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Lithium-ion battery based on "Lithiated Multicomponent Oxides–Silicon Nanofibers" System for Portable Applications

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Abstract

Lithium-ion battery based on a new electrochemical system with a positive electrode based on lithiated multicomponent oxides and a negative electrode based on silicon nanofibers has been developed. The battery is intended for portable applications. The energy density of the battery is about 230 Wh kg^{-1}.

Keywords: *Lithium-ion battery, lithiated multicomponent oxides, silicon nanofibers, energy density*

1. Introduction

In terms of energy density traditional electrochemical system of lithium-ion battery, manufactured since 1991 (lithium cobaltate–graphite), approaches its theoretical limit [1]. The energy density of a battery is determined by the specific capacity of active substances in its positive and negative electrodes, its voltage, and the efficiency of its design [2]. The preference of active material of negative electrodes of lithium-ion batteries is given to silicon-based materials (pure silicon or its composites), which have the specific capacity of above 2000 mAh g^{-1} and work at the discharge potentials of ca. 0.2 V more positive than carbon materials [3]. It can be assumed that lithiated multicomponent oxides are ones of the best candidates for the active material of positive electrodes. Such materials operate at potential about 3.9 – 4.0 V and therefore it can be used together with traditional electrolytes based on mixture of ethylene carbonate-diethyl carbonate-dimethyl carbonate [4]. One of the new electrochemical systems of lithium-ion battery, such as lithiated multicomponent oxides – silicon nanofibers, has ultimately higher energy density. Theoretical energy density of such electrochemical system can achieve 550 Wh kg^{-1}.

2. Experimental

2.1 Synthesis of electrode materials

The samples of lithiated multicomponent oxides $LiCo_{0.968}Mg_{0.014}Ti_{0.018}O_2$ were synthesized by solid-state method from $Li_2(CO_3)$, MgO, Co_3O_4 and TiO_2. Firstly, stoichiometric amounts of starting materials (with some excess of lithium carbonate for compensation of possible Li_2O evaporation during following heat-treating) were treated in planetary mill for 30 s. Then the mixture was dried and calcined for 3 to 16 hours at the temperature 650−950 ^oC in air [4].

The synthesis of silicon nanofibers was carried out by electrolysis of SiO_2 solution in KF(40.5) – KCl(49.5) – K_2SiF_6(10) melt at 750°C. The SiO_2 concentration was 2-3 mol. %. The silicon electrodeposition was performed on a graphite cathode. The obtained deposit was washed with a dilute aqueous solution of hydrochloric acid. In all electrolysis runs, the source of direct current was provided by a GWINSTEK PSH-3610 potentiostat/galvanostat. The temperature in the furnace was set with a Varta TP 403 thermoregulator. The cell voltage was controlled with APPA 109 N multimeter with high input impedance. Methods for the synthesis of silicon nanofibers as well as method of melts preparation have been already described in detail elsewhere [5-8].

2.2 Electrode preparation

Cathode and anode active masses for electrodes were prepared using the ratios as follows: 85 wt. % of $LiCo_{0.968}Mg_{0.014}Ti_{0.018}O_2$ (or silicon nanofibers), 10 wt. % of carbon black, 5 wt. % of polyvinylidene fluoride. The latter was dissolved in N-methylpyrrolidone. Active

masses based on $LiCo_{0.968}Mg_{0.014}Ti_{0.018}O_2$ or silicon nanofibers were heated and applied onto aluminum (for positive electrode) or titanium (for negative electrode) foil substrates with MSK-AFA-II-Automatic Thick Film Coater. After drying, electrode plates were placed in roller press. Semi-finished product was pressed at 2 t. Rolled electrode sheets were cut into ready electrodes sized 55x55 mm^2 with MiniMarker A2 laser marker, which were subsequently used for assembling batteries. To determine specific electrochemical capacity of cathode and anode material, small electrodes sized 1.5x1.5 cm^2 were cut out, and galvanostatic studies were carried out in three-electrode electrochemical cells. Thickness of the positive electrode's active layer was 90 µm. Thickness of the negative electrode's active layer was about 20 µm. The difference in thickness was conditioned by the difference in specific capacity of $LiCo_{0.968}Mg_{0.014}Ti_{0.018}O_2$ and silicon nanofibers. Batteries and electrochemical cells were assembled in a glove box in a dry argon atmosphere (OJC "Specrum-system", Moscow). The 1 M $LiPF_6$ in a mixture of ethylene carbonate-diethyl carbonate-dimethyl carbonate (1:1:1) prepared in the laboratory of the Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences from Battery Grade commercial reagents was used as an electrolyte.

3. Results and discussion

3.1 Scanning electron microscopy

Following the results of scanning electron microscopy, the particle size of $LiCo_{0.968}Mg_{0.014}Ti_{0.018}O_2$ is about 500 nm. The particles form agglomerates from 5 µm to 10 µm (Figure 1).

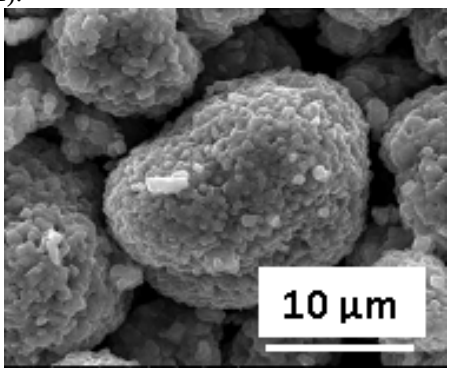

Fig. 1. Micrograph of $LiCo_{0.968}Mg_{0.014}Ti_{0.018}O_2$

According to the data of the scanning electron microscopy, synthesized samples of silicon represent nanofibers with diameter from 50 to 250 nm (Figure 2).

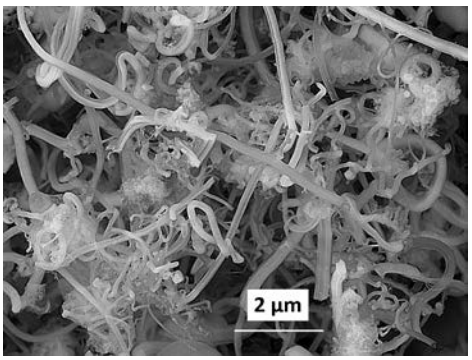

Fig. 2. Micrograph of silicon nanofibers

3.2 Electrochemical performances of the electrodes

The results of galvanostatic cycling presented in Figure 3 revealed that the specific discharge capacity of $LiCo_{0.968}Mg_{0.014}Ti_{0.018}O_2$ at the current density of 20 mA g^{-1}, which corresponds to C/10 was about 150 mAh g^{-1}. The increased current density logically resulted in the decreased discharge capacity. At the current load of 5C the discharge capacity was about 45 mAh g^{-1}.

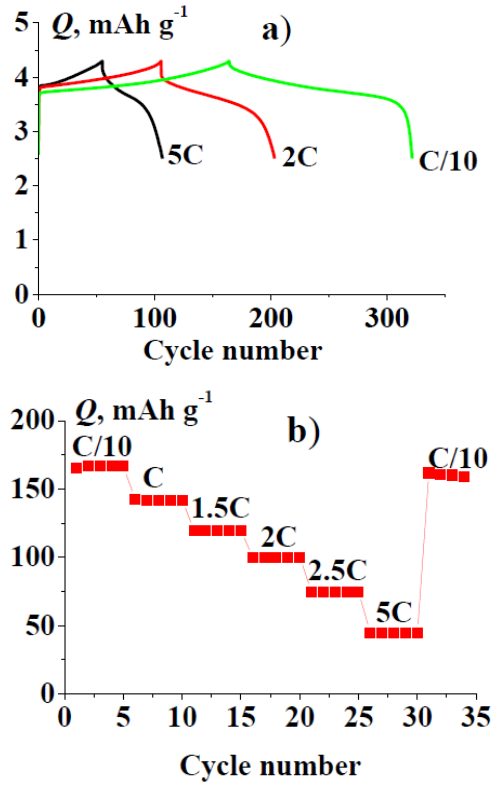

Fig. 3. Charge-discharge curves (a) and dependence of the discharge capacity on the current density (b) of $LiCo_{0.968}Mg_{0.014}Ti_{0.018}O_2$

The discharge potential of $LiCo_{0.968}Mg_{0.014}Ti_{0.018}O_2$ at low current load (C/10) was about 3.82 V. At increased loads (5C), the discharge potential of $LiCo_{0.968}Mg_{0.014}Ti_{0.018}O_2$ lowered insignificantly and was about 3.63 V.

The results of galvanostatic cycling of negative electrodes from silicon nanofibers are represented in Figure 4. The charge-discharge curve of silicone nanofibers represents a classical charge-discharge curve of a silicone electrode. At the same time, the average potential of insertion and extraction of lithium at current density of 100 mA g^{-1} was about 0.25 and 0.5 V, respectively. The current density of 400 mA g^{-1} corresponds to the current C/10. Discharge capacity was about 1000 mAh g^{-1}. The increase in current density has led to decrease in discharge capacity up to 200 mAh g^{-1} at current 5C (20 000 mA g^{-1}).

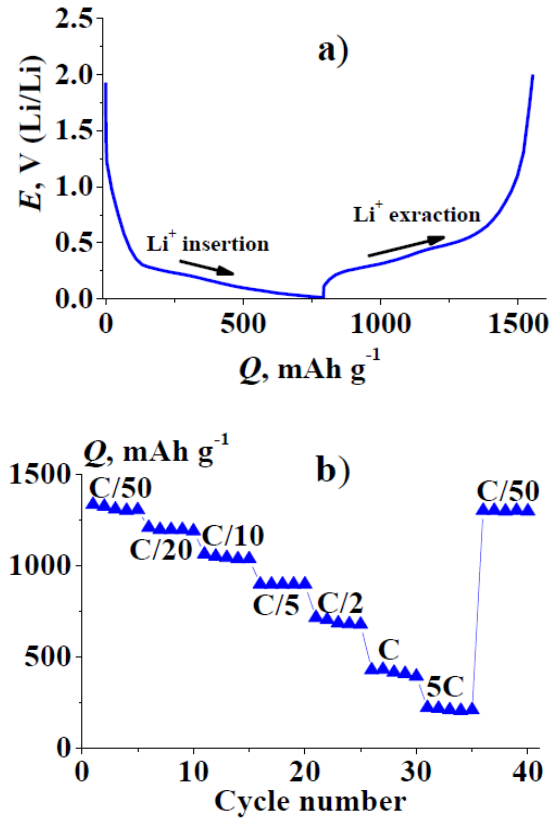

Fig. 4. Charge-discharge curves (a) and dependence of the discharge capacity on the current density (b) of silicon nanofibers

Seven (7) negative and seven (7) positive electrodes were used to manufacture a stack battery of 1 Ah rated capacity. The results of cycling are represented in Figure 5. As the figure 5a shows, the battery discharge capacity at the current of C/10 equals to the rated capacity, and the average discharge voltage is about 3.4V, which evidences of the battery's insignificant ohmic resistance. When the current density is increased, the battery's discharge capacity and average discharge voltage are reduced. Degradation and cycle life of the lithiated multicomponent oxides – silicon nanofibers system battery were determined at the charging-discharging current 0.2 A, which corresponded to the so called cycle service C/5. As the Figure 5b shows, change in the discharge capacity during the cycling for 50 cycles was 58 mAh on average, which is about of 5.8 % of the rated capacity. Thus, degradation during the cycling was 0. 11 % per cycle.

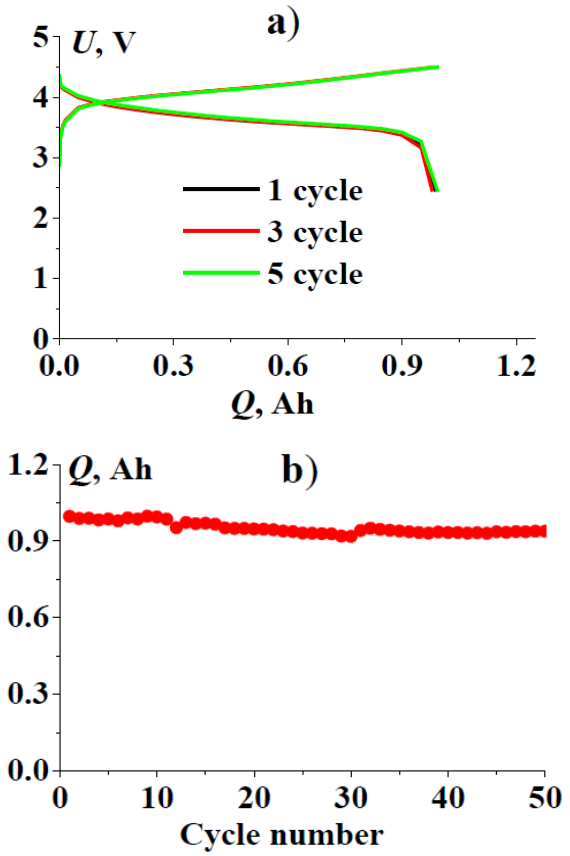

Fig 5. Charge-discharge curves (a) and change in the discharge capacity (b) of the lithiated multicomponent oxides – silicon nanofibers system battery. Nominal capacity was 1 Ah. Current of 200 mAh.

4. Conclusions

In order to develop a battery with increased energy specifications, new materials for lithium-ion battery were synthesized: cathode material based on lithiated multicomponent oxides ($LiCo_{0.968}Mg_{0.014}Ti_{0.018}O_2$) and anode material based on silicon nanofibers. Lithium-ion battery of the lithiated multicomponent oxides – silicon

nanofibers system was developed based on these materials. Energy density of the battery was about 230 Wh kg^{-1}. The battery of this electrochemical system is intended for power supply of portable electronic devices.

Acknowledgments

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