

PLASMA ENHANCED ATOMIC LAYER DEPOSITION OF SOLID-STATE ELECTROLYTE LI-TA-O FOR SOLID-STATE BATTERIES

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Abstract

Solid-state batteries (SSBs) are regarded as the next step in energy storage technology. One of the main problems in developing such batteries is developing and synthesizing solid-state electrolytes (SSE). The main factor that stops the introduction of SSBs into everyday life is the low ionic conductivity of Li ions in modern SSEs. Therefore, the primary purposes of the work are to establish the reasons for the manifestation of this inhibiting factor and to assess the possibility of using new materials for SSLIB. Solution these problems ultimately can give an impetus to the development and promotion of such type batteries. In this work, SSE was obtained by the atomic layer deposition (ALD) method, allowing the formation of homogeneous coatings with precision control of the thickness. ALD of Li_xTaO_y thin films on silicon and stainless steel substrates using $\text{Ta}(\text{OEt})_5$ and LiOtBu was studied. The synthesis temperature was 300 °C, which is based on the previous research. Samples were synthesized with different ratios of $\text{Li}:\text{Ta} = 1:2, 1:3, 1:7$, and depending on the ratio of metals, the growth rate per supercycle varied from 0.21 to 0.46 nm. The film thickness was determined by spectral ellipsometry. A scanning electron microscopy was used to determine the conformity and morphology of the coatings. X-ray Photoelectron Spectroscopy was used to determine the elemental composition on the surface and in the bulk of SSE. According to X-ray diffraction, thin films are amorphous. Cyclic voltammetry has been used to study how thin films will respond to different voltages. The cathodic region cycling at various discharge currents (from 20 to 80 $\mu\text{A}/\text{cm}^2$) presents a low capacity.

Keywords: Atomic layer deposition, lithiated tantalum oxide, solid-state electrolyte, thin films, solid-state batteries

1. INTRODUCTION

Lithium-ion batteries (LIBs), due to their unique characteristics (specific energy, specific power, wide operating temperature range, recharge resource, etc.), have already taken root in many areas of human activity, from industrial technology to household and portable appliances [1]. But due to the use of a liquid organic electrolyte in LIBs, they are characterized by the following disadvantages: first of all, we need to introduce additional process - formation, which complicates the operation of their production, and the second drawback is the decrease in output parameters and maximum capacity with use due to the formation of solid-electrolyte interphase (SEI) [2,3]. Therefore, today in lithium-ion energy, quite a lot of research is devoted to solid-state batteries (SSBs). This is because they use a solid inorganic compound instead of the usual liquid electrolyte

[4]. Just because of this, the main factor that distinguishes SSBs from ordinary LIBs has increased levels of fire and explosion safety due to a decrease in the proportion of combustible material. So it becomes possible to introduce lithium-ion energy in new promising areas, such as electric vehicles.

Compounds similar in structure to LISICON (Li Super Ion CONductors) [5] are chosen as a solid electrolyte: $\text{Li}_{1+x}\text{Ti}_{2-x}\text{M}_x(\text{PO}_4)_3$ ($\text{M} = \text{Ge}, \text{Ti}, \text{Sn}, \text{Zn}, \text{Hf}$ [5]), $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$, and others [6]. As specific examples, we can cite studies of structures: $\text{Li}_x\text{La}_3\text{Zr}_2\text{O}_{12}$, $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, etc. [1,7,8,9]. The standard method for obtaining these structures is the sol-gel method [5, 6]. Still, the growing popularity of synthesis using atomic layer deposition (ALD) can be considered a progressive and better method for obtaining solid electrolytes. The most important advantages of ALD over the sol-gel method, in this case, can be called: obtaining conformal coatings, obtaining the required thickness with a minimum error, and the possibility of covering complex geometric shapes [1,10]. Less important, but still advantages can be called: the repeatability of the process, its self-limiting, and synthesis at relatively low temperatures [10,11,12].

This article describes the results of studies of obtained LiTaO thin films on steel and silicon substrates by the ALD method. We studied samples with the ratio Li:Ta = 1:2, 1:3, and 1:7, their growth rate on the substrate, and the elemental composition in-depth. Based on which the optimal Li-Ta-O films were selected for subsequent syntheses on the cathode material [13].

2. MATERIALS AND METHODS

The deposition of Li-O and Ta-O for Li-Ta-O films was carried out by ALD with Picosun R-150 setup at 300 °C at a base pressure of 8-12 hPa. Lithium tert-butoxide (LiOtBu , 97 %, Sigma Aldrich) and tantalum(V) ethoxide ($\text{Ta}(\text{OEt})_5$, 99,98 % Sigma-Aldrich), were used as metal-containing reagents. Remote oxygen plasma ($\text{O}_2\text{-p}$) was applied as a counter-reagent.

Precursors' containers were heated to 190 °C for $\text{Ta}(\text{OEt})_5$ and 220 °C for LiO^iBu . All depositions were performed as follows. After pulsing of metal-containing reagent ($\text{Ta}(\text{OEt})_5$ - 1.5s or LiO^iBu - 3.0s) the excess of the precursor was purged with nitrogen (99.999 %) within 10s. Pulse times for O_2 plasma was 10s. For deposition of Li-Ta-O thin films we used super cycles consisting of one $\text{LiO}^i\text{Bu}/\text{O}_2\text{-p}$ pulses and two, three or seven $\text{Ta}(\text{OEt})_5/\text{O}_2\text{-p}$ pulses: $[\text{LiO}^i\text{Bu}/\text{O}_2\text{-p}] + [\text{Ta}(\text{OEt})_5/\text{O}_2\text{-p}] * 2 = \text{LiTaO-1/2}$, $[\text{LiO}^i\text{Bu}/\text{O}_2\text{-p}] + [\text{Ta}(\text{OEt})_5/\text{O}_2\text{-p}] * 3 = \text{LiTaO-1/3}$, $[\text{LiO}^i\text{Bu}/\text{O}_2\text{-p}] + [\text{Ta}(\text{OEt})_5/\text{O}_2\text{-p}] * 7 = \text{LiTaO-1/7}$. To obtain the required films, 100-150 synthesis supercycles were performed. Estimated growth rates for Ta-O was 0.05 nm/cycle, for Li-O - 0.11 nm/cycle.

Monocrystalline silicon wafers (surface orientation 100, the size 4x4 cm, Telecom-STV Co., LTD, Zelenograd, Moscow, Russia) and stainless-steel plates (316SS, Tob New Energy Technology Co., LTD, diameter 15.8 mm) were used as substrates.

The thicknesses of the films were measured by spectral ellipsometry (wavelength range 350-1000 nm) using Ellips-1891 SAG ellipsometer (CNT, Novosibirsk, Russia). The morphology of the films was studied by scanning electron micrographs of flat and cross-sections were obtained by a Supra 55 VP scanning electron microscope (SEM, Zeiss, Oberkochen, Germany). X-ray diffraction (XRD) studies were performed using a Bruker D8 ADVANCE (Cu-K α). The obtained results were processed by the Rietveld method using TOPAS 5 software (XRD). Finally, the chemical composition of the films was studied by X-ray photoelectron spectra (XPS) and was obtained on an Escalab 250Xi spectrometer (Thermo Fisher Scientific, Waltham, MA, USA).

Electrochemical studies were performed in CR2032 coin cells, the samples of Li-Ta-O were deposited on the 316SS surface. Lithium foil, polyolefin porous film 2325 (Celgard, Charlotte, NC, USA), and TC- E918 (Tinci, Guangzhou, China) solution were used as the counter electrode, separator, and electrolyte, respectively. The coin cells (CR2032) were assembled in OMNI-LAB (VAC) glove box under argon atmosphere. Cyclic voltammetry (CV) was performed using a potentiostat PGSTAT302N+ (Autolab, Utrecht, the Netherlands) in the range of 0.1 - 4.3 V with a scan rate of 0.5 mV/s. Cyclic charge/discharge was performed using the battery

testing system CT-3008W-5V10mA (Neware, Shenzhen, China) at room temperature in the range of voltage 3.0-4.3 V, at current 20-80 $\mu\text{A}/\text{cm}^2$.

3. RESULTS AND DISCUSSIONS

3.1. Synthesis of Li-Ta-O structures

Previous experiments with the synthesis of tantalum structures as thin films [1,14] made it possible to select the conditions for obtaining the Li-Ta-O system; the corresponding synthesis parameters are presented in the Materials and Methods section.

A series of experiments were carried out to obtain Li-Ta-O with the ratios of the pulse $\text{LiO}^i\text{Bu}/\text{Ta}(\text{OEt})_5$ in the supercycle: 1:2, 1:3, and 1:7. The ratios were selected based on research results published elsewhere [15]. As a result, the investigated growth rate of LiTaO-1/2 corresponds to the expected - 0.21 nm/supercycle (**Table 1**). According to spectral ellipsometry, the samples LiTaO-1/3 and LiTaO-1/7 have a higher growth rate than expected, possibly caused by the stimulation of growth with an increase in the number of pulse $\text{Ta}(\text{OEt})_5$.

Table 1 The thicknesses of the Li-Ta-O films measured using SEM and ellipsometry and the growth parameters of the films according to the ellipsometry data

Samples - Li/Ta ratio	SEM average thickness, nm	Ellipsometry average thickness, nm	Number of supercycles	Growth rate, nm/supercycle	Estimated growth rate, nm/supercycle
LiTaO-1/2	45.05	30.9	150	0.21	0.21
LiTaO-1/3	39.44	37.9	120	0.32	0.26
LiTaO-1/7	58.75	62.61	100	0.63	0.46

The thicknesses measured by SEM (**Table 1**) for the LiTaO-1/3 and LiTaO-1/7 samples are close to the data obtained by ellipsometry. For LiTaO-1/2, there is a discrepancy between the two measurement methods. This may be due to the film thickness gradient and edge effects when measuring thin films on SEM. According to the SEM micrograph (**Figure 1**), the surface of LiTaO-1/7 is homogeneous without visible defects.

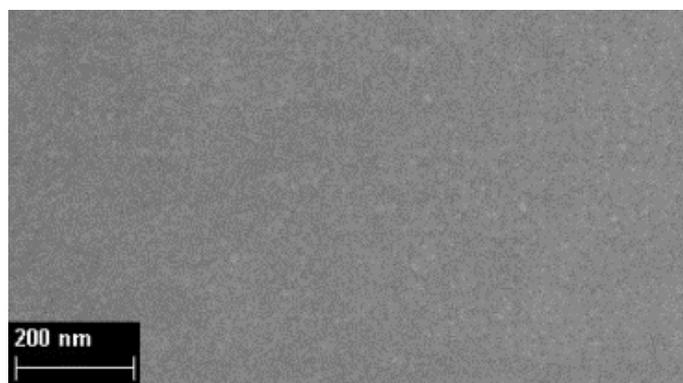


Figure 1 SEM image demonstrates a LiTaO-1/7 coating sample on the silicon substrate

For a detailed study of the chemical composition of the Li-Ta-O system, studies were carried out by the XPS method (LiTaO-1/7 - **Table 2**). As a result, the composition of the samples' surface and the bulk of the coating were investigated before and after etching the surface layer with argon ions (90 and 300 sec, 500 eV). As a result, the following elements were found on the sample's surface: lithium, tantalum, oxygen, and carbon (**Table 2**). Also, by the etching proceeds, it can be seen the number of lithium decreases and the proportion

of tantalum increases. This may be due to the presence of a gradient of elements in the bulk of the film. Thus, the surface is enriched with lithium, while tantalum is found mainly in the bulk of the film.

According to the C1s peaks of carbon (**Figure 2**), before etching, C is present on the surface in the composition of compounds, including the C-OH, C-C, C-H groups, and C=O bonds (peak shoulder at 284.8 eV) and COOH (289 eV peak). After 90 sec etching of the surface layer, the carbon signal has dropped noticeably, which indicates its absence in bulk (concentration in the analysed sample is below the detection threshold).

The spectra of Li1s (**Figure 2**), obtained without preliminary etching and after 90 and 300 sec etching, exhibit a broad maximum in the region of manifestation of lithium compounds. In the region of the location of the maximum, bands appear that characterize the presence of lithium in various compounds: Li₂O, Li₂CO₃, LiOH. The low intensity and signal/interference ratio of the Li1s spectra do not allow one to reveal the preferred state. After etching, the intensity of the peak drops by almost a factor of two.

The position of the maxima in the Ta4f spectrum (**Figure 2**) before etching corresponds to the TaO₂ compound, which is inconsistent with the data obtained from the O1s (Ta₂O₅) spectrum. This discrepancy can be caused by the high described difficulties and errors in the calibration of the position of the peaks (charge compensation). Nevertheless, in the spectra after 90 sec etching, the appearance of new peaks (components) in the region of lower energies is noticeable, these peaks correspond to the Ta⁰ and Ta²⁺ states of tantalum. Therefore, an unambiguous conclusion can be made about reducing tantalum (possibly even to metallic Ta) during etching.

Table 2 Element ratios before and after etching a Li-Ta-O-1/7 film

Element	Before etching (at. %)	After etching 90 s (at. %)	After etching 300 s (at. %)
O	47.65	55.29	3.15
Ta	12.45	31.94	1.15
Li	20.96	12.78	-
C	18.95	-	0.97
Si	-	-	94.74

After etching for 300 s, most of the signals from the silicon substrate and weak signals of pure tantalum are present in the spectra, so after 300 s, the film is completely etched away, so the etching rate is about 0.21 nm/s.

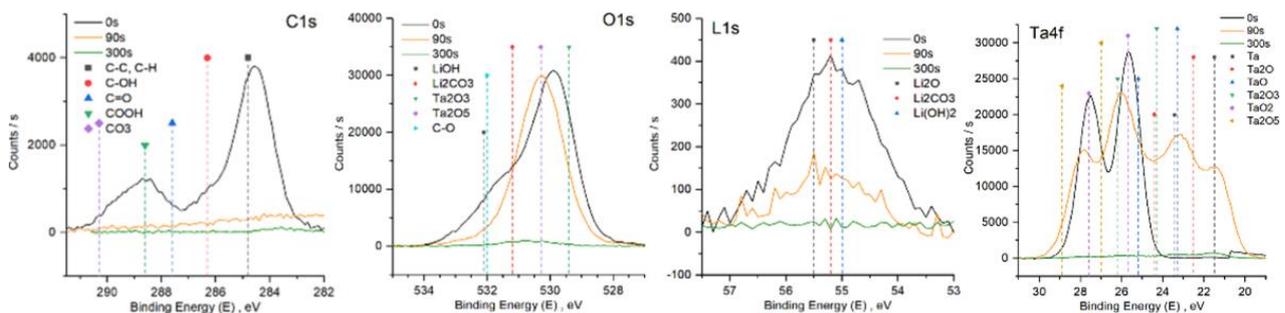


Figure 2 XPS spectra of the Li-Ta-O-1/7 film before and after etching

The X-ray phase analysis pattern (**Figure 3**) shows two relatively intense peaks characteristic of the Ta structures in the region 27° (TaO₂) and 33° (TaO), as well as one less intense peak in area 62 (TaO₂). An ultra-intense peak of 33° is also observed, which can be associated with a defect in the silicon substrate. Comparing the obtained diffractogram with cards from the database of diffractograms PDF, we can conclude that the obtained LiTaO-1/7 film is X-ray amorphous.

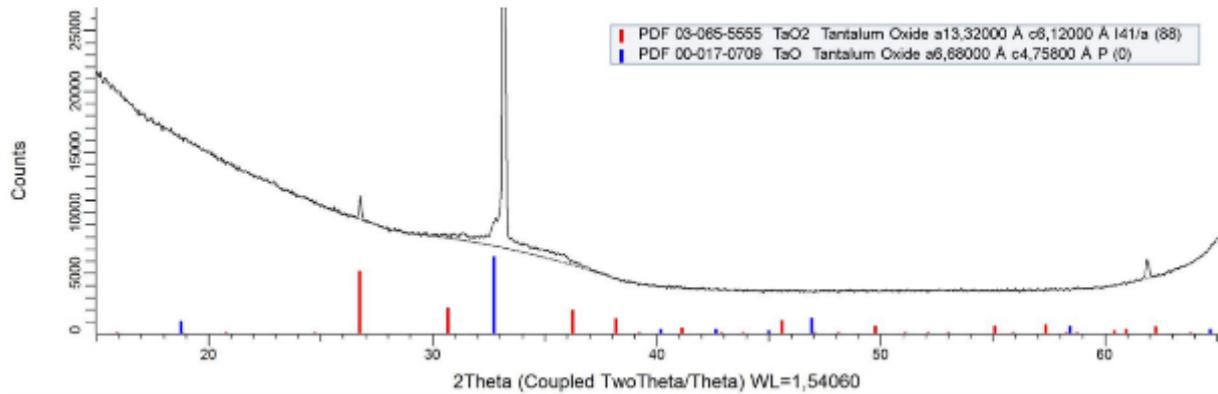


Figure 3 Diffraction pattern of the LiTaO-1/7 sample (Si substrate)

3.2. Electrochemical tests of Li-Ta-O structures

The LiTaO-1/2 samples on steel (SS_LiTaO-1/2) with a calculated ratio Li/Ta = 1/1 were selected to study the electrochemical characteristics. This ratio was selected based on research results published elsewhere [15], which showed that with an increase of lithium content (from $x = 0.32$ to 0.98 in Li_xTaO_y), the lithium-ion conductivity is improved by two orders of magnitude. Based on the results of work [15] and the obtained XPS graphs (**Figure 3**), we can conclude that with an increase in the Li concentration ($x = 1.73$), it tends to form harmful bonds with carbon (Li_2CO_3), hydroxide ($\text{Li}(\text{OH})_2$) and oxygen (Li_2O), instead of being in a free state in the $[\text{TaO}_6]$ crystal lattice. As a result of the formation of such bonds, we lose lithium ions, thereby lowering the overall conductivity of the material.

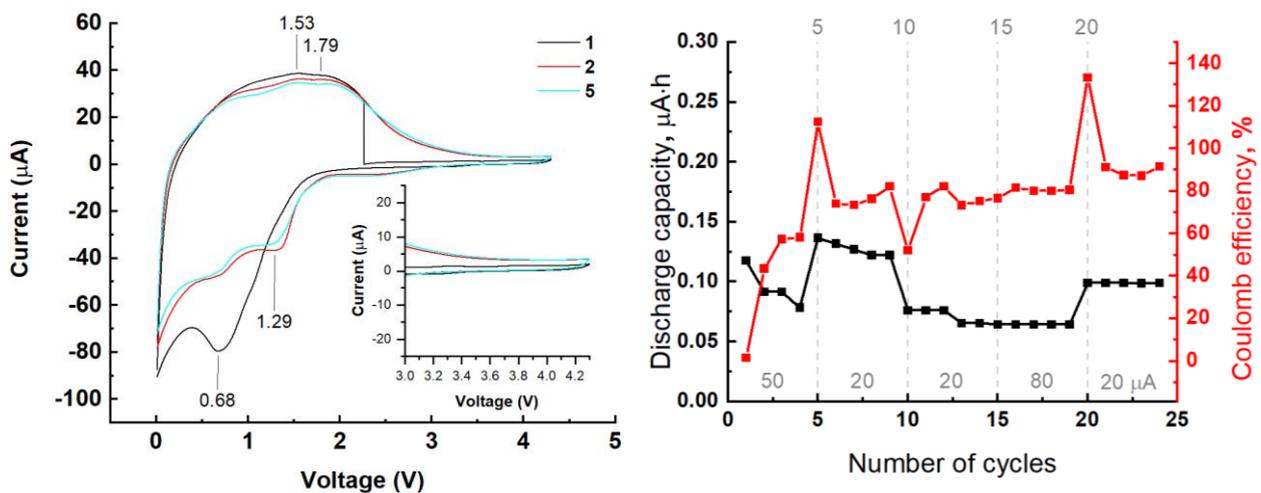


Figure 4 Cyclic voltammetry (CV) curves and results of cyclic tests at different discharge currents

The CV curves of a series of SS_LiTaO-1/2 samples (**Figure 4**) and coatings of the Ta-O system have a general trend: in the anodic region (3.0-0.1 V), there is current amplification, which is most likely associated with the formation of SEI film [16], and no current increases are observed in the potential cathode range (4.3-3.0 V - inset in **Figure 4**). Further cycling at currents from 20 to 80 $\mu\text{A}/\text{cm}^2$ in the cathode potential range (4.3-3.0 V) showed the presence of a minimum capacity of about 2.0-1.5 $\mu\text{A}\cdot\text{h}\cdot\mu\text{m}^{-1}\cdot\text{cm}^{-2}$ (0.14-0.07 $\mu\text{A}\cdot\text{h}$), for example in our previous work on the lithium-nickel-silicon oxide cathode study [1], the capacity of the cathode material was 30-20 $\mu\text{A}\cdot\text{h}\cdot\mu\text{m}^{-1}\cdot\text{cm}^{-2}$, so we can consider that this thin film of LiTaO-1/2 does not affect on the final capacity. Thus, the investigated coatings of the LiTaO-1/2 system do not significantly contribute to the electrochemical capacity in the potential cathode range. Therefore, this thin film can be studied like cathode-solid electrolyte systems in the future.

4. CONCLUSION

First, thin films carried out at different synthesis ratios showed different growth rates for LiTaO-1/2, LiTaO-1/3, and LiTaO-1/7: 0.21, 0.32, and 0.63 nm/supercycle respectively. Secondly, the physicochemical analysis showed: thin films are amorphous; lithium diffuses from the bulk closer to the surface, while tantalum is concentrated in bulk or bottom of coating; traces of carbon (which are absent in bulk) were also found on the surface, which may indicate its interaction with lithium or the formation of organic acids/bases/substances. Finally, electrochemical tests have shown no current amplification in the cathode region (4.3-3.0 V); also, Li-Ta-O films do not mainly introduce additional capacity, at currents equal $2.0\text{-}1.5 \mu\text{A}\cdot\text{h}\cdot\mu\text{m}^{-1}\cdot\text{cm}^{-2}$.

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