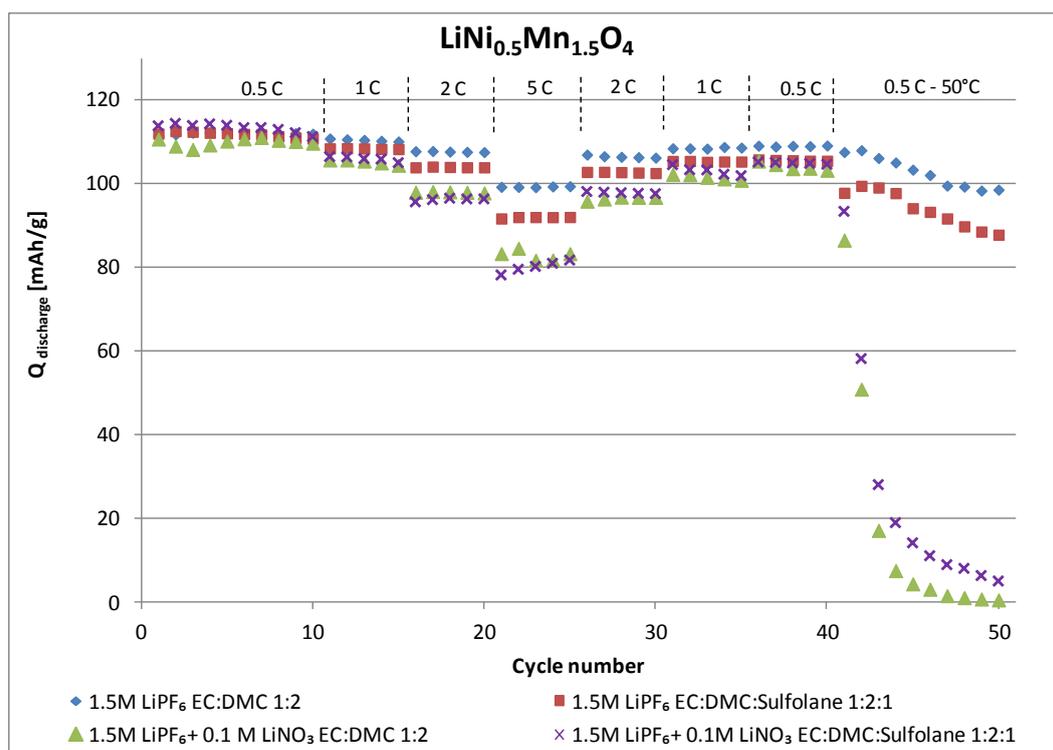


Figure 8. Comparison of capacity change depending on load and temperature changes for the material LiNi_{0.5}Mn_{1.5}O₄ with different electrolytes

The cathode material with the highest capacity in the last cycle at 0.5 C at room temperature was the one with the electrolyte 1.5M LiPF₆ EC:DMC 1:2 that after forty cycles at different loads lost 2.1 % of the capacity from the first cycle. It was followed by the sample with electrolyte 1.5M LiPF₆ EC:DMC:Sulfolane 1:2:1 which lost 5.8 % of its capacity in comparison with the first cycle. The highest decrease was observed in the sample with electrolyte 1.5M LiPF₆ + 0.1M LiNO₃ EC:DMC:Sulfolane 1:2:1 which capacity decreased by 8.1 %. The decrease of capacity can be seen for all samples during cycling at 50 °C. This is very significant for the samples with electrolyte containing LiNO₃ and the cell practically stops working. The most stable material is the one with electrolyte 1.5M LiPF₆ EC:DMC 1:2 where the decrease of the capacity is gradual and from the sixth cycle the capacity stabilizes. The capacity of this sample at the end of the cycling was 88.5 % of the capacity from the first cycle. The cycling of the sample with electrolyte 1.5M LiPF₆ EC:DMC:Sulfolane 1:2:1 provided similar results. The capacity was somewhat lower - it was equal to 78.4 % of the capacity in the first cycle at the end of cycling at 50°C.

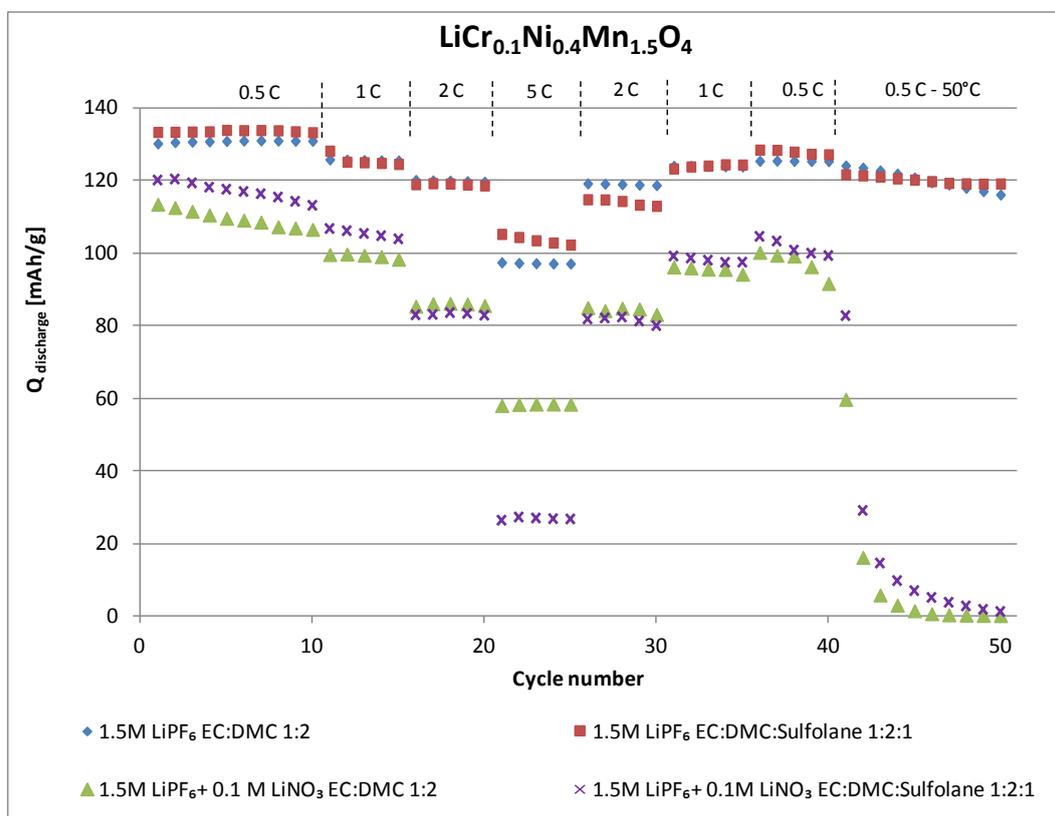
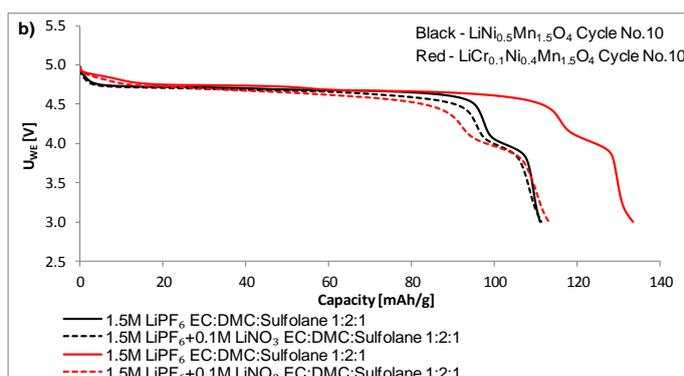
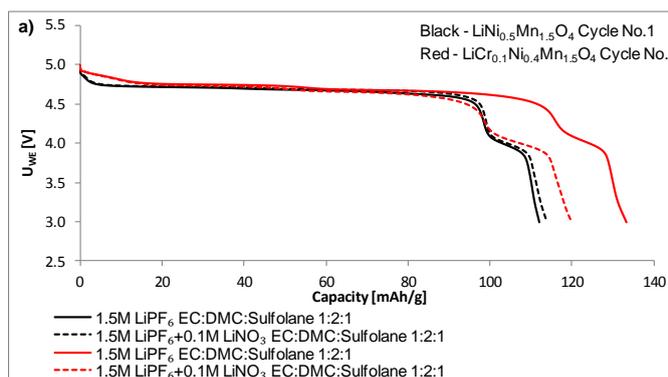


Figure 9. Comparison of capacity change depending on load and temperature changes in materials LiCr_{0.1}Ni_{0.4}Mn_{1.5}O₄ with different electrolytes

Fig.9 shows the cycling of the material LiCr_{0.1}Ni_{0.4}Mn_{1.5}O₄ in combination with different electrolytes at different loads similarly as in the case of material LiNi_{0.5}Mn_{1.5}O₄. Material LiCr_{0.1}Ni_{0.4}Mn_{1.5}O₄ showed higher capacity than LiNi_{0.5}Mn_{1.5}O₄ during the first ten cycles. Their capacity was around 130 mAh/g in the case of the electrode an electrolyte of which did not contain the

LiNO₃ salt. Electrolytes with LiNO₃ salt exhibited during the first ten cycles the capacity between 120 mAh/g and 110 mAh/g. The most stable was LiCr_{0.1}Ni_{0.4}Mn_{1.5}O₄ in combination with the electrolyte 1.5M LiPF₆ EC:DMC 1:2 which showed slightly higher capacity in the tenth cycle (130.9 mAh/g) that was the capacity in the first cycle (130.2 mAh/g) and the electrolyte 1.5M LiPF₆ EC:DMC:Sulfolane 1:2:1 which showed the decrease of 0.1 % after ten cycles (to 133.2 mAh/g). The highest decrease showed the sample with the electrolyte 1.5M LiPF₆ + 0.1M LiNO₃ EC:DMC 1:2 - after the first ten cycles there was the decrease of 6.1 %. It was again followed by cycling at various loads up to 5 C. The decrease of capacity occurred during the rising of the load. The most stable sample during the increase of the load was the one with electrolyte 1.5M LiPF₆ EC:DMC:Sulfolane 1:2:1 which achieved the highest capacity. The material with electrolyte 1.5M LiPF₆ EC:DMC:Sulfolane 1:2:1 achieved after five cycles at 5 C the capacity of 102.3 mAh/g which is 76.7 % of the capacity in the first cycle. The sample LiCr_{0.1}Ni_{0.4}Mn_{1.5}O₄ in combination with the electrolyte 1.5M LiPF₆ + 0.1M LiNO₃ EC:DMC:Sulfolane 1:2:1 showed the highest capacity decrease, it achieved 22.2 % of the capacity during the first cycle. The most stable sample during the load reduction was again the one with electrolyte 1.5 M LiPF₆ EC:DMC:Sulfolane 1:2:1 which, at the end of cycling at 0.5 C, exhibited the highest capacity (127.2 mAh/g). This was followed by ten cycles at 50 °C during which there was a sharp decline in the capacity of the cells with the electrolyte containing LiNO₃. This is similar as in the case of combination of this electrolyte with the cathode material of LiNi_{0.5}Mn_{1.5}O₄. The samples with electrolyte 1.5 M LiPF₆ EC:DMC:Sulfolane 1:2:1 and 1.5M LiPF₆ EC:DMC 1:2 showed good stability during cycling at high temperature.



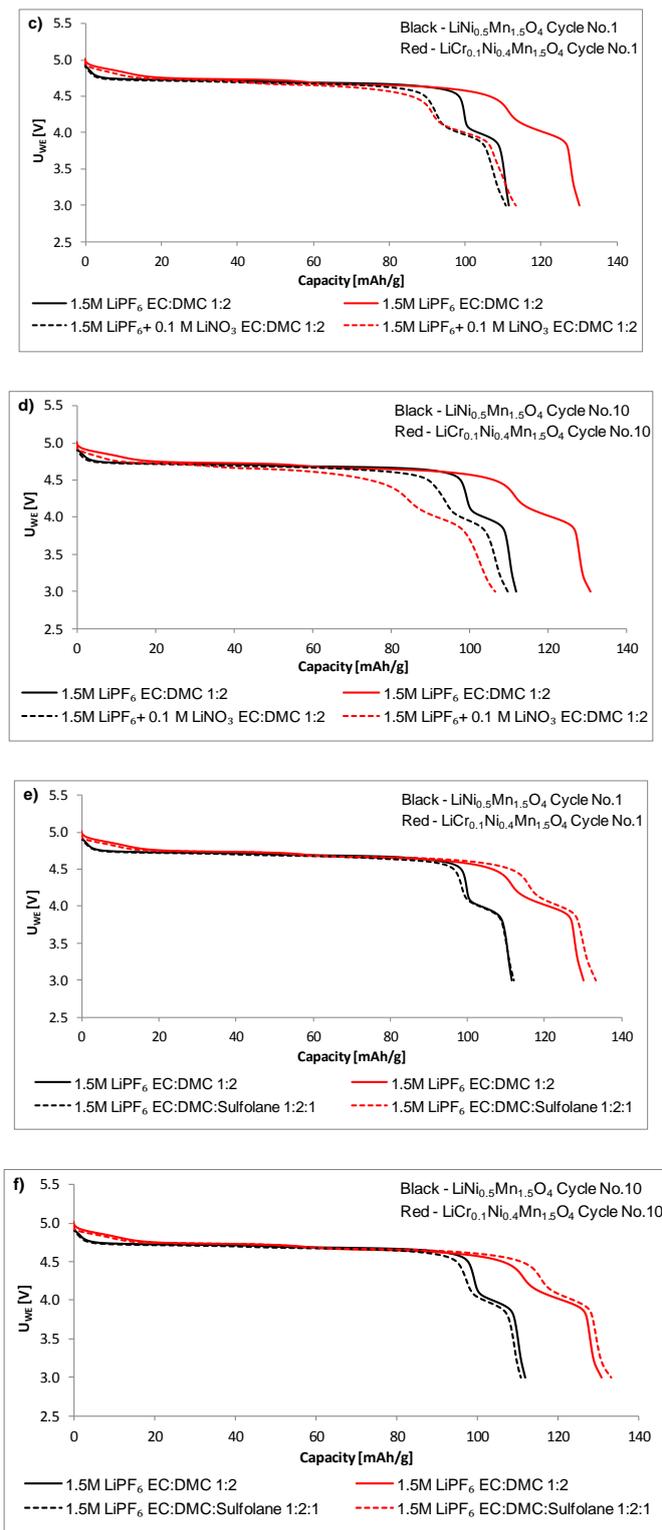


Figure 10. Comparison of the first and the tenth discharge cycle of the cycling at 0.5 C for both cathode materials $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (black) and $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ (red) **a)** 1st cycle electrolyte 1.5 M LiPF_6 EC:DMC:Sulfolane 1:2:1 and with addition of LiNO_3 **b)** 10th cycle electrolyte 1.5 M LiPF_6 EC:DMC:Sulfolane 1:2:1 and with addition of LiNO_3 **c)** 1st cycle electrolyte 1.5 M LiPF_6 EC:DMC 1:2 and with addition of LiNO_3 **d)** 10th cycle electrolyte 1.5 M LiPF_6 EC:DMC 1:2 and with addition of LiNO_3 **e)** 1st cycle electrolyte 1.5 M LiPF_6 EC:DMC 1:2 and with addition of Sulfolane **f)** 10th cycle electrolyte 1.5 M LiPF_6 EC:DMC 1:2 and with addition of Sulfolane

If we compare this samples with this combination of electrolytes we can see that sample $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ in the combination with electrolyte 1.5 M LiPF_6 EC:DMC:Sulfolane 1:2:1 show slightly higher stability during cycling at high temperature and in the end of cycling is his capacity 119.2 mAh/g which is 98.6 % of capacity from the firs cycle of all cycling.

Fig. 10 shows the comparison of discharge curves for both cathode materials before and after adding the additive to the electrolyte. We can see the comparison of cathode materials when using the electrolyte 1.5 M LiPF_6 EC:DMC:Sulfolane 1:2:1 and after addition of 0.1M LiNO_3 in Fig. 10 a) and b). It was observed during the first cycle that the cathode material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with the electrolyte 1.5M LiPF_6 + 0.1 M LiNO_3 EC:DMC:Sulfolane 1:2:1 showed a higher capacity than the electrolyte without the addition of 0.1 M LiNO_3 . The capacity of the cathode material $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$ with the electrolyte 1.5 M LiPF_6 EC:DMC:Sulfolane 1:2:1 was higher than with the electrolyte with an addition of 0.1 M LiNO_3 . There is a noticeable drop of capacity and a faster decline of the discharge plateau after ten cycles for both cathode materials which use the electrolyte 1.5 M LiPF_6 + 0.1 M LiNO_3 EC:DMC:Sulfolane 1:2:1 than for those which use the electrolyte 1.5 M LiPF_6 EC:DMC:Sulfolane. Fig. 10 c) and d) show the comparison of discharge curves of cathode materials when using the electrolyte 1.5 M LiPF_6 EC:DMC 1:2 and after the addition of 0.1 M LiNO_3 . Quicker decrease in discharge plateau is observed for the cathode materials using electrolyte 1.5 M LiPF_6 + 0.1 M LiNO_3 EC:DMC 1:2 already during the first cycle. This decline is more evident after ten cycles and it is also accompanied by the decrease of capacity. We can see the comparison of cathode materials when using electrolyte 1.5 M LiPF_6 EC:DMC 1:2 and after addition of Sulfolane in Fig. 10 e) and f). It is evident that capacity obtained in the first cycle for the cathode material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is for both electrolytes the same but there is greater decline in capacity after ten cycles leads for the sample using the electrolyte 1.5 M LiPF_6 EC:DMC:Sulfolane 1:2:1. The sample with electrolyte 1.5 M LiPF_6 EC:DMC:Sulfolane 1:2:1 achieves in the first and the tenth cycle greater capacity for cathode material $\text{LiCr}_{0.1}\text{Ni}_{0.4}\text{Mn}_{1.5}\text{O}_4$. This could be due to higher stability of this electrolyte in combination with the higher discharge plateau of this type of cathode material.

4. CONCLUSION

It was found out by the LSV method that electrolytes using LiTFSI as salt exhibit high instability at both Scan Rate speeds in the given potential window as shown in Fig. 1 and Fig. 2. It is evident that these electrolytes become unstable when crossing the threshold of 4 V. That was the reason why electrolytes with LiTFSI were discarded in the following measurements with cathode materials. All electrolyte samples with the addition of Sulfolane showed improved stability. However, comparing the stability of electrolytes 1.5 M LiPF_6 EC:DMC 1:2, and 1.5M LiPF_6 EC:DMC:Sulfolane 1:2:1 before and after addition of 0.1 M LiNO_3 salt, we can see increased stability of the electrolyte without Sulfolane, while the electrolyte with Sulfolane shows stability decrease. Structure of both types of created cathode materials was crystalline as we can see in Fig. 3. Fig. 4 further confirms good distribution of the elements in the materials of both prepared samples. It is evident that the capacity during the first cycling at 0.5 C is lower in the case of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode and the capacity of the

LiCr_{0.1}Ni_{0.4}Mn_{1.5}O₄ cathode is about 20 mAh/g higher, depending on the type of electrolyte. The material LiNi_{0.5}Mn_{1.5}O₄ shows very stable capacity in combination with the electrolyte 1.5 M LiPF₆ EC:DMC 1:2 and it displays low sensitivity to load changes. Similar results can be obtained using the electrolyte 1.5 M LiPF₆ EC:DMC:Sulfolane 1:2:1 which behaved similarly to the electrolyte without Sulfolane, while the material was more sensitive to the load change. These two electrolytes were also the only ones with which the material LiNi_{0.5}Mn_{1.5}O₄ worked at the high temperature. Other electrolytes showed much lower stability. Similar results were achieved during the testing with LiCr_{0.1}Ni_{0.4}Mn_{1.5}O₄, but this material exhibited higher stability with the electrolyte 1.5 M LiPF₆ EC:DMC:Sulfolane 1:2:1 than with 1.5 M LiPF₆ EC:DMC 1:2. The cathode material LiCr_{0.1}Ni_{0.4}Mn_{1.5}O₄ in combination with the electrolyte 1.5 M LiPF₆ EC:DMC:Sulfolane 1:2:1 and electrolyte 1.5 M LiPF₆ EC:DMC was also very stable during cycling at high temperatures; it was better than LiNi_{0.5}Mn_{1.5}O₄ with higher capacity and higher thermal stability confirmed by TGA, which confirmed that the addition of chromium improved the structural stability. The combination of the cathode material LiCr_{0.1}Ni_{0.4}Mn_{1.5}O₄ with the electrolyte 1.5 M LiPF₆ EC:DMC:Sulfolane 1:2:1 was the most stable of all the tested combinations. The drop of the capacity at the end of cycling was 10.6 %. These findings are very important because they have not been reported in any previous articles so far, since electrolytes are usually tested with the cathode material LiNi_{0.5}Mn_{1.5}O₄ and not with its alternative doped by Cr with a higher plateau and higher demands on the properties of electrolyte. Lower stability of the samples with electrolytes with addition of 0.1 M LiNO₃ salts was proved. Generally it can be stated that electrolytes with the addition of 0.1 M LiNO₃ showed worse results in terms of stability and that by adding Sulfolane we can achieve similar or better results than with the electrolyte 1.5 M LiPF₆ EC:DMC 1:2.

ACKNOWLEDGEMENTS

This research work has been carried out in the Centre for Research and Utilization of Renewable Energy (CVVOZE). Authors gratefully acknowledge financial support from the Ministry of Education, Youth and Sports of the Czech Republic under NPU I programme (project No. LO1210).

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