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**Electrochemically Active In Situ Crystalline Lithium-Organic Thin Films by ALD/MLD**

Jenna Multia, † Juho Heiska, † Aida Khayyami, and Maarit Karppinen*

**ABSTRACT:** Intercalated metal–organic framework (iMOF) type electrochemically active aromatic metal carboxylates are intriguing material candidates for various energy storage devices and microelectronics. In this work, we grow in situ crystalline thin films of such materials through atomic/molecular layer deposition (ALD/MLD); the remarkable benefit of this approach is the possibility to evaluate their electrochemical properties in a simple cell configuration without any additives. Five organic linkers are investigated in combination with lithium: terephthalic acid (TPA), 3,5-pyridinedicarboxylic acid (PDC), 2,6-naphthalenedicarboxylic acid (NDC), 4,4′-biphenyldicarboxylic acid (BPDC), and 4,4′-azobenzenedicarboxylic acid (AZO). In particular, the electrochemical activity of Li-PDC and the crystal structure of Li-AZO are addressed here for the first time. We believe that the in situ gas-phase thin-film deposition is a crucial requirement to benefit from the iMOF-type electrode materials in, e.g., microelectronics and wearable devices.

**KEYWORDS:** atomic layer deposition, molecular layer deposition, thin film, metal–organic framework, energy storage, organic electrode

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**INTRODUCTION**

Certain metal–organic compounds, sometimes referred to as intercalated metal–organic frameworks (iMOFs), possess the extremely attractive attribute of experiencing only minimal changes in crystal structure upon (electrochemical) metal ion intercalation/deintercalation. Such materials could provide us novel solutions to overcome one of the notorious drawbacks of conventional metal oxide electrode materials in Li-ion battery technology, that is, the capacity decay on cycling due to the substantial volume changes during the Li⁺-ion intercalation. Another attractive feature of the iMOF structures is that they are not ion specific but could be—besides the Li⁺ ions—utilized in next-generation battery technologies based on, e.g., Na⁺ ions. An iMOF could be defined as (i) a layer-structured inorganic–organic material, in which (ii) the intercalated metal ions in the inorganic layer originate from the redox-active organic moiety and which is (iii) highly robust against structural changes upon this metal-ion intercalation. The metal-ion (de)intercalation in iMOFs is dominated by a flexible organic moiety. This scheme is significantly different from the conventional inorganic electrode materials in which there is a rigid lattice site for the moving metal ions, making them very ion specific. The Li⁺-ion storage mechanism of iMOFs has been studied in detail for aromatic π-conjugated carboxyls; the Li-oxide layer provides both the transport pathway and storage site for ions, while the organic layer acts as the electron transport pathway and the redox center.

Owing to their peculiar electrochemical properties, iMOF-like materials are intriguing electrode candidates for various energy storage devices. Moreover, thanks to their organic components, they are mechanically flexible and thus particularly appealing, e.g., for wearable electronics. Also, these materials could be used as hybrid capacitors, since their potential lies within the desired range, making them safer than graphite (no dendrites) and better than, e.g., lithium titanate regarding the power density. In addition, it has been shown that lithium 2,6-naphthalenedicarboxylate (Li-NDC) and lithium 4,4′-biphenyldicarboxylate (Li-BPDC) become electronically conductive in their fully lithiated state (with a built-in thermal shut-down mechanism), which could open up a plethora of other applications, e.g., organic transistors.

In Figure 1, well-established examples of electrochemical active Li-based iMOFs are shown, for which the “zero-volume-change condition” upon a full electrochemical charge/discharge cycle has been demonstrated; these include—besides the aforementioned Li-NDC and Li-BPDC—compounds—lithium terephthalate (Li-TPA). Pyridinedicarboxylate...
(PDC) structures are also interesting candidates for iMOF materials; indeed, for some of them, electrochemical activity has already been reported, e.g., Li-2,6-PDC,16 Na-2,5-PDC,17 Mn-3,5-PDC,18 and Zn-2,5-PDC.19 Considering the possible Li-based iMOF candidates, for lithium 3,5-pyridinedicarboxylic acid (referred to as Li-PDC in the following), the crystal structure is known,20 but the electrochemical performance has not been investigated.

The iMOF materials are exceptionally lightweight, which is also reflected in the names of their structures, i.e., ULMOF\(^4\) (UL = ultralight). For example, the structures of Li-NDC, Li-BPDC, and Li-PDC are known as ULMOF-1,\(^4\) ULMOF-2,\(^21\) and ULMOF-4,\(^20\) respectively. Among these, the ULMOF-1 and ULMOF-2 structures are isoreticular, while the ULMOF-4 structure of Li-PDC is different in the sense that there are multiple coordination sites (N and O acceptors) which can participate in metal bonding in a multidentate fashion.\(^20\)

From the redox standpoint, Li-TPA, Li-NDC, and Li-BPDC behave similarly, the only difference being in their redox potentials.\(^2,3,15\) By increasing the size of the conjugated organic backbone, the LUMO of the carbonyl group can be lowered, the redox potential decreased, and the structural stability increased against the metal-ion intercalation.\(^22\) However, the larger organic backbone also leads to lower volumetric/gravimetric capacity.\(^9\)

In order to truly benefit from the iMOF materials in, e.g., microelectronics and wearable devices, development of industry-feasible solvent-free thin-film fabrication techniques with precise thickness control and a possibility to deposit the film over various 3D surface architectures would be necessary. The strongly emerging atomic/molecular layer deposition (ALD/MLD) thin-film technique\(^23\)–\(^25\) provides us with unique advantages. Unlike its parent commercially well-established ALD technology, the combined ALD/MLD technique for hybrid inorganic–organics is based on self-limiting gas-surface reactions of alternatingly pulsed gaseous precursors. This enables the large-area uniformity and precise thickness control of the resultant thin films. Using the industry-feasible ALD/MLD technique could be an important step along the roadmap toward devices based on new exciting metal–organic materials for, e.g., microelectronics and sensing applications.\(^26\)\(^,\)\(^27\)

So far, new ALD/MLD processes have been developed for tens of amorphous and crystalline inorganic–organic materials, both previously known and completely new.\(^28\)–\(^38\) In particular, we recently fabricated a series of crystalline s-block-metal-based TPA and PDC thin films through ALD/MLD.\(^28\)\(^,\)\(^30\)\(^,\)\(^32\)\(^,\)\(^34\)\(^,\)\(^35\) Here in this work, we investigate the ALD/MLD growth, structures, and electrochemical activity of five different lithium dicarboxylate (iMOF) materials; see Figure 2 for the molecular structures of their organic components. Prior to the present work, ALD/MLD processes were already known for Li-TPA and Li-PDC, while for Li-NDC, Li-BPDC, and Li-AZO new processes were first developed. Recently, Lausund et al.\(^38\) utilized the NDC and BPDC precursors in combination with ZrCl\(_4\) (followed by post-deposition acid treatment) to prepare crystalline thin films with a known MOF phase. The NDC precursor has also been used earlier with zinc acetate to yield IRMOF-8 films after a post-deposition treatment with dimethylformamide.\(^39\) As for the AZO precursor, we recently employed it for the deposition of amorphous Zn-AZO\(^40\) and crystalline Fe-AZO\(^41\) films. It should also be noted that bulk samples of Li-AZO were recently synthesized through solvothermal synthesis, but the crystal structure was not reported.\(^42\) Nevertheless, the material showed very promising electrochemical performance; during the electrochemical cycling, the N=N bond is apparently cleaved, making the mechanism very different from those of other carboxylates.

## MATERIALS AND METHODS

**Thin-Film Deposition.** In our ALD/MLD processes, we employed Li(thd) complex (thd = 2,6,6-tetramethyl-3,5-heptane-dione; synthesized in-house) as the metal precursor and terephthalic acid (TPA; Tokyo Chemical Industry Co., Ltd., >99.0% purity), 3,5-pyridinedicarboxylic acid (PDC; Tokyo Chemical Industry Co., Ltd., 98.0% purity), 2,6-naphthalenedicarboxylic acid (NDC; Tokyo Chemical Industry Co., Ltd., >98.0% purity), 4,4′-biphenyldicarboxylic acid (BPDC; Tokyo Chemical Industry Co., Ltd., >97.0% purity), and 4,4′-azobenzedicarboxylic acid (AZO; Tokyo Chemical Industry Co., 95% purity) as the organic precursors. The depositions were carried out in a commercial flow-type hot-wall ALD reactor (F-120 by ASM Microchemistry Ltd.); for the details of the reactor configuration, see the Supporting Information (Figure S8). The solid precursors were kept in open glass crucibles inside the reactor. The reactor pressure was ∼3 mbar, and nitrogen (99.999%; Parker Hannifin HFN 5000 N\(_2\) generator) was used as both the purging and carrier gas.

The thin films were deposited on Si(100) substrates (3.0 × 3.0 cm\(^2\)) at different temperatures in the range 210–300 °C. Table 1 summarizes the sublimation temperatures and final deposition temperatures chosen for each ALD/MLD process. Sublimation temperatures were derived from our thermal analysis of the organic precursor samples.\(^43\) These thermogravimetric measurements were run on a modified PerkinElmer TGA 7 thermobalance under a flowing nitrogen atmosphere at a low pressure of ca. 4 mbar. In a typical experiment, a sample of 5−10 mg was heated with a rate of 2 °C/min; the area of the crucible was 0.181 cm\(^2\).

**Characterization.** The crystallinity/crystal structure was confirmed for the films using grazing incidence X-ray diffraction (GIXRD); X’Pert Pro, PANalytical; Cu Kα) measurements. The film thickness and density were determined through X-ray reflectivity (XRR) measurements using the same equipment. In the measurements, the
time per step was set at 20 and 6 s in GIXRD and XRR, respectively, and in the GIXRD measurements, an incidence angle of 0.5° was used. The film thickness values were determined from the averages of the values calculated using the direct calculation and the Fourier methods. For the thickest films (>100 nm), the thicknesses were determined with spectroscopic ellipsometer measurements by a Woollam Spectroscopic Ellipsometer using CompleteEASE software for data analysis. The density of the films was deduced from the critical angle θc in the XRR patterns, as follows: \( \rho_e = (\theta_c^2 \lambda) / (2 r_e) \), where \( \rho_e \) is the mean electron density, \( \lambda \) is the X-ray wavelength, and \( r_e \) is the classical electron radius. By assuming the elemental composition being that of pure lithium-dicarboxylate, the mass density was estimated from \( \rho_m = (\rho_e A) / (N_A Z) \), where \( A \) is the average molar mass, \( N_A \) is the Avogadro constant, and \( Z \) is the average atomic number. GIXRD of the Li-AZO was compared to other structures, and it was assumed to share a space group with other dicarboxylates. Four peak positions (100), (110), (111), and (112) were chosen to calculate the lattice parameters of Li-AZO using the d-spacing formula for a monoclinic lattice. The interaxial angle was estimated to be similar to Li-BPDC.

Chemical composition/bonding was studied by Fourier transform infrared (FTIR) spectroscopy. The measurements were carried out in transmission mode with a Bruker alpha II instrument in the range 400–4000 cm\(^{-1}\) using a resolution of 4 cm\(^{-1}\) and analyzed from 24 measured spectra. A spectrum of blank Si was subtracted from the spectra to compensate for the effect of the substrate. Scanning electron microscope (SEM) images were recorded with a Tescan Mira 3 FEG-SEM instrument using an in-beam detector and secondary electrons with a 10 kV accelerating voltage. The samples were coated with 8.2 Au/Pd prior to imaging.

Electrochemical characterizations were carried out for thin films deposited on stainless steel substrates (Ø 15.5 mm). The film thickness could not be measured from the steel substrate, and therefore, we chose to only show the areal capacity of the electrodes and focus on the intrinsic properties of the electrodes. The electrode thickness was chosen to be ca. 110 nm, approximated from the growth behavior on a silicon wafer. Before transferring the samples into the glovebox (<1 ppm of oxygen and <0.1 ppm of H\(_2\)O), they were dried overnight at 110 °C in a vacuum oven. The thin-film electrodes were assembled in a glovebox and directly applied as electrodes in a CR2016 coin cell with a lithium metal counter electrode. The electrolyte was 1 M LiPF\(_6\) in 1:1 EC:DMC. The cells were left to stabilize for 24 h before measurements. The galvanostatic cycling was conducted in a Neware battery testing unit with various current densities. Cyclic voltammetry (CV) was carried out on an Autolab potentiostat (PGSTAT302N) using Nova software with scan rates of 0.1, 0.5, 1.0, and 5.0 mV. Before the scan, the potential was swept to 2.0 V, which was used as a starting point for CV.

### RESULTS AND DISCUSSION

**ALD/MLD Process Development.** Among the five Li-based iMOF materials targeted in this work, ALD/MLD processes were already developed in earlier works for Li-TPA and Li-PDC; then, among the newly developed processes for Li-NDC, Li-BPDC, and Li-AZO materials, the first one was most thoroughly investigated. In the following, we summarize these process optimization results for the Li-NDC films as an exemplary case.

First, we investigated the growth-per-cycle (GPC) values as a function of the precursor pulse lengths for Li-NDC films; for these experiments, the deposition temperature was fixed to 220 °C (for others, see Table 1) and the number of ALD/MLD cycles to 150. The GPC values were calculated from the XRR-determined film thickness values; an example of a typical XRR curve is shown in the inset of Figure 3c. From Figure 3b, it can be seen that the GPC value is saturated when the Li(thd) pulse length is 4 s (N\(_2\) purge 4 s) and the NDC pulse length is 10 s (N\(_2\) purge 20 s). These values are in line with those previously observed for Li-TPA and Li-PDC.24,29,33,37 Next, we investigated the growth rate at different temperatures (Figure 3a), to find out that the GPC decreases with increasing deposition temperature, which is a common but poorly understood feature in ALD/MLD.33,44,45 The organics employed have very low vapor pressures in addition to their bifunctionality, which makes them sticky, possibly causing some molecules to stick on the film and act as an extra surface site especially in the lower temperature regime.46 Nevertheless, even if this is the case, our Li-NDC process can be controlled in an essentially ideal manner as the GPC value saturates over the precursor pulsing time. Finally, the expected fact that the film thickness increases with the number of ALD/MLD cycles applied can be verified from Figure 3c; note that for the films thicker than 50 nm the thickness was measured with a

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**Table 1. Precursor Sublimation Temperatures (Chosen Based on Thermogravimetric Analysis in a N\(_2\) Vacuum), Pulse/Purge Lengths, and Deposition Temperatures Used**

<table>
<thead>
<tr>
<th>precursor</th>
<th>( T_{subl.} ) (°C)</th>
<th>( T_{calc} ) (°C)</th>
<th>TG (°C)</th>
<th>pulse/purge lengths (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(thd)</td>
<td>174</td>
<td>185</td>
<td>236</td>
<td>10/30</td>
</tr>
<tr>
<td>TPA</td>
<td>220</td>
<td>190</td>
<td>210</td>
<td>15/30</td>
</tr>
<tr>
<td>PDC</td>
<td>220</td>
<td>220</td>
<td>275</td>
<td>10/20</td>
</tr>
<tr>
<td>NDC</td>
<td>220</td>
<td>210</td>
<td>289</td>
<td>20/30</td>
</tr>
<tr>
<td>BPDC</td>
<td>240</td>
<td>240</td>
<td>325</td>
<td>20/30</td>
</tr>
<tr>
<td>AZO</td>
<td>270</td>
<td>250</td>
<td>325</td>
<td>20/30</td>
</tr>
</tbody>
</table>

---

**Figure 3.** GPC values for the Li-NDC process as a function of (a) deposition temperature and (b) precursor pulse lengths. (c) Thickness of the films as a function of the number of ALD/MLD cycles; the inset shows a representative XRR pattern and its fitting; the number of ALD/MLD cycles is 150 in parts a and b and the inset of part c; the Li(thd)/NDC precursor pulse lengths are 4 s/10 s in parts a and c.
spectroscopic ellipsometer and for the rest with both XRR and a spectroscopic ellipsometer.

Parallel process optimizations (similar to those described above) yielded the optimized GPC values for the five processes as follows (in Å/cycle): Li-PDC 2.5, Li-TPA 3.0, Li-NDC 2.3, Li-BPDC 7.0, and Li-AZO 7.0. These values are comparable to those reported for processes with the same organic precursors, i.e., Zr-NDC (8 Å/cycle), Zn-NDC (4.0–4.9 Å/cycle), and Zr-BPDC (10–12 Å/cycle).

Particularly interesting is to note that our Li-AZO process yielding crystalline films has a higher GPC (7.0 Å/cycle) compared to that earlier seen for amorphous Zn-AZO (3.0 Å/cycle) films but lower compared to the case of the crystalline Fe-AZO (25 Å/cycle) films. Apparently, the choice of the metal precursor also plays a role, as the more bulky ligands would yield lower surface site densities, allowing the bulky organic molecules to more easily get to the surface, even though this could lead to slower growth rates.

All of our Li(thd)+dicarboxylate processes were found to yield highly crystalline and air-stable thin films for which the GIXRD patterns could be readily indexed—in cases when relevant—according to the structures previously reported for the same materials in bulk samples. In Figure 4, we plot the GIXRD patterns for our Li-PDC, Li-TPA, Li-NDC, Li-BPDC, and Li-AZO films. Three of the structures (Li-TPA, Li-NDC, and Li-BPDC) have the same space group $P2_1/c$, and in the corresponding bulk samples, the $b$-axis ranges between 5.13 and 5.35 Å and the $c$-axis between 8.00 and 8.66 Å. The Li-NDC and Li-BPDC structures consist of antifluorite-type layers of corner- and edge-sharing LiO$_4$ tetrahedra connected by the 2,6-NDC or 4,4$'$-BPDC linkers to form a 3-D framework, where $\pi$-$\pi$ interactions between the naphthalene or biphenyl herringbone stacked rings exist. Li-TPA forms a similar layered structure with tetrahedrally coordinated lithium cations and the packing of the terephthalate in the herringbone way.

Table 2. Density Values Determined from XRR Data for Our Thin-Film Samples in Comparison to Crystal Structures (and Ideal Densities Calculated from the Crystal Structure Data) Reported in the Literature for Bulk Samples*

<table>
<thead>
<tr>
<th>Compound/Structure</th>
<th>Space Group</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (deg.)</th>
<th>$V$ (Å$^3$)</th>
<th>Ideal Density (g/cm$^3$)</th>
<th>Exp. Density (g/cm$^3$)</th>
<th>Org. Backbone Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-PDC</td>
<td>$C21$</td>
<td>12.69</td>
<td>10.98</td>
<td>11.20</td>
<td>105.8</td>
<td>1501.2</td>
<td>1.58</td>
<td>1.4</td>
<td>5.2</td>
</tr>
<tr>
<td>LiC$_7$H$_8$O$_4$N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-TPA</td>
<td>$P2_1/c$</td>
<td>8.36</td>
<td>5.13</td>
<td>8.48</td>
<td>93.15</td>
<td>363.5</td>
<td>1.63</td>
<td>1.4</td>
<td>6.8</td>
</tr>
<tr>
<td>LiC$_2$H$_4$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-NDC</td>
<td>$P2_1/c$</td>
<td>10.30</td>
<td>5.35</td>
<td>8.66</td>
<td>98.66</td>
<td>471.6</td>
<td>1.61</td>
<td>1.5</td>
<td>8.9</td>
</tr>
<tr>
<td>LiC$_6$H$_6$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-BPDC</td>
<td>$P2_1/c$</td>
<td>12.76</td>
<td>5.14</td>
<td>8.00</td>
<td>97.23</td>
<td>520.6</td>
<td>1.54</td>
<td>1.5</td>
<td>11.0</td>
</tr>
<tr>
<td>LiC$_6$H$_6$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-AZO</td>
<td>$P2_1/c$</td>
<td>14.3</td>
<td>5.0</td>
<td>8.4</td>
<td>97</td>
<td>599</td>
<td>1.56</td>
<td>1.4</td>
<td>12.8</td>
</tr>
<tr>
<td>LiC$_8$H$_4$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

“Structural parameters for known bulk structures and calculated Li-AZO structure parameters estimated from the parameters of similar compounds.

Figure 4. GIXRD patterns for Li-PDC, Li-TPA, Li-NDC, Li-BPDC, and Li-AZO films. The calculated patterns below the measured ones were produced from the reported crystal structures using VESTA software; the experimental patterns were indexed accordingly. For Li-AZO, no previous structure determination data exist, but visual comparison of our GIXRD pattern with the XRD pattern published for a bulk Li-AZO sample (Figure S6a in ref 42) revealed similar peaks (with similar intensity ratios), e.g., at 2$\theta$ values of 19, 22, 23, and 29$\theta$.
5.0 Å, and $c = 8.4$ Å; these values reflect well the trend expected based on the organic backbone lengths (Table 2). Moreover, we give in Table 2 both the ideal density values calculated from the crystal structure data and the experimental values determined from the XRR data; it can be seen that the experimental values for our thin films are systematically slightly lower than the ideal values.

The morphology of the samples was investigated with SEM (Figure S1). The polycrystalline nature of the films is evident from the images and the overall appearance of the Li-TPA, Li-NDC, Li-BPDC, and Li-PDC films is very similar, although slight differences in the shape and arrangement of the crystallites are seen; Li-AZO in particular deviates from the rest of the samples, as it clearly consists of smaller crystallites which grow and merge with the film growth. A similar trend is visible in the crystallite size, such that for Li-AZO significantly smaller crystallites were seen compared to the other films (Supporting Information).

In Figure 6, we display the FTIR spectra for the films. First, the spectral range around $3400 \text{ cm}^{-1}$ is free from any features related to incorporated water (Figure S4); this is in line with previous knowledge on bulk-synthesized lithium carboxylates; Li-PDC, Li-TPA, Li-NDC, Li-BPDC, and Li-PDC do not absorb water molecules and are stable up to temperatures of $550, 350, 15$ cm$^{-1}$, $610, 575, 410$ cm$^{-1}$, respectively. We also note that for all of our Li-dicarboxylate thin films the region around $1720 \text{ cm}^{-1}$ lacks the absorption band due to free COOH groups; this confirms that during the ALD/MLD process the dicarboxylic acid precursor indeed reacts with lithium. The dominant absorption bands are seen in all of the spectra around 1400 and 1600 cm$^{-1}$, arising from the asymmetric and symmetric stretch of the carboxylate group, respectively. The visibly sharp COO$^-$ asymmetric and symmetric stretch of the carboxylate group, $\Delta$, $\Delta$, $\Delta$, $\Delta$, and $\Delta$, and $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$, $\Delta$.
rationalize the possible reasons for the present observations which partly differ from those reported for bulk samples.

From Figure 7, both Li-AZO and Li-PDC perform very well, although the comparison to other Li-dicarboxylates is not entirely feasible because of the different electrochemical redox mechanisms. Our Li-AZO thin-film sample shows very similar performance to that previously reported for bulk Li-AZO samples, with two plateaus and similar values for redox potential, polarization, and capacity retention. Therefore, it can be concluded that lithium is inserted with the same N=N cleavage mechanism and the material is working in excellent fashion as a thin-film electrode. The Li-PDC thin film also
performs well, but it has a different (sloping) voltage profile after the first cycle. Previous reports of pyridine-type compounds have shown that carboxylates in the para position tend to yield plateaus that resemble those of their terephthalate analogues, although the redox potentials are typically higher.\textsuperscript{17,18} On the other hand, the sloping voltage profile is often seen in polymer batteries, where the state of lithiation heavily affects the redox potential. This is an indication of more connected redox units, compared to the isolated carboxylate units, e.g., in terephthalate.\textsuperscript{15,55} Thus, further experiments are required to fully verify the redox mechanism of our Li-PDC films and answer the question of whether it involves the carboxylate groups or the pyridine ring.\textsuperscript{55,57} Nevertheless, as there is no plateau nor peaks in CV, we tentatively believe that the reaction is not Faradaic in nature.

From Figure 8, the lithiation (discharge) potentials for our Li-TPA, Li-NDC, and Li-BPDC thin films are found to be ca. 0.83, 0.76, and 0.68 V, respectively, well in line with those reported for bulk materials.\textsuperscript{2,3} The polarization of the plateau also decreases—as expected—with increasing size of the aromatic core, from 0.14 V of Li-TPA to 0.09 V of Li-NDC and further to 0.02 V for Li-BPDC. For Li-TPA and Li-NDC, only one continuous plateau can be distinguished; Li-BPDC shows two (at 0.70 and 0.66 V), in line with the previous reports where the mechanism was confirmed to be step-by-step lithiation of the carboxylates.\textsuperscript{22} The sloping part of the (dis)charge curve (ca. 0.7−0.4 V) is possibly caused by the “superlithiation”, i.e., lithiation of the aromatic core.\textsuperscript{58}

The same voltage profile is retained by the Li-dicarboxylates even with high current densities and at least up to 50 cycles. However, by 150 cycles, all of the carboxylates have lost their typical voltage profiles and have transformed into sloping voltage profiles (Figures 7f and 8). In a previous study by Lee et al.\textsuperscript{58} with Li-TPA bulk samples, this was attributed to the lithiation of the aromatic skeleton where the same changes in the voltage profile and increased polarization were observed over extended cycling.\textsuperscript{58} We also argued this to be the case with another terephthalate analogue studied in thin-film form, for which we saw the degradation of crystallinity upon extended cycling.\textsuperscript{59} As these materials are very similar to the materials studied in this study, this might suggest that the amorphization or gradual degradation of the crystal structure could be a rather common feature of these Li-dicarboxylates when cycled between 3.0 and 0.4 V.

The Coulombic efficiency (CE) of these materials is also behaving rather interestingly. With the low current density, i.e., when the intercalation speed of lithium is slow, the CE for Li-TPA, Li-NDC, and Li-BPDC was found to be ca. 98, 94, and 92%, respectively, while, with high current density, it was 99% for all of our Li-dicarboxylate films. The carbonyl reaction itself should be fast.\textsuperscript{60} However, the lithiation reaction of the aromatic skeleton could be considered to be a slow one and kinetically controlled;\textsuperscript{60−62} in such a situation when the cell is cycled with higher current density, the slower reaction may not have enough time to occur before the cut-off potential is reached.

A plausible explanation for the low CE with the low current densities could be amorphization/gradual degradation of the structure; the fact that the CE is lowered in particular with the larger organic backbones for which there are more sites for the lithiation of the aromatic skeleton to occur\textsuperscript{51,62} further supports this explanation. To study this, we conducted post-mortem GIXRD and ATR-FTIR analyses for the Li-TPA, Li-NDC, and Li-BPDC electrodes (Figures S5−S7). The GIXRD clearly showed that the crystallinity of the materials was degraded upon cycling. The main reflections became almost completely invisible, and in the Li-BPDC case, a new unidentified peak appeared. The ATR-FTIR spectra for the cycled electrodes actually look very similar at a first glance, indicating that the SEI or the degradation product of these materials is very similar. Nevertheless, tiny differences are seen in the 1800−1300 cm\(^{-1}\) range, i.e., in the range originating from the asymmetric and symmetric carboxylate vibrations. In the cycled electrodes, there are no shoulders or peaks visible in the exact positions where the asymmetric carboxylate peak lies in the pristine electrode. The asymmetric carboxylate peak is a better indicator of the changes in the structure than the symmetric one, since it is more sensitive to possible changes in the electron and coordination structure.\textsuperscript{63} Therefore, we believe that these materials are undergoing changes upon long-term cycling indicated by changes in voltage plateau and the post-mortem analysis.

In previous works, the higher CE values with the larger current densities are sometimes attributed to the slow kinetics of the lithiation or the conductive carbon present in the cell design;\textsuperscript{55,54,64,65} however, in our thin-film electrodes, conductive carbon is not present. We also note that the crystal structure could be an important factor to achieve good cyclability and capacity.\textsuperscript{66} Fêdèle et al.\textsuperscript{22} also proposed solvent co-intercalation with the Li\(^+\) ions with Li-BPDC. To address these questions in future studies, choosing narrower potential ranges or minimizing the possible electrolyte co-intercalation or other side reactions, e.g., by coating could be considered.\textsuperscript{6,30,61,87−89}

\section*{CONCLUSIONS}

We have demonstrated that an entire family of in situ crystalline thin films of lithium-based iMOF-type materials can be readily fabricated from gaseous precursors using the ALD/MLD technique. In our comparative study, we combined the lithium precursor Li(thd) with five different organic precursors: TPA (terephthalic acid), PDC (3,5-pyridinedicarboxylic acid), NDC (2,6-naphthalenedicarboxylic acid), BPDC (4,4′-biphenyldicarboxylic acid), and AZO (4,4′-azobenzenedicarboxylic acid). The deposition processes carried out at 220−270 °C yielded high-quality air-stable thin films at the appreciably high growth rate ranging from 2.3 to 7.0 Å/cycle.

For four of the Li-dicarboxylate thin-film materials studied (Li-TPA, Li-PDC, Li-NDC, Li-BPDC), crystal structures could be assigned based on their GIXRD and FTIR data to those previously reported for corresponding bulk samples. For Li-AZO, based on the close resemblance of the GIXRD and FTIR data, we assumed the same monoclinic P2\(_{1}\)/\(c\) space group as that for Li-TPA, Li-NDC, and Li-BPDC and indexed the major diffraction peaks accordingly to corroborate the monoclinic symmetry and estimate the unit cell parameters. We also determined the densities for all five thin films based on XRR data, to confirm that they were in line (systematically slightly lower) than the ideal density values calculated from the crystal structures.

Galvanostatic cycling experiments verified the electrochemical activity expected for an iMOF, i.e., lithium (de-)intercalation, for all five of the Li-dicarboxylates investigated, notably, for the first time in the case of Li-PDC. Also importantly, our approach (gas-phase electrode fabrication without additives and parallel experimental procedures for all
samples) allowed us—for the first time—to address the intrinsic electrochemical characteristics of the different I-MOF materials in a comparative manner. With this comparison, we managed to shed light on the possible degradation mechanism of the Li-dicarboxylates, which is still poorly understood but vital information for the actual applicability of these materials.

The I-MOF-type electrode materials possess a number of superior chemical features over the traditional transition metal oxide electrode materials. We thus believe that our work will boost the research on these materials as intriguing new components for various energy storage devices, in particular in applications requiring the electrode materials in high-quality flexible thin-film form. Moreover, we would like to emphasize that our approach is not limited only to the Li-based carboxylates taken as a model case here.

**ASSOCIATED CONTENT**

1. Supporting Information
   The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsami.0c11822.

   Figure S1, SEM image of the films; Figure S2, voltammmograms of the films; Figure S3, thermogravimetric analysis graphs of the organic precursors; Figure S4, full FTIR spectra of the films; Figures S5–S7, post-mortem analysis of the electrodes; Figure S8, schematic of the ALD reactor; Table S1, FWHM values of the thin films; Scherrer equation for determining crystallite size and appropriate data (PDF).

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**ABBREVIATIONS**

I-MOF, intercalated metal–organic framework; ALD/MLD, atomic/molecular layer deposition; UL, ultralight; TPA, terephthalic acid; PDC, 3,5-pyridinedicarboxylic acid; NDC, 2,6-naphthalenedicarboxylic acid; BPDC, 4,4′-biphenyldicarboxylic acid; AZO, 4,4′-azobenzenedicarboxylic acid; GIXRD, grazing incidence X-ray diffraction; XRD, X-ray reflectivity; FTIR, Fourier transform infrared; thd, 2,2,6,6-tetramethyl-3,5-heptanedione.

**REFERENCES**


