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

A.V. Desyatov, M.Yu. Chaika, V.V. Besedin*, E.V. Bulavina, A.V. Denisenko, N.A. Shibanov

Global CO LLC, 2, Nagornoye Shosse, Khimki, 141407, Russia

* Corresponding author. Tel.: +7 498 624 44 86; fax: +7 498 624 44 86; E-mail: vl.besed@gmail.com

Abstract

In this paper, we investigated the effect of the cathode material additive LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$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; LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC111); hybrid cathode; active carbon.

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Introduction

Low specific power (<1000 W/kg), short service life (<4000 charge-discharge cycles) of lithium-ion batteries (LIB) and insufficient specific energy of supercapacitors (SC; 5–10 W-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 LIA 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

| Parameter          | LIB                        | LISC                       | DEC                        |
|--------------------|----------------------------|----------------------------|-----------------------------|
| Cathode            | Complex lithium oxides     | AC, complex lithium oxides | AC, graphene, carbon        |
|                    | Graphite, Si/C,            | Graphite, hyperdense carbon,| nanotubes, etc.             |
|                    | metal oxides, etc.         | Li4Ti5O12, etc.             |                             |
| Anode              |                            |                            |                             |
| 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$_2$O$_4$ [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 LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ as part of the HLISC mixed cathode. In this case, Li$_4$Ti$_5$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 LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$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 LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ + AC / graphite is a promising device for use in energy storage systems.

**Experimental**

**Electrode massfabrication**

Electrode mass obtaining of the investigated assemblies was carried out according to the following methods. Powder LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$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 μm, and the HLISC cathodes were 280 μm. 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 μm, HLISC – 140 μm. 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 μm, OOO Stanko-Inter, Russia) onto a current supply of copper foil 17 μm thick.
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.

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 Figs. 3, 4.

**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 LiPF₆ 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. 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. 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.
The dependences of the charge-discharge characteristics on the current value were investigated. The LISC model 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 HLISC model 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/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 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.
Table 2

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

| I, mA/g<sub>graphite</sub> | Q (discharge), mA⋅h/g<sub>pure graphite</sub> | C (charge), F/g<sub>cathode mixture</sub> | E (discharge), W⋅h/kg<sub>cathode mixture</sub> |
|---------------------------|---------------------------------|---------------------------------|---------------------------------|
|                           | LISC                            | HLISC                           | LISC                            | HLISC                           |
| 100                       | 45                              | 149                             | 123                             | 205                             |
| 200                       | 42                              | 135                             | 115                             | 191                             |
| 400                       | 37                              | 111                             | 101                             | 165                             |

Fig. 9. The dependence of the capacitance LISK (1) and GLISK (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<sub>graphite</sub>; 102 at a current of 400 mA/g<sub>graphite</sub>) including at high currents. As the current increases from 50 to 400 mA/g<sub>graphite</sub>, 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.

Acknowledgments

We express our gratitude to the management of global SO LLC, Khimki, for financial support and providing the material base for the research.

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