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Plasma-Assisted ALD of LiPO(N) for Solid State Batteries

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All solid state 3D batteries are pursued for their increased safety and high power capabilities. At present conformal coating of the solid electrolyte remains one of the key hurdles for the implementation of such devices. In the present work we investigate atomic layer deposition (ALD) as means of conformal deposition of lithium phosphate (Li$_3$PO$_4$) and nitrogen doped lithium phosphates (LiPON). These processes are characterized here to obtain the highest possible Li-ion conductivity. Li$_3$PO$_4$ is shown to yield a conductivity of $10^{-5}$ S/cm at 25°C. On the other hand, an optimized LiPON process gave rise to a Li-ion conductivity of $5 \times 10^{-4}$ S/cm at 25°C. In addition, good conformity of the LiPON process was shown on high aspect ratio pillars. Furthermore, a solid state battery device was fabricated comprising a Li$_4$Ti$_5$O$_12$ cathode, a 70 nm thick ALD LiPON solid electrolyte and a metallic lithium anode. This finding indicates that a layer down to 70 nm can be made pinhole free.

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Figure 1. XRD patterns of 40 nm Li₃PO₄ films deposited at different processing temperatures. Crystallinity of the layers is seen to increase with increasing temperature.

For the fabrication of a battery stack a 200 nm Li₄Ti₅O₁₂ layer was deposited by RF sputtering (Pfeiffer, Spider) from a 4-in. Li₄Ti₅O₁₂ target on a 100 nm Pt/TiOₓ coated SiO₂ substrate. This layer received a crystallization anneal for 20 min at 800°C. Subsequently a 70 nm ALD LiPON layer is deposited as solid electrolyte. To conclude, 1 μm metallic lithium was thermally evaporated and functions here as anode, leading to the formation of a 1.5 V battery. The created battery was characterized using an autolab (Metrohm) potentiostat operated by Nova software (Metrohm Autolab).

Results and Discussion

Li₃PO₄ characterization.—As was mentioned before, the ionic conductivity of Li₃PO₄ is greatly impacted by the crystallinity of the material. Therefore the crystallinity of layers deposited using different processing temperatures were examined using XRD (Figure 1). Figure 1 shows a clear reduction of the crystallinity of 40 nm Li₃PO₄ films when decreasing processing temperature. At 200°C nearly amorphous films are formed. At processing temperatures lower than 200°C the growth per cycle (GPC) drops significantly. These conditions were not further investigated.

The stoichiometry of different Li₃PO₄ films was investigated using ERD. This technique allows for highly accurate stoichiometry determination of films constituted of light elements. In addition it can also detect hydrogen, contrary to e.g. XPS. For the different Li₃PO₄ layers, stoichiometries were found in the range Li₁₂±₁.3PO₁₃.5. However, with decreasing processing temperature an increase of the amount of hydrogen is detected in the layer. This is likely caused by the incomplete reaction between the TMP and the LiOTBu.

The ionic conductivity of the material was determined by SIS measurements using a metal-electrolyte-metal device. The obtained impedance spectra were fitted using an equivalent circuit model. This model consisted of a series resistance followed by two R-CPE branches and terminated with another constant phase element (CPE), the model is shown in the supplementary information (SI). As such it can be represented as R₁(R₂-CPE)(R₃-CPE)CPE, where the Rᵥ corresponds to the series resistance of the contact and wiring, the first R₁-CPE branch can be linked to the formation of an interface film, the second R₂-CPE to the bulk conductivity.¹³ The final CPE element accounts for the usage of a blocking contact and the associated double layer. The total impedance contribution of the solid electrolyte thus consists of the sum of R₁ and R₂. In the present work the ionic conductivity is calculated from the sum of these components.

Figure 2b depicts a strong increase in the Li-ion conductivity with decreasing processing temperature for 40 nm Li₃PO₄ layers, attributed to the decrease of the crystallinity on reducing the processing temperature. Layers deposited at 200°C exhibit the largest ionic conductivity reaching a value of 1.4 · 10⁻¹² S/cm at 25°C. Note the layers measured here were only 40 nm thick and showed low electronic leakage current.

LiPON characterization.—When a nitrogen plasma is added to the Li₃PO₄ deposition process, LiPON (nitrogen doped Li₃PO₄ glass) can be formed. In the present work a nitrogen plasma exposure time of 20 s was used in all depositions. Both the effect of processing temperature and plasma power on the Li-ion conductivity were examined.

The incorporation of nitrogen into the Li₃PO₄ layers results in shortening of the P-O-P chains as explained above. In this way a more disordered structure is created which increases ion conductivity. The addition of a nitrogen plasma step to the Li₃PO₄ process also results in the formation of amorphous material, independent of the deposition temperature (Data not shown).

The ionic conductivity of the LiPON layers depends on the amount of incorporated nitrogen. This was more closely investigated by...
Table I. N and Li content of LiPON layers deposited under different nitrogen plasma power and processing temperature settings. A clear increase in the amount of nitrogen is seen when increasing the plasma power. Simultaneously, the amount of nitrogen is increased by reducing the processing temperature. As expected, the amount of Li is found to decrease when the amount of nitrogen in the layer increases. This can be understood by the fact that the nitrogen substitutes oxygen in the LiPO4 and, as oxygen is associated with a lithium ion, its removal also leads to a lower lithium content.

<table>
<thead>
<tr>
<th>LiPON XPS Characterization</th>
<th>275°C</th>
<th>275°C</th>
<th>275°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>N (%)</td>
<td>2.9</td>
<td>3.5</td>
<td>4.3</td>
<td>6.3</td>
</tr>
<tr>
<td>Li (%)</td>
<td>41</td>
<td>38.7</td>
<td>35.9</td>
<td>34.2</td>
</tr>
</tbody>
</table>

XPS (results depicted in Table I). As the plasma power increases more nitrogen is incorporated in the layers, increasing from 2.9% at 100 W up to 4.3% at 300 W. Additionally, more nitrogen is also incorporated when the temperature is lowered, reaching a maximum of 6.3% for a layer deposited at 100°C using a plasma power of 100 W.

As XPS does not allow the detection of hydrogen, the stoichiometry of the LiPON layers was measured using ERD. A stoichiometry of Li1.9P2.5O2.6N0.23 was found for a sample deposited at 275°C 100 W and a composition of Li1.8P2.5O2.7N0.25 was found for a sample deposited at 275°C 200 W. In these layers the hydrogen content was 0.5% and carbon content was 0.2%. This is attributed to the high reactivity of the nitrogen plasma which efficiently removes impurities.

The incorporation of nitrogen into LiPON can occur by forming a double bond (P-N-P, doubly coordinated nitrogen) or 3 single bonds (P-N<, triply coordinated nitrogen) as explained above. The ratio of triply to doubly coordinated nitrogen has a significant impact on the ionic conductivity. Therefore the effect of the deposition conditions on the nitrogen binding states was investigated using XPS (shown in Figure 3a).

Figure 3a shows that on lowering the processing temperature the amount of incorporated nitrogen increases. Additionally it can be seen that when increasing the plasma power the amount of incorporated nitrogen increases as well but more importantly also the amount in a triply coordinated fashion. As this is most efficient in disrupting the O-P-O chains, increasing the plasma power is expected to lead to an increased Li-ion conductivity.

The ionic conductivity of the fabricated LiPON layers was again investigated using impedance spectroscopy measurements in a MEMS-configuration. Fitting of the obtained impedance spectrum was performed using the model described above. The results of the impedance characterization is depicted in Figure 3b.

Figure 3b addresses the changes in Li-ion conductivity of the LiPON films upon addition of a N2 plasma increase in plasma power and decrease in substrate temperature. As predicted by the discussion on the characterization of the material properties (Fig. 3a and Table I), the N2 plasma is essential in promoting the increase in Li-ion conductivity up to 10⁻⁸ S/cm at 25°C. The increase in plasma power further promotes the conductivity, up to a value of 2.10⁻⁷ S/cm at 25°C, as a result of the increase in triple coordination of N with respect to double coordination. Moreover, a decrease in temperature down to 200°C, enhances the conductivity up to 5.10⁻⁷ S/cm at 25°C because of further incorporation of N in the layer. No further improvements in conductivity are detected when further lowering the temperature down to 100°C.

Also the conformality of the deposition was checked using SEM at different positions on a silicon etched pillar. These structures serve as large area structures for usage in 3D all solid state batteries. The used pillars were 50 μm high, had a diameter of 2 μm and were coated with a ~30 nm TiN current collector. On these pillars a 90 nm LiPON layer was deposited at a processing temperature of 275°C and a plasma power of 100 W. Figure 4 shows three SEM pictures at different heights along the pillar. Image (a) is taken at the top of the pillar and shows a TiN layer of ~25 nm and a LiPON layer of ~90 nm. Image (b) is taken half way the pillar and depicts a 30 nm TiN layer and 80 nm LiPON. The final image (c) is taken at the bottom of the pillar and shows a TiN layer of 28 nm and 70 nm of LiPON. These results indicate that the conformality for this process is good.

**Solid state stack characterization.**—To demonstrate the functionality of the LiPON solid electrolyte, a solid state battery was fabricated using Li4Ti5O12 (LTO) as cathode, a lithium metal anode and a 70 nm
Figure 4. Investigation of conformance of the LiPON process at 275°C using a plasma power of 100W. Micropillars of 50 μm high and a diameter of 2 μm are used for this purpose. The pillars are coated with a 30 nm TiN layer on top of which a 90 nm layer of LiPON was deposited. Images (a), (b) and (c) show the LiPON/TiN layer at respectively the top, middle and bottom of the pillars. Good conformance is obtained for the process, showing a thickness variation from 90 to 70 nm.

Figure 5. (a) Schematic of the solid state cell fabricated here. The battery constitutes a Li metal anode, a LiPON electrolyte and an LTO cathode. (b) Constant current charge-discharge curve of the solid state battery shown in (a). A capacity of 0.3 Ah/cm³ is found at rate of 5C.

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