Features of electrophoretic deposition process of nanostructured electrode materials for planar Li-ion batteries

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Abstract. The features of electrophoretic deposition process of composite LiCoO₂-based cathode and Si-based anode materials were researched. The influence of the deposition process parameters on the structure and composition of the deposit was revealed. The possibility of a local deposition of composites on a planar lithium-ion battery structure was demonstrated.

1. Introduction

In recent years researchers focused their interest on the development of miniature electronic devices, such as MEMS, sensors and implantable systems. All of these devices require an energy supply. However, traditional batteries are difficult to scale. Therefore, it is necessary to develop fundamentally new electrochemical power sources with planar structure, in which both cathode and anode located in the same plane. Such problem can’t be resolved with traditional methods, that currently in use. So it is demanded to work out a novel technique of the electrode materials creation.

From the overview of different possibilities electrophoretic deposition (EPD) seems to be incredibly perspective for the applying. Electrophoresis is the electrokinetic phenomenon of the particles movement in the liquid or gaseous medium under the applying of the external electric field [1]. Main advantages of this method are simplicity, low operating temperature and cost, possibility of a local and multicomponent deposition. The schematic depiction of the EPD cell is presented in Figure 1. The most simple one includes two electrodes, descended in suspension, and a potential source.

![Figure 1. Schematic representation of the electrophoretic deposition.](image-url)
The necessity of the composite materials creation is determined by charge storage mechanism characters in lithium-ion accumulators. In Table 1 essential characteristics of mostly common anode materials are presented [2, 3, 4].

**Table 1. Characteristics of Li-ion anode materials**

|                | Si   | C    | Sn   | Li   |
|----------------|------|------|------|------|
| Lithiated phases | Li_{4.4}Si | LiC_6  | Li_{4.4}Sn | Li |
| Theoretical specific capacity (mAh g\(^{-1}\)) | 4200 | 372  | 994  | 386  |
| Volume change (%) | 320  | 12   | 260  | 100  |
| Potential vs. Li (V) | 0.4  | 0.05 | 0.6  | 0    |

It is clearly seen, that silicon based compound many times overtops other anode materials because of the high specific capacity, that comes out due to possibility of the compound formation, in which 1 Si atom bonds about 4 Li atoms. But in the same time triple volume increasing of the material takes place when charging. This problem can be solved by the creation of the carbon nanotubes-based composite, wherein CNTs will constitute the connected network, meanwhile Si particles will be smoothly distributed in it. So silicon can provide high capacity with CNTs procuring high conductivity and mechanical sustainability.

By analogy, characteristics of traditional cathode materials [5, 6], presented in Table 2, can be improved.

**Table 2. Characteristics of Li-ion cathode materials**

| Cathode material | Avg. Potential Li/Li⁺ | Th. capacity (mAh g\(^{-1}\)) | Pract. capacity (mAh g\(^{-1}\)) |
|------------------|-----------------------|-------------------------------|----------------------------------|
| LiCoO₂            | 3.9                   | 274                           | 120-130                          |
| LiNiO₂            | 3.8                   | 275                           | 120-150                          |
| LiMn₂O₄           | 4.0                   | 148                           | 120                             |
| LiFePO₄           | 3.3                   | 170                           | 120-140                          |

Advantageous position is occupied by lithium cobalt oxide (LiCoO₂), being able to provide accumulators working in lower temperatures, saving prolonged life time, having relatively high theoretical capacity, characteristics stability and synthesis simplicity [7]. In traditional batteries LiCoO₂ is employed in composition of multicomponent material, which also includes graphite as conducting agent and polyvinylidene difluoride (PVDF) as binder. The development of the composite with CNTs will allow not only refuse from graphite, but also partially from PVDF, because the CNTs-formed connected network will provide mechanical strength. In the actual paper an approach in composite materials, based on Si-CNT and LiCoO₂-CNT, creation with electrophoretic method for usage in Li-ion accumulators is studied. Investigation of process, materials’ structure and consistency features is carried out.

2. **Experimental**

Composites of silicon and graphite or CNT has been aimed as an anode and composites of LiCoO₂ spinel with PVDF and graphite or CNT has been aimed as a cathode materials. The deposition was carried out from suspension made of solvent, listed powder components and citric acid as a charger. Formulations of suspensions is represented in Table 3. Coatings were shaped by EPD on Ti foils. As the counter electrode in the electrophoresis cell gold foil was settled in parallel 1 cm apart. EPD was
performed in potentiostatic regime, using a high voltage power source. The voltage applied in all cases was 5-140 V during times from 30 to 300 s. Process was periodic and consisted of deposition and drying stages with different durations. Number of cycles was ranged from 1 to 10. All of these processes were realized at room temperature. Morphology and composition of received layers were controlled by scanning electron microscopy and energy dispersive X-ray analysis JEOL model JSM-6010 PLUS/LA.

Table 3. Formulations of suspensions for cathode and anode materials deposition

| Material | Active component | Carbon component | Binder | Charger | Solvent          |
|----------|-----------------|------------------|--------|---------|------------------|
| Anode    | Si, 12.5mg      | CNT, 5mg         | -      | Citric acid, 12.5 mg | Acetone, 50ml    |
|          |                 | Graphite, 5mg    |        |         | Isopropyl alcohol, 50ml |
| Cathode  | LiCoO₂, 250mg   | CNT, 10mg        | PVDF   | Citric acid 10 mg | Acetone, 50ml    |
|          |                 | Graphite, 10mg   | 10-40mg|         | Ethanol, 50ml     |
|          |                 |                  |        |         | n-methyl-pyrrolidone, 50ml |
|          |                 |                  |        |         | Isopropyl alcohol, 50ml |

Planar Li-ion battery is based on the structure which consists of two nested into each other metal combs on the surface of the substrate. This structure allows to place two electrodes in the same plane and dispose of separator. All of suchlike experimental samples were prepared using standard integral technology and equipment. The schematic depicture of key manufacturing stages is presented on Figure 2.

Figure 2. Technological route of interdigital structure fabrication process.

The fabrication process was began with wet cleaning and thermal oxidation of a bare silicon wafer (Figure 2, 1) in order to isolate the substrate from the electrodes. After that, Ti was evaporated onto the substrate till the thickness of 300 nm (Figure 2, 2). Ti acts as a current collector. Photoresist was spin-coated on substrate (Figure 2, 3) and then photolithography was carried out to pattern two comb-like electrodes and contact pads (Figure 2, 4). A photoresist lift-off (Figure 2, 5) followed to remove the metal on unwanted areas using wet etching processes (Figure 2, 6).
3. Results
Multiple test processes of the anode composite materials deposition on titan foil was carried out. When as a solvent isopropyl alcohol was used, very porous layers of the deposit were obtained, which tended to detach from substrate. The maximum precipitate thickness was 80 μm.
In the Figure 3a morphology of the Si-graphite composite, obtained at 60 V in EPD, surface is represented. Figure 3b represents Si-CNT surface morphology. It can be observed, that CNTs-including material has more porous structure. This has positive effect on the anode properties, as it makes easier for lithium ions to traverse during the cycling process. Also, the CNTs-constituted matrix, as we consider, helps to get down mechanical strain of silicon during the lithium ions intercalation in the accumulator charging process.

In the Figures 4a and 4b a Si-graphite and Si-CNT composite materials layers thickness relations on applied voltage after 10 EPD cycles of 30 seconds each are represented. It is clearly seen, that in both cases results laying in linear dependency, and the deviations can be explained by the thickness unevenness and the measurement peculiarity. With increasing of the potential under 120 V the deposit structure becomes more friable and begins to crumble, that makes it difficult to determine the thickness correctly. With potential less than 5 V the deposition wasn’t implemented because of the too low rate. Significant difference in the deposits thicknesses for Si-CNT and Si-graphite composites can be explained by the distinguish inequality in CNT and graphite particles sizes.

![Figure 3(a, b).](image)

**Figure 3(a, b).** (a) SEM image of the composite anode material based on Si-graphite; (b) SEM image of the composite anode material based on Si-CNT.

![Figure 4(a, b).](image)

**Figure 4(a, b).** (a) Dependence of the thickness on the applied voltage for Si-graphite; (b) Dependence of the thickness on the applied voltage for Si-CNT.
Also, series of LiCoO$_2$-graphite and LiCoO$_2$-CNT cathode composite materials deposition experiments has been carried out. The most successful one happened to be with ethanol as the solvent. Good adhesion, high deposition rate and continuity of the deposit was observed. The maximum stated precipitate thickness was 100 μm.

In Figure 5a SEM image of the obtained LiCoO$_2$-graphite composite material is depicted. As can be seen a porous layer was received. In the Figure 5b SEM image of the LiCoO$_2$-CNT composite material, where LiCoO$_2$ particles covered with CNTs, which form connected network, can be observed.

![Figure 5(a, b). (a) SEM image of the composite cathode material based on LiCoO$_2$-graphite; (b) SEM image of the composite cathode material based on LiCoO$_2$-CNT.](image)

In the Figure 6a the plot of the 10-cycles deposit specific weight dependence from the applied potential is represented. The deviation from a linear dependency can be associated with the deposition area measurement error. With increasing of the potential under 120 V the deposit structure changes and becomes cellular, and after the complete drying begins to crumble, that makes it difficult to determine the weight correctly.

![Figure 6(a, b). (a) Dependence of the specific weight on the applied voltage for LiCoO$_2$-CNT; (b) Dependence of the carbon to cobalt ratio from PVDF presence.](image)

Also, series of LiCoO$_2$-CNT with PVDF as binder cathode composite materials deposition experiments has been carried out. So an interesting dependency has been discovered, presented in Figure 6b. It shows the increment of the carbon to cobalt atomic percent content ratio in the deposit with the increment of PVDF substance. This can be associated with co-deposition of PVDF and CNTs because of their possible binding in the suspension.
Furthermore, test experiments on the local deposition at the planar accumulator structure of the Si-CNT composite cathode material has been carried out. The results are presented in Figure 7.

![Figure 7(a, b, c). (a) SEM image of the planar structure after the local EPD of the Si-CNT composite; (b) Silicon EDX mapping; (c) Carbon EDX mapping.](image)

It can be clearly seen (Figure 7a), that the deposition occurred mainly on the top current collector, which was connected to the potential source. Elemental analysis confirmed the presence of silicon (Figure 7b) and carbon (Figure 7c) in the deposit.

### 4. Conclusions
In this paper an approach for composite Li-ion accumulator electrode materials with different content creation through the EPD technique is represented. Influence of suspension substance and technical parameters on deposits characteristics is researched. Planar Li-ion accumulator structure is created, and the local deposition of the Si-CNT composite electrode material is carried out on its surface.

### Acknowledgments
The Russian Science Foundation supported this work (project №16-19-10625).

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