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Atomic/Molecular Layer Deposition of Lithium Terephthalate Thin Films as High Rate Capability Li-Ion Battery Anodes

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1 Atomic/molecular layer deposition of lithium
2 terephthalate thin films as high rate capability Li-ion
3 battery anodes

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6
7 Keywords: Atomic layer deposition, molecular layer deposition, thin film battery, organic
8 electrode

9 ABSTRACT: We demonstrate the fabrication of high-quality electrochemically active organic
10 lithium electrode thin films by the currently strongly emerging combined atomic/molecular layer
11 deposition (ALD/MLD) technique using lithium terephthalate, a recently found anode material for
12 lithium-ion battery (LIB), as a proof-of-the-concept material. Our deposition process for Li-
13 terephthalate is shown to well comply with the basic principles of ALD-type growth including the
14 sequential self-saturated surface reactions, a necessity when aiming at micro-LIB devices with 3D
15 architectures. The as-deposited films are found crystalline across the deposition temperature range
16 of 200 – 280 °C, which is a trait highly desired for an electrode material but rather unusual for
17 hybrid organic-inorganic thin films. Excellent rate capability is ascertained for the Li-terephthalate
18 films with no conductive additives required. The electrode performance can be further enhanced

19 by depositing a thin protective LiPON solid-state electrolyte layer on top of Li-terephthalate; this
20 yields highly stable structures with capacity retention of over 97 % after 200 charge/discharge
21 cycles at 3.2 C.

22
23
24 The miniaturization of electronic devices demands for energy storage systems of equal
25 dimensions. In order to retain reasonable energy and power densities, all-solid-state thin-film
26 microbatteries based on three-dimensional (3D) microstructured architectures are seen as a viable
27 solution. Compared to 2D thin-film batteries, the increased specific surface area of 3D
28 microstructures provides us with enhanced energy density while the electrodes can still be kept
29 thin enough for short Li diffusion paths and thereby good power density.¹⁻³ Such an approach
30 places an apparent need for a thin-film deposition method capable of manufacturing the electrode
31 and electrolyte materials on high-aspect-ratio substrates. Atomic layer deposition (ALD) is an
32 established thin-film technology for producing conformal coatings on such high-aspect-ratio
33 structures.^{4,5} It is based on sequential exposure of gaseous precursors on the target substrate where
34 surface-saturation limited reactions allow the layer-by-layer deposition of high-quality thin films
35 with sub-monolayer accuracy.⁶ However there is an apparent need for broadening the currently
36 rather narrow range of available deposition processes for Li-ion electrode materials.

37 Organic electrode materials would possess several attractive features compared to the current
38 transition-metal based inorganic materials. They are composed of cheap, earth-abundant,
39 environmentally friendly and light elements, and owing to the low molecular mass together with a
40 possibility for multiple redox processes per molecule, organic electrodes display very high
41 theoretical specific capacities of several hundred mAh per gram. Moreover, the redox properties
42 can be tuned by the addition of electron donating/withdrawing functional groups. The biggest

43 obstacles in putting organic electrode materials into practical use in next-generation LIBs are their
44 instability/dissolution in the commonly employed liquid electrolytes and their negligible electronic
45 conductivity which dictates the need for very large amounts of conductive additives resulting in
46 greatly reduced actual capacities.^{7,8} In an all-solid-state thin-film LIB these obstacles could
47 possibly be circumvented: the dissolution issue would be completely avoided by replacing the
48 liquid electrolyte by a solid one, while the reduced dimensions in thin films should contribute
49 towards mitigating the effect of intrinsically poor electronic conductivity of organics.

50 Owing to the recent progress in combining the ALD technique for inorganic materials with the
51 strongly emerging molecular layer deposition (MLD) technique for organics it has become
52 possible to fabricate inorganic-organic hybrid thin films in a well-controlled atomic/molecular
53 layer-by-layer manner; for a recent review of the combined ALD/MLD technique see ref. 9. A
54 number of ALD/MLD processes with different organic constituents have already been developed.
55 However, the range of the metal components is yet limited, and as far as we know no ALD/MLD
56 processes for lithium-organic thin films have been reported. Here we demonstrate that the
57 ALD/MLD technique indeed is commendably suited for the deposition of organic LIB electrodes;
58 our proof-of-the-concept data are for lithium terephthalate ($\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$ or LiTP). The
59 electrochemical activity of bulk LiTP was discovered by Tarascon *et al.*;¹⁰ their data revealed high
60 gravimetric capacity of 300 mAh/g associated with a flat reduction potential at around 0.8 V vs.
61 Li^+/Li . As such LiTP is indeed an attractive anode material as it offers considerably higher specific
62 energy compared to other electrode material candidates for thin-film LIBs including TiO_2 and
63 $\text{Li}_4\text{Ti}_5\text{O}_{12}$.² Moreover, computational predictions indicate that the volume change of LiTP during
64 (de)lithiation is relatively small, i.e. ~6%.¹¹ Hence LiTP would be preferable also over the
65 traditional high-capacity anode materials such as silicon and transition-metal oxides for which the

66 large volume expansion during lithiation results in poor cycle life of the material.¹² The major
67 findings of the present study are three-fold. First, we succeeded in fabricating crystalline organic
68 LIB electrode thin films for the first time through a gas-phase deposition technique. Secondly, the
69 films were found to be electrochemically active with excellent rate capability without relying on
70 any conductive additives thus demonstrating that LiTP can perform as a high-rate anode material
71 if the electronic conductivity issue can be overcome. Lastly we show that by applying a protective
72 layer consisting of the lithium phosphorus oxynitride (LiPON) solid-state electrolyte deposited by
73 ALD, the LiTP electrodes can be stabilized even in LiPF₆-based liquid electrolytes resulting in an
74 excellent cycle life.

75 The LiTP thin films were deposited using Li(thd) (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate)
76 and terephthalic acid (TPA) as precursors. The defining feature of an ALD/MLD process is the
77 self-limiting film growth, that is, after a certain threshold value, the growth-per-cycle (GPC)
78 calculated from the resultant film thickness value (determined in our case by spectroscopic
79 ellipsometry) becomes constant regardless the pulsing times of the precursors. To verify the
80 ALD/MLD-type film growth, the deposition rate for our Li(thd)-TPA process was studied as a
81 function of the precursor pulse lengths at a deposition temperature of 200 °C using 200 ALD/MLD
82 cycles. As shown in Figure 1a, in the case of Li(thd), saturation is achieved with a pulse length of
83 4 s whereas TPA requires a longer pulse length of 10 s. With these optimized pulse lengths the
84 saturation-limited growth rate at 200 °C is ~3.0 Å/cycle. The saturation limited growth was further
85 investigated by depositing LiTP thin films on microstructured silicon substrates consisting of
86 trenches ~50 μm deep and 7.5 μm wide using the aforementioned pulse and purge lengths with
87 400 deposition cycles. As shown in Figure S1 in Supporting Information, essentially conformal
88 films are achieved even with parameters optimized for planar substrates.

89 Using the same pulse lengths, the growth rate was further studied in a temperature range of 200
90 – 280 °C using 400 ALD/MLD cycles. From Figure 1b, no region of constant GPC value, i.e. a
91 so-called ALD window, is observed; instead there is a rather monotonous decrease in GPC with
92 increasing deposition temperature which is actually a common feature for a majority of ALD/MLD
93 processes.^{9,13,14} The density of the films, as obtained from the X-ray reflectivity (XRR) data,
94 appears to remain essentially constant in the deposition temperature range of 200 – 240 °C (Figure
95 1b). At temperatures higher than this, the decrease in density might arise from thermal
96 decomposition of either of the precursors resulting in inclusion of carbon impurities. Within the
97 uniform density region, the resultant film density of $\sim 1.4 \text{ g/cm}^3$ is in a rather good agreement with
98 the ideal density of bulk LiTP (1.6 g/cm^3) calculated from its crystal structure proposed in ref. 18.
99 As shown in Figure 1c, instead of the expected linear relationship between the film thickness and
100 the number of deposition cycles, the growth rate increases with increasing number of deposition
101 cycles. The growth rate nears constant after 200 deposition cycles. Simultaneously, an opposite
102 trend is seen in the film density which decreases until reaching a stable value of 1.4 g/cm^3 after
103 200 deposition cycles. The film thicknesses up to 100 deposition cycles were crosschecked using
104 X-ray reflectivity (XRR) measurements (Table S1). As the roughness of the samples prevented the
105 use of XRR on the thicker samples, the thickness of the sample with 400 deposition cycles was
106 measured also from a scanning electron microscopy (SEM) cross-section image.

107 Atomic force microscopy (AFM) image taken after 70 deposition cycles (Figure 2a) shows
108 distinct granular shapes with voids in between. The average feature height of 20 nm matches well
109 with the film thickness obtained with ellipsometry. In the AFM image taken after 400 deposition
110 cycles (Figure 2b) the granular features have gained in size and coalesced forming a more
111 continuous film. In between the granules there appear to be deep voids and the overall roughness

112 of the sample is quite high. As such, the nonlinearity of could possibly be explained by the island
113 growth model of crystalline films.^{15,16} The initial nucleation and growth is not uniform; instead,
114 distinct islands are formed, which grow in size as the deposition proceeds. A constant-growth
115 regime is achieved only after the islands have coalesced and formed a continuous layer. As the
116 growth rate along different lattice planes varies, during the coalescence parts of the film can
117 become inaccessible forming voids within the films thus explaining the decrease in the apparent
118 density.

119 Grazing incidence X-ray diffraction (GIXRD) data do indeed confirm that the as-deposited films
120 are highly crystalline at all deposition temperatures which is unusual for ALD/MLD inorganic-
121 organic hybrid thin films.⁹ To our best knowledge, thus far only one report exists on crystalline
122 ALD/MLD thin films.¹⁷ The GIXRD patterns could be indexed in space group $P2_1/c$ according to
123 the crystal structure proposed by Kaduk¹⁸ for LiTP with no additional reflections (Figure 2c). The
124 lattice parameters were determined to be, $a = 8.36 \text{ \AA}$, $b = 5.12 \text{ \AA}$, $c = 8.46 \text{ \AA}$, $\beta = 93.08^\circ$, in an
125 excellent agreement with those reported for bulk LiTP.^{10,18} The FWHM value of the 011 peak
126 (Figure S2a and S2b) decreases with increasing number of deposition cycles indicating an increase
127 in the crystallite size. Such an observation is in line with the proposed island-type growth mode.
128 As with the GPC and density values, the FWHM values appear to level off after 200 deposition
129 cycles. Additional X-ray diffraction measurements conducted in the Bragg-Brentano configuration
130 revealed only the most prominent 110 and 102 peaks indicating that the films are polycrystalline
131 without any evident orientation effect.

132 Fourier transform infrared spectroscopy (FTIR) studies were carried out to further elucidate the
133 structure of our LiTP thin films. In the FTIR spectrum (Figure 2d) the dominant absorption peaks
134 at 1392 and 1570 cm^{-1} arise from the symmetric and asymmetric stretching of the carboxylate

135 group, respectively. The values are in good agreement with those reported for bulk LiTP.^{10,19} The
136 peak separation, i.e. 178 cm^{-1} , indicates towards a structure where Li is in a bridging position,^{20,21}
137 in accordance with the crystal structure proposed for LiTP. Additionally, at $\sim 523\text{ cm}^{-1}$ a
138 characteristic peak of Li-O bond can be observed. The lack of characteristic absorption bands due
139 to -OH stretching in the region of $2500 - 3000\text{ cm}^{-1}$ indicates that during the deposition process
140 TPA has fully reacted as intended with no inclusions of the unreacted precursor in the films.²² Also
141 no traces of Li_2CO_3 and LiOH were detected and no changes were seen in the FTIR spectrum even
142 after extended storage (6 months) of the films in ambient atmosphere (Figure S3). The surface
143 composition for a fresh and aged sample were probed with X-ray photoelectron spectroscopy
144 (XPS). As shown in Figure S4, the long storage time has not resulted in significant changes in the
145 spectrum. While the similarities of the chemical environments of carbonate and carboxylate group
146 make the analysis somewhat ambiguous, we conclude that Li_2CO_3 is not formed on the films
147 surface based on the following observations. For lithium carbonate, the CO_3^{2-} signal should be
148 seen at 290 eV. Instead, a peak at 289.0 eV is detected, which matches with values reported for
149 the carboxylate group.²³ Furthermore, the Li 1s peak is detected at 55.8 eV, while for Li_2CO_3 the
150 peak should be located at 55.2 - 55.4 eV. While the shift is relatively minor, it is in the opposite
151 direction as compared to the carboxylate/carbonate peak thus ruling out a systematic error in the
152 measurements. Lastly, the ratio of oxygen vs. carboxylate-type carbon is 1.9:1, which matches
153 quite well with the expected ratio of 2:1

154 The electrochemical performance of the LiTP films was evaluated using conventional LiPF_6
155 based liquid electrolyte coin cells in order to establish that the electrochemical characteristics
156 match those previously reported¹⁰ for bulk LiTP electrodes. LiTP deposited on a stainless steel
157 substrate was employed as the working electrode and Li foil as the counter electrode. In order to

158 shield the electrodes from the liquid electrolyte and to mimic the situation in all-solid-state LIBs
159 regarding the electrode-solid electrolyte interface, samples with 600 ALD cycles of LiPON solid
160 electrolyte layer on the surface were manufactured using our recently developed ALD process for
161 LiPON.²⁴ Assuming a growth rate of $\sim 0.7 \text{ \AA/cycle}$, this would add up to a layer of $\sim 40 \text{ nm}$. Figures
162 3a and 3b display the cyclic voltammograms recorded for the bare and LiPON-coated LiTP films,
163 respectively. The as-deposited films are indeed electrochemically active but for the bare LiTP film
164 the initial cycle differs greatly from the following ones with a broad reduction peak appearing at
165 around 0.4 V . For the subsequent two cycles, a much sharper peak at 0.76 V is observed but the
166 peak current density decreases from 52 to 42 \mu A/cm^2 between the second and third cycle. The
167 anodic sweep is identical for each cycle with three oxidation peaks appearing at 0.89 , 1.00 , and
168 1.06 V . For the LiTP-LiPON case, the initial wide reduction peak is not seen, but instead a sharp
169 reduction peak with a constant peak current density of 40 \mu A/cm^2 appears at 0.79 V during each
170 cycle. Also, the anodic peak at 1.06 V is not existing and the one at 0.89 is significantly reduced.
171 Thus the data seem to implicate that a solid electrolyte interface (SEI) layer is formed on the bare
172 LiTP anode either directly due to immersion in the liquid electrolyte or during the initial cathodic
173 scan. Furthermore, during subsequent CV measurements at varying scan rates (data not shown
174 here), the initial broad reduction peak was always observed after the cell had been left to stabilize
175 in between the scans. The LiPON layer however was found to stabilize the LiTP-anode without
176 reducing the peak currents, i.e. not increasing the cell resistance, and the reduction peaks remained
177 sharp and consistent also with the higher scan rates.

178 Similar behavior was observed also in the initial charge/discharge conducted at a voltage range
179 of $0.4 - 3.0 \text{ V vs Li}^+/\text{Li}$ with a current rate of 0.5 \mu A/cm^2 (Figure 3c). During the initial discharging
180 a distinct plateau at 0.8 V is observed for both the bare and the LiPON-coated LiTP electrodes

181 with the latter one demonstrating a slightly lower polarization consistent with the CV data.
182 However the amount of irreversible capacity is much higher with the bare LiTP film resulting in
183 an initial coulombic efficiency of 0.50 while the LiPON coating increases the efficiency to 0.64.
184 The larger irreversible capacity of the bare LiTP also implies formation of a SEI layer during the
185 cycling.

186 The electrochemical performance was further tested by cycling the electrodes at various current
187 rates at a voltage range of 0.4 - 3.0 V vs Li⁺/Li. Because the mass of the electrodes could not be
188 reliably assessed, here the C-rates are calculated assuming the reversible capacity obtained from
189 the initial charge/discharge conducted at a very low current rate of 0.5 $\mu\text{A}/\text{cm}^2$ to be equal of the
190 full capacity. Assuming an electrode thickness of 170 nm and density of 1.4 g/cm^3 as obtained
191 from ellipsometry and XRR measurements, respectively, for a comparable sample deposited on
192 silicon, the measured reversible capacity would correspond to a specific capacity of approximately
193 350 mAh/g. As we were unable to measure the thickness directly from the stainless steel substrate,
194 the value is only directional due to possible differences in the growth rate. While higher than the
195 theoretical capacity assuming two electron transfer reactions per molecule, it is not unreasonable
196 as recently Lee *et al.*²⁵ revealed that LiTP may undergo further lithium insertions when cycled
197 below 0.7 V vs Li⁺/Li bringing the actual specific capacity up to 522 mAh/g when discharged to
198 0.0 V vs. Li/Li⁺. As shown in Figure 4a, both LiTP and LiTP-LiPON perform very well up to 6.4
199 C retaining approximately 69 and 66 % of the initial capacity, respectively at that current rate. At
200 higher current rates, the bare LiTP electrode fails completely while the LiPON-coated LiTP
201 electrode retains a very respectable performance delivering over 50 % of the initial capacity at ~20
202 C, i.e. charge/discharge in 3 min, and even at 64 C, i.e. charge/discharge in 56 s, the electrode still
203 retains 23 % of the full capacity. The high rate performance is not unexpected as according to

204 density functional theory calculations conducted by Zhang et al.¹¹, the rate capability of LiTP
205 should inherently be excellent due to the low activation energy of lithium diffusion. Thus it is
206 apparent that the limited performance of bulk LiTP is indeed due to the poor electronic
207 conductivity, and this can be circumvented with the reduced dimensions of our thin-film electrodes
208 without relying on conductive additives. The reason for the sudden failure of the bare LiTP is
209 evident from the voltage curves recorded at increasing current rates shown in Figures 4b and 4c.
210 The bare LiTP electrode displays much higher overvoltages at the onset of the discharge plateau
211 as the current rate increases. At 12.8 C where the failure is observed, the initial overvoltage exceeds
212 the cut-off voltage ending the lithiation of the electrode prematurely. The LiPON protective layer
213 appears to stabilize the electrode resulting in a flat discharge plateau even at 12.8 C. Further
214 evidence for the resistive nature of the supposed SEI layer is revealed from electrochemical
215 impedance spectroscopy (EIS) measurements. In the Nyquist plots (Figure 4d) an additional
216 semicircle at mid-frequencies can be seen in the bare LiTP sample indicating increased cell
217 resistance. Since the measurements were conducted in a two electrode setup, further deciphering
218 of the EIS data was not attempted as it is not possible to separate the contributions of the LiTP
219 working electrode and the Li-metal counter electrode.

220 The cycle life of the LiPON-coated LiTP electrode was investigated at current rates of 3.2 and
221 6.4 C (Figure 4e). At 3.2 C the electrode performance is exceptionally stable: 97.4 % of the initial
222 capacity is retained even after 200 charge/discharge cycles. Accordingly, the coulombic efficiency
223 is very high, 99.7 % on the average. As the current rate is increased to 6.4 C, a steady capacity
224 fade can be observed. After 500 cycles the capacity remains at 81.8 % in respect to the 1st 6.4 C
225 charge/discharge cycle while the coulombic efficiency remains high at 99.8 % on the average.
226 From the voltage curves recorded at different stages of cycling, it could be confirmed that the

227 voltage profile remains stable throughout the cycling with no additional overpotentials associated
228 with the aging of the electrodes (Figure S5a and S5b). Combined with the high coulombic
229 efficiency, this seems to implicate that the capacity fade is mostly due to dissolution of the active
230 material, which has previously been noted to be a contributing cause to the capacity fade of LiTP,¹⁹
231 and not due to unwanted side reactions, e.g. formation of a resistive surface layer. Thus, while the
232 intended application for the LiTP thin films is in all-solid-state LIBs, the current results may prove
233 to be helpful also for bulk organic electrode materials highlighting the usefulness of a protective
234 surface coating on the stability of the materials. Moreover, although more sophisticated analysis
235 is needed, these results seem to implicate that also the LiTP-LiPON interface remains stable, which
236 is crucial for the performance of an all-solid-state LIB.

237 In conclusion, we developed a simple reproducible ALD/MLD process for Li-containing
238 inorganic-organic hybrid thin films. Our as-deposited Li terephthalate thin films were crystalline
239 exhibiting the same layered crystal structure previously reported for bulk LiTP. Moreover
240 demonstrated was that the films are electrochemically highly active showing excellent rate
241 capabilities without any conductive additives. Most remarkably, a thin LiPON electrolyte coating
242 applied using our recently reported ALD process was found to suppress the unwanted side
243 reactions with the LiPF₆-based liquid electrolyte without increasing the cell resistance. Although
244 further studies using an all-solid-state setup are required, the present findings appear to indicate
245 that LiTP is a very promising candidate for a high-rate high-capacity anode material for thin-film
246 LIBs. We believe that our work is a step towards the all-solid-state organic-electrode-based LIB
247 technology, and has furthermore demonstrated the potential power of the ALD/MLD technique in
248 realizing this technology.

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251

252 **Experimental Section**

253 The LiTP thin films were deposited using an F-120 flow-type hot-wall ALD reactor (ASM
254 Microchemistry Ltd.), from lithium 2,2,6,6-tetramethyl-3,5-heptanedionate (Li(thd)) and
255 terephthalic acid (TPA). Li(thd) was synthesized in-house by mixing 50-% EtOH solutions of
256 LiOH and Hthd. The resulting white precipitate was dried in vacuum and purified by sublimation.
257 TPA (>99.0 %) was acquired from Tokyo Chemical Industry Co., Ltd. Both precursors were kept
258 inside the reactor at temperatures of 175 °C for Li(thd) and 185 °C for TPA. Nitrogen (99.999%,
259 produced from air by Schmidlin UHPN 3000 nitrogen generator) was used both as purging and
260 carrier gas. The purging times were kept constant at 4 s for Li(thd) and 30 s for TPA. The films
261 were deposited on Si(100) substrates for structural characterization and on stainless steel disks
262 (15.5 mm diameter) for the electrochemical characterization. The reactor pressure was ~5 mbar.
263 For the deposition of the LiPON coatings, lithium hexamethyldisilazide and diethyl
264 phosphoramidate were used as the precursors.²⁴ The pulse/purge lengths were 2 s/2 s for both
265 precursors with a total of 600 deposition cycles applied. The deposition temperature was 300 °C.

266 The thickness of the films was measured using a Semilab SE-2000 spectroscopic ellipsometer
267 equipped with a xenon lamp. The crystallinity of the films was studied by grazing incidence X-ray
268 diffraction using a PANanalytical X'Pert Pro diffractometer with a Cu K X-ray source while the
269 density of the films was deduced from X-ray reflectivity measurements using the same device. The
270 density of the films was calculated from the XRR patterns based on the dependency of the critical
271 angle, θ_c , on the mean electron density, ρ_e , of the material; namely $\rho_e = (\theta_c^2 \pi) / (\lambda^2 r_e)$, where λ is the
272 X-ray wavelength and r_e is the classical electron radius. By assuming the elemental composition
273 being that of pure LiTP, i.e. $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$, the mass density can be estimated from $\rho_m = (\rho_e A) / (N_A Z)$,
274 where A is the average molar mass, N_A is the Avogadro constant and Z is the average atomic

275 number.²⁶ We note that the assumption on chemical composition and ambiguity in determining the
276 exact critical angle result in uncertainties in the absolute value but still allows for extracting trends
277 within a sample series. For samples up to 100 deposition cycles, XRR was also used to cross check
278 the film thickness. The lattice constants were determined from the GIXRD pattern by Le Bail
279 profile fitting procedure using the FullProf Software Suite.²⁷ The surface composition was
280 analyzed with X-ray photoelectron spectroscopy (Kratos Analytical AXIS Ultra) with
281 monochromatic Al-K α radiation. The binding energy was calibrated based on C1s peak set to 285
282 eV. The FTIR measurements were conducted in a transmission mode on samples deposited on Si
283 with a Nicolet Magna 750 spectrometer in range of 400-4000 cm⁻¹ using a resolution of 4 cm⁻¹.
284 The SEM images were collected on a JEOL JSM-7500FA scanning electron microscope. AFM
285 measurements were conducted with a Veeco Dimension 5000 operated in tapping mode. For the
286 electrochemical measurements, the films deposited on stainless steel substrates were dried in
287 vacuum at 110 °C for 24 h and then used as the working electrode in a CR2016 coin cell. Lithium
288 metal was used as the counter electrode and the electrolyte was 1 M LiPF₆ in 50:50 ethylene
289 carbonate/dimethyl carbonate solution. The cell assembly was conducted in an Ar filled glove box
290 with O₂ level less than 1 ppm and H₂O level less than 0.1 ppm. The cyclic voltammetry and
291 electrochemical impedance spectroscopy measurements were carried out using an Autolab
292 PGSTAT302N potentiostat/galvanostat. The EIS measurements were carried out in the frequency
293 range of 500 kHz - 1 mHz using an amplitude of 10 mV. The galvanostatic measurements were
294 conducted using a Neware battery testing unit.

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299 ASSOCIATED CONTENT

300 **Supporting information.** SEM image of LiTP thin film deposited on microstructured Si-
301 substrate, evolution of FWHM values of the 011 peak of LiTP from GIXRD as a function of film
302 thickness, FTIR and XPS analysis on the aging of LiTP thin films, voltage profiles recorded during
303 the cycling stability testing. This material is available free of charge via the Internet at
304 <http://pubs.acs.org>.

305

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309 **Notes**

310 The authors declare no competing financial interest.

311 **Author Contributions**

312 The manuscript was written through contributions of all authors. All authors have given approval
313 to the final version of the manuscript.

314

315

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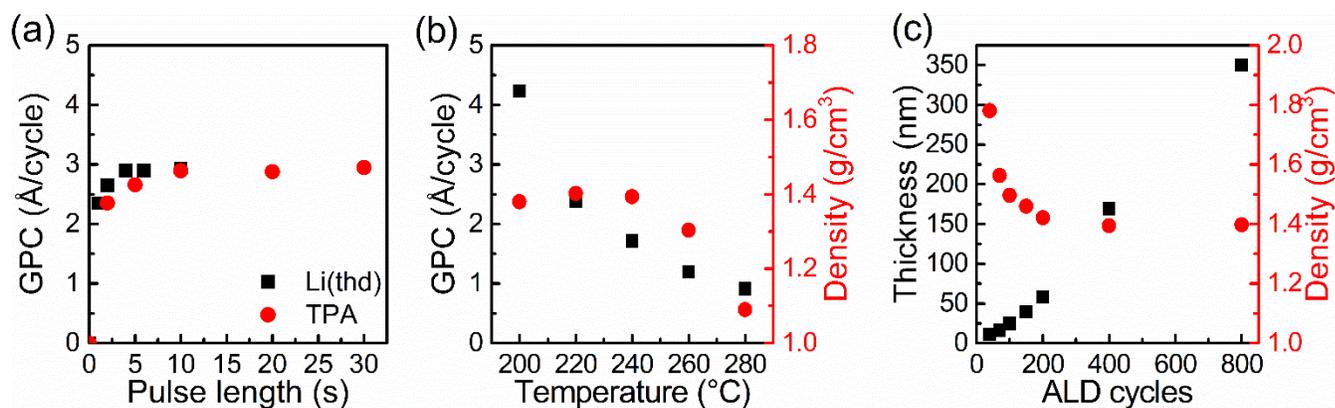
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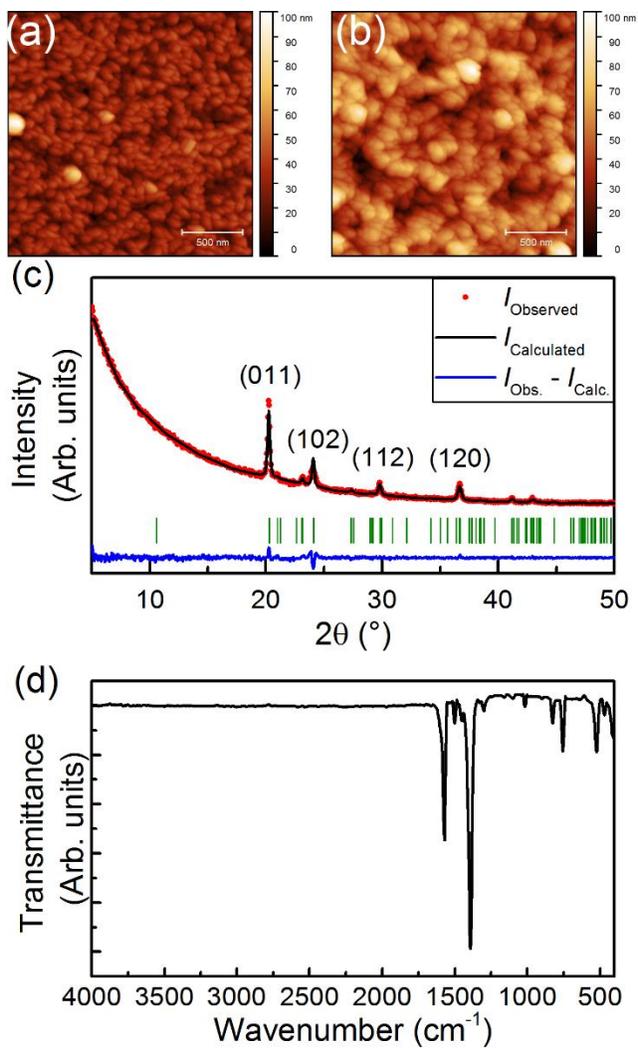
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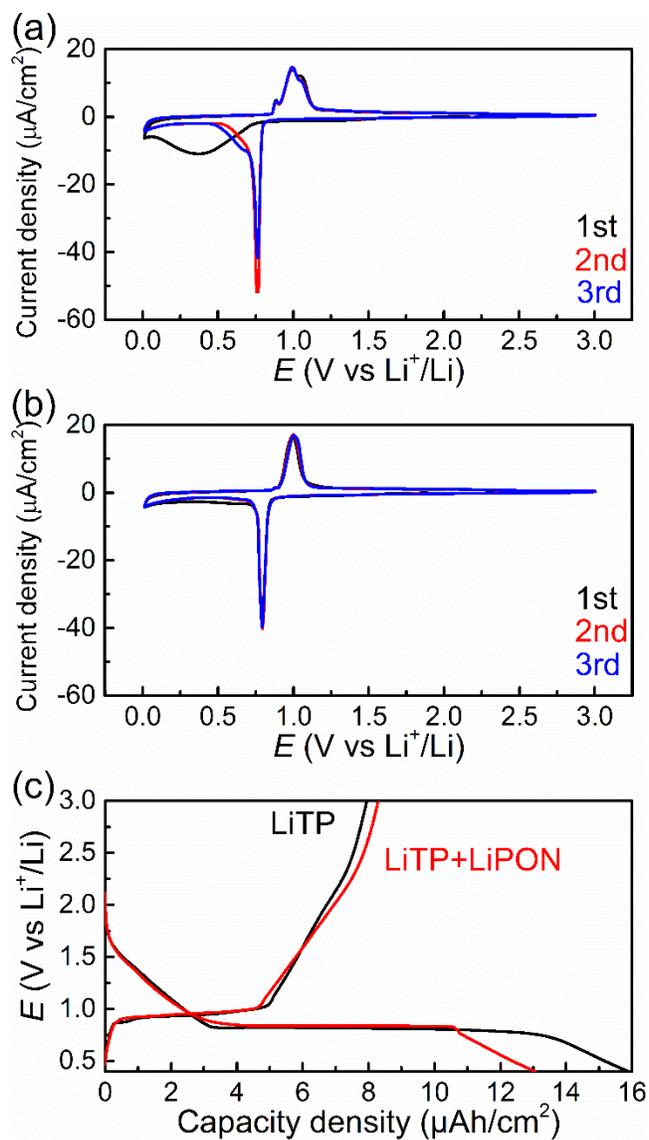


367
 368 **Figure 1.** (a) Growth-per-cycle (GPC) of LiTP thin films as a function of Li(thd) (black squares)
 369 and TPA (red circles) pulse lengths. The deposition temperature was 200 °C and the pulse/purge
 370 lengths of the other precursor were fixed to 4 s/4 s for Li(thd) and to 10 s/30 s for TPA. (b) GPC
 371 (black squares) and film density (red circles) of LiTP as a function of deposition temperature. The
 372 pulse/purge lengths were 4 s/4 s and 10 s/30 s for Li(thd) and TPA, respectively. (c) Film thickness
 373 (black squares) and density (red circles) of LiTP versus number of deposition cycles. The
 374 deposition temperature was 200 °C and the pulse/purge lengths were 4 s/4 s and 10 s/30 s for
 375 Li(thd) and TPA, respectively.

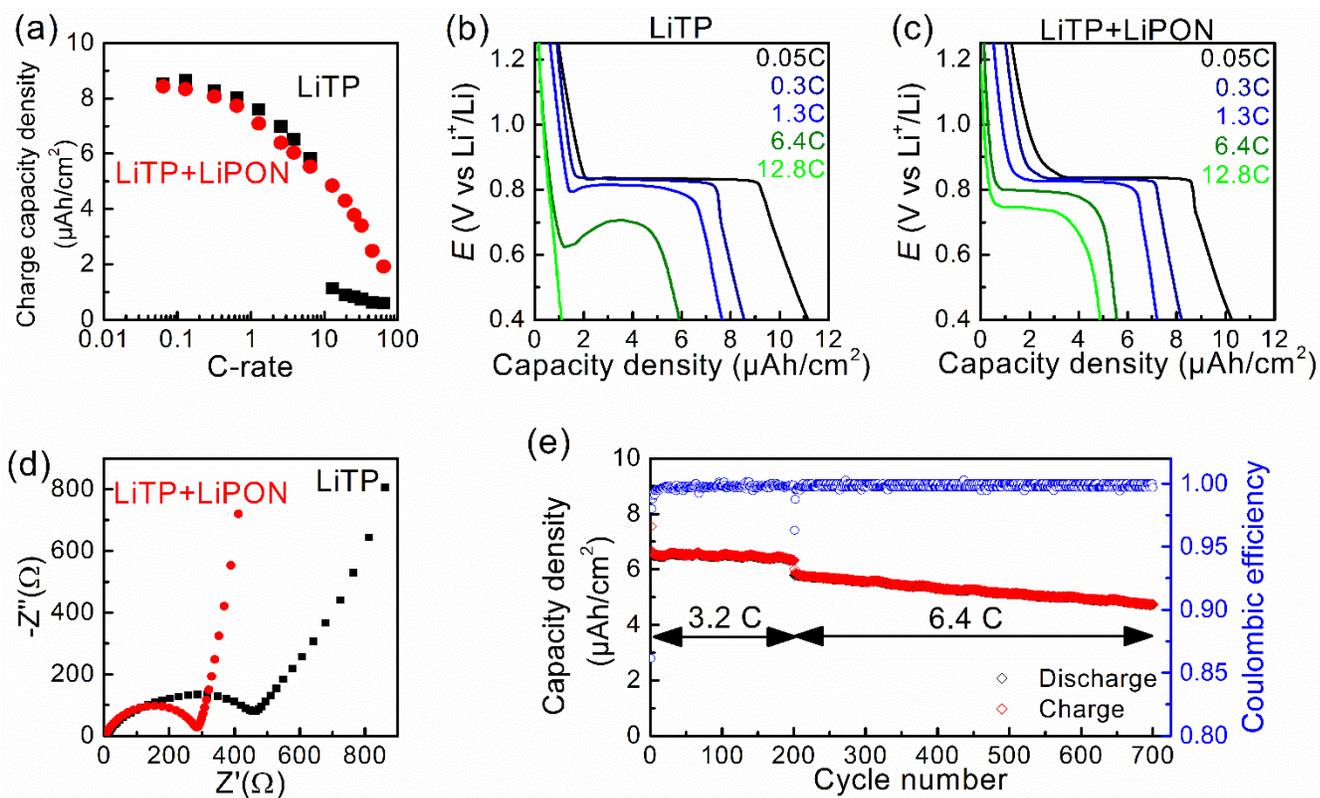
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 380 **Figure 2.** AFM images of samples with (a) 70 and (b) 400 deposition cycles, (c) GIXRD pattern
 381 for a LiTP film deposited at 200 $^\circ\text{C}$ using 400 deposition cycles. (d) FTIR spectrum of the same
 382 film.

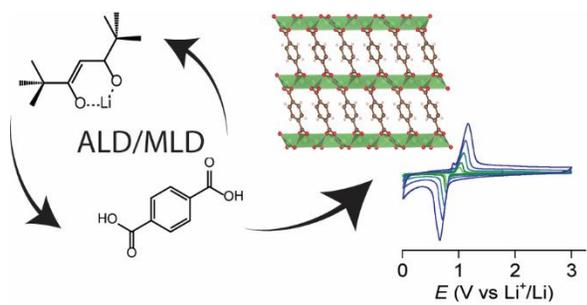


383
 384 **Figure 3.** Cyclic voltammograms of (a) bare, and (b) LiPON-coated LiTP conducted at a scan rate
 385 of 0.1 mV/s. (c) The initial charge/discharge curves of LiTP (black line) and LiTP-LiPON (red
 386 line) recorded using a current density of $0.5 \mu\text{A}/\text{cm}^2$ ($\sim 0.05 \text{ C}$).



387
 388 **Figure 4.** (a) Rate capability of bare LiTP (black squares) and LiPON-coated LiTP (red circles) as
 389 determined from the charge capacity. Discharge curves at different current rates for (b) LiTP, and
 390 (c) LiPON-coated LiTP. In the bare LiTP at 12.8 C the overvoltage exceeds the cut-off potential
 391 ending the lithiation prematurely. (d) Nyquist plots of the EIS measurements for LiTP (black
 392 squares) and LiPON-coated LiTP (red circles). (e) Cycle life of LiPON-coated LiTP measured at
 393 current rates of 3.2 and 6.4 C.

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