

As you can see from table 2 the analysis is too less sensitive. The recovery is higher than the actual concentration of fluoride after 30 min that can be caused by influence of  $\text{Fe}^{2+}$  ions in solutions. Nevertheless after 60 min electrocoagulation the increasing potential shows a decreasing concentration of fluoride to 36,9-38,4mg/l that shows the sorption of  $\text{F}^-$  ion on surface of large flocs which start to form only after 40 min electrocoagulation. However, if we continue electrocoagulation the concentration of fluoride does not change because the process of coagulation has finished until 60 min of electrolysis.

For electrocoagulation experiment, a decreasing concentration of the solution could be determined. Possible reasons could be the increased amount of used testing solution and incomplete oxidation of iron to  $\text{Fe}^{2+}$  (shown by the green to blue color of the solution after about 40 min). These conditions allow increasing the concentration of  $\text{Fe}^{2+}$ , their transfer to  $\text{Fe}^{3+}$  and formation of large flocs, finally, and it improve removing of  $\text{F}^-$  ion.

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#### **THIN-LAYER CO-DOPED $\text{LiMn}_2\text{O}_4$ SPINEL COMPOSITE WITH CARBON NANOTUBES FOR LITHIUM-ION BATTERIES AT LOW TEMPERATURE**

With technical progress development the demand for high energy autonomous power sources particularly for lithium-ion batteries (LIB) increases. Success of LIB basic research and practice applications are regarded as conspicuous progress in the electrochemistry of last decades. However it is necessity in LIB improvement with aim of their cost decrease

and play for safety. Alternative to expensive and toxicity  $\text{LiCoO}_2$  used generally in LIB is low price and toxicity  $\text{LiMn}_2\text{O}_4$  spinel. Along with merits of  $\text{LiMn}_2\text{O}_4$  spinel it possesses the demerits it inter alia is the low discharge rate and the decrease of discharge capacity of  $\text{LiMn}_2\text{O}_4$  during cycling particularly at the low temperatures.

In our works [1, 2] well-directed efforts on the improvement of the discharge characteristics  $\text{LiMn}_2\text{O}_4$  spinel were carried out. The positive effect was achieved with  $\text{LiMn}_2\text{O}_4$ , carbon nanotubes (CNT) compositions which were madden by mechanical embedding of the mixture of  $\text{LiMn}_2\text{O}_4$  spinel powder with CNT (90:10% mass) into Al-matrix. The high coulomb efficiency of thin-layer composite electrode (0.5-0.8  $\mu\text{m}$ ) performance in redox reaction with Li observes as the result of an increase of composite conductivity [1]. The discharge capacity of  $\text{LiMn}_2\text{O}_4$ , CNT-electrodes in the first cycles reaches to 117-119  $\text{mAh}\cdot\text{g}^{-1}$  at discharge rate of 1 C (98-100  $\text{mAh}\cdot\text{g}^{-1}$  at 22.4 C) and cycling continued at high discharge rate during more than 500 charge-discharge cycles at  $T=290\text{-}298$  K.

The improvement of discharge characteristics of  $\text{LiMn}_2\text{O}_4$  compositions with CNT is achieved by Co-doping of  $\text{LiMn}_2\text{O}_4$  [2]. Surface Co-doping promotes to increase of electro conductivity of pressed  $\text{LiMn}_2\text{O}_4$  spinel at temperatures of 293 and 323 K. The advantage of Co-doped  $\text{LiMn}_2\text{O}_4$  in composition with CNT over one's without Co is shown in the increase of cyclic efficiency and the rate of  $\text{Li}^+$ -intercalation/deintercalation. Discharge capacity of Co-doped  $\text{LiMn}_2\text{O}_4$ , CNT-electrodes at rate of 40 C and  $T=293\text{-}298$  K is equal to 75% (90  $\text{mAh}\cdot\text{g}^{-1}$ ) of one obtained in the first cycle. The capacity of  $\text{LiMn}_2\text{O}_4$ , CNT-electrodes without cobalt reaches as soon as 80  $\text{mAh}\cdot\text{g}^{-1}$  at 20 C. Satisfactory cycling performance of Co-doped  $\text{LiMn}_2\text{O}_4$ , CNT-electrodes was obtained at 1 C and low temperature (258 K). At same time their high discharges characteristics change for the worse at low  $T=273, 258$  K when the charge rate increased to 10 C. Low temperature investigations of LIB become necessary with increased requirement of their effective operation at low temperature for various applications. The preceding investigations considered not profoundly low temperature effects. The interest to low temperature behavior of LIB with carbon anode becomes recently rise after aircraft with the 787 Dreamliner. The catastrophe was caused by Li-dendrite short circuit in LIB at low temperature [3]. At low temperature lithium plating in LIB becomes negatively affected by resistance of charge transfer  $R_{\text{ct}}$  and blocking characters of surface film [4]. The cell over potential rises quickly leading to lithium deposition on carbon electrode surface instead Li-intercalation into carbon. It promotes to the dendrite formation. When the surface abnormal litiation becomes possible on the carbon anode the

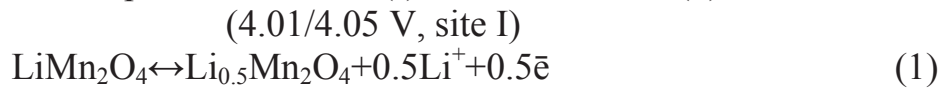
LIB system operates as Li accumulator. The investigations of Co-spinel, CNT/Li accumulator system presents as actual one for the understanding of high cell polarization at low temperatures.

It was begin the exposure of the causes of discharge capacity decrease of Co-doped  $\text{LiMn}_2\text{O}_4$ , CNT-electrodes in redox reaction with lithium at the long cycling and low temperatures. In the work it was attempt to analyze of relationship of galvanostatic charge-discharge curves, cycling voltammograms (CV) and impedance characteristics (IS) of thin-layer Co-doped  $\text{LiMn}_2\text{O}_4$ , CNT-electrodes.

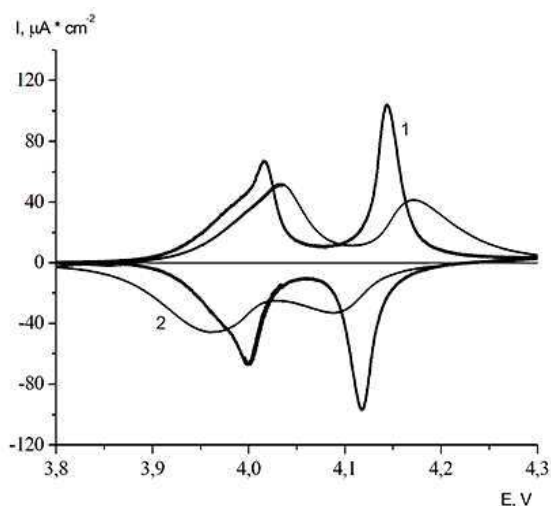
Co-doped  $\text{LiMn}_2\text{O}_4$  spinel was synthesized and used in thin-layer electrodes. Surface Co-doping of  $\text{LiMn}_2\text{O}_4$  spinel ( $\text{LiCo}_{0.04}\text{Mn}_{1.96}\text{O}_4$ ) was produced by the thermal treatment of stoichiometric mixture (98:2%) of  $\text{LiMn}_2\text{O}_4$  powder (Merck) with  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  [1]. Carbon nanotubes were synthesized by catalytic pyrolysis of ethylene and used as a conductive addition. The outer diameter of nanotubes is about 10-30 nm.

The electrochemical investigations of  $\text{LiCo}_{0.04}\text{Mn}_{1.96}\text{O}_4$ , CNT-electrodes were performed in the sealed 3-electrode cell with Li counter electrode,  $\text{Li}/\text{Li}^+$  reference electrode and also in 2-electrode cell with Li counter electrode. Cells filled up in argon atmosphere by electrolyte of the composition: ethylene carbonate (Merck), dimethyl carbonate (Merck), 1 mole  $\text{l}^{-1}$   $\text{LiClO}_4$ . The charge-discharge characteristics were plotted on a test bench with computer control and registration. IS and CV obtained using VoltaLab PGZ 301 analytical radiometer. IS were acquired under application of the electrical perturbation of 5-10 mV in frequency series of  $10^{-6}$ - $10^{-2}$  Hz at T K: 258, 296. Zplot, Zview (Version 2.1 b) software's were used for registration and analysis of IS.

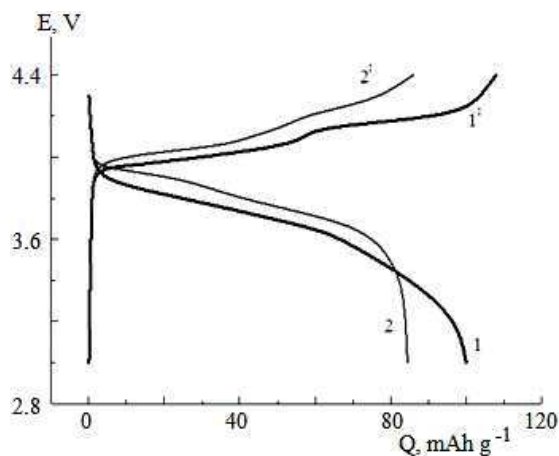
CV (Fig.1, curve 1) of  $\text{LiCo}_{0.04}\text{Mn}_{1.96}\text{O}_4$ , CNT-electrode in electrolyte in the beginning of long cycling at  $T=296$  K show reversible behavior of the system due to two-phase  $\text{LiMn}_2\text{O}_4$  performance (1, 2) as the characteristic of redox couples 4.01/4.05 V (I) and 4.12/4.14 V (2):



The essential kinetic limits appear in the system at the low temperature (Fig.1, curve 2).



**Figure 1 – Cyclic voltammograms of  $\text{LiCo}_{0.04}\text{Mn}_{1.96}\text{O}_4$ , CNT-electrode at T K: 1 – 296; 2 – 258. Rate of potential scan is  $1 \cdot 10^{-4} \text{ V} \cdot \text{s}^{-1}$ .**



**Figure 2 – Charge-discharge characteristics of  $\text{LiCo}_{0.04}\text{Mn}_{1.96}\text{O}_4$ , CNT at charge rate 1 C (curves 1<sup>1</sup>), 10 C (curve 2<sup>1</sup>) and discharge rate 10 C (curves 1, 2) at T=258 K.**

If sum the presented results at 296 K it could say just about nonessential decrease of discharge capacity of  $\text{LiCo}_{0.04}\text{Mn}_{1.96}\text{O}_4$ , CNT-electrodes in redox reaction with lithium (2.0-3.6%) at the increase of intercalation/deintercalation rate from 1 C to 10 C at  $T_{\text{room}}$ .

Because of high anodic polarization of  $\text{LiCo}_{0.04}\text{Mn}_{1.96}\text{O}_4$ , CNT-electrode at 10 C at T=258 K in charging of the composite with final voltage 4.3 V usually employed for  $\text{LiMn}_2\text{O}_4$  spinel is insufficient for the maintenance of reversible capacity (Fig. 2, curves 2-2<sup>1</sup>). At the rate of the deintercalation 1 C, discharge rate 10 C and T=258 K the discharge capacity is high (Fig. 2, curve 1-1<sup>1</sup>) but the discharge profile is greatly differs from one at 296 K at the expense of  $iR$ -component. The charge capacity and corresponding discharge capacity at 10 C decreases at charge current rate of 10 C (Fig. 2, curves 2<sup>1</sup>, and 2).

At T=296 K the difference of discharge capacity of  $\text{LiCo}_{0.04}\text{Mn}_{1.96}\text{O}_4$ , CNT-electrodes obtained in 3-electrode cell and in 2-electrode cell at charging by 1 C and 10 C averages to 1.0% when discharge rate is 10 C. At the low temperature (258 K) the difference averages to 4.5% at charging by 1 C and one to 19.0% at charging by 10 C when discharge rate is 10 C.

The data of galvanostatic and CV studies analyzed in parallel with the evolution of impedance spectra IS in site II at the potential 4.14 V at low temperature and long cycling. The IS changes at low temperatures (258 K) are expressed in increase of the resistance of surface film ( $R_{\text{SEI}}$ ) by 3.0-3.5 times and also one of the resistance  $R_{\text{ct}}$  by the order of the value.

At discharge capacity decrease to  $74 \text{ mAh}\cdot\text{g}^{-1}$  in the 270<sup>th</sup> cycle at  $T=258 \text{ K}$  effective exchange current decreases by the order (to  $0.90\cdot 10^{-5} \text{ A}\cdot\text{cm}^{-2}$ ). The decomposition of the electrolyte near potential  $4.13 \text{ V}$  vs.  $\text{Li}/\text{Li}^+$ -electrode is accompanied by the formation of the resistive surface film as was shown by analyses of CV-, IS-, galvanostatic results.

Such causes of the decline in discharge electrode capacity have been established as limiting electrode kinetics, increased polarization of the electrolyte and solid-state phase resistance, and also decreasing ionic permeability of SEI film at low temperature ( $258 \text{ K}$ ). The decrease of the capacity upon long cycling in these compounds can be attributed to the loss of the electrode ability of full Li deintercalation because of increasing polarization of electrolyte decomposition with formation of resistive film. Further the optimization of the electrolyte with using of the effective multifunctional additions and co-solvents for the new investigated spinel composite might be one from the possible ways of the improvement of the obtained results. Formation of more conductive passivation films as known provided by fluoroethyl carbonate and butyl sulfone, and further low temperature phase transfer modification in spinel might be highly beneficial to rate performance of spinel composite at low temperature.

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