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The method of formation of planar lithium-ion batteries with composite electrode materials

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Abstract. A novel approach was developed to locally fabricate planar lithium-ion batteries using composite electrode materials. The method involved electrophoretic deposition to create a composite cathode material comprising NCA and Super C45, while the anode was formed through localized electrochemical deposition of germanium nanofibers. This technique successfully formed planar batteries with heterogeneous composite electrodes on a single plane, offering advantages such as efficient ion transport, minimized electrode polarization, and enhanced electrochemical performance. The integration of electrochemical and electrophoretic deposition methods allowed for precise control of layer composition and deposition parameters, optimizing the properties of planar batteries in terms of specific capacitance and electrical conductivity. The study also focused on laser engraving topology and optimized modes for planar battery structures, enabling the integration of multiple processes in a single manufacturing cycle. Capacitive characteristics were assessed using specialized polypropylene tooling, and the planar battery prototypes demonstrated comparable capacity (4 μ Ah) to existing commercial alternatives.

Keywords: planar lithium-ion battery, electrophoretic deposition, electrochemical deposition, cathode material, anode material

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Метод формирования планарных литий-ионных аккумуляторов с композитными электродными материалами

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Аннотация. В данной работе был исследован метод формирования планарных литий-ионных аккумуляторов с композитными электродными материалами. Для формирования композитного катодного материала на основе NCA ($\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$) и Super C45 был использован процесс электрофоретического осаждения, а анод был сформирован путем локального электрохимического осаждения германия в виде нановолокон. Была продемонстрирована принципиальная возможность формирования и работоспособность планарных литий-ионных аккумуляторов с гетерогенными композитными электродными материалами, расположенными на одной плоскости.

Ключевые слова: планарный литий-ионный аккумулятор, электрофоретическое осаждение, электрохимическое осаждение, анодный материал, катодный материал

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Introduction

Microsized lithium-ion batteries (μLIB) with a sandwich structure have been developed for wearable electronics and microsystem devices [1]. These batteries, composed of superimposed electrodes and electrolytes, are compact and lightweight. However, integrating them with other miniature devices can be challenging.

Transition metal oxide systems like NCA offer high energy density, stability, and durability, making them ideal for wearable microelectronics [2]. Planar batteries with an interdigitated design provide an attractive alternative [3]. This architecture offers increased electrode surface area, leading to improved electrochemical reactions and battery performance. It also ensures uniform voltage and current distribution, enhancing efficiency and cyclic stability. Furthermore, planar batteries with interdigitated topology exhibit high mechanical strength and stability, making them resistant to deformation and damage.

To achieve optimal implementation of planar batteries with an interdigitated topology, selecting the appropriate method for forming the cathode material is crucial. Electrophoretic deposition is a promising approach, offering simplicity, cost-effectiveness, and precise control over structure and composition [4]. It enables uniform and stable deposition of cathode material layers, ensuring homogeneity and effectiveness in battery operation.

This study proposes a method for creating a planar μ LIB structure on a conductive substrate. It involves local electrophoretic deposition (EPD) of composite cathode materials (NCA and Super C45) on one current collector and local electrochemical deposition (ECD) of germanium nanofibers on the other. This approach allows for the fabrication of a planar battery in a single process cycle with a power consumer.

Overall, this research explores the optimization of deposition parameters, selection of suitable suspensions or solutions, and characterization of the electro-physical properties of planar battery samples.

Materials and Methods

The substrates for the planar batteries were sital plates with a 250 nm Cr conductive layer. Using laser engraving on a CNC machine, the structures of planar batteries were formed, representing the structures of a counter-pin converter - two combs nested into each other.

An electrophoretic cell consisting of two electrodes connected to a power supply and immersed in a beaker with a suspension was used for local formation of composite cathode materials by the EPD method. The electric field strength was varied from 30 V/cm to 110 V/cm and the process duration was 2 minutes. The suspension used in this work contained 1.8 mg of NCA and 0.2 mg of the carbon conductive additive Super C45 per 1 ml of isopropyl alcohol and acetone-based solvent in a 1:1 ratio. To improve the electrophoretic mobility of the active material, nickel nitrate hexahydrate at a concentration of 0.1 per 1 ml of solvent was used.

Germanium nanofiber structure was formed on one current collector. Indium catalyst arrays were deposited on the substrate surface using electrochemical deposition. The indium deposition solution contained citric acid, indium chloride (InCl_3), and a wetting agent dissolved in deionized water. The deposition was performed at room temperature with a constant stirring and a current density of 1 mA/cm² for 5 minutes. The germanium nanofibers were deposited in an electrolyte solution containing germanium oxide (GeO_2), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), and succinic acid. The solution pH was adjusted to 6.5 using NH_4OH . The deposition process was carried out at 85°C with a current density of 2 mA/cm² for 30 minutes, followed by an additional hour at 4 mA/cm².

To control the composition of the obtained samples, the method of energy dispersive X-ray spectroscopy was used. The morphology of the obtained layers was studied using a scanning electron microscope. The capacitive characteristics of the planar battery samples were studied on the basis of charge-discharge characteristics and cyclic sweeps.

To create a planar battery, a polypropylene tolling was designed to prevent damage to the electrode materials. The working electrodes were pre-dried under vacuum at 120°C for 8 hours to remove any traces of water. The electrolyte used was a mixture of 1M LiClO_4 in a propylene carbonate-dimethoxyethane (7:3) solution. The water content in the electrolyte, measured by Fischer coulometric titration, was no more than 15 ppm.

The assembly of the electrochemical cells was carried out in a sealed glove box with an argon atmosphere. The water and oxygen content in the box was approximately 1 ppm. Electrochemical investigations of the electrodes were conducted in a galvanostatic mode with a current of 0.5 μA .

Results and Discussion

In this study, the influence of various additives on the stability and deposition rate of the composite cathode materials NCA and Super C45 was investigated. Specifically, dispersing and surfactant additives such as nickel nitrate hexahydrate and hydroxypropyl cellulose were used. Nickel nitrate hexahydrate served as a source of nickel ions, which adsorb onto the particle surfaces and change their zeta potential. Hydroxypropyl cellulose was used as a dispersant and for viscosity modification of the suspension.

Experiments showed that at a nickel concentration of 0.1 mg/mL, the deposition rate was 0.7 mg/cm²min (Fig. 1, *a*). At higher concentrations of nickel ions, charged particles can collide with each other, leading to electrostatic repulsion. Hydroxypropyl cellulose prevents particle agglomeration, thereby increasing the deposition rate at an optimal concentration of 0.03 mg/mL. However, increasing the cellulose concentration results in higher viscosity, which slows down particle movement.

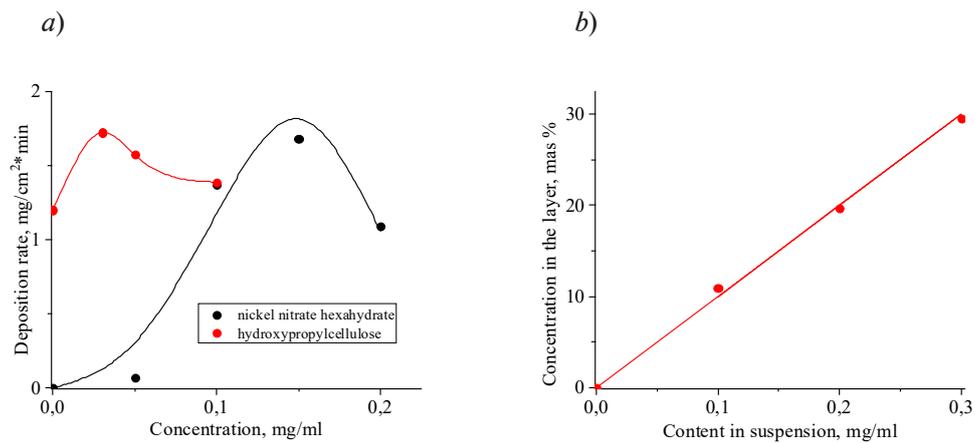


Fig. 1. Dependency (a) of deposition rate on the concentration of nickel nitrate hexahydrate and hydroxypropyl cellulose in the suspension, and (b) of carbon conducting additive concentration in the active material on its quantity in the suspension

The concentration of carbon in the cathode material influences the electrochemical properties and electrical conductivity. The impact of Super C45 concentration on the graphite content in the composite cathode material was investigated (Fig. 1,b). It was shown that the carbon additive concentration in the active material is directly proportional to the Super C45 content in the suspension, enabling the regulation of the composition of the composite cathode material for specific needs.

In order to create planar accumulators in this study, both the anode and the cathode electrodes were formed in the same plane and in close proximity to each other on the surface of thin-film current collectors. It was necessary to ensure electrical isolation between the formed electrodes. For this purpose, a set of planar accumulator samples with deposited cathode and anode materials was prepared to study the localization of electrode deposition.

The correct sequence of electrode material deposition was experimentally determined for creating planar battery samples. Thus, localized electrochemical deposition of germanium nanofibers was performed first, followed by localized electrophoretic deposition of the composite cathode material. Since water-based solution is used in localized electrochemical deposition, the deposited layer of cathode material is separated from the substrate due to the capillary effect.

A distribution map of elements was constructed using energy-dispersive X-ray spectroscopy to determine the localization of deposition of different electrode materials (Fig. 2). The map reveals that carbon, nickel, cobalt, aluminum, and oxygen (components of NCA) are concentrated on one electrode, while germanium (anode component) is uniformly distributed on the other electrode. The absence of overlap between the two materials indicates the localized formation of electrode materials.

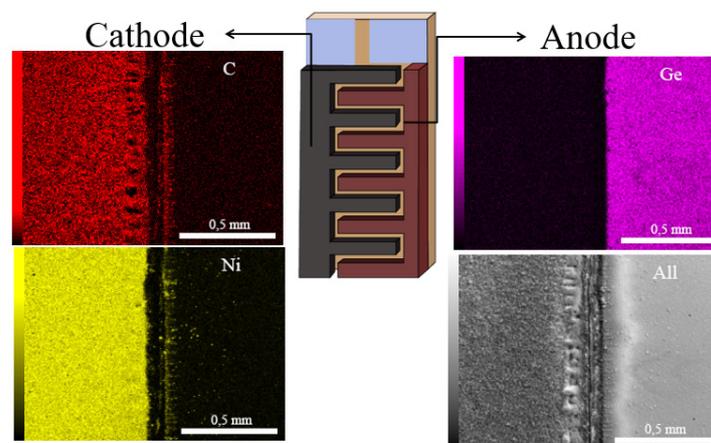


Fig. 2. Distribution map of elements in a planar battery

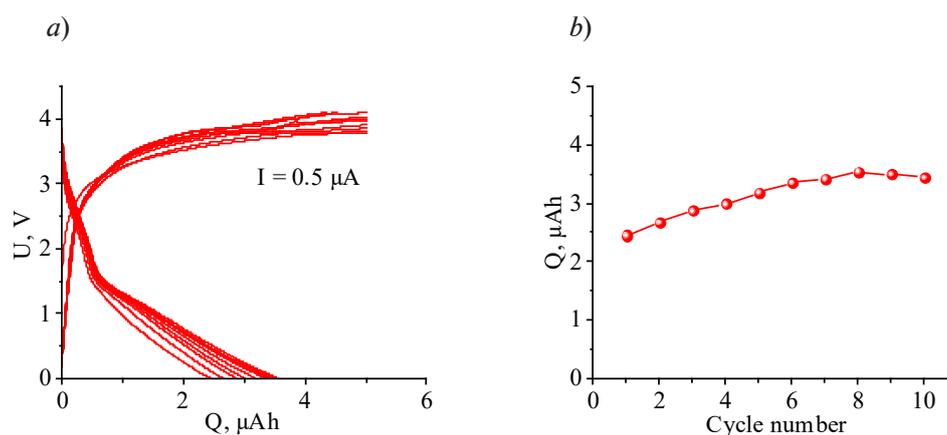


Fig. 3. Charge-discharge curves (*a*) and variation of discharge capacity of the NCA-Ge battery prototype (*b*)

The charge-discharge curves of the battery (Fig. 3,*a*) and the dependence of discharge capacity during cycling at a constant current density (Fig. 3,*b*) reflect the characteristics of the battery.

It can be observed that the average voltage during charging is approximately 3.8, while during discharging, it is around 1.3. The low voltage during discharging is not typical for the NCA-Ge electrochemical system and may be attributed to high internal resistance of the battery. The discharge capacity increases in the initial cycles and stabilizes around the 8th to 10th cycle. The increase in discharge capacity may be associated with the increase in the discharge capacity of germanium in the initial cycles [5].

Conclusion

This study developed a method for fabricating composite cathode materials for integrated batteries. The main focus was on optimizing the suspension composition and investigating the influence of dispersing and surfactant additives on the stability of the suspension and the electrophoretic mobility of the active material.

The conducted experiments showed that the optimal suspension recipe includes a 1:1 ratio of acetone and isopropyl alcohol as the solvent. The addition of nickel nitrate hexahydrate at a concentration of 0.1 mg/mL of the solvent resulted in a deposition rate of the active material at a level of 0.7 mg/cm²·min. The addition of hydroxypropyl cellulose at a concentration of 0.03 mg/mL of the solvent increased the stability of the suspension by 25%. It was also confirmed that the concentration of carbon conductive additive is directly proportional to its content in the composite cathode material.

To form the structure of a planar battery, a methodology was developed, which includes creating a topological pattern using laser engraving on the conducting coating, local electrochemical deposition of germanium nanofibers, and local electrophoretic deposition of the composite cathode material.

The results of cyclic voltammetry measurements showed that the specific capacity of the planar lithium-ion accumulator is 4 μAh, which corresponds to the level of commercial analogs.

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