

## SYNTHESIS OF LITHIUM AND COBALT OXIDES SYSTEMS BY THE ALD METHOD TO OBTAIN LITHIUM COBALT OXIDE CATHODE FOR THIN-FILM LIBS

Ilya MITROFANOV, Ilya EZHOV, Yury KOSHTYAL, Denis NAZAROV, Artem KIM, Aleksander RUMYANTSEV, Anatoly POPOVICH, Maxim MAXIMOV

<sup>1</sup>Peter the Great Saint-Petersburg Polytechnic University, Saint-Petersburg, Russian Federation, [maximspbstu@mail.ru](mailto:maximspbstu@mail.ru)

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### Abstract

The development of micro- and nanoscale power sources for micro size electronic devices such as wireless sensors, biomedical implants, and smart cards is an important task. In this work, the processes of synthesis uniform lithium oxide, cobalt oxide, and lithium cobalt oxide thin films using atomic layer deposition (ALD) method were studied. Lithium tert-butoxide (LiOtBu) and cobaltocene (Co(Cp)<sub>2</sub>) were used as precursors. Remote oxygen plasma was used as a counter-reagent. The synthesis was carried out at 300 °C. The growth rate and uniformity of the films were controlled by adjustment the precursor's evaporation temperature, reagent pulse time, and purge times. Monocrystalline silicon and stainless steel (SS316) were used as substrates. The films were studied by spectral ellipsometry, energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction analysis (XRD). Results showed that an increase the purge time to 10 s after the reagent pulse positively affects the uniformity of the films. The growth rates of Li-O and Co-O systems were 0.080±0.010 nm/cycle and 0.022±0.003 nm/cycle, respectively. XRD data showed the presence of the crystalline CoO phase for the Co-O and the presence of the LiCoO<sub>2</sub> for Li-Co-O samples. The optimized synthesis parameters determined for Li-O and Co-O were subsequently used to synthesize Li-Co-O (LiCoO<sub>2-x</sub>) system. According to the growth rates of Li-O and Co-O, the ratio of Li and Co pulses was set as 1/5. XRD data showed well crystalline LiCoO<sub>2</sub> textured in (003) direction for as-deposited Li-Co-O thin films. According to cyclic voltammetry (CV), there is a pronounced peak characterizing of the change in the oxidation state of cobalt from 3+ to 4+. Based on cyclic tests, the Li-Co-O films have high coulombic efficiency.

**Keywords:** Atomic layer deposition, lithium oxide, cobalt oxide, lithium cobalt oxide, lithium-ion batteries, solid-state lithium-ion batteries

### 1. INTRODUCTION

Today lithium-ion batteries (LIBs) are widespread for power supply in modern portable electronics, sensors, medical devices, etc. The downscale trend in portable electronics requires the on-board power supply device to be of smaller dimensions, higher energy, and power density. Therefore, the production of thin-film anode and cathode materials is one of the most important task for the development modern portable electronic devices. Atomic layer deposition (ALD) is the most promising technology for synthesis inorganic thin films due to the ability to control the composition and thickness of the films with high precision. ALD is based on self-limited chemical reactions of gas-phase reagent with substrate surface [1,2]. Some examples of synthesis electrode materials by ALD method and their electrochemical properties can be found somewhere [3-5]. However, most of the work on the use of ALD for preparation of active materials is devoted to the synthesis of thin film anodes. There is much less work to synthesize cathode materials. The problem is the cathode materials contain lithium, which is difficult to produce by ALD due to hydrolysis when using water as a counter-reagent. However, the use of oxygen plasma as a counter-agent can solve this problem. LiCoO<sub>2</sub> is the most commonly used cathode material in commercial LIBs due to its high energy density, low self-discharge and excellent cyclability. Therefore in this work we synthesized the lithium cobalt oxide thin films by ALD using oxygen plasma as counter-reagent and studied its electrochemical performance.

## 2. MATERIALS AND METHODS

The deposition of Li-O, Co-O, Li-Co-O films was carried out by ALD with Picosun R-150 setup at 300 °C at base pressure of 8-12 hPa. Lithium tert-butoxide (LiOtBu, 97%, Sigma Aldrich) and bis(cyclopentadienyl) Cobalt(II) (Co(Cp)<sub>2</sub>, 99% Sigma-Aldrich), were used as metal-containing reagents. Remote oxygen plasma (O<sub>2</sub>-p) applied as a counter-reagent. The temperatures of reagent containers were 218 °C for LiOtBu, and 100-175 °C for Co(Cp)<sub>2</sub>. All depositions were performed as follows. After pulsing of metal-containing reagent (LiOtBu - 1.0s or Co(Cp)<sub>2</sub> - 1.6-3.0s) the excess of the precursor was purged with nitrogen (99.999%) before the counter-reagent was introduced. For increasing of vapor pressure of LiOtBu boosting ALD regime [6] was tested. Boosting parameters (Picohot™ Boosting), 500 sccm /0.5s/1.2s/0s (boost/pre empty/master fill/post-empty) was used. Pulse times for O<sub>2</sub> plasma was 10s. To prevent Li-O thin films hydrolysis, 50 ALD cycles of trimethylaluminum (TMA)-H<sub>2</sub>O were applied for deposition of alumina protective coatings [7]. For deposition of Li-Co-O thin films we used super cycles consisting of one LiOtBu/O<sub>2</sub>-p pulses and five Co(Cp)<sub>2</sub>/O<sub>2</sub>-p pulses: [LiOtBu/O<sub>2</sub>-p] + [Co(Cp)<sub>2</sub>/O<sub>2</sub>-p]\*5. We used 100 and 400 supercycles. 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. Before deposition, silicon substrates were cleaned in an ultrasonic bath in acetone and deionized water for 15 min.

The thicknesses of the films were measured by spectral ellipsometry (wavelength range 350-1000 nm) using Ellips-1891 SAG ellipsometer (CNT, Novosibirsk, Russia). X-ray diffraction (XRD) studies were performed using a Bruker D8 ADVANCE (Cu-Kα). The obtained results were processed by the Rietveld method using TOPAS 5 software (XRD). The morphology and chemical composition of the films was studied by energy-dispersive X-ray spectroscopy (EDX) using Mira-3M (Tescan, Quanta 200, FEI).

Electrochemical studies were performed in CR2032 coin cells. The samples of Li-Co-O deposited on the 316SS surface were used. 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. Coin cells were assembled in an argon glove box OMNI-LAB (VAC). Cyclic voltammetry (CV) was performed using a potentiostat PGSTAT302N+ (Autolab, Utrecht, the Netherlands) in the range of 3.0 - 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 potential 3.0 - 4.3 V, at current 20 - 80 μA.

## 3. RESULTS AND DISCUSSION

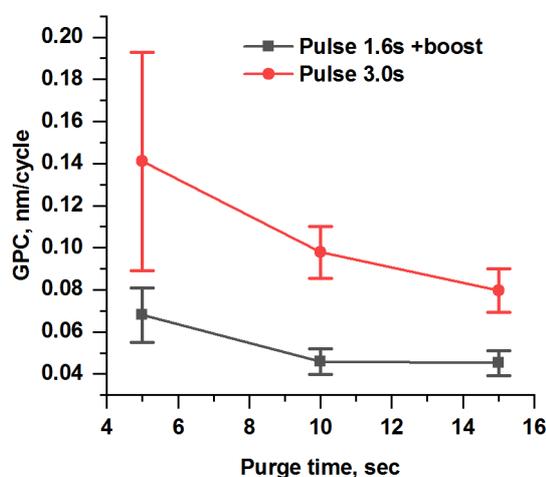
### 3.1. Li-O system

Lithium butoxide is the most commonly used reagent for the synthesis of lithium-containing thin films by ALD [8]. The temperature of evaporation of lithium butoxide varies over a wide range from 90 to 180 °C [4,9]. Such a large temperature difference depends on the design features of the setups [4,9]. Our results showed that the Li-O growth of the films occurs only at the maximum possible temperature of the evaporator (218 °C) on the installation used (Picosun R-150) with a pulse duration of 3 seconds. In this regard, experiments were carried out to study the uniformity of coatings at various purge times and two precursor pulse modes: line boost mode (Picohot™ Boosting) and under standard mode. Picohot™ Boosting is provided by the manufacturer for the low volatile reagent to reduce the temperature of the evaporator. In this work, the lithium reagent pulse time is 1.6 s (Boosting) and 3.0 (Standard mode). The temperature of the evaporator at Standard and Boosting modes was 218 °C.

It should be noted that the reagent is low volatile and stable up to 250 °C [10], which imposes restrictions on the minimum temperature for the synthesis of lithium-containing films. Based on the literature data and taking into account the physicochemical characteristics of the reagents, the reactor temperature was set at 300 °C.

All films, in accordance with our previous studies [7] on the preparation of lithium-containing films, were coated with a protective layer of alumina (50 ALD cycles - TMA+H<sub>2</sub>O) and stored in an inert atmosphere of argon.

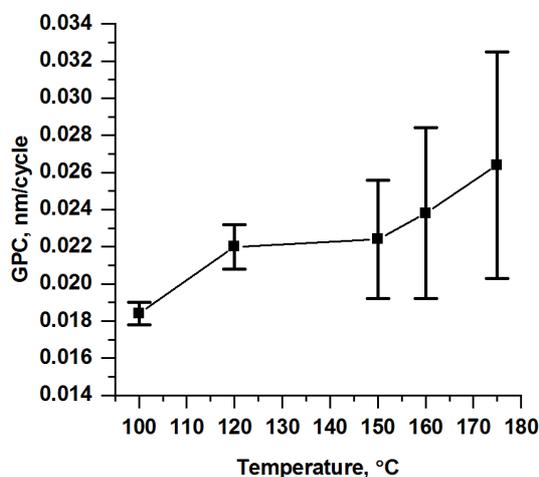
The effect of purge time on the growth rate and uniformity of the films using two types of reagent pulse modes (Standard and Boosting) shown in **Figure 1**. With increasing purge time, uniformity of coatings increases and the growth rate decreases for both modes. Acceptable growth rate and uniformity of the films was obtained by pulse 10 - 15 s. To optimize the synthesis time, a purge of 10 s was chosen for subsequent experiments. It is worth noting that when using Boosting, the growth rate more than 2 times lower than with Standard pulse mode. To increase the growth rate of the films, the conditions with the highest growth rates with similar uniformity were chosen for Li-Co-O deposition. XRD data didn't show presence of any crystalline phase.



**Figure 1** The change of growth per cycle (GPC) with an increase in the purge time of LiOtBu

### 3.2. Co-O system

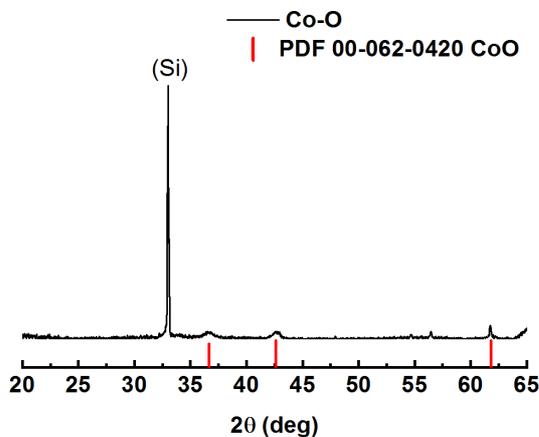
The literature provides information on the synthesis of CoO<sub>x</sub> films by the ALD in a wide temperature range using cobaltocene and ozone or oxygen plasma as a counter-reagent. The synthesis is carried out in a wide temperature range (140 - 350 °C) [11,12]. However, to synthesize the lithium cobaltate, it is necessary to combine the deposition temperature of cobalt and lithium oxides (for Li-O the temperature is at least 300 °C). Therefore to optimize the deposition conditions of cobalt oxide, we used a temperature of 300 °C.



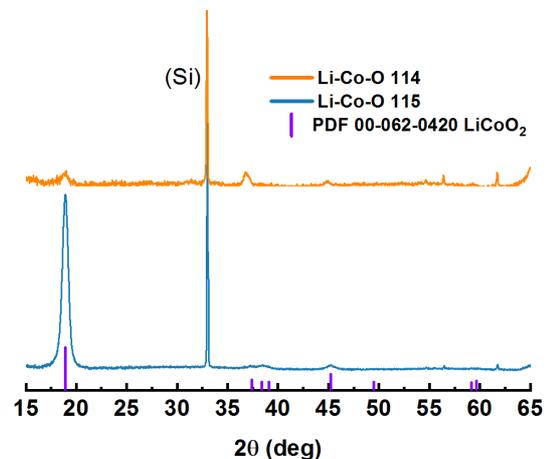
**Figure 2** The change of growth per cycle (GPC) with an increase in the evaporation temperature of Co(Cp)<sub>2</sub>

Based on our previous work [13], when the nickelocene ( $\text{NiCp}_2$ ) was used as ALD precursor for  $\text{NiO}_x$  thin film synthesis we used 1.0 second for pulse and 10 second for purge. As we found out earlier, the temperature of the source is of great importance when using metallocenes. In this regard, we studied the effect of evaporator temperature on growth rate and uniformity  $\text{Co-O}$  films (**Figure 2**). The optimal temperature range was from 120 to 150 °C. At higher temperatures, the growth rate increases, but the gradient of film thickness also increases significantly, which may be caused by the decomposition of cobaltocene.

EDX data showed the presence of cobalt in the film. **Figure 3** shows the diffraction pattern of  $\text{Co-O}$  sample deposited on silicon surface. Three peaks at 33, 55 and 57 degree are associated with the imperfection of the crystal structure of the silicon substrate. The other peaks correspond to the  $\text{CoO}$  phase (Fm-3m). The coincidence of the intensities of these peaks with the table value indicates the absence of texture in the film.



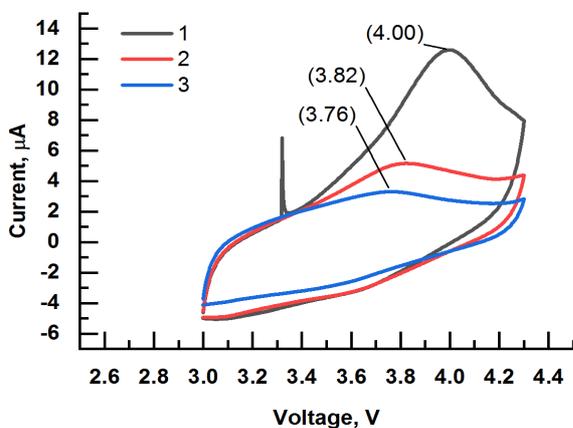
**Figure 3** XRD of  $\text{Co-O}$  thin film



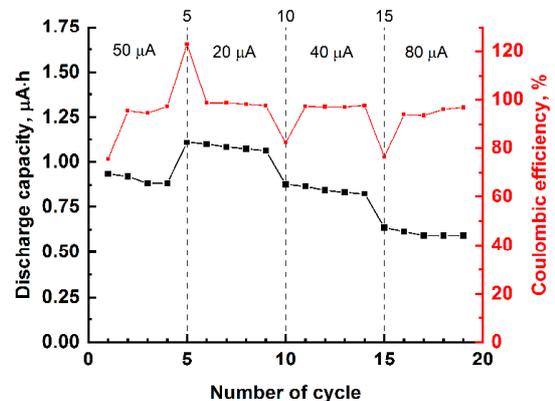
**Figure 4** XRD of  $\text{Li-Co-O}$  thin films

### 3.3. $\text{Li-Co-O}$ system synthesis and electrochemical performance

Based on the results of experiments with  $\text{Li-O}$  and  $\text{Co-O}$ , the optimal parameters were used for the synthesis of  $\text{Li-Co-O}$  films. We synthesize 2 samples using 100 and 400 super cycles. Each supercycle consisted of one  $\text{LiOtBu/O}_2\text{-p}$  pulses and five  $\text{Co(Cp)}_2/\text{O}_2\text{-p}$  pulses:  $[\text{LiOtBu/O}_2\text{-p}] + [\text{Co(Cp)}_2/\text{O}_2\text{-p}] * 5$ . The thickness of the films were  $34.2 \pm 4.2$  and  $70.6 \pm 11.6$  nm respectively.



**Figure 5** CV of  $\text{Li-Co-O}$  115 thin film



**Figure 6** Effect of discharge current on capacity of  $\text{Li-Co-O}$  115 film

Presence of cobalt in the films were confirmed by EDX data. At the diffraction patterns of the samples (**Figure 4**) clearly visibly peaks of the silicon substrate (33, 55, 57 degree). But the other peaks are characteristic by the LiCoO<sub>2</sub> structure with the space group (R $\bar{3}m$ ). The X-ray diffraction pattern of sample with a larger film thickness shows a strong texturing of the LiCoO<sub>2</sub> phase into the (003) direction which is perpendicular to the substrate surface. The March-Dallas coefficient was 0.3752±0.0064. The unit cell parameters calculated by the Rietvelt method for samples thin and thick films were: a = 2.856 ± 0.009, c = 14.046 ± 0.016 and a = 2.815 ± 0.002, c = 14.065 ± 0.002 respectively. which fits well with tabular values [14]. The difference in the lattice parameter “a” for a thin film may be due to surface effects.

The resulting samples were investigated by cyclic voltammetry (**Figure 5**). An intense peak in region 4V is characteristic of the process of cobalt oxidation from 3+ to 4+. [15,16], while there is no pronounced peak for the reverse process (reduction processes from 4+ to 3+). Also, there is a decrease in the anode peak and its displacement in the region of lower potentials. All of the above can be associated with the involvement of the substrate material in the process [13]. The areas of the anodic and cathodic curves on cycles 2 and 3 are comparable, which may indicate good reversibility of the process. **Figure 5b** shows the dependence of the discharge capacitance on the number of cycles at various currents. A stepwise increase in the discharge current from 20 to 80  $\mu$ A leads to a marked decrease in the discharge capacitance, which is similar for all electrode materials. Coulombic efficiency is about 95 %. (**Figure 6**) The average discharge capacity was 0.85 $\mu$ Ah. The average specific discharge capacity is 37 mAh/g, which is less than the values obtained in practice for powder analogues (practical capacity of LiCoO<sub>2</sub> is only ~137 mAh/g, while the theoretical capacity of ~274 mAh/g [15]), this may be due to the involvement of the substrate material in the process.

#### 4. CONCLUSION

ALD-growth of Li-O, Co-O, and Li-Co-O films was carried out using lithium butoxide, cabaltocene, and remote oxygen plasma. The growth rates of Li-O and Co-O systems were 0.080 ± 0.010 nm/cycle and 0.022 ± 0.003 nm/cycle, respectively. Results showed that an increase the purge time to 10 s positively affects the uniformity of the films. The presence of cobalt in the films was confirmed by the EDX method. In contrast to the results presented in literature [3,11] the synthesized Co-O and Li-Co-O films contain well crystalline CoO and LiCoO<sub>2</sub> phases respectively. For as-deposited Li-Co-O thin films, LiCoO<sub>2</sub> phase textured in (003) direction. According to CV study, there is a pronounced peak characterizing of the change in the oxidation state of cobalt from 3+ to 4+. Based on cyclic tests, the Li-Co-O films have high coulombic efficiency.

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#### REFERENCES

- [1] MALYGIN, A.A.; DROZD, V.E.; MALKOV, A.A.; SMIRNOV, V.M. From V. B. Aleskovskii's "Framework" Hypothesis to the Method of Molecular Layering/Atomic Layer Deposition. *Chem. Vap. Depos.* 2015, 21, 216-240.
- [2] PUURUNEN, R.L. Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process. *J. Appl. Phys.* 2005, 97.
- [3] NILSEN, O.; MIIKKULAINEN, V.; GANDRUD, K.B.; ØSTRENG, E.; RUUD, A.; FJELLVÅG, H. Atomic layer deposition of functional films for Li-ion microbatteries. *Phys. status solidi* 2014, 211, 357-367.
- [4] WANG, B.; LIU, J.; SUN, Q.; LI, R.; SHAM, T.-K.; SUN, X. Atomic layer deposition of lithium phosphates as solid-state electrolytes for all-solid-state microbatteries. *Nanotechnology* 2014, 25, 504007.

- [5] MAXIMOV, M.Y.; KOSHTYAL, Y.; MITROFANOV, I.; EZHOV, I.; RUMYANTSEV, A.; POPOVICH, A. Features of the synthesis of lithium-based ternary oxide nanofilms by atomic layer deposition with LHMDs for thin-film LIBs. In Proceedings of the Materials Today: Proceedings; INESS-2019, 2019.
- [6] PFEIFFER, K.; SCHULZ, U.; TÜNNERMANN, A.; SZEGHALMI, A. Ta<sub>2</sub>O<sub>5</sub> / Al<sub>2</sub>O<sub>3</sub> / SiO<sub>2</sub> - antireflective coating for non-planar optical surfaces by atomic layer deposition.; von Freymann, G., Schoenfeld, W. V., Rumpf, R.C., Eds.; 2017; p. 1011513.
- [7] NAZAROV, D.; EZHOV, I.; MITROFANOV, I.; MAXIMOV, M. The use of the TMA as stabilizing reagent for the Li-O system obtained by atomic layer deposition. *Key Eng. Mater.* 2019, 822, 787-794.
- [8] NILSEN, O.; MIIKKULAINEN, V.; GANDRUD, K.B.; ØSTRENG, E.; RUUD, A. Atomic layer deposition of functional films for Li-ion microbatteries. In Proceedings of the Physica Status Solidi (A) Applications and Materials Science; 2014; Vol. 211, pp. 357-367.
- [9] HÄMÄLÄINEN, J.; HOLOPAINEN, J.; MUNNIK, F.; HATANPÄÄ, T.; HEIKKILÄ, M.; RITALA, M.; LESKELÄ, M. Lithium Phosphate Thin Films Grown by Atomic Layer Deposition. *J. Electrochem. Soc.* 2012, 159, A259-A263.
- [10] CHISHOLM, M.H.; DRAKE, S.R.; NAIINI, A.A.; STREIB, W.E. The synthesis and characterization of volatile lithium alkoxides, and the single crystal X-ray structure of [LiOCMe<sub>2</sub>Ph]<sub>6</sub>. *Polyhedron* 1991, 10, 805-810.
- [11] DONDEERS, M.E.; ARNOLDBIK, W.M.; KNOOPS, H.C.M.; KESSELS, W.M.M.; NOTTEN, P.H.L. Atomic layer deposition of LiCoO<sub>2</sub> thin-film electrodes for all-solid-state Li-ion micro-batteries. *J. Electrochem. Soc.* 2013, 160.
- [12] DISKUS, M.; NILSEN, O.; FJELLVÅG, H. Thin Films of Cobalt Oxide Deposited on High Aspect Ratio Supports by Atomic Layer Deposition. *Chem. Vap. Depos.* 2011, 17, 135-140.
- [13] KOSHTYAL, Y.; NAZAROV, D.; EZHOV, I.; MITROFANOV, I.; KIM, A.; RYMYANTSEV, A.; LYUTAKOV, O.; POPOVICH, A.; MAXIMOV, M. Atomic Layer Deposition of NiO to Produce Active Material for Thin-Film Lithium-Ion Batteries. *Coatings* 2019, 9, 301.
- [14] SITA, L.E.; DA SILVA, S.P.; DA SILVA, P.R.C.; SCARMINIO, J. Re-synthesis of LiCoO<sub>2</sub> extracted from spent Li-ion batteries with low and high state of health. *Mater. Chem. Phys.* 2017, 194, 97-104.
- [15] NIE, P.; SHEN, L.; LUO, H.; LI, H.; XU, G.; ZHANG, X. Synthesis of nanostructured materials by using metal-cyanide coordination polymers and their lithium storage properties. *Nanoscale* 2013, 5, 11087.
- [16] JULIEN; MAUGER; HUSSAIN Sputtered LiCoO<sub>2</sub> Cathode Materials for All-solid-state Thin-film Lithium Microbatteries. *Materials (Basel)*. 2019, 12, 2687.