Supporting information: Electrochemically Active In Situ Crystalline Lithium-Organic Thin Films by ALD/MLD

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Table S1. FWHM values of the thin films

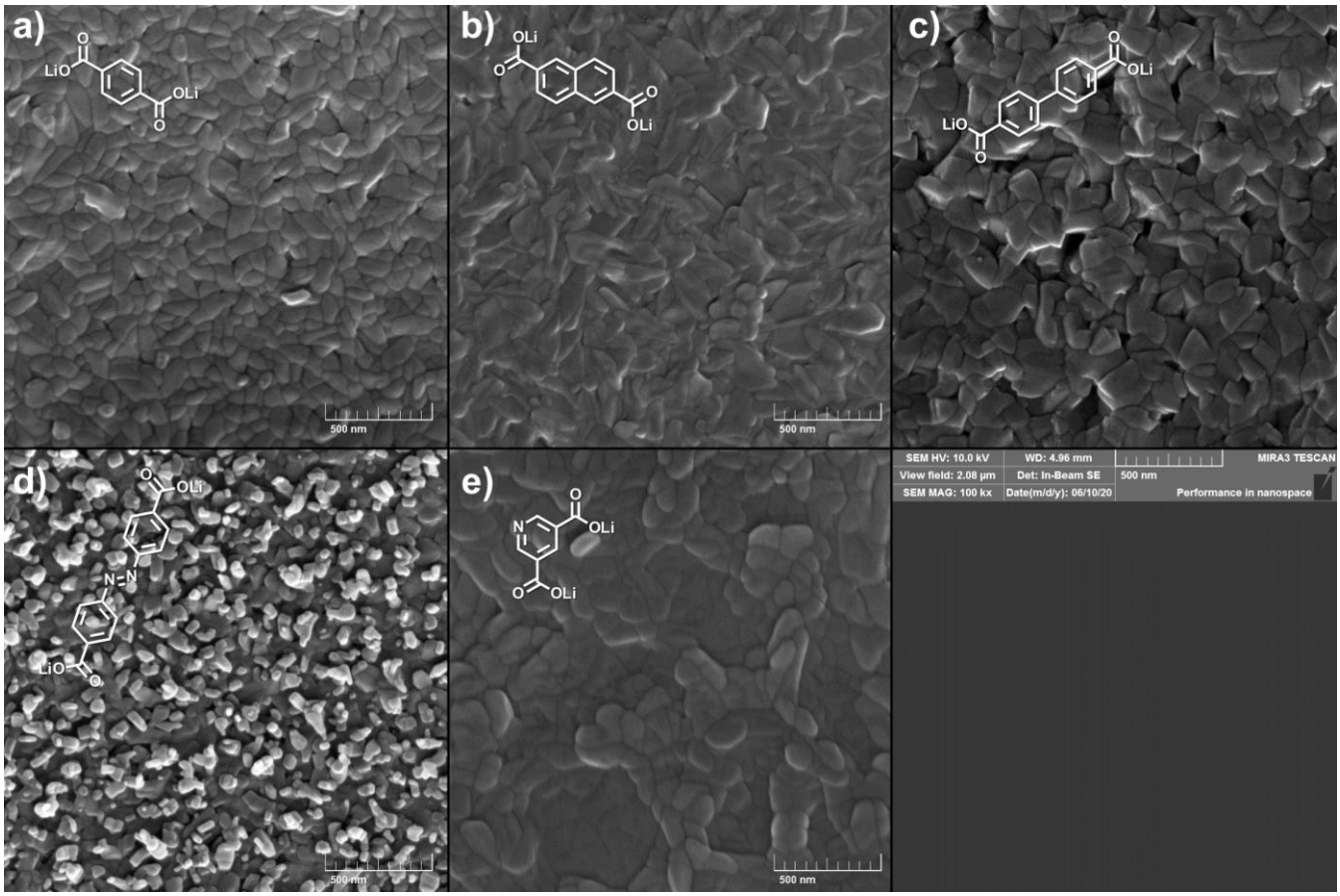


Figure S1. SEM images of the active materials. (a) Li-TPA, (b) Li-NDC, (c) Li-BPDC, (d) Li-AZO, (e) Li-PDC.

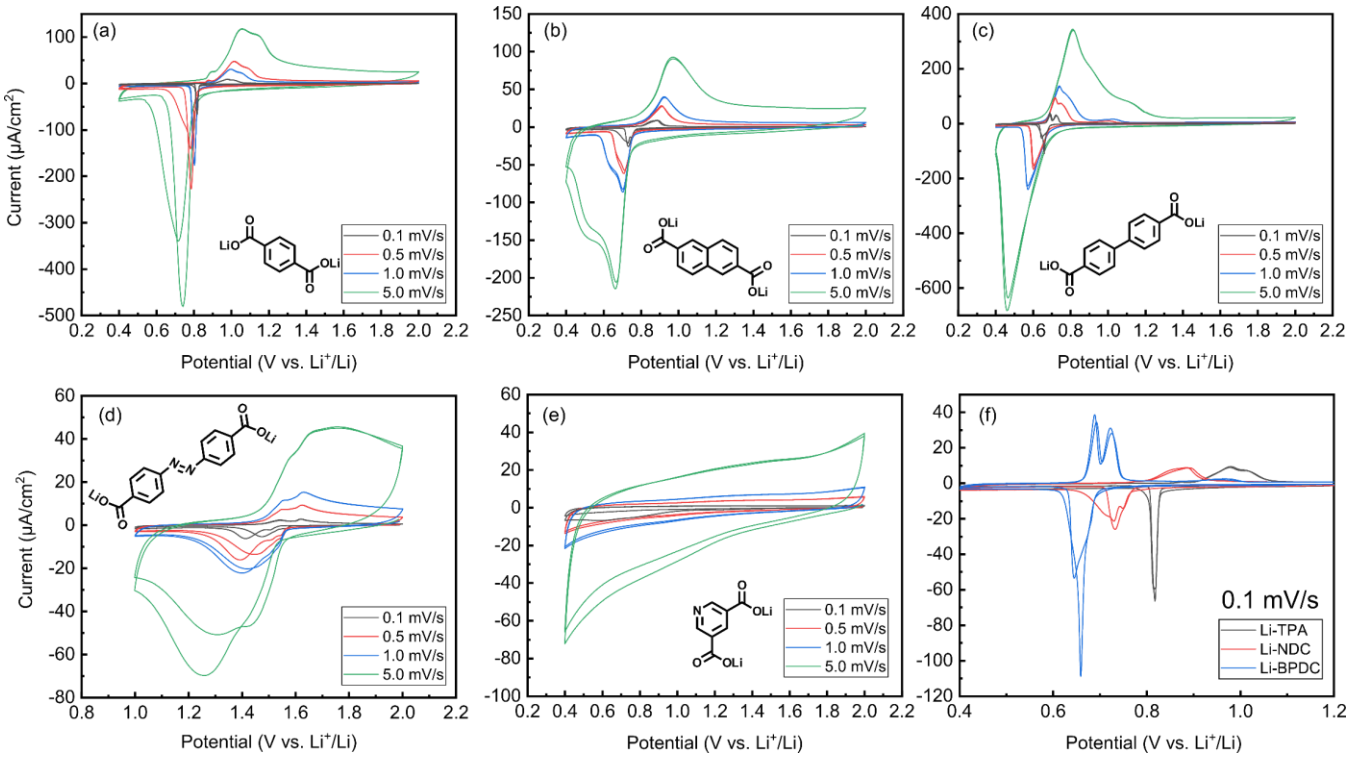


Figure S2. Voltammograms of the active materials with increasing scan rate. (a) Li-TPA, (b) Li-NDC, (c) Li-BPDC, (d) Li-AZO, (e) Li-PDC. In (f) magnification of the 0.1 mV/s scan rate for Li-dicarboxylates.

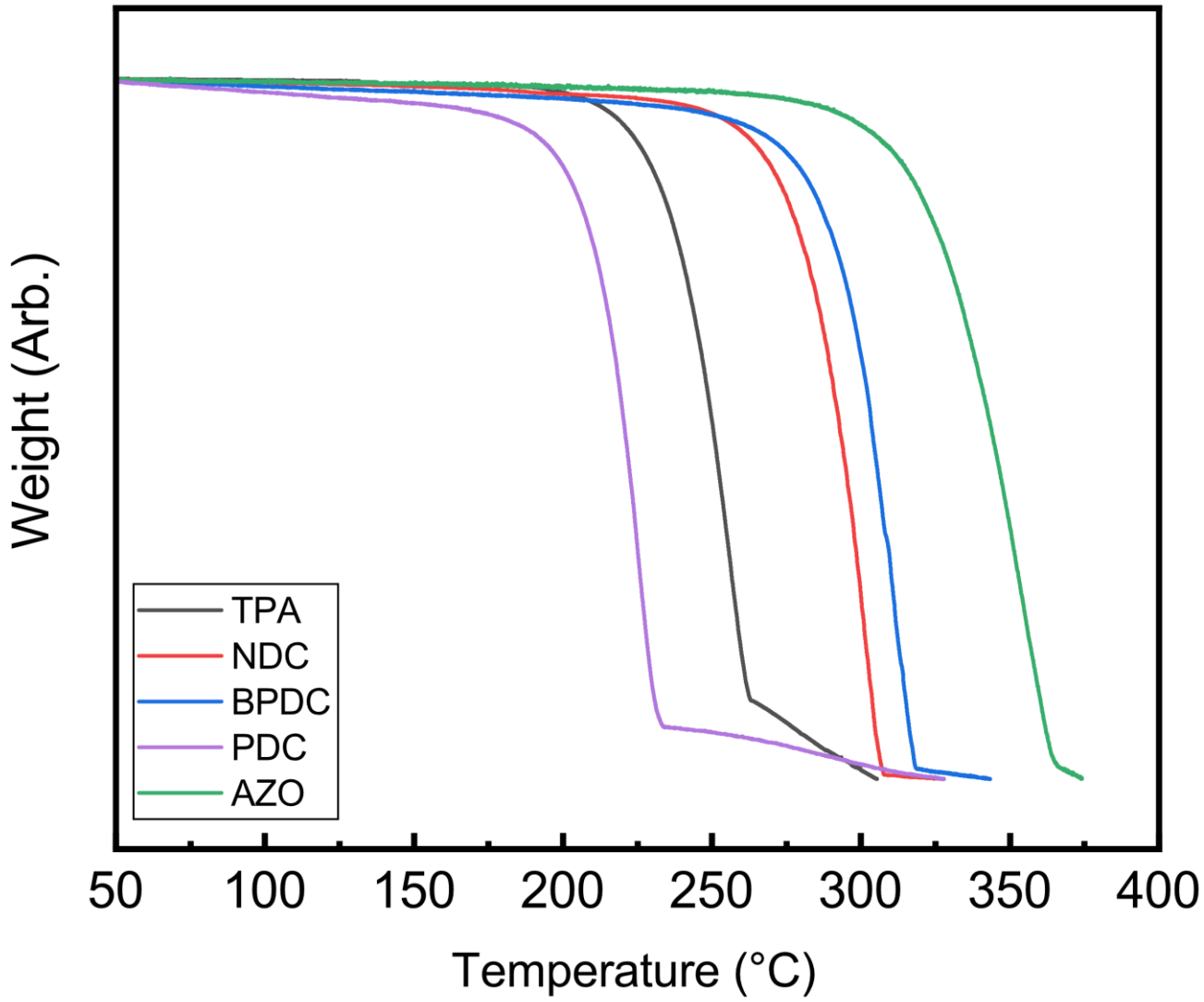


Figure S3. TG curves of the organic precursors employed in this study. The weight scale is normalized.

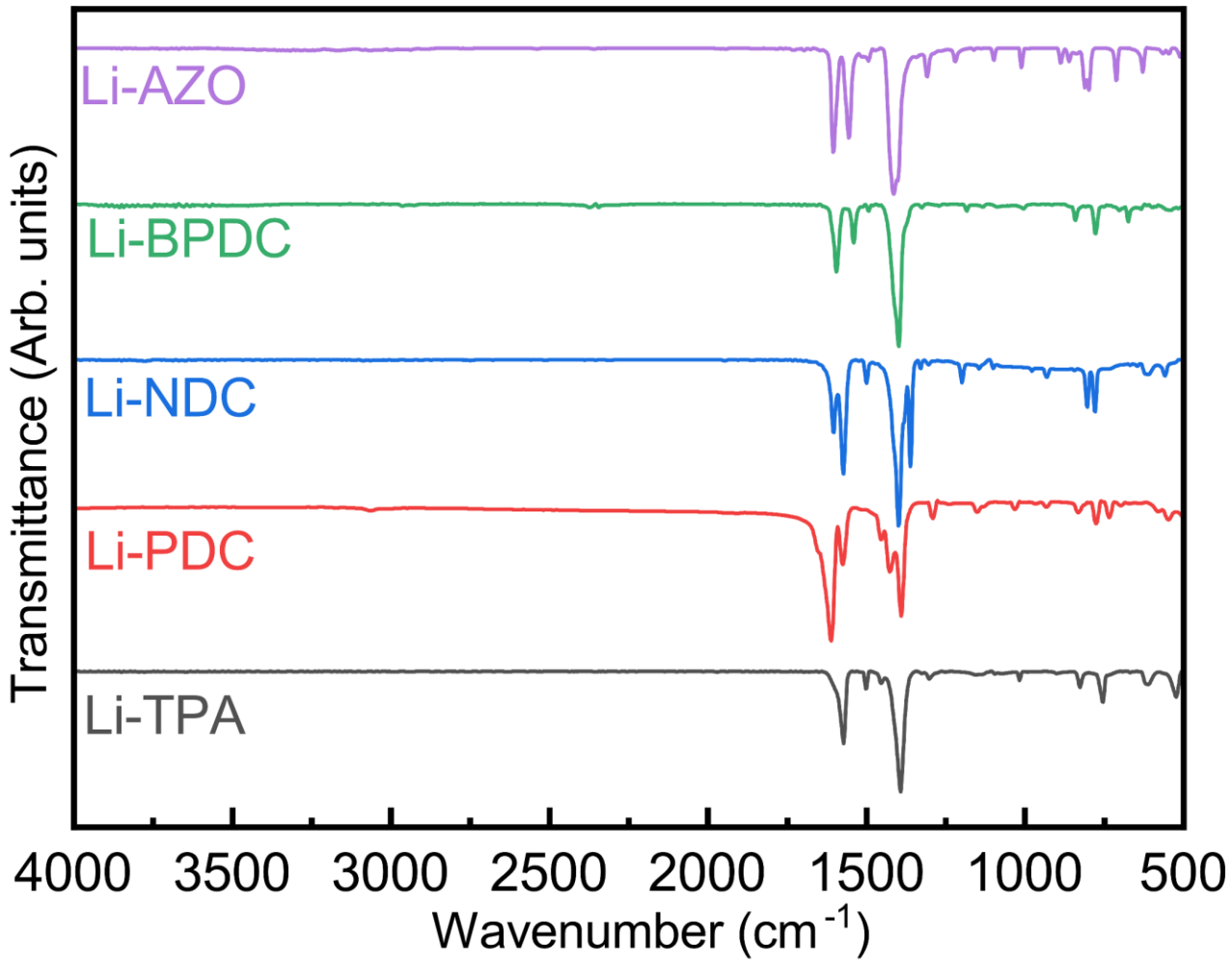


Figure S4. FTIR spectra for Li-TPA, Li-PDC, Li-NDC, Li-BPDC and Li-AZO films.

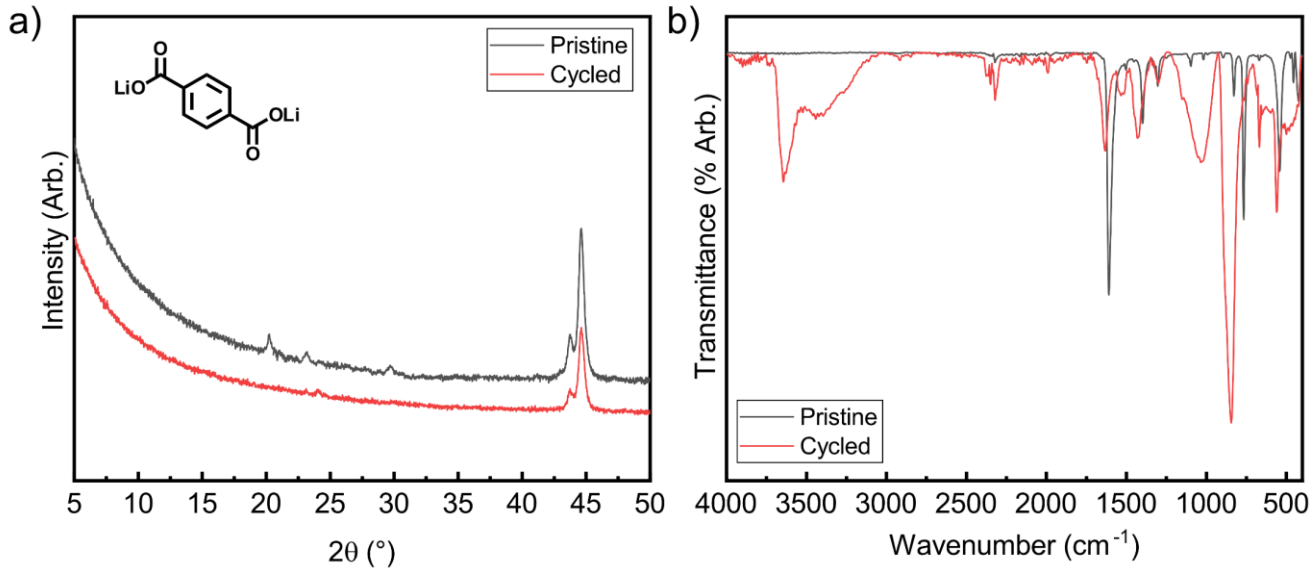


Figure S5. (a) GIXRD and (b) ATR-FTIR for pristine and cycled Li-TPA electrode.

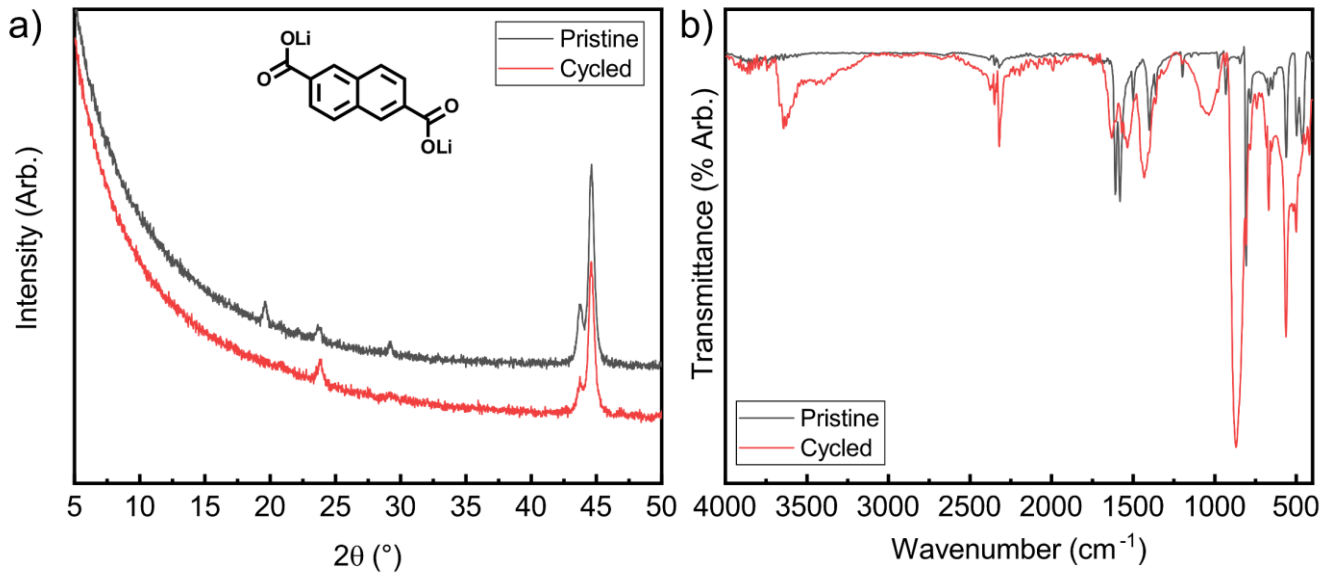
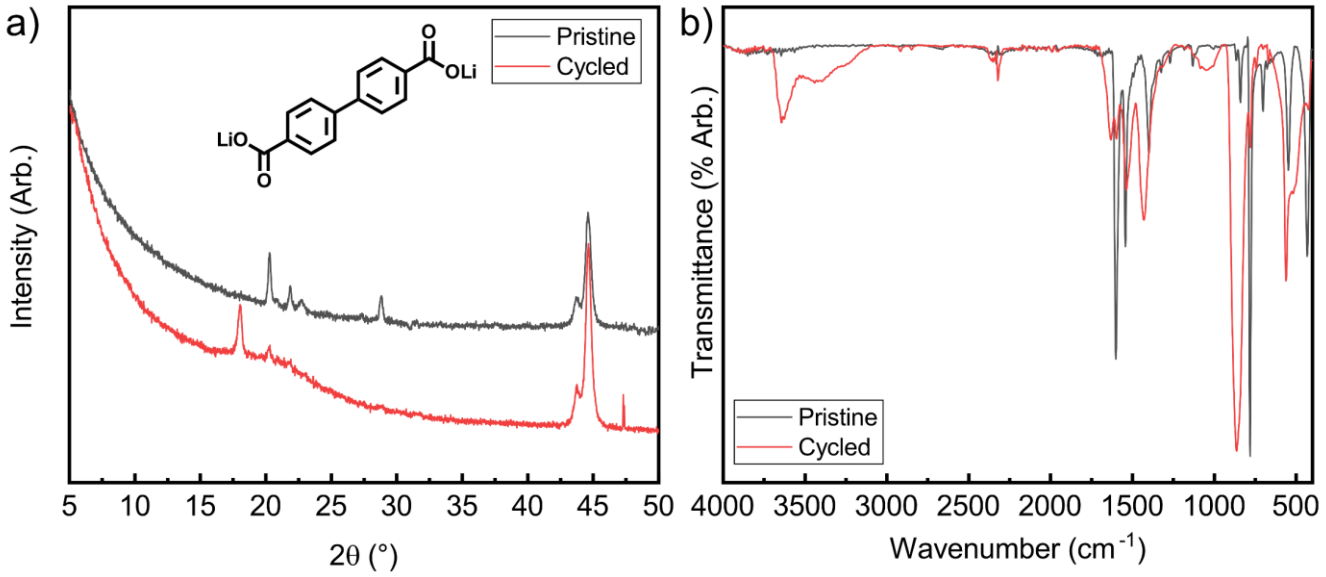


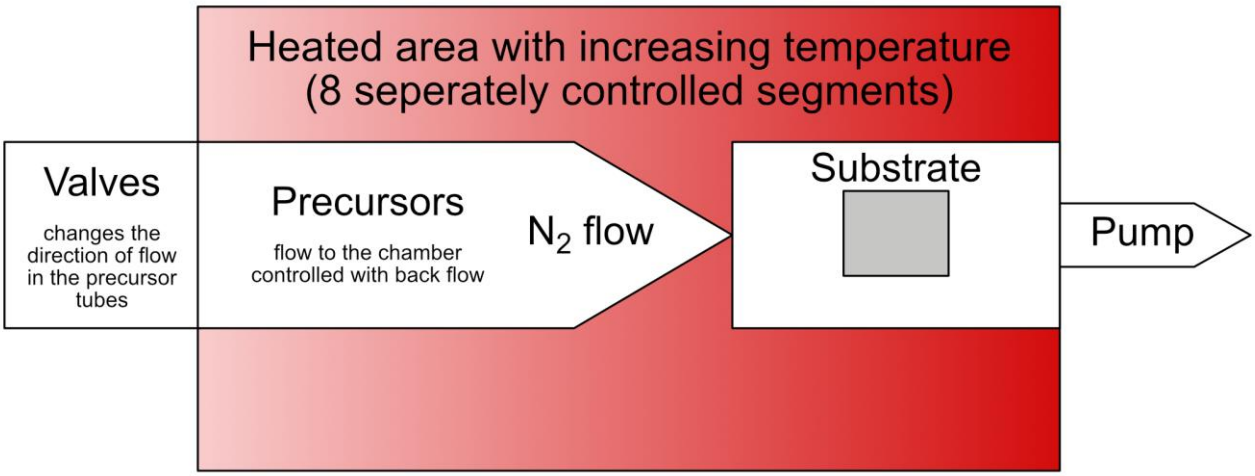
Figure S6. (a) GIXRD and (b) ATR-FTIR for pristine and cycled Li-NDC electrode.



SI Figure 7. (a) GIXRD and (b) ATR-FTIR for pristine and cycled Li-BPDC electrode.

ALD reactor design

The F120 ALD reactor is a first commercial reactor by ASM Microchemistry Ltd. Our reactor design is a slight modification from the original. The basic schematic is given in SI Figure 8 as detailed blueprints are confidential. Precursors which require heating are held inside the reactor in one of the eight separately controlled heating areas. There are six separate glass tubes connected to the chamber, although there is only one inlet. Precursors are inside two glass tubes, with the outer tube having the N_2 flow direction always towards the chamber and the pump. The inner glass tube's flow direction is by default away from the chamber. The flow direction in it can be controlled with a simple valve, which on activation changes the flow direction in the inner glass tube and allows the precursor to flow to the reaction chamber. As these valves can be individually controlled, depositing in cyclic manner becomes trivial. This setup allows us to use very high sublimation temperatures for the organics and other solid precursors as only the glass parts are heated, and the actual valves are not.



SI Figure 8. Schematic of our ALD equipment.

Scherrerr equation for determining crystallite size

The Scherrerr equation is determined as[1]:

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

where τ is mean size of the ordered crystallite domains, K is a dimensionless factor for the shape of the crystallites, λ is the X-ray wavelength, β is the FWHM (full width half maximum) value of the diffraction peak, and θ is angle of incidence. The calculated values will contain a relatively large error due to GIXRD measurement rather than XRD, film rather than a powder sample and without exact information about the value K. Nevertheless, as the measurement conditions are the same for all the samples, we should be able to compare them in series when the thickness of the film is similar, and we compare the same reflection (011). For Li-PDC we had to choose reflection (021) since (011) is not visible and in addition it has a different space group and therefore does not fit very well into this comparison. This however means that the formula can be reduced basically just comparing the FWHM value of the samples. The collected data is shown in table below.

MATERIAL	Li-PDC	Li-TPA	Li-NDC	Li-BPDC	Li-AZO
FWHM	0.21	0.22	0.19	0.2	0.41
CRYSTALLITE SIZE (Å)	431	411	476	453	221

Li-TPA, Li-NDC, and Li-BPDC, have very similar crystallite size, while Li-AZO with the same space group have significantly smaller crystallite size, which might be the reason for the different morphology observed in the SEM images.

References

(1) Patterson, A. L. *The Scherrer Formula for I-Ray Particle Size Determination*; 1939; Vol. 56.