

Increasing of a Lithium-Ion Supercapacitor Specific Energy by Introducing $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ Additive into the Active Carbon-Based Cathode Material

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Abstract

In this paper, we investigated the effect of the cathode material additive $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111) on the capacity and specific energy of a hybrid lithium-ion supercapacitor (HLISC) with a positive electrode based on active carbon, a negative electrode based on graphite, and an auxiliary lithium electrode. The introduction of 35 % of the mass. NMC111 made it possible to increase the specific capacity of the storage device energy by ~ 77 % compared to a lithium-ion supercapacitor (LISC) with a cathode based on pure, non-doped active carbon. It was found that cycling at high current densities does not cause significant changes in the HLISC characteristics. This type of hybrid element proved to have two advantages. At low current densities, it exhibits charge-discharge properties of a lithium-ion battery with a high specific energy, and at high current densities, it exhibits the properties of a lithium-ion supercapacitor with a high specific power.

Keywords

Lithium-ion supercapacitor; $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111); hybrid cathode; active carbon.

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Introduction

Low specific power ($< 1000 \text{ W/kg}$), short service life (< 4000 charge-discharge cycles) of lithium-ion batteries (LIB) and insufficient specific energy of supercapacitors (SC, $5 - 10 \text{ W}\cdot\text{h/kg}$) limit the possibilities of their further development in the electric power industry and related fields. For this reason, continuous development of new electrochemical energy storage devices (EESD), which could combine the advantages of LIB and SC, is observed.

One of the proposed types of drives that can overcome the disadvantages of LIB and SC are lithium-ion supercapacitors (LISC) (Fig. 1).

LISCs are interesting in that they have an increased specific power and a large number of cycles compared to LIB, as well as a higher specific energy compared to SC. A typical LIB consists of a cathode containing chemically bonded lithium, a separator, an electrolyte, and an anode [2]. During its operation, Li^+ ions move between the positive and negative electrodes, which is accompanied by intercalation-

deintercalation in the electrode masses. SC, depending on the mechanism of charge accumulation, can be divided into pseudo-capacitors (PC) and double-layer electrochemical capacitors (DEC) [3]. The energy in PC accumulates due to rapid redox reactions on the surface of electrode materials, such as oxides, metal sulfides and conductive polymers. In DEC, energy is accumulated due to a double electric layer that is formed during the rapid adsorption-desorption of ions on the surface of porous carbon materials with a high specific surface area. In fact, LISC can be considered as a combination of a positive DEC electrode and a negative LIB electrode (Fig. 2) [4–7]. Thanks to this configuration, the shortcomings of SC and LIB are leveled (Table 1). LISCs are usually divided into conventional types according to the type of electrode materials used: all-carbon, non-carbon and hybrid [8].

Hybrid LISCs can be created using an internal serial or parallel circuit [9]. Hybrid capacitors with an internal serial circuit are also called asymmetric hybrid lithium-ion capacitors [7, 10].

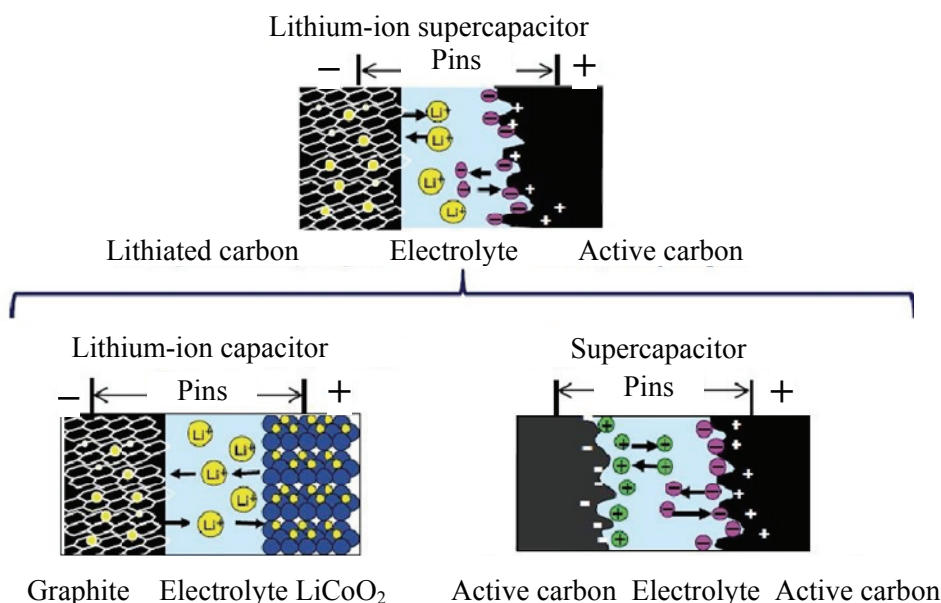


Fig. 1. The principle of operation of LIB, SC and LISC [1]

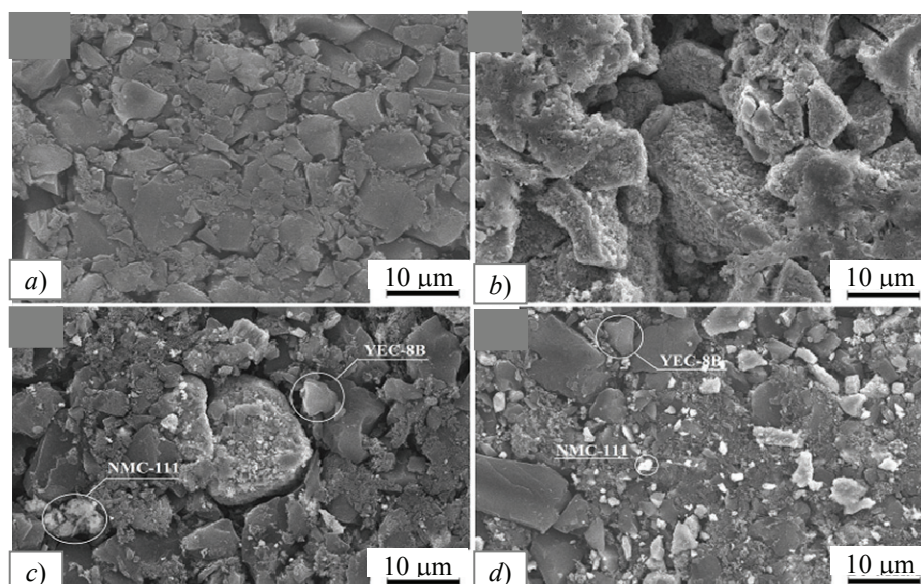


Fig. 2. Electronic micrographs of electrodes containing various active materials:
a – coal YEC-8B; *b* – NMC111; *c* – a mixture of YEC-8B and 35 % unmilled NMC111;
d – a mixture of YEC-8B and 35 % milled NMC111

Table 1

Some parameters of LIB, SC and LISC [1]

Parameter	LIB	LISC	DEC
Cathode	Complex lithium oxides	AC, complex lithium oxides	AC, graphene, carbon nanotubes, etc.
Anode	Graphite, Si/C, metal oxides, etc.	Graphite, hyperdense carbon, Li ₄ Ti ₅ O ₁₂ , etc.	
Service life, cycles	< 4000	> 10000	> 100000
Operating voltage, V	4.2 – 4.35	3.8 – 4.0	2.5 – 2.7
Specific energy, W · h/kg	150 – 200	~ 100	5 – 10
Specific power, W/kg	< 1000	10000 – 40000	> 10000

Until now, various complex lithium compounds, such as LiCoO_2 [11], LiMn_2O_4 [12], etc., have been used to fabricate mixed cathodes of hybrid capacitors with an internal parallel circuit. Until now, there have been no studies on the use of a material with a layered structure $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ as part of the HLISC mixed cathode. In this case, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, graphite or hyperdense carbon can be used as the anode active substance. Among them, graphite seems to be the most attractive, due to its low negative potential of intercalation – deintercalation of lithium and high specific capacity [10]. At the moment, a rather small number of studies on HLISC with an internal parallel circuit are available [7, 11 – 19].

In this study, a mixed cathode material was prepared based on crushed $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC111) and AC. The structure of the electrodes was defined using scanning electron microscopy (SEM) in comparison with a mixed material based on unmilled NMC111 and AC. Studies were conducted of the material electrochemical properties as a part of the positive electrode of a hybrid HLISC element with a graphite-based anode. The values of the operating characteristics of this GLISC were obtained: reversible discharge capacity, specific energy, and cyclic stability. A comparison of the characteristics of the developed HLISC with LISC manufactured by Global SO LLC with a cathode based on only AC and a graphite based anode is demonstrated. Combining high specific energy with a high charge rate, the hybrid element $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2 + \text{AC} / \text{graphite}$ is a promising device for use in energy storage systems.

Experimental

Electrode mass fabrication

Electrode mass obtaining of the investigated assemblies was carried out according to the following methods. Powder $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC111, XIAMEN TOB NEW ENERGY TECHNOLOGY Co., LTD, China) was mixed with isopropyl alcohol (IPA, ChP, ZAO “ECOS-1”, Russia) in a ratio of 1 : 1 by weight in agate bowl with a capacity of 125 cm^3 and subjected to grinding with agate balls at a speed of 400 rpm in a planetary ball mill Retsch PM200 for 10 hours. The resulting mixture was dried in air overnight at 70°C .

To prepare a carbon mass with a binder and an electrically conductive additive (88.4 % active carbon, 5.5 % binder and 6.1 % carbon black by weight) carbon black TOB-S-16 “Super P” (LLC Stanko-Inter, Russia) were dispersed in IPA to homogeneity using an

overhead stirrer at a rotation speed of 800 rpm. Then, YEC-8B AC (Stanko-Inter LLC, Russia) was added to the resulting suspension, and then it was dispersed in a vacuum mixer at a speed of 1200 rpm within 3 hours. Then, polytetrafluoroethylene (PTFE, mass fraction of dry matter 57.5 %, LLC Halopolimer Perm, Russia) was added to the resulting suspension and mixed on a vacuum mixer at a speed of 550 rpm 3 hours. The resulting carbon mass was mixed with an appropriate amount of NMC111 powder using a laboratory knife mill. The manufacture of electrode tape was carried out using a doctor blade.

Cathode fabrication

The cathodes for LISC were fabricated by pressing an appropriate electrode-based electrode tape on an aluminum grid 20 microns thick (NPP Kvarta, Russia), coated with a layer of electrically conductive adhesive consisting of carbon black and PVC in a ratio of 2 : 3 by weight.

HLISC cathodes were fabricated by pressing an NMC / AC-based tape onto an aluminum mesh 20 microns thick (NPP Kvarta, Russia) coated with a layer of electrically conductive adhesive consisting of carbon black and PVC in a ratio of 2:3 by weight.

The thickness of the active layer (excluding the current supply) of the obtained LISC cathodes was $210 \mu\text{m}$, and the HLISC cathodes were $280 \mu\text{m}$. The finished cathodes were dried in a vacuum oven at 120°C for 24 hours.

Anodes and auxiliary electrodes fabrication

For the manufacture of anodes, we used a mixture of 92 % T-S360 graphite (Stanko-Inter LLC, Russia), 2 % carbon black and 6 % PVDF (Stanko-Inter LLC, Russia) in N-methylpyrrolidone (ChC, “Component-Reagent”, Russia). The specified mixture was applied using a squeegee on both sides of a 30-micron thick copper mesh (NPP Kvarta, Russia), on both sides coated with a layer of electrically conductive adhesive consisting of carbon black and PVC in a ratio of 2 : 3 by weight. The thickness of the active layer (excluding current supply) of the LISC anode was $44 \mu\text{m}$, HLISC – $140 \mu\text{m}$. The finished anodes were dried in a vacuum oven at 120°C for 24 hours.

Auxiliary lithium electrodes were fabricated by pressing lithium foil (thickness $60 \mu\text{m}$, OOO Stanko-Inter, Russia) onto a current supply of copper foil $17 \mu\text{m}$ thick.

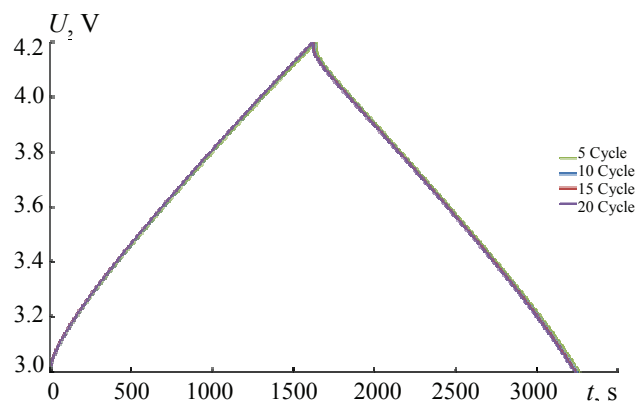


Fig. 3. Charging and discharge characteristics of the LISC (voltage U , V versus time t , s) in the voltage range 3.00–4.20 V at a constant current density of 100 mA/g_{graphite} (2C)

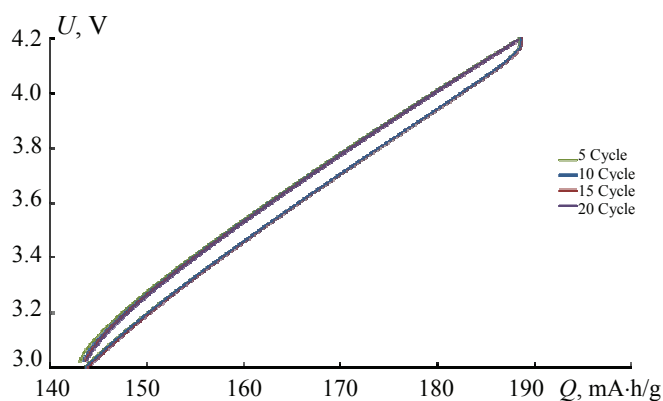


Fig. 4. Charging and discharge characteristics of LISC (voltage U , V versus capacity Q , mA·h/g) in the voltage range 3.00–4.20 V at a constant current density of 100 mA/g_{graphite} (2C)

The charge-discharge characteristics of HLISC in the voltage range from 3.00 to 4.20 V at a constant current density of 50 mA/g_{graphite} are shown in Fig. 5 and for 5, 15 and 20 cycles – in Fig. 6.

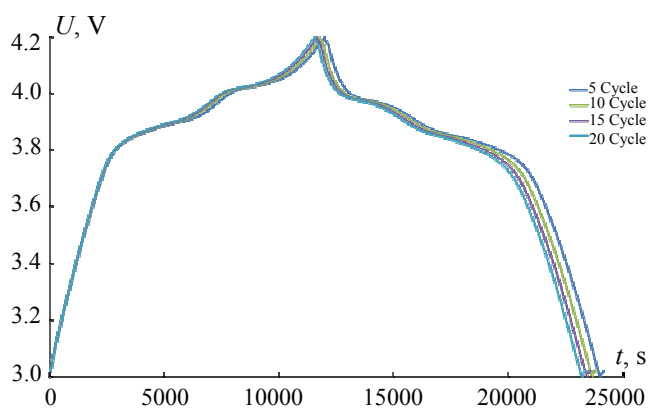


Fig. 5. Charging and discharge characteristics of HLISC (voltage U , V vs. time t , s) in the voltage range 3.00 – 4.20 V at a constant current density of 50 mA/g_{graphite} (0.3C)

Formation of assemblies

The size of the active region of the cathodes was 98×98 mm, the size of the anodes was 100×100 mm.

As an electrolyte, a LiPF_6 solution of a concentration of 1.2 mol/L in a mixture of 50 % ethylene carbonate with 50 % (Stanko-Inter LLC, Russia) by weight was used.

The separator was used of the PP20 grade and 30 microns thick (Stanko-Inter LLC, Russia). It was dried at 40 °C for 12 hours in a vacuum oven before use.

The elements were assembled in a glove box in an atmosphere of dry argon by combining one double-sided anode, separator, two single-sided cathodes, a separator and one auxiliary electrode with an additional current collector made of copper foil 9 μm thick.

Study of the electrodes structure

The microstructure of the electrodes was investigated using a scanning electron microscope (SEM) JSM-6510LV “JEOL”, Japan. Accelerating voltage during image acquisition was 15 kV.

Test procedure

To conduct anode lithiation, the first LISC charge cycle was carried out with a current of 5 mA/g_{graphite} and ended when the charge reached 250 mA·h/g_{graphite}. The voltage of the cell after the completion of lithiation was 3.1 V. The first HLISC charge cycle was carried out with a current of 10 mA/g_{graphite} and ended when the charge reached 180 mA·h/g_{graphite}. The voltage of the element after the completion of lithiation was 3.1 V. LISC was cycled in the potential region of 3.0–4.2 V using a charge/discharge current of 100, 200, 300, 400 mA/g_{graphite}, at room temperature. HLISC was cycled in the range of potentials of 3.0–4.2 V using a charge/discharge current of 100, 200, 300, 400 mA/g_{graphite} at room temperature. The studies were conducted on the potentiostat “P-150X Elins”.

Results and Discussion

In order to study the surface morphology and establish a relationship between the particle size and electrochemical properties of the electrodes, micrographs of the surface of the electrodes were obtained by scanning electron microscopy, see Fig. 2.

As can be seen from Fig. 2, the average particle size of YEC-8B activated carbon is 5–10 μm (Fig. 2a), NMC111 is 5–20 μm (Fig. 2b). The charge-discharge characteristics of LISCs in the voltage range from 3.0 to 4.2 V at a constant current density of 100 mA/g_{graphite} are shown in Figs. 3, 4.

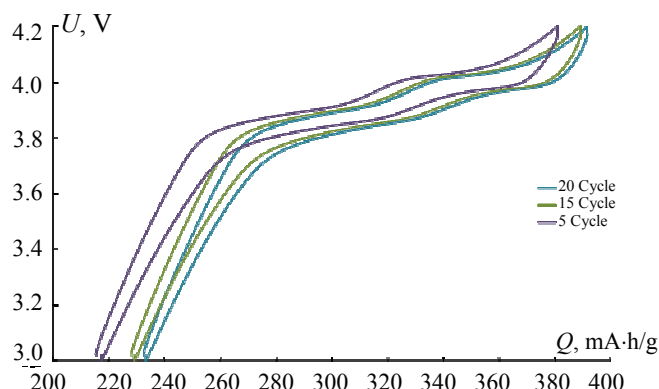


Fig. 6. Charging-discharge characteristics of HLISC (dependence of voltage U , V on capacity Q , mA·h/g) in the voltage range 3.00 – 4.20 V at a constant current density of 50 mA/g_{graphite} (0.3C)

It is obvious that when the voltage of the HLISC is less than 3.8 V, the main contribution to the capacitance is made by the AC. In the voltage range of 3.8–4.2 V, 2 waves with a large charge appear due to the contribution of the NMC capacitance.

Next, the element main characteristics dependence on the current value was investigated. The LISCmodel was cycled in the voltage range of 3.00 – 4.20 V with currents of 100, 200, and 400 mA/g_{graphite}. The dependences of the charge-discharge characteristics on the current value are shown in Fig. 7.

The HLISCmodel was cycled in the voltage range of 3.00 – 4.20 V with currents of 50, 100, 150, 200, 300, and 400 mA/g_{graphite}. The dependences of the charge-discharge characteristics on the current value are shown in Fig. 8.

Thus an increase in the charge-discharge current is accompanied by a decrease in the HLISC capacity. Basically, a decrease in HLISC capacity with increasing current is associated with a decrease in the contribution of NMC capacitance. However, NMC manages to partially realize its capacity at high currents. The main specific characteristics of LISC and HLISC at different currents are given in Table 2. With an increase in current from 100 to 400 mA·h/g_{graphite}, the capacity of HLISC decreased by 26 % from 149 to 111 mA·h/g_{graphite}, and the energy intensity by 28 % from 231 to 167 W·h/kg HLISC positive electrode mixture. At the same time, the LISC capacity decreased by 17 %, and the energy intensity by 18%, with an increase in the charge / discharge current from 100 to 400 mA·h/g_{graphite}.

Figure 9 show the graphical dependences of the LISC and HLISC assemblies capacities, expressed in

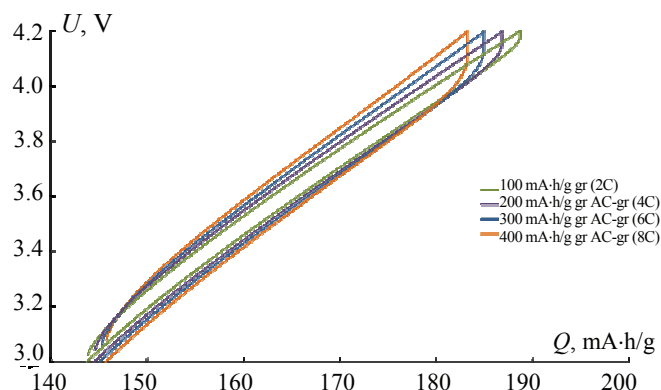


Fig. 7. Charging and discharge characteristics of LISC (voltage U , V versus capacity Q , mA·h/g) in the voltage range 3.00 – 4.20 V at different current densities

farads and mAh on the charge-discharge current strength during cycling in the voltage range 3.00 – 4.20 V.

It is seen that the decrease in capacitance with increasing current is linear. It is important to note that the capacitance of the HLISC positive electrode is noticeably higher than that of conventional carbon electrodes, and with increasing current from 50 to 400 mA/g_{graphite} changes from 212 to 165 F/g of the cathode active mass (the capacity of carbon electrodes varies from 120 to 102 F/g of the cathode active mass at a current transition from 50 to 400 mA/g). The undoubted value of HLISC is that at a current of 400 mA/g_{graphite}, the hybrid element charges in 17 minutes. From the totality of the data obtained it follows that HLISC with a hybrid (coal + NMC) cathode has advantages over LISC with a carbon electrode, including when operating at high currents.

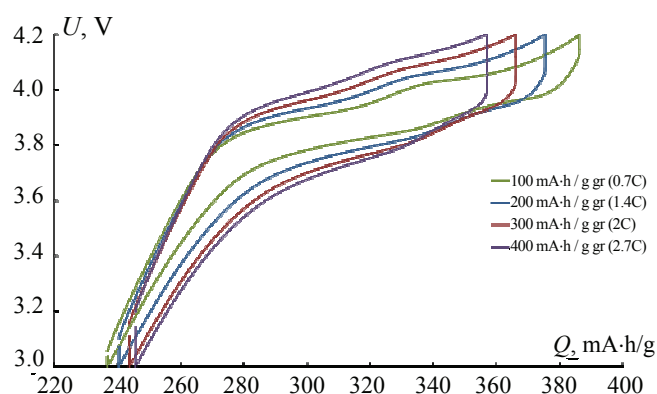


Fig. 8. Charging and discharge characteristics of GLISK (dependence of voltage U , V on capacity Q , mAh/g) in the voltage range 3.00 – 4.20 V at different current densities

Table 2

The dependence of the elements main specific characteristics on the current density

I , mA/g _{graphite}	Q (discharge), mA·h/g _{pure graphite}		C (charge), F/g _{cathode mixture}		E (discharge), W·h/kg _{cathode mixture}	
	LISC	HLISC	LISC	HLISC	LISC	HLISC
100	45	149	123	205	148	231
200	42	135	115	191	138	206
400	37	111	101	165	121	167

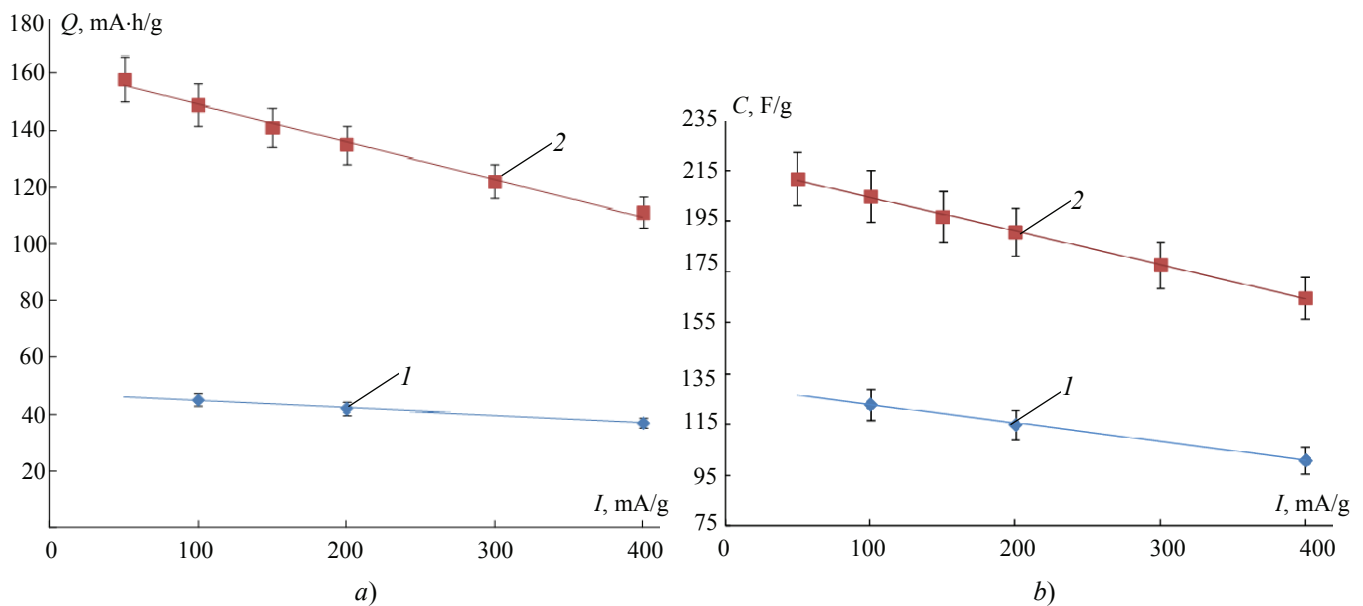


Fig. 9. The dependence of the capacitance LISC (1) and GLISC (2) on the strength of the charge-discharge current: a – mA h/g; b – F/g positive electrode

Conclusions

The capacity of the HLISC positive electrode (with a 35 % NMC additive in the carbon electrode) is ~ 77 % higher than conventional carbon electrodes (120 F/g of the positive electrode active mass at a current of 50 mA/g_{graphite}; 102 at a current of 400 mA/g_{graphite}) including at high currents. As the current increases from 50 to 400 mA/g_{graphite}, the capacity of the electrode decreases from 212 to 165 F/g of the active mass of the positive electrode.

The totality of the data obtained shows that HLISC with (carbon + 35 % NMC) cathode material has advantages over LISC with a carbon electrode, including when operating at high currents.

In addition, test results show that the addition of NMC does not affect the operation of the cell at high currents. The contribution of each of the active materials that make up the cathode largely depends on the current density. In applications where high energy

intensity is required, the cathode material due to the properties of NMC included in its composition will allow replacing the use of a separate energy storage device.

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