Thin-film coating technologies on porous materials for chemical current sources

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Abstract. This paper investigates the technologies for the formation of the thin-film electrode material of the chemical current sources. To get the high specific energy density of the electrode we used the grinding of chemically active material (LiCoO₂), which the most widely used for cathode materials of chemical current sources to deposit on the materialized carbon-based electrode materials. The tested results show that the specific energy density of the electrode reaches to 210 mAh/g, which is more than thick-film technologies can reach (150 mAh/g).

1. Introduction

Chemical current sources are used in various fields of science and technology: electronics, medicine, aviation, and astronautics. In particular energy storage is used for satellites, spacesuits (extra-ship activities), launch vehicles and portable devices such as computers and video cameras. By comparing with the other type of devices rechargeable lithium-ion battery (LIB) has proven to be a reliable energy storage device since its first market introduction in 1991 because of its high energy density, light weight, low maintenance, long service life, and high efficiency [1].

The characteristics of these energy storage systems largely depend on the electrode materials. Electrode materials must meet the following requirements: high specific energy intensity, good reversibility of electrode processes (cyclability), high conductivity for lithium, the high diffusion rate of lithium.

Among the various cathode materials studied, Layered oxides with the formula LiMO₂ (M = Co, Mn, Ni) have been the most widely used/commercialized cathode materials for chemical current sources [1-3]. Lithium cobalt offered many crucial advantages such as its stability in ambient conditions (moisture), a significantly higher Li-ion insertion voltage. The complex oxide LiCoO₂ has a layered structure in which the Li and Co ions take place orderly in alternating planes. The presence of planes occupied exclusively by lithium ions provides the possibility of complete deintercalation of the alkali metal and the applicability of this compound as a cathode material in chemical current sources [4, 5]. The material with layered lattice shows better electrochemical performance compared to that with a cubic spinel lattice. The unit cell of the layered form consists of three slabs of edge-sharing CoO₆ octahedra separated by interstitial layers of Li (figure 1). LiCoO₂ has a theoretical capacity of 274 mAh/g when one mole of Li was extracted from one mole of LiCoO₂, but the practical capacity
reaches only 150 mAh/g when using standard thick-film technology for applying chemically active material [1, 2].

![Crystal structure of LiCoO2](image)

**Figure 1.** Crystal structure of LiCoO2. In the LiMO2 (M = Co, Mn, Ni) the metal layer is occupied by Mn, Ni, and Co in a random manner [1].

Thin-film electrodes exhibit excellent specific capacitance which could be due to possession of lower contact resistance between film matrix and current collector, and providing a shorter ion diffusion path length [6]. And it points out that the modern thick-film deposition technologies have reached their limit and that need to use the thin-film technology for cathode materials which can use the chemically active material more efficiently [7]. LiCoO2 with a particle size of 8-50 microns is used in the standard thick-film coating technology [8, 9]. There is the technology to possible to disperse the powder to particle sizes of 150-350 nm while maintaining the structure of the material and increasing the effective surface area and energy intensity [10]. In this paper, we will investigate the impregnation of the metallized electrode with 100 to 350 nanometers size of lithium cobalt oxide particles to thin-film electrode material and report the test results of the electrode material.

The purpose of this work is the grinding of chemically active material (LiCoO2) filling the carbon matrix with it in order to create a thin-film cathode material.

2. Materials and research methods

In the research high-porous carbon fiber Busofit is used as an electrode material that meets the requirements for chemical current sources. The use of highly porous carbon as a matrix for LiCoO2 allows switching from a standard thick-film technology using chemically active material to the thin-film using a fine dispersed powder of LiCoO2. And LiCoO2 powder is precipitated in the pore space of carbon fiber type Busofit. The smaller the size of LiCoO2 particles, the greater the effective surface area and the more Li ions can participate in the chemical reaction.

In this paper, the metallized carbon fiber "Busofit-UL-50" is impregnated by using LiCoO2 dispersion in the electrolyte medium based on propylene carbonate (PC). Metallization of the Busofit before impregnation was carried out to reduce the equivalent resistance between the elements of chemical current sources. Metallization was carried out in a vacuum installation equipped with two magnetrons (figure 2), which can apply titanium coatings at a speed of 0.1 μm per minute. As a result, the 1–3 microlayer of titanium was received and the materialized electrode Busofit with the specific capacity of 200–250 F/g was produced. The advantage of the technology is electro-pulse processing of the Busofit in a liquid medium containing metal nanoclusters. This processing leads to the additional increase of electrical capacitance, the reduction of electrical resistance and stabilization of the parameters of the electrode material.
The deposition of titanium to carbon fabric Busofit increases the specific surface, which allows to increase the energy intensity of supercapacitor systems. Also, titanium can improve lithium intercalation and increase the cyclicity of chemical current sources. Figure 3 shows the comparison between clean single thread Busofit and single thread Busofit coated with a layer of titanium.
Grinding of lithium cobalt was carried out in a bead mill produced by Netzsch, LabStar type at a speed of rotation of the main shaft 3000 rpm for 8 hours in propylene carbonate (PC). A grinding chamber with a volume of 600 ml was used, which was 70% filled with yttria-stabilized zirconia beads and with a diameter of (0.4-0.6) mm. 600 ml of PC was poured into the mill, then 500 g of lithium cobaltate was added in portions of 60 g each, after which 200 ml of solvent was added until the mill working volume was completely filled. To measure the size, samples were taken in a volume of 1 ml, and then dried on an electric stove at a temperature of 200 °C until complete removal of the PC. The dried powder was dispersed in ethylene glycol using an ultrasonic bath for 15 minutes. Measurement observed in ethylene glycol. According to the results of the measurement, the 100 to 350 nanometers size of lithium cobalt particles was obtained from grinding (figure 4).

![Size Distribution by Intensity](image.png)

Figure 4. Particle size distribution (three measurements at 30 second intervals).

Impregnation with the prepared dispersion was carried out in a vacuum impregnation unit. Inside the glass cover, the temperature-controlled device is installed to create the required temperature for impregnation.

The carbon fabric should be cleaned of impurities and dried before the vacuum impregnation procedure so that the electrolyte mixed with LiCoO₂ can freely penetrate into the empty pores and fill them.

After closing the lid of the tank, a vacuum of at least 10 Pa is created in it by using a vacuum pump, and the air is removed from the open pores. After the "vacuum drying" stage, the electrode material is placed in the electrolyte and impregnated for 30 minutes. The vacuum pump is stopped at the end of the impregnation operation, and atmospheric pressure is restored. The open pores are filled due to the pressure difference between the vacuum and atmosphere.

3. Results and discussion

The relation between surface area of the electrode and the specific energy density of the electrode was studied. According to the measurements, the increase in the area of the electrode material by 3 times allows to increase the energy density of the material by 21% as well as to reduce the internal resistance (ESR) of chemical current source by 2.5 times.

Electrode material with metallization that achieved 670 cm² can reach a specific capacity of 17 F/g and ESR 0.1 Om. There is a comparison of results between electrode with metallization and without
metallization in the figures 5 and 6. Metallized Busofit has a specific energy similar to other carbon materials of the same area [11], but allows to simultaneously form a chemical current source based on it.

Figure 5. Dependence of a specific electrical capacity on the contact area of electrode materials in the cell: without metallization (blue); with metallization (red).

Figure 6. Dependence of a ESR on the contact area of electrode materials in the cell: without metallization (blue); with metallization (red).

The weight of the chemically active cathode material should be 50% to achieve the highest energy intensity in standard cells [11]. By using the technology from this research, the weight of LiCoO₂ in the chemical current sources was 50% of the weight of the chemical current cells.
Figure 7 shows a photograph of a filament of carbon material impregnated with a dispersion of LiCoO$_2$ + PC and a graph of the composition of the material deposited on the fiber. The obtained data with SEM show that dispersion made it possible to obtain the required particle size of LiCoO$_2$ less than 300 nm and there are no excess impurities in the formed coating. Figure 7 also shows that the dispersed lithium cobaltate stuck around the Busofit thread 5 microns thick from all sides. Vacuum impregnation made it possible to impregnate Busofit not only in the upper layers, but also in depth, which allowed to increase the entire chemically active material and increase the specific surface area of the electrode material.

Figure 7. Impregnation of Busofit with dispersion LiCoO$_2$ + PC.

Figure 8 shows that, in addition to titanium and cobalt, there are no other materials when impregnated, which indicates the purity and repeatability of the technology.

Figure 8. X-ray analysis of the applied LiCoO$_2$ + PC layer on the Busofit filament.
Table 1 shows the specific energy density of the cathode material after impregnation with LiCoO$_2$. Dispersing lithium cobalt and placing it in the pore space allows increasing the specific capacity of the cathode material from working 145-160 mAh/g [1, 2] to 210 mAh/g, which will increase the overall energy density of the chemical current sources. And also we can see from work [1, 2] that the 40 µm thickness thin-film electrode only achieved the charge capacities 141 to 151 mA h/g, and the discharge capacities 140 to 148 mAh/g. Thus, the dispersion of lithium cobaltate and the impregnation of Busofit obtained with the dispersion of carbon fabric made it possible to increase the energy intensity of the electrode material with lithium cobaltate without dispersion up to 30%. However, after 4 charge-discharge cycles, the energy intensity began to decrease, which is apparently due to the movement of dispersed lithium cobaltate inside the cell through a separator and the polarization of the surface layer of the reactive material was occurred.

| No. of cycle | 1  | 2  | 3  | 4  | 5  | 6  |
|--------------|----|----|----|----|----|----|
| Discharge (mAh/g) | 210 | 210 | 146.4 | 160.7 | 69.4 | 87.5 |
| Charge (mAh/g)    | 239.3 | 240.3 | - | 251 | 149.3 | - |

In comparison with [1, 2], lithium cobaltate-based electrolytic cells can operate at the same voltage (3V), but the number of charge-discharge cycles is much smaller, which may be due to a lack of information about the chemical processes that occur when using Busofit as a matrix for lithium cobaltate. This phenomenon requires further study.

4. Conclusions
The obtained results allow drawing the following conclusions:
- The dispersion with a particle size of LiCoO$_2$ less than 300 nm was obtained.
- In accordance with the SEM images, it was obtained a carbon fabric material Busofit soaked with dispersed LiCoO$_2$ around each strand into the depth of the material.
- Dispersing lithium cobalt and placing it in the pore space allows increasing the specific energy density of the cathode material LiCoO$_2$ up to 210 mAh/g, which can increase the overall energy density of the chemical current sources.

Acknowledgment
The study is carried out with the financial support from the State represented by the Ministry of Education and Science of the Russian Federation. Subsidies Provision Agreement No. RFMEFI57717X0275.

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