

APPLICATION OF ATOMIC LAYER DEPOSITION IN LI-ION BATTERIES

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Abstract

Li-ion batteries (LIBs) are widely used as portable power sources. The development of new electrode materials for LIBs is an important challenge for material science. The application of modern methods and approaches can facilitate the implementation of this task. One of the new methods which can be used for improvement of Li-ion batteries is an atomic layer deposition (ALD). The method is based on conducting of self-terminating reactions between functional surface groups of solids and low molecular precursors. The thickness of deposited film can be set by number of treatment cycles. In present work we describe the examples of ALD application for the improvement of lithium-ion batteries. In particular, the capacity retention of positive electrodes comprising LiCoO₂ and Li_{1.25}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂ has been improved after deposition of thin (1-3 nm) alumina films. The application of ALD for deposition of thin films which can be used in lithium solid state 3D batteries is shown. Thin (80 nm) films of SnO₂ showed high specific capacity (850-900 mA·h/g) stable during 400 cycles at 1C discharge current density.

Keywords: Li-ion batteries, ALD, SnO₂, lithium cobalt oxide, lithium-rich cathode, coatings, composite electrode

INTRODUCTIONS

Lithium-ion batteries (LIB) became an integral part of our everyday lives. They have a number of benefits that make them suitable for portable electronic devices, electric vehicles, uninterruptible power supplies. Development of new electrode materials for LIBs is an important challenge for material science. Without use of modern methods and approaches, it will become an impossible problem.

In order to increase stability of cathode and electrolyte in a wide range of voltages it is applied electrochemically inactive protective coating [1]. Metal oxides are usually used for this purpose. One of new methods for LIB application is an Atomic Layer Deposition (ALD) in Russian literature known as Molecular Layering (ML). ALD allows obtaining functional coatings (oxides, sulphides etc. [2]) inside the pore space [3] and therefore can be used for covering composite electrodes. The method is based on conducting of self-terminating reactions between functional surface groups of solids and low molecular precursors. The thickness of deposited film can be set by number of treatment cycles [4]. Alumina is used as protective coating for cathode materials. Application of ALD method allows depositing of protective coatings not only on cathode particles but also on porous composite electrodes. The first studies devoted to modification of cathode material appeared in 2010 [5] and they were focused on influence of aluminum oxide coating on electrochemical properties of LiCoO₂.

Currently in the Web of Science the overall amount of articles concerning the modification of cathode materials for lithium-ion cells with use of ALD/ML exceeds 70 and they are highly cited (more than 1900 citations). In present work we communicate a brief summary of literature review as well as some results achieved by our group.

According to literature review, the films deposited by ALD method:

- hinders the dissolution of cathode material [6];

- protects cathode material during cycling at high temperatures (50-55°C) [7];
- diminishes thickness of SEI film [8];
- decreases extent of electrolyte decomposition [9];
- reduces intensity of irreversible phase transformations of cathode materials during cycling [10].

Modified cathode materials have better capacity retention [1] and rate capability as well as increased performance at high temperatures [7].

ALD deserves specific attention due to its unique features, such as good conformity and absence of pinholes and defects, high precision of thickness and composition controllability and a capability to deposit high quality coating both on planar, high aspect ratio and complex 3-dimensional substrates [2, 4]. Thus, it can be applied for thin film power sources production. This type of batteries is the most progressive and sometimes the only possible ones for smart cards, microchips with integrated power supplies, various portable devices, medical implants, etc. [11]. Today lithium metal is used as anode in most of solid state power sources which results in safety issues such kind of devices. Tin dioxide is considered to be a promising anode material for solid state batteries due to its high theoretical specific capacity about 1491 mA·h / g, cycleability and safety during recharging [12, 13]. In case of high electrochemical performance thin films of tin dioxide synthesized by ALD method could be applied in thin film power sources.

1. THE METHODOLOGICAL BASES AND EXPERIMENTAL PART

1.1. Cathode preparation

$\text{Li}_{1,25}\text{Ni}_{0,13}\text{Co}_{0,13}\text{Mn}_{0,54}\text{O}_2$ powder cathode material was synthesized with use of spray-drying method followed by calcination at 900 °C during 7 hours from metals nitrate solution. The average diameter (D50) of the secondary particles according to static light scattering was $\approx 20 \mu\text{m}$. The size of initial particles measured by SEM was about 100 nm. The relation of transition metals in the formula was proved by EDX. Commercial LiCoO_2 is LC108R, Shanghai Shanshan, China.

Positive electrodes were prepared according to a standard procedure used for lithium-ion electrodes preparation. They consist of active mass (commercial LiCoO_2 or synthesized $\text{Li}_{1,25}\text{Ni}_{0,13}\text{Co}_{0,13}\text{Mn}_{0,54}\text{O}_2$ - 90 wt.%, PVDF (Kynar 761A) - 5 wt.%, Carbon black (Timcal Super C65) - 5 wt.%) layer (70 μm) deposited on the aluminum foil (20 μm).

The synthesis of aluminum oxide thin films with various thicknesses directly on a porous electrode was conducted using Picosun R-150 reactor at temperature 150 °C and pressure about 1000 Pa. Trimethylaluminum (TMA) and double distilled water were used as the precursors. After placing of electrodes in the chamber the latter was evacuated and purged by nitrogen during several minutes. One cycle of synthesis included following steps: TMA pulse (0.1 seconds, 150 sccm), nitrogen purge (12 seconds, 400 sccm), H₂O pulse (0.1 seconds, 200 sccm), nitrogen purge (15 seconds, 400 sccm). The purity of the reagents and ALD gases was no less than 99.995%. The parameters of synthesis were chosen based on the previous research results [14, 15].

1.2. Synthesis of SnO_2 thin films by ALD

Thin films of tin(IV) oxide were synthesized from tetraethyltin (TET, $\text{Sn}(\text{C}_2\text{H}_5)_4$, CAS No. 597-64-8, purity 99.995%) with the use of inductively coupled remote oxygen plasma (Picosun R-150 installation, laboratory "Functional Materials", SPbPU) and ozone (Solar-ML setup, the Resource Center "Innovative Technologies of Composite Nanomaterials", SPbSU). The power of plasma was 2500 W, the frequency was varied 1.9-3.2 MHz. 316SS stainless steel plates 16 mm in diameter were used as wafer. The parameters of synthesis SnO_2

were chosen based on the previous research results [16, 17]. The ALD timing sequence is compactly expressed as $t_1:t_2:t_3:t_4$, where t_1 and t_3 correspond to the pulse lengths of TET and those of coreactants respectively, and t_2 and t_4 to nitrogen purge times following these doses. The timing $t_1:t_2:t_3:t_4$ were 0.1:10:10:10 (plasma) and 2:10:2:10 (ozone). Reactor pressure was 8-10 hPa. For plasma process the vessel with TET was heated up to 65 °C, for ozone it was 27 °C. The process with plasma was completed after performing the 1000 number of cycles and thickness of the deposited thin films were 78 and 83 nm for synthesis temperature 250 and 300 °C, respectively. For ozone process, there were 2200 (88 nm) and 1900 (85 nm) ALD cycles for the temperatures of 250 and 300 °C, respectively.

1.3. Electrochemical performance

The electrodes based on commercial LiCoO_2 and synthesized $\text{Li}_{1,25}\text{Ni}_{0,13}\text{Co}_{0,13}\text{Mn}_{0,54}\text{O}_2$ cathode materials with and without coatings were used to fabricate coin cells batteries (CR2032) in a glove box (VGB-6) with argon atmosphere (water content <5 ppm). For commercial LiCoO_2 and synthesized $\text{Li}_{1,25}\text{Ni}_{0,13}\text{Co}_{0,13}\text{Mn}_{0,54}\text{O}_2$ FSN-1 (Shanghai Shanshan, China) carbon material and lithium foil were used as the negative electrodes, correspondingly. A solution of LiPF_6 in a mixture of organic carbonates served as the electrolyte (TC-E918, Tinci, China). Celgard 2325 was used as separator. Measurements were made at room temperature on a CT-3008W-5V10mA automated charge-discharge stand (Neware, China). The electrochemical performance for commercial LiCoO_2 was made using following parameters. The final charge voltage was 4.3 V at a charge current density of 0.5 C, and the final discharge voltage was 2.8 V at a discharge current density of 1 C (during the first 7 cycles, the final discharge voltage was 4.2 V at a charge discharge current of 0.25 C). The activation of $\text{Li}_{1,25}\text{Ni}_{0,13}\text{Co}_{0,13}\text{Mn}_{0,54}\text{O}_2$ cathode materials was made during 4 cycles (2.8 - 4.8 V). Then the coin cells were charged/discharged with use of 0.5C current in 2.8 - 4.4 V range.

Electrochemical studies of SnO_2 electrodes were performed in disk casings of CR2032 size vs. lithium metal with TC-E918 electrolyte (Tinci) and 2325 separator (Celgard). The cells were assembled in a dry argon atmosphere. The final charging voltage was 0.8 V and the final discharging voltage was 0.05 V at a various current density 25 - 100 $\mu\text{A}/\text{cm}^2$ [16]. Charging/discharging time at 25 $\mu\text{A}/\text{cm}^2$ was 60 min (1C).

2. RESULTS AND DISCUSSION

2.1. Electrode passivation using Al_2O_3 by ALD for cycle stability improvement of cathode materials

As a part of studying influence of Al_2O_3 coating on cycling stability of cathode materials there were made coatings directly on cathode electrodes based on commercial LiCoO_2 and synthesized $\text{Li}_{1,25}\text{Ni}_{0,13}\text{Co}_{0,13}\text{Mn}_{0,54}\text{O}_2$. During electrochemical tests, the specific capacity of the LiCoO_2 -based electrodes was 148 mA·h / g and the Al_2O_3 coating had no effect on the specific capacity of the material. The coulomb efficiency was 99.2 - 99.6 % during more than 400 charge-discharge cycles. No negative effect of the passivating coating on the internal resistance of the battery was observed for samples with 10 ALD cycles, the differences in the charge and discharge curves are insignificant [14]. According to the obtained results (**Figure 1**), samples with coatings have a 30% longer cycle life. For synthesized $\text{Li}_{1,25}\text{Ni}_{0,13}\text{Co}_{0,13}\text{Mn}_{0,54}\text{O}_2$ cathode material the discharge capacities after activation were almost 210 mA·h / g for initial and modified electrodes. According to electrochemical measurements the capacity of uncoated and modified electrodes reduced to 80% of their initial capacity after 200 and 300 cycles correspondingly (**Figure 1**). There was no significant difference in performance of electrodes modified after 10 and 20 cycles of TMA and H_2O treatment [15]. The increase of cycle life can be explained by the fact that the coating prevents unwanted degradation of cathode at the interface electrolyte-cathode [18].

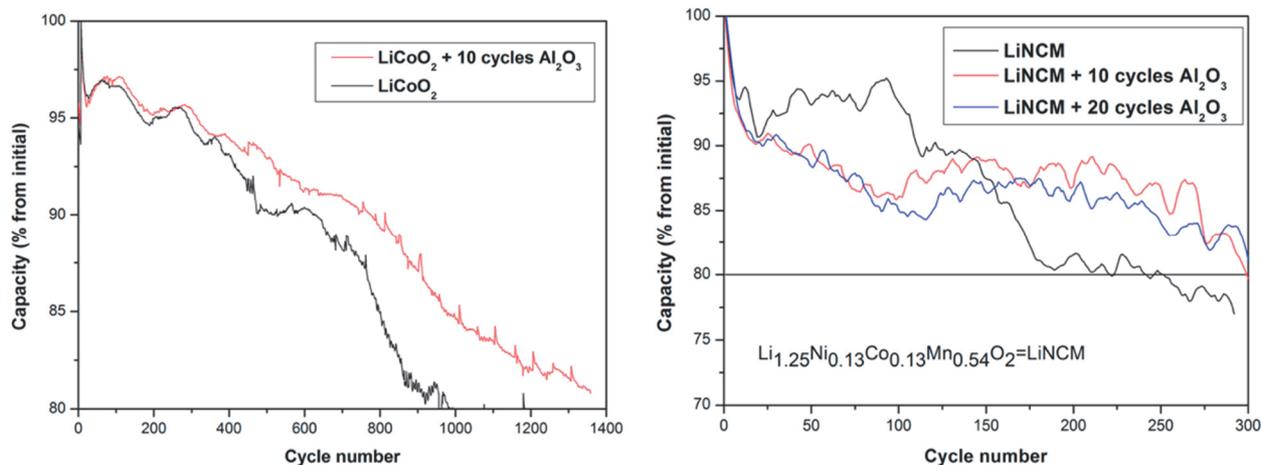


Figure 1 Cyclic stability of LiCoO_2 and $\text{Li}_{1.25}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ with and without Al_2O_3 coatings

2.2. Superior stability with high capacity of SnO_2 thin films synthesized by ALD

SnO_2 thin films were synthesized at 250 °C and 300 °C according to the XRD data they had amorphous and crystalline structure, respectively. The XPS data demonstrate that Sn3d level contains only one component with the value of peak maximums equal to 486.6 and 495 eV, common for Sn^{4+} [17].

In-plane and cross-section images were obtained for the films deposited on steel substrates (Figure 2). The cross-section was made using focused gallium ions beam. Morphology of tin dioxide synthesized using plasma and ozone are different. Thin films obtained by ozone are denser. It is also confirming by cross-section images (Figure 2).

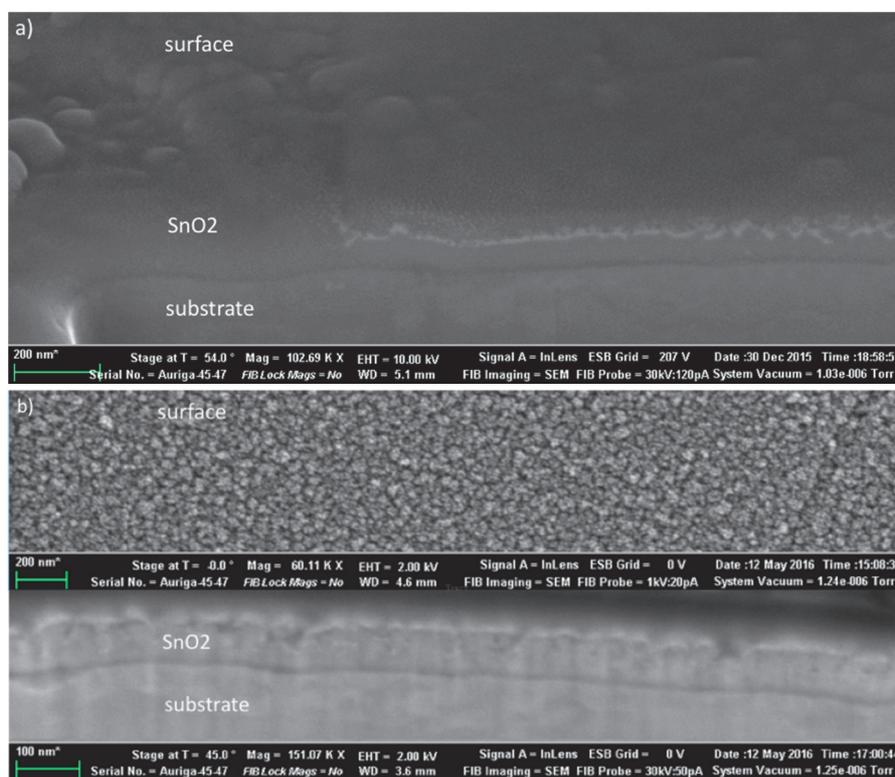


Figure 2 SEM images of SnO_2 thin films synthesized by ALD at 300 °C using TET, a) - ozone; b) - O_2 plasma

The cyclic stability of tin dioxide thin films has been studied during more than 400 charge/discharge cycles (**Figure 3**). According to the obtained results, the coulombic efficiency was 99.0-99.7%. Charge voltage was limited by 0.8 V, based on the previous research [16]. During cycling in the voltage range 0.8 - 0.05 V the process (1) takes place [13]:



Samples synthesized at different conditions are stable during cycling at various current densities. The fall in capacity after 400 charge/discharge cycles is around 5-7 %. The specific capacity of tin oxide thin films electrodes, independently from the charge/discharge rate for the samples obtained at the same parameters does not differ by more than 20 %. The difference in the specific capacity for the tin dioxide samples is probably caused by the fact that the films obtained with ozone are denser and homogeneous. Samples obtained at 300 °C have higher capacity than at 250 °C. It may be due to the crystalline structure of the thin films and material density, since the specific capacities of the thin films were estimated on the basis of cassiterite density, the higher their density is, the lower the specific capacity is.

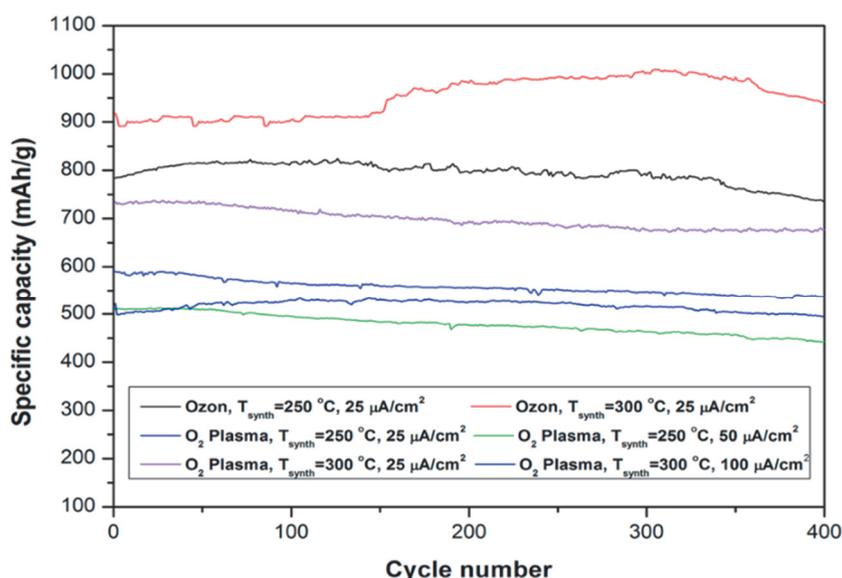


Figure 3 Cyclic stability at various current densities of SnO₂ thin films synthesized by ALD

Obtained in this work results of investigation specific capacity and cyclic stability for thin films of SnO₂ synthesized by ALD exceed values mentioned in the literature. For example, in [12] there is an overview of tin dioxide electrochemical performance. Most promising results (specific capacity, cyclic stability) were obtained by depositing tin oxide into graphene or mixing with it. It should be taken into account that increase of specific capacity may be caused by forming compounds lithium with carbon (LiC₆). Electrochemical characteristics of tin oxide deposited on graphene layers by ALD presented in [19] is about 800 mA-h / g during 160 cycles. In [20] authors demonstrated properties of tin oxide doped by other electrochemically active elements (Co, Fe) and mixed with graphene. In this case Plasma specific capacity exceeds 1000 mAh / g during 100 cycles.

3. CONCLUSION

Thus, it was shown that ALD method can be successfully applied for modification of porous positive electrodes used in li-ion batteries and for deposition of solid state batteries anode. The deposition of alumina layers on electrode comprising commercial LiCoO₂ or synthesized Li_{1.25}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂ led to the improvement of capacity retention. The number of cycles conducted before discharge capacity has reached the 80% of initial one for modified cathodes increased up to more than 30% compared to unmodified electrodes. Moreover,

SnO₂ thin films have been successfully synthesized by the atomic layer deposition method at temperatures 250 and 300 °C using tetraethyl tin, ozone and inductively coupled oxygen plasma. Studying of SnO₂ electrochemical performance have shown stable charge/discharge process throughout more than 400 cycles at current density from 25 to 100 μA / cm² in voltage range of 0.05-0.8 V. Specific capacity of tin dioxide films obtained at 300 °C is higher than samples synthesized at 250 °C and for ozone it is approximately 850-900 mA·h / g. In addition, in this work were discussed high electrochemical properties of synthesized SnO₂ thin films compared to the modern research.

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