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In-situ lithiated quinone cathode for ALD/MLD-fabricated high-power thin-film battery

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ABSTRACT: We demonstrate that the high-capacity organic electrode material, *p*-benzoquinone, is able to sustain ultrahigh redox reaction rates without any conductive additives when applied as ultrathin layers in an all-solid-state thin-film battery setup, viable for e.g. high-performance power sources in microelectronic devices. The combined atomic/molecular layer deposition (ALD/MLD) technique employed for the fabrication allows the *in-situ* deposition of the quinone cathode in its lithiated state. The LiPON solid electrolyte is fabricated by ALD as a remarkably thin layer down to 30 nm. Our proof-of-the-concept setup is able to reach 50 % of the full capacity in less than 0.25 s, with energy/power densities of 108 mWh/cm³ and 508 W/cm³. These characteristics are of considerable promise towards bridging the gap between microbatteries and microsupercapacitors. Moreover, we demonstrate an all-ALD/MLD-made organic battery where the lithium quinone and LiPON layers are combined with a lithium terephthalate anode layer.

Keywords: Atomic layer deposition, molecular layer deposition, quinone, thin film battery

1. INTRODUCTION

Organic Li-ion battery electrode materials such as quinones have gained interest due to their low-cost, abundant and environmentally benign constituents, and high specific capacity, but in bulk form their poor electronic conductivity significantly hinders the rate performance.^{1,2} Enhanced redox kinetics have been achieved with surface functionalization of carbonaceous and conductive polymer substrates with quinone moieties for both battery^{3,4} and supercapacitor applications,⁵⁻⁷ but only at the cost of a significantly reduced energy density. Thin films can be seen as an intermediate between the conventional bulk and the surface-functionalized materials, and thus as a promising platform to fuse some of the benefits from the two extremes.

28 For an organic n-type cathode material, the quinone family provides the most prominent candidates.
29 Quinones can undergo a two-step reduction by enolization of the carbonyl groups with a semiquinone
30 radical intermediate product (Figure 1a). The dianion is stabilized by charge delocalization within the
31 conjugated system, and the negative charge is balanced by ion-coordination to cations such as Li^+ . The
32 simplest member of the quinone family is *p*-benzoquinone (BQ). With its theoretical maximum capacity
33 of 496 mAh/g and the relatively high redox potential of 2.8 V vs. Li/Li^+ , BQ also ranks high regarding
34 the electrochemical performance. However, its high solubility in liquid electrolytes practically prevents
35 its use in conventional wet-cell Li-ion batteries.^{8,9} Obviously, in an all-solid-state thin film setup the
36 dissolution issue is completely avoided.

37 Recently, we demonstrated that high-quality Li-organic thin films can be deposited using the
38 combined atomic/molecular layer deposition (ALD/MLD) technique; our pioneering work moreover
39 revealed excellent electrochemical performance for the lithium terephthalate anode material.¹⁰ A major
40 difficulty in using the quinones as cathode materials in a Li-ion battery is that they do not contain lithium
41 in their neutral form. Here we demonstrate that the ALD/MLD approach is commendably suited for the
42 *in-situ* deposition of the lithiated, dianionic (i.e. discharged) form of BQ by deprotonating the
43 hydroquinone (HQ) organic precursor molecules with lithium bis(trimethylsilyl)amide (LiHMDS) used
44 as the source of lithium; in this process hexamethyldisilazane is released as the volatile by-product
45 (Figure 1b). The surface saturation limited layer-by-layer process yields high-quality thin films of
46 dilithium-1,4-benzenediolate (Li_2Q) with nanometer-scale thickness control.¹¹

47 Also importantly, the recent progress in ALD of solid electrolyte materials and in particular lithium
48 phosphorous oxynitride (LiPON)^{12,13} has enabled the manufacturing of all-solid-state thin-film batteries
49 with sub-100-nm thick electrolyte layers;^{14,15} this is the key requirement in high-power applications.
50 Now, in the present work we demonstrate that combining the LiHMDS-HQ process for Li_2Q with our
51 previously reported ALD LiPON process,¹² we are able to manufacture all-solid-state thin-film batteries
52 with an organic cathode material without relying on an external lithium source in the cell setup. For the
53 negative electrode, the cells rely on the *in-situ* formed metallic Li – a concept earlier introduced by
54 Neudecker et al.¹⁶ for an inorganic thin-film battery. Namely, during the first charge of the cell, a layer
55 of Li forms on the Cu negative current collector, which is then consumed on the discharge. Despite the
56 insulating nature of quinone molecules, the thin-film approach allows for the use of extremely high C-
57 rates up to 6500. In addition, by using our previously reported ALD/MLD-fabricated lithium

terephthalate as the negative electrode, we demonstrate an all-organic solid-state thin-film battery capable of extended charge-discharge cycling.

Figure 1. (a) The redox scheme of *p*-benzoquinone. (b) The ALD/MLD process for the Li_2Q thin films.

2. EXPERIMENTAL

The cell manufacturing was carried out in three phases. First, 300 mm Si wafers were coated with 500 ALD cycles (~ 23 nm) of Pt using (methylcyclopentadienyl)trimethylplatinum and oxygen as reported elsewhere.¹⁷ The Pt depositions were carried out with a Picosun R-200 Advanced ALD-reactor. The wafers were then cut into 3×3 cm² pieces, and the Li_2Q and LiPON layers were deposited on top of the Pt layer in succession without breaking the vacuum in between. These depositions were carried out in an F-120 flow-type hot-wall ALD reactor (ASM Microchemistry Ltd.) using our previously reported ALD/MLD processes.^{11,12} In short, the Li_2Q layers were deposited using LiHMDS (97 %, Sigma-Aldrich) and hydroquinone (HQ, >99 %, Sigma-Aldrich) as the precursors. The deposition temperature was 160 °C with pulse/purge times of 2 s/2 s and 10 s/20 s for LiHMDS and HQ, respectively. The LiPON layer was deposited at 300 °C using LiHMDS and diethyl phosphoramidate (DEPA) as the precursors with pulse/purge times of 2 s/2 s for both precursors. For sufficient volatility, LiHMDS, HQ and DEPA were heated to 60, 95 and 85 °C, respectively.

With each sample, two reference substrates (Si(100) and Pt) were simultaneously coated for the sake of characterization. The Si reference substrate was required as in scanning electron microscopy (SEM)

cross-section images the contrast between LiPON and Li₂Q was not sufficient to discern their individual layer thicknesses, while in the X-ray reflectivity (XRR) measurements the high density Pt substrate hindered the analysis of the other layers of the whole cell. A corner of each Pt substrate was masked with a piece of silicon wafer to preserve electric contact to the electrode. After the LiPON deposition, the samples were transferred to a Leybold-Heraeus UNIVEX300 thermal evaporator, which was used to deposit the Cu top contacts (~70 nm thickness, diameter = 3 mm) using a shadow mask resulting in 20–30 individual cells per sample. The Li₂Q/LiPON/Ge cell was manufactured similarly, with an addition of Cu current collector for the Ge electrode. Due to incompatible deposition processes, the Li₂Q-Li₂TP cells were manufactured with the following deposition order: Pt/Li₂TP/LiPON/Li₂Q/Cu. The Li₂TP layer (70 ALD/MLD cycles) was deposited at 200 °C using the previously reported process¹⁰ with the exception that LiHMDS was used as the lithium precursor. During the transfer from the ALD reactor to the evaporator, all the samples were exposed to ambient air for several minutes.

The presence of Li₂Q and LiPON in the samples was confirmed using Fourier transform infrared spectroscopy (FTIR; Nicolet Magna 750, transmission mode, 400–4000 cm⁻¹, 4 cm⁻¹ resolution), which also allowed semiquantitative analysis on the layer thickness. The layer thicknesses were obtained from X-ray reflectivity (XRR, PANalytical X'Pert Pro, Cu K α X-ray source) measurements. The individual layer thicknesses were obtained by fitting the XRR data from the Si(100) substrate. The SEM images were acquired with a Tescan Mira3 FE-SEM.

The electrochemical measurements were carried out using an Autolab PGSTAT302N potentiostat/galvanostat. Given the limited cycle life of the *in-situ* anode design, a pristine cell was used for each measurement (i.e. for each scan rate/current density). The contact to the top electrode was made using a self-made spring-loaded Pt wire.

3. RESULTS AND DISCUSSION

The structure of our Li₂Q/LiPON/Cu cells deposited on platinum is schematically shown in Figure 2(a). The thickness of the Li₂Q cathode layer was varied from 5 to 42 nm, while the thickness of the LiPON electrolyte layer was kept at 30 nm, unless otherwise mentioned. In our original work where the ALD/MLD process of Li₂Q was developed the films of the same thickness scale as investigated here were crystalline;¹¹ nevertheless, all the present films deposited on Pt substrates were seemingly amorphous. From FTIR, the presence of both Li₂Q and LiPON in the samples was confirmed, with the

absorption intensities scaling linearly with the respective layer thickness as expected, see Figure 2(b) and Figure S1(b); reference FTIR spectra of Li₂Q and LiPON are shown in Figure S1(a). The individual layer thicknesses were determined from parallel samples grown on silicon by fitting the XRR patterns with a three-layer model consisting of the Si substrate, Li₂Q, and LiPON layers. An exemplary fit of XRR data is shown in Figure 2(c). The results yielded the expected linear behavior of thickness as a function of the number of ALD/MLD cycles (Inset, Figure 2(c)). The linear growth was also confirmed for LiPON (Figure S2(a)). The layer roughness, as judged from the XRR fit, is in the range of 1 to 2.5 nm in our films (Figure S2(b)).

Figure 2. (a) Schematic presentation of the Li₂Q/LiPON/Cu cells used to evaluate the electrochemical performance of Li₂Q. The *in-situ* Li negative electrode is electroplated on the Cu current collector upon the first charge of the cell. (b) FTIR spectra confirming the presence of both Li₂Q and LiPON in the samples. (c) Representative XRR fit used to extract the individual layer thicknesses in a Li₂Q/LiPON stack. The inset demonstrates the expected linear dependence of the Li₂Q layer thickness on the number of deposition cycles.

Cyclic voltammetry (CV) and chronopotentiometry were used to establish the electrochemical activity of the Li₂Q films. As the cell design prevented the use of a reference electrode the results reflect the

126 properties of the whole cell instead of solely arising from the Li₂Q positive electrode. Hence the results
 127 are treated in terms of the terminal voltage of the cell. In Figure S3(a) we present a voltammogram
 128 recorded for a 10-nm sample at 0.2 mV/s from 0.1 to 4 V. A single prominent oxidation peak is seen at
 129 3.38 V on the initial anodic sweep, whereas on the return sweep, the reduction occurs in two phases such
 130 that the more prominent is seen peak at 2.57 V with an overlapping shoulder at 2.49 V. With the
 131 theoretical maximum capacity of 439.5 mAh/g and assuming a density of 1.2 g/cm³ as determined from
 132 XRR measurements, the total integrated charge $Q_{\text{Ox,total}}$ obtained from the 10 nm layer should be 0.50
 133 $\mu\text{Ah}/\text{cm}^2$. The total charge for the anodic sweep is 1.0 $\mu\text{Ah}/\text{cm}^2$, and for the cathodic sweep 0.53
 134 $\mu\text{Ah}/\text{cm}^2$. However, the area under the anodic peak $Q_{\text{Ox,peak}}$ (onset determined from the first derivative
 135 of the curve) is 0.48 $\mu\text{Ah}/\text{cm}^2$, while being only 0.35 $\mu\text{Ah}/\text{cm}^2$ for the cathodic peak. Parallel behavior
 136 is seen with the chronopotentiometric measurements. On the first charging of the cell at 2 $\mu\text{A}/\text{cm}^2$, the
 137 obtained capacity 1.0 μAh equals to the $Q_{\text{Ox,total}}$ of the CV measurement, whereas the total discharge
 138 capacity is 0.55 $\mu\text{Ah}/\text{cm}^2$. The coulombic efficiency is improved on the subsequent cycles, where also
 139 the charge capacity is close to the theoretical maximum (Figure S3(b)). The charge plateau occurs at 3.29
 140 V, whereas from the discharge curve two plateaus at 2.57 and 2.43 V are discerned in an agreement with
 141 the CV data. The linear change in the potential at the end of discharge is tentatively ascribed to double-
 142 layer capacitance. The capacity associated with the plateaus exactly matches those of the anodic/cathodic
 143 peak in the CV measurements. Therefore, we ascribe the initial excess charge capacity of $\sim 0.46 \mu\text{Ah}/\text{cm}^2$
 144 on a parasitic side reaction. In our additional tests with a Pt/LiPON/Cu setup, the initial charging capacity
 145 corresponds to the excess capacity observed in the Li₂Q sample with little subsequent electrochemical
 146 activity (Figure S3(c)). In Figures S3(d) and S4(e), the irreversible oxidation is further confirmed with
 147 cyclic voltammetry. On the first anodic sweep, two small peaks are seen at 1.5 and 2.3 V, which are not
 148 present on the subsequent cycles. The parasitic reaction is suspected to be due to the decomposition of
 149 LiPON at the solid electrolyte/negative electrode interface. Recent experimental and theoretical studies
 150 indicate that at low electrode potentials and in contact with metallic lithium LiPON decomposes to Li₃N,
 151 Li₂O and Li₃P.¹⁸⁻²⁰ Unfortunately, we were not able to directly observe the decomposition products but
 152 our observations for the electrochemical behavior of the cells are consistent with the aforementioned
 153 interpretation. The decomposition is expected to be self-limiting due the formation of an inert SEI layer.
 154 Indeed, the excess capacity occurs only on the first charge, after which the cell capacity is relatively
 155 constant for the next cycles. Thus, judging from the values of $Q_{\text{Ox,peak}}$ and the voltage plateau in the
 156 constant current measurement, we conclude that during the oxidation both the Li⁺ ions of each quinone

molecule are involved. Whether the process is fully reversible, cannot be conclusively established using the present method as the *in-situ* formed Li anode is known to instill capacity loss during cycling.¹⁶ Also in this study, post-mortem analysis of the cells using SEM revealed that upon cycling, the *in-situ* formed Li layer penetrates into the Cu current collectors leaving behind deposits presumably of LiOH or Li₂O. In previous works the formation of such deposits has been attributed to reaction with O₂/H₂O traces present in the glove box atmosphere. We found that the amount of the deposits depends on the current rate and the number of charge/discharge cycles, which is in line with the electrochemical measurement data (Figure S5(a)-(c)).

The full capacity is achieved only for the thinnest electrode layers. As shown in Figure 3a, at a scan rate (v) of 2 mV/s the capacity follows the theoretical line only up to 10-nm thick Li₂Q layers. From 15 nm up to 42 nm, the integrated charge associated with the anodic peak ($Q_{\text{Ox,peak}}$) remains constant at 0.55 $\mu\text{Ah}/\text{cm}^2$. The corresponding voltammograms are shown in Supplementary Figure S5(a). The peak shift is highly asymmetric for the anodic sweep with ΔE_{Peak} values of up to 1 V, whereas a comparatively minor shift is observed for the cathodic peak position (Supplementary Figure S5(b)). The restricted cell capacity is not affected by the electrolyte layer thickness; increasing the thickness up to 90 nm increases the ohmic loss as is seen in the symmetric increase in the peak separation and peak broadening typical for an increased cell resistance (Supplementary Figure S6). The redox peak area however stays constant. The same effect is observed also in the constant current charge/discharge curves, where at a current density of 2 $\mu\text{A}/\text{cm}^2$ the capacity increases linearly only up to the 10-nm layer thickness and plateauing at 15 nm (Supplementary Figure S7). When the current density is increased to 20 $\mu\text{A}/\text{cm}^2$, the difference in cell polarization between the 15 nm and 30 nm samples becomes apparent (Supplementary Figure S8). Similar saturation of capacity has previously been observed for other quinone and nitroxide radical containing thin films.^{21,22}

Up to the Li₂Q-layer thickness of 15 nm the rate performance is excellent. The discharge voltage profiles measured at current rates from 2 to 5000 $\mu\text{A}/\text{cm}^2$ are shown in Figure 3(b). Even at 5000 $\mu\text{A}/\text{cm}^2$ (C-rate of ~6500 assuming full theoretical capacity for a 15 nm thick Li₂Q layer), a discharge capacity of 0.31 $\mu\text{Ah}/\text{cm}^2$ (or appr. 176 mAh/g) is obtained. In other words, the cell is capable in delivering almost 50 % of the initial capacity with a charge/discharge time of 0.25 s. The flat voltage profile is maintained even with the highest current rates. The rate capability exceeds even that of the ultrafast nitroxide radical thin films in aqueous media²³. As the use of a solid electrolyte allows for high operation voltages in

187 comparison to aqueous electrolytes and the voltage remains stable throughout the discharge, reasonably
 188 high energy density values can be obtained despite the ultrathin nature of the Li_2Q electrode. At 2
 189 $\mu\text{A}/\text{cm}^2$, an energy density of $1.55 \mu\text{Wh}/\text{cm}^2$ is obtained and even at $5000 \mu\text{A}/\text{cm}^2$ one third of this, i.e.
 190 $0.51 \mu\text{Wh}/\text{cm}^2$, is still obtained. The corresponding power densities range from 4.6 to $7265 \mu\text{W}/\text{cm}^2$. To
 191 widen the perspective, we should also look at the volumetric energy/power densities. At the low current
 192 density, the volumetric energy density reaches a value of $108 \text{ mWh}/\text{cm}^3$, and at $5000 \mu\text{A}/\text{cm}^2$ the
 193 volumetric power density reaches $508 \text{ W}/\text{cm}^3$ while the energy density yet remains at the reasonably high
 194 value of $35.5 \text{ mWh}/\text{cm}^3$. Here we should emphasize that the volumetric values were calculated using the
 195 volume of the full stack including the current collectors, even though the device is by no means optimized
 196 for the volumetric performance, e.g. the arbitrarily thick Cu current collector accounts in this setup for
 197 half of the total cell thickness.

198
 199 **Figure 3.** (a) Integrated capacity corresponding to the redox peaks of the solid-state cells as a function
 200 of Li_2Q layer thickness. The experimental values follow the theoretical maximum (dashed line) up to
 201 Li_2Q thickness of 10 nm. (b) Discharge voltage curves with current density ranging from $2 \mu\text{A}/\text{cm}^2$
 202 (approximately 2.6 C) to $5000 \mu\text{A}/\text{cm}^2$ (6500 C) for Li_2Q layer thickness of 15 nm. (c) and (d) Cyclic

voltammograms between 2 and 100 mV/s and 100 – 10000 mV/s, respectively with Li₂Q layer thickness of 10 nm. The inset in (c) highlights the cathodic peak for the scan rates between 2 and 20 mV/s whereas the inset in (d) shows the redox peak separation as a function of the scan rate.

To gain deeper comprehension of the seemingly fast charge storage, chronoamperometry and cyclic voltammetry measurements were conducted. In Figures S9(a) and S9(b) the chronoamperometric responses for charging and discharging are plotted as $It^{0.5}$ vs $\log t$. The observed current transient is asymmetric regarding the oxidation and reduction with significantly faster reaction for the latter. With increasing Li₂Q layer thickness, it seems that the redox reaction transition from kinetic to diffusion control. The integrated charge plotted against t shown in Figure S9(c) reveals that the reduction of the 10 nm films occurs very rapidly with 80 % of the total capacity obtained in just 0.1 s. The CV measurements were conducted with scan rates from 0.2 to 10000 mV/s. As seen in Figures 3(c) and 3(d), prominent redox peaks are visible all the way up to 10000 mV/s. The shift in the reduction peak potential is minimal up to 100 mV/s (Figures 3(c) and 2(d), insets). The $Q_{Ox,peak}$ remains constant at 0.5 $\mu\text{Ah}/\text{cm}^2$ up to 2 V/s implying fast redox reaction kinetics (Figure S10). To elucidate the nature of the charge storage, we plot (see Supplementary Figures S11(a) and (b)) the logarithm of the peak current density i_p against $\log(v)$: a slope value of 1 points towards capacitive charge storage according to

$$i = C v \quad (1)$$

whereas a slope of 0.5 is expected for a purely diffusion controlled reaction as per the Randles-Sevcik equation

$$i_p = 0.4463nFc_{o,0}\sqrt{\frac{nF}{RT}}D^{0.5}v^{0.5} \quad (2)$$

Using the CV data from pristine cells, the slopes for the first/second cycle are determined to be 0.77/0.82 for the anodic current and 0.88/0.84 for the cathodic current 0.88/0.84. Above 2000 mV/s, both the anodic and the cathodic current deviate from linearity. Based on the interpretation above, the current should be dominantly capacitive, yet the prominent redox peaks are clearly from a faradaic redox process. Fast faradaic redox reaction kinetics have been associated with pseudocapacitance,²⁴ but in the present case

229 such a mechanism cannot be invoked as the redox peaks together with the voltage plateau in the
230 galvanostatic measurements clearly indicate battery-like behavior.^{25,26} Instead, a linear dependency of i_p
231 *versus* v is also a fundamental property of molecular surface layers.²⁷ For surface films beyond a
232 monolayer thickness, the surface-like dependency may persist depending on the efficiency of the charge
233 carrier transport inside the film, and also the film thickness.²⁸ Considering the insulating nature of Li₂Q,
234 a possible explanation could be that the charge propagates through electron self-exchange of adjacent
235 quinone molecules as has previously been observed for organic radical polymer layers.²⁹ Such a behavior
236 would lead to a buildup of fully oxidized BQ molecules at the current collector/electrode interface, which
237 at a certain thickness would terminate the efficient charge propagation, thus explaining the depressed
238 performance observed for the cells with Li₂Q layers thicker than 15 nm.

239 Another unexpected feature is the rather large voltage hysteresis, which is ill suited for high power
240 applications. Previous experimental results indicate the redox potential of BQ to be ~2.8 V with no
241 significant hysteresis between oxidation and reduction.⁸ A rudimentary galvanostatic intermittent
242 titration (GITT) measurement (Supplementary Figure S12) indicates that with the solid-state cells, the
243 charge/discharge overpotential is indeed significant, i.e. 0.5/0.35 V, with the open circuit voltage close
244 to the literature values. Here poor redox reaction kinetics are clearly ruled out as the underlying reason.
245 Nucleation of metallic lithium could have some contribution but the overpotential for the nucleation is
246 not likely to exceed some tens of millivolts.³⁰ A larger impact could arise from the phase transition within
247 the Li₂Q/BQ layer,³¹ or alternatively as suggested by Precht et al.³² from the electron transport across the
248 metal-organic interface. Depending on the Fermi level alignment of the current collector with the HOMO
249 and LUMO levels of the organic electrode, an electron injection barrier of several tenths of eV could
250 form. As the HOMO-LUMO levels are dependent on the degree of lithiation,³³ the overpotential can be
251 highly asymmetric regarding the charge/discharge. When Cu was utilized as the positive electrode
252 current collector, only a very minor decrease in the cell polarization was observed (Figure S13). Further
253 studies are needed to elucidate the origin of the unexpectedly large activation overpotential.

254 Finally, in Figure 4(a) we compare the capacity retention of our Li₂Q solid-state device constructed
255 with three different negative electrode schemes: the *in-situ* plated Li, thermally evaporated Ge, and
256 ALD/MLD-grown lithium terephthalate (Li₂TP). With the *in-situ* plated Li and Ge anodes, the cells
257 lasted only for about 20 cycles before a rapid loss of capacity regardless of the current density used with
258 an increase in the voltage polarization at each cycle (Figures 4(b) and 4(c)). Electrochemical impedance
259 spectroscopy (EIS) conducted at 5 charge/discharge cycle interval reveals that the cell impedance

260 gradually increases upon cycling (Figure S14(a)). An additional component is seen in the Bode plots at
 261 end-of-life conditions (Figure S14(b)). However, given the two-electrode setup, its origin cannot
 262 conclusively be discerned. To complement the EIS measurements, *post-mortem* SEM analysis of the
 263 aged cells was also performed (Figures S4(d-f)). Significant amounts of deposits were observed on the
 264 anode current collector surface. In addition, the current collector itself was found to degrade, as cracking
 265 of the surface and erosion of the edges were clearly visible. Thus, the poor cycle life seems to stem from
 266 loss of lithium and degradation/delamination of the negative electrode current collector. In contrary, with
 267 Li_2TP as the anode the cell performs more evenly retaining ~74 % of the initial capacity over 100
 268 charge/discharge cycles. The improved performance further suggest that the poor cycle life of the Li and
 269 Ge cells is due to the negative electrode. Here we should stress that the present cell designs were rather
 270 primitive. For instance, with proper protective layers, cycle life of above 1000 charge/discharge cycles
 271 has been achieved with an *in-situ* plated Li anode with sputtered LiCoO_2 cathode and LiPON solid
 272 electrolyte.¹⁶

273

274

275 **Figure 3.** (a) Comparison of the cycling stability of the all-solid-state cells with different anode materials;
 276 *in-situ* formed Li (black), germanium (red) and lithium terephthalate (blue). The open diamond/square

markers represent the charge/discharge capacity, respectively. For visualization purposes, the data is normalized to the initial discharge capacity; 0.63, 0.54, and 0.41 $\mu\text{Ah}/\text{cm}^2$ for in-situ Li, Ge, and Li_2TP , respectively. The corresponding voltage profiles are shown in (b) for in-situ Li, (c) for Ge, and (d) for Li_2TP .

4. CONCLUSIONS

We have presented ultrathin quinone thin films as an exciting cathode material for the all-solid-state thin-film Li-ion battery. Atomic/molecular layer deposition allows the fabrication of these films with a high precision and with the remarkable advantage that the cathode can be prepared in the lithiated form, thus simplifying the scheme, as the cells do not require any post-deposition lithiation treatments. Moreover, our organic all-solid-state cells are fully functional without any conductive additives; this fact could be of great benefit in fundamental studies on e.g. the redox kinetics. Most impressively, the work has demonstrated that nanoscaling is indeed the access to the extremely high redox reaction rate of quinones that further benefit from the ultra-thin solid electrolyte layer made possible by the ALD approach. Even though the cycle life of the current devices leaves much to improve on, we believe that the concept presented could be an important step towards devices merging the energy density of batteries with the power density of supercapacitors.

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344 ASSOCIATED CONTENT

345 **Supplementary information**

346 Supplementary graphs for initial electrochemical response of the solid-state cells, additional CV,
347 chronoamperometry and charge/discharge graphs on the effect of varying Li₂Q and LiPON layer
348 thickness, cell capacity and log-log plots as a function of the CV scan rate, and GITT measurement details
349 and results.

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361 Competing financial interests

362 The authors declare no competing financial interests.

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