Thin-film solid-state lithium-ion batteries. Materials and technology

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Abstract. The results on the study of functional layers of a solid-state thin-film lithium-ion batteries are presented. Thin-films of lithium cobaltite (positive electrode), silicon nanocomposite (negative electrode) and lithium phosphorus-oxynitride (solid electrolyte) were studied by the methods of electron microscopy, energy dispersive analysis and X-ray phase analysis. Technological modes have been determined which make it possible to obtain functional layers with a large-block and columnar structure providing the full depth of electrodes lithiation-delithiation and high ionic conductivity of the solid electrolyte.

1. Introduction
Currently the most common chemical power sources for portable electronics are lithium-ion batteries (LIB). The electrodes of such batteries are manufactured by the method of squeegee application of pastes on the down conductor made of metal foil, and have a thickness of several tens of microns. Industrial LIBs are produced in the form of cylindrical and prismatic elements, as well as in the form of pouches. The last two types of batteries structurally are stacks of electrodes separated by sheets of non-woven polypropylene 15 - 20 microns thick, impregnated with electrolyte. These stacks are placed in a sealed metal can or polymer pouch. Thus, the minimum thickness of pouches with liquid electrolyte exceeds several millimeters, and the thickness of prismatic LIBs is even higher. At the same time, to feed miniature electronic devices, smart cards, RFID tags, wearable gadgets, implants, etc. batteries of significantly less thickness are required, i.e. less than one millimeter. Such thicknesses is attainable only for thin-film solid-state lithium-ion batteries (SSLIB) [1-3].

In the industrial production of SSLIBs, LiCoO₂ – LiPON – Li and LiCoO₂ – LiPON – Si electrochemical systems are most widely used. The choice of the negative electrode in these systems is due to the fact that Li and Si have the highest capacity towards the reversible insertion of lithium. In batteries with a silicon thin-film electrode, the film thickness does not exceed 1 μm, while silicon itself has an amorphous structure. With a greater thickness or crystal structure of silicon, lithium intercalation results in mechanical stresses growth destroying the film. The thickness of the positive electrode varies from 1 μm to 3 μm, and the thickness of the solid electrolyte is about is 1 μm or even slightly less. For the deposition of functional layers PVD (Physical Vapor Deposition) methods are used, of which the magnetron sputtering method is most flexible and efficient [4].

The main disadvantage of SSLIBs is that their specific capacity is much lower than that of LIB with liquid electrolyte. This is due to the lower conductivity of the solid electrolyte (usually LiPON)
and the smaller specific contact area of the electrolyte with the electrode material. If in a battery with liquid electrolyte the latter penetrates into the pores of the electrode material, thereby increasing the contact area, in the case of a solid electrolyte, only the outer surface of the electrode participates in the formation of a contact. Nevertheless, to increase the capacity of SSLIB, the electrode films are tried to be made as porous as possible. This is necessary in order to increase the transfer of lithium due to surface diffusion along crystallite boundaries. In addition, the high porosity makes it possible to reduce the mechanical stresses, arising from lithium intercalation, and increase the film stability. To stabilize the films of the negative electrodes based on silicon, they are made of Si@Al composition where silicon is partially oxidized to prevent the formation of a Li15Si4 crystalline phase [5].

It can be seen from the foregoing that the capacitive characteristics and service life of SSLIBs of any electrochemical system are determined by the phase composition, morphology and elemental composition of functional layers. This work describes the technology of LiCoO2 / LiPON / Si@O@Al system formation by magnetron sputtering and the results of layers’ studying by scanning electron microscopy, energy-dispersive analysis and X-ray phase analysis. It is shown that the selected technological parameters of films deposition ensure the formation of battery layers of the required morphology and chemical composition with the necessary adhesion between the layers.

2. Manufacturing of solid-state thin-film lithium-ion batteries

Batches of SSLIB of electrochemical system LiCoO2 / LiPON / Si@O@Al were manufactured using mask technology. For the deposition of functional layers, masks made of steel or copper with a thickness of 0.5 - 0.8 mm were used. The lateral size of all masks was 100×100 mm², and the size of the windows in the masks decreased for each next layer by 2 mm on each side. In addition, the masks were provided with windows for the manufacture of test structures. Sketches of a set of masks with indicating the purpose and sequence of their application are shown in Table 1.

The functional layers were deposited by radio-frequency magnetron sputtering at a SCR 651 Tetra system. SSLIB substrate, which also served as a down conductor, was made of titanium foil 10 µm thick. The substrate was preliminarily treated in an aqueous solution containing 5% sulfuric and 4% hydrofluoric acids to form a surface relief that improves the adhesion of the electrode film (LiCoO2 or Si@O@Al) to the substrate. Immediately before the electrode layer deposition, the substrate was cleaned by ion bombardment.

The Si@O@Al composite layer was deposited using two targets — one made of a Si-Al alloy (9:1) and one made of pure aluminum. In this case, argon with an admixture of 0.3% oxygen served as the working gas.

Solid electrolyte (LiPON) was deposited by sputtering a Li3PO4 target. The target was made of Li3PO4 powder by gradient pressing followed by annealing. To prevent cracking, the target was fixed in a copper holder, which ensures uniform temperature distribution and efficient heat dissipation during sputtering. In this case, the working gas was nitrogen.

The LiCoO2 layer was deposited by sputtering a target manufactured by Girmet Inc. (Russia) in argon-oxygen gas mixture (4:1).

Two types of batteries SSLIB Ti / Si@O@Al / LiPON / LiCoO2 / Ti(10 µm) and Ti / LiCoO2 / LiPON / Si@O@Al / Ti(10 µm) were manufactured. The order of the layers is from top to bottom. Modes of SSLIB functional layers deposition are given in Table 2.

3. Study of morphology, elemental and phase composition of SSLIB functional layers

The morphology, elemental and phase composition of the Si@O@Al, LiPON and LiCoO2 layers were investigated by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray phase analysis (XPA). Particular attention was paid to the effect of the substrate surface
roughness on the structure of the deposited functional layer. The structure hereinafter is understood as porosity and the presence or absence of a pronounced block or columnar structure of the film. So, deposited on a rough surface of a titanium foil, composite films Si@O@Al or LiCoO$_2$ have a structure close to the morphology of the surface of the foil. Figs. 1 and 2 show cleavages of Si@O@Al and LiCoO$_2$ films deposited on a titanium foil. The Si@O@Al film (Figure 1) has a large-block structure, in which each block grows during deposition in a direction close to perpendicular to the substrate. The film LiCoO$_2$ in Figure 2 has a combined structure, where each separate large block has a columnar structure with a predominant growth direction perpendicular to the substrate.

Table 1. Sketches of a set of masks and the sequence of their application in the SSLIB manufacturing.

| Mask number and purpose | Mask sketch |
|-------------------------|-------------|
| 1 - Anode (cathode) layer | Window in a mask 6×6 cm$^2$ in size |
| 2 – Solid electrolyte | |
| 3 - Cathode (anode) layer | |
| 4 - Upper metal down conductor | |
Table 2. Technological parameters of manufacturing SSLIB with Ti/Si@O@/LiCoO₂/LiPON/Al/Ti structure. Layers order – from top to bottom.

| Layer     | Residual vacuum, \(\text{bar}\) | Heating, \(\text{°C}\) | Ionic cleaning, \(\text{V, c}\) | Pressure, \(\text{bar}\) | Gas 1 flow, \(\text{sccm}\) | Gas 2 flow, \(\text{sccm}\) | Magnetron power, \(\text{W}\) | Deposition time | Layer thickness, \(\text{m}\) |
|-----------|----------------------------------|-------------------------|-------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-----------------|------------------|
| LiCoO₂    | \(<10^{-3}\)                    | 15V, 15s                 | 10                            | \(\text{O}_2=5\)         | \(\text{Ar}=20\)       | 200                     | 4h 5m                   | Interoperative time 12h in vacuum |
| LiPON     | \(<10^{-3}\)                    | -                        | 20V, 20s                      | 10                       | -                       | 150                     | 2h 45m                  | Interoperative time 1h 30m with mask change |
| SiOAl     | \(<10^{-3}\)                    | -                        | 10V, 20s                      | Ar=200                  | 250                     | 25m                     | Interoperative time 12h in vacuum |
| Ti        | \(<10^{-3}\)                    | -                        | 10V, 10s                      | Ar=20                   | 300                     | 25m                     | 0.55                    |

After depositing a 1 \(\mu\)m thick LiPON film, the surface gets planarized, thus the depositing of the next functional layer \(\text{LiCoO}_2\) (Figure 1) or \(\text{Si@O@Al}\) (Figure 2) proceeds onto a smoothed surface. This kind of surface smoothing affects the structure and morphology of the upper film. The top film \(\text{LiCoO}_2\) or \(\text{Si@O@Al}\) deposited upon a smooth LiPON surface has fewer defects, which reduces the diffusion rate of lithium and layers adhesion. If the film in Fig. 1 shows a columnar structure, then the \(\text{Si@O@Al}\) film in Figure 2 looks dense, without any signs of structuredness. Based on this, it can be assumed that SSLIB with the structure shown in Figure 1 will be more efficient at high currents than the SSLIB with a dense \(\text{Si@O@Al}\) layer, shown in Figure 2.

The determination of the elemental composition of the SSLIBs’ functional layers and their control during the development of the technology and the SSLIBs manufacture was carried out by energy dispersive analysis on a Quanta 3D 200i SEM equipped with an EDAX X-ray energy dispersive spectrometer. Elemental analysis of the SSLIBs’ functional layers was used primarily to improve the technology and control the \(\text{Si@O@Al}\) composition. In each technological process of \(\text{Si@O@Al}\) deposition near Ti substrate was placed a Si substrate or so called “witness”, which served for further measurements of the thickness and elemental composition. In addition, the presence of the mask windows enables to obtain test structures for all functional layers on titanium foil as well.

Elemental analysis of aluminosilicates was carried out on the basis of the software of the EDAX energy dispersive attachment, then its results were refined using aluminosilicate minerals of known composition and the corresponding corrections to the measurement data were made. Depending on the film thickness, the accelerating voltage at which the spectra were recorded was selected. Films on silicon substrates or on titanium foil were analyzed at various accelerating voltages from 3 kV to 10 kV. For functional layer thicknesses of 0.5 - 2.0 \(\mu\)m, the values of the element concentrations were measured at an accelerating voltage of 5 kV. Under such shooting conditions, the probe beam did not pass through the film and the reliability of the results increases.
Figure 1. Functional layers of LiCoO$_2$ / LiPON / Si@O@Al SSLIB. The SEM image shows that the Si@O@Al nanocomposite has a large-block structure, while LiCoO$_2$ consists of blocks, each of which has a columnar structure.

Figure 2. Functional layers of Si@O@Al / LiPON / LiCoO$_2$ SSLIB. The image shows that LiCoO$_2$ has a columnar structure, while the Si@O@Al nanocomposite film looks absolutely uniform.

The X-ray energy dispersive attachment EDAX does not allow recording the energy spectrum of the characteristic X-ray radiation of lithium, therefore, the concentration of lithium atoms cannot be determined by this method. In lithium-containing materials such as LiPON (LiPO$_x$N$_{1-x}$), by the energy dispersive method one usually determines the concentration of elements P, O, and N without considering Li concentration. This is done to determine the percentage of oxygen atoms replaced by nitrogen atoms, or the N/O ratio. Tab. 3 shows the concentration of elements in the SSLIB functional layers Si@O@Al and LiPON.

The elemental analysis of the cathode LiCoO$_2$ by the energy dispersive method was not carried out due to the impossibility of determining the Li concentration. For these materials, X-ray phase analysis was used, which allows to determine the formula of a lithium-containing material if at least a fine-crystalline phase is present in it.

As a result, the concentration of the following elements contained in the functional layers of SSLIB was determined by the method of energy dispersive analysis:
- in the Si@O@Al layers, the oxygen concentration varied from 13.55 at.% to 24.36 at.%. The Al concentration in Si@O@Al varied from 12.37 at.% to 42.73 at.%. The Si concentration in Si@O@Al varied from 40.73 at.% to 69.14 at.%;
- in the LiPON layers, the N/O ratio ranged from 0.076 to 0.286.
In the indicated ranges of element concentrations, functional layers \(\text{Si} @ \text{O} @ \text{Al}\) as a part of SSLIB have shown good performance.

**Table 3.** Concentrations of elements in \(\text{Si} @ \text{O} @ \text{Al}\) and LiPON functional layers of SSLIB.

| Sample # | 1 | 2  | 3  | 4  | 5  | 6  | 7  |
|----------|---|----|----|----|----|----|----|
| Functional layer | \(\text{Si} @ \text{O} @ \text{Al}\) | \(\text{LiPON}\) | \(\text{Si} @ \text{O} @ \text{Al}\) | \(\text{Si} @ \text{O} @ \text{Al}\) | \(\text{LiPON}\) | \(\text{Si} @ \text{O} @ \text{Al}\) | \(\text{Si} @ \text{O} @ \text{Ti}\) |
| Accelerating voltage, kV | 5 | 5 | 5 | 5 | 5 | 5 | 7.5 |
| C concentration, at.% | 2.69 | 4.13 | 2.18 | | | | | |
| O concentration, at.% | 13.7 | 69.95 | 24.36 | 23.41 | 58.7 | 13.55 | 5.96 |
| N concentration, at.% | | 5.37 | 5.13 | | | | | |
| Al concentration, at.% | 42.73 | 25.36 | 13.29 | | | | | |
| Si concentration, at.% | 40.89 | 42.96 | 63.29 | | | | | |
| P concentration, at.% | | 20.55 | 24.51 | | | | | |
| Ti concentration, at.% | | | | | | | 11.59 |
| Ar concentration, at.% | | | | | | | 0.85 |

Investigations of SSLIB functional layers by X-ray phase analysis (XPA) were carried out on an ARL X'tra X-ray diffractometer using Cu – K\(\alpha_1\) radiation in 2\(\theta\) geometry with Bragg-Brentano focusing and X-ray tube operating mode 30 kV at 30 mA. Solid electrolyte LiPON after deposition on the anode or cathode layer should be amorphous and remain so after high-temperature exposure. To confirm the fulfillment of this requirement, four test samples were made by depositing \(\text{LiCoO}_2\) and \(\text{LiCoO}_2 / \text{LiPON}\) layers on the Ti foil. Two samples were not annealed, and two other samples were annealed at a temperature of 500°C in an inert Ar atmosphere. The phase compositions of the samples with and without annealing are compared in Figure 3. In addition to the titanium peaks (ICDD # 01-089-3073), the diffraction patterns show characteristic peaks of the system \(\text{LiCoO}_2\) (LCO) with different degrees of crystallization. No crystallized LiPON phase was found. Thus, annealing of LiPON films in an inert medium up to 500°C does not lead to their crystallization.

**Figure 3.** Diffraction patterns of annealed and unannealed Ti / \(\text{LiCoO}_2\) (LCO) and Ti / \(\text{LiCoO}_2 / \text{LiPON}\) structures. Annealing conditions are shown in the graph.

4. Conclusion

The study of SSLIBs' functional layers by high-resolution scanning electron microscopy allows to determine the morphology and structure preferable for SSLIB. According to the charge-discharge characteristics of SSLIB, anode and cathode layers of a porous, large-block and columnar structure have an advantage over dense defect-free films. They provide the penetration of lithium to the entire
depth of the film, which allows to use charge-discharge modes of more than 10 C without noticeable degradation of battery layers. On the contrary, in dense defect-free films, lithium diffuses only into the near-surface volume of the electrode layer, which not only does not provide acceptable capacitive cycling characteristics of SSLIB, but also in some cases does not allow initiating the anode lithiation.

The study of the elemental composition of functional layers carried out by the energy dispersive method has shown that the Si@O@Al anode layer is efficient at oxygen concentrations 13-23 at.%, aluminium concentration 12-42 at.% and silicon concentration 40-70 at.%. For solid electrolyte LiPON, the N/O ratio at which SSLIBs are efficient is defined as 0.08-0.29.

According to the results of SSLIB studies by the XPA method, it was confirmed that LiPON and Si@O@Al, after their deposition by the magnetron method, are always amorphous. Carrying out high-temperature anneals at 500°C did not reveal crystallization of LiPON.

The cathode material LiCoO$_2$, after deposition by magnetron sputtering, usually has a microcrystalline structure, as indicated by diffraction peaks. High-temperature annealing at 500°C and higher has little effect on the degree of crystallization of these films.

5. References
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