View Article Online
Journal Homepage
Cite This: J. Mater. Chem. A 2019, 7, 7327–7333
DOI: 10.1039/C8TA10604C

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

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Received 15th January 2019 , Accepted 27th March 2019

First published on 29th March 2019

Abstract

We demonstrate that the high-capacity organic electrode material, polyquinoxaline, is able to sustain ultrahigh-rate reaction rates without any conductive additives when applied as cathode layer in an all-solid-state thin-film battery setup, viable for 4 μg high-performance power sources in electronic 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 LPON solid-electrolyte is deposited by ALD as the anode layer. The layer-by-layer assembly of the cell is finished by ALD of a thin metallic Pt film with the full capacity in less than 0.25 s, with energy-power densities of 230 mW h cm^{-3} and 918 W cm^{-3}. These characteristics are of considerable promise towards bridging the gap between the lithium-ion batteries and supercapacitors. We moreover demonstrate an all-ALD/MLD-made battery where the lithium-quinone and LPON layers are combined with a lithium-terephthalate anode layer.

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.[1–3] Enhanced redox kinetics have been achieved with surface functionalization of carbonaceous and conductive polymer substrates with quinone moieties for both battery[4–6] and supercapacitor applications,[7] but only at the cost of a significantly reduced energy density. This then has to be seen as an inherent trade-off between the energy density and the surface functionalized material, and thus as a promising platform to form some of the benefits from the two extremes.

For an organic Li-ion battery cathode material, the benefits from the two prominent candidates: Quinones can undergo a two-step reduction by installation of the carbonyl groups with a semiquinone radical intermediate product (Fig. 1a). The duration is established by charge-discharge rate-limiting Li$^+$ ion migration, and the energy density is governed by ion-coordination to anions such as Li$^+$. The simplest member of the quinone family is *p*-benzoquinone (BQ). With its theoretical maximum capacity of 496 mA h g^{-1} and the relatively high redox potential of 2.8 V *vs.* Li$^+$/Li, BQ also readily forms organic charge-transfer complexes with conductive polymers.[8] However, its high solubility in liquid electrolytes practically prevents its use in conventional wet cell Li-ion batteries.[9] Obviously, in an all-solid-state thin-film setup the dissolution issue is completely avoided.

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

Recently, we demonstrated that high-quality Li-organic thin films can be deposited using the combined atomic/molecular layer deposition (ALD/MLD) technique in a hot-wall reactor system.[10] Quinone moieties were successfully incorporated in the lithium terephthalate anode matrixes.[11] A major difficulty in using the quinones as cathode materials in a Li-ion battery is that they do not contain lithium in their structure. We have now prepared the ALD/MLD quinone cathode layers as lithiated (i_nQ, Fig. 1b) by deposition of the trilithiated, aluminum (i.e. discharged) form of BQ by employing the heterocyclic LiHQ organic precursor molecules with the Li-ion battery anode deposition in mind. The lithiated quinone cathode is then combined with the LPON solid-electrolyte layer suitable for the process (Fig. 1b). The surface saturation limited layer-by-layer process yields high-quality thin films with excellent conformality.[12,13]

Also importantly, the recent progress in ALD of solid electrolyte materials and in particular lithium phosphorous oxynitride (LiPON)[14–16] has made the deposition of all-solid-state thin-film batteries with the cell-level energy densities beyond 1 mW h cm^{-2} μm^{-1} a key requirement in high-power applications. Now, in the present work we demonstrate that combining the LiHQ/BQ-ALD process for i_nQ with our previously developed LPON process for the solid electrolyte we are able to manufacture all-solid-state thin-film batteries with an organic cathode material utilizing not an external lithium source in the cell setup. For the negative electrode, the cells rely on the *in situ*-formed metallic Li – a concept well established for rechargeable thin-film batteries.[17] The complete cell is finished by a cathode-free, yet, a layer of Pt forms on the Cu-organic current collector, which is then consumed on the discharge. Despite the insulating nature of quinone materials, the cells operate without the use of conductivity additives up to 5000 C rates. In addition, by using the previously reported ALD/MLD-fabricated lithium terephthalate as the anode, demonstrate an all-organic solid-state battery that is entirely free of extended charge-discharge cycling.

2. Experimental

The cell manufacturing was carried out in three phases. First, 300 mm Si wafers were coated with 500 ALD cycles (~15 nm) of Pt using (methylcyclopentadienyl)trimethylplatinum and oxygen as the precursors in a hot-wall reactor.[18] The depositions were carried out with a Picosun R-200 Advanced ALD reactor. The wafers were then cut into 2 × 3 cm^2 pieces, and the Cu and LPON layers were deposited on top of the Pt layer in successive depositions by using the same reactor. These depositions were carried out at 225 °C by employing the hot-wall ALD reactor (ASM Microchemistry LTD.) using our previously reported ALD/MLD processes.[11,19] In short, the i_nQ layers were deposited using LiHMDS (LiN(SiMe$_3$)$_2$; Sigma-Aldrich) and hydroquinone (HQ; Sigma-Aldrich) as the precursors. The hydroquinone was sublimated at 160 °C with pulse/purge times of 1.2 and 2.0 s for LiHMDS and HQ, respectively. The LPON layer was deposited at 265 °C using LiHMDS and diethyl phosphoramidate (DEPA; Sigma-Aldrich) as the precursors with pulse/purge times of 1.2/3.0 s for the precursors. For sufficient adhesion, LiHMDS, HQ and DEPA were heated to 60, 90 and 95 °C, respectively.

With each substrate, two reference materials for LPON and i_nQ were simultaneously coated for the sake of characterization. The Si reference substrate was deposited as a starting electrochemistry (SEA) cross-section image the contrast between LPON and i_nQ was not sufficient to discern the two layers from each other. Therefore, while in the X-ray reflectivity (XRR) measurements the i_nQ layer was on the substrate instead of relying on an external lithium source in the cell setup. For the negative electrode, the cells rely on the *in situ*-formed metallic Li – a concept well established for rechargeable thin-film batteries.[17] The complete cell is finished by a cathode-free, yet, a layer of Pt forms on the Cu-organic current collector, which is then consumed on the discharge. Despite the insulating nature of quinone materials, the cells operate without the use of conductivity additives up to 5000 C rates. In addition, by using the previously reported ALD/MLD-fabricated lithium terephthalate as the anode, demonstrate an all-organic solid-state battery that is entirely free of extended charge-discharge cycling.

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3. Results and discussion

The structure of an i_nQ/LPON/Cu/Pt cell deposited on platinum is schematically shown in Fig. 2(a). The thickness of the i_nQ cathode layer was varied from 5 to 40 nm, whereas the thickness of the LPON electrolyte layer was kept at ~90 nm, unless otherwise mentioned. In our original work where the ALD/MLD process of i_nQ was developed the films of the same thickness scale as investigated here were characterized by X-ray reflectivity (XRR) and X-ray photoelectron spectroscopy annealing studies.[10] From the present XRR data, 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 also verified by cross-sectional SEM images (Fig. 2(b)) from the SEA/QCM images and analyzed with a Tescan Mira3 FE-SEM.

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

Fig. 2 (a) Schematic presentation of the i_nQ/LPON/Cu/Pt cells used to evaluate the electrochemical performance of i_nQ. The *in situ*-Li negative electrode is electrodeposited on the Cu-current collector upon the first charge of the cell. (b) FIB cross-sectioning the presence of both i_nQ and LPON layers in the SEM image. (c) Representative XRR fit used to extract the individual layer thicknesses in i_nQ/LPON stack. The inset demonstrates the expected linear dependence of the i_nQ layer thickness on the number of deposition cycles.

Cyclic voltammetry (CV) and chronopotentiometry were used to establish the electrochemical activity of the i_nQ films. As the cell-design presented the use of a reference electrode the results reflect the properties of the whole cell instead of solely arising from the i_nQ-positive electrode. Hence the results are treated in terms of the energy density of the cell. In Fig. 3(a) CVs are presented. A voltammogram recorded for a 20 nm-thick i_nQ layer at 0.1 mV s^{-1} from 3 to 4.5 V with a high-prominent oxidation peak is seen at 3.39 V on the initial anodic sweep, whereas on the subsequent cathodic sweeps a broad reduction is seen between the peak-potentials of 3.23 and 2.17 V with an overlapping shoulder at 2.49 V. With the theoretical maximum capacity of 495.9 mA h g^{-1} and assuming a density of 1.2 g cm^{-3} calculated from XRR measurements, the theoretical capacity of the 20 nm-thick i_nQ layer is 1.19 mA h cm^{-2} μm^{-1}. The total charge for the anodic sweep is 1.5 μA h cm^{-2}, and for the cathodic sweep 0.9 μA h cm^{-2}. However, the area under the anodic peak ($Q_{ox,peak}$) corresponds to the oxidation of the current to 0.4 mA h cm^{-2} μm^{-1} (Fig. 3(a) inset). The ratio of $Q_{ox,peak}$ to the cathodic peak Q_{red} is 0.27 which is near the chronopotentiometric measurements. On the first charging of the cell at 1 μA cm^{-2}, the potential rises to 3.4 V, and then levels off to a plateau-region at 3.3 V, corresponding to the anodic peak in the CV. The coulombic efficiency is improved on the subsequent cycles, where also the charge capacity is close to the theoretical maximum (Fig. S2(b)†). The charge capacity is also retained when the discharge current was increased to 5 μA cm^{-2} and 10 μA cm^{-2} which is in agreement with the CV data. The lower charge in the potential at the end of discharge is tentatively ascribed to double-layer capacitance. The results are also in agreement with the previous reports on the electrochemical activity of the bulk quinone materials.[1–3] Therefore, we ascribe the initial excess charge capacity of ~0.46 μA h cm^{-2} as a parasitic side-reaction. In our additional tests with a PTCDA/PTCDI_{C8} anode the first cycle irreversibility was also observed (Fig. S3†). The effect of R_{series} on the charge-discharge curves is investigated by electrochemical activity (Fig. S3(c)†). In Fig. 3(b) and S4(a),† the irreversible oxidation is further confirmed with cyclic voltammetry measurements. The first anodic sweep is recorded at 1 mV s^{-1} between 3 and 4.5 V, and the cathodic sweep is recorded from 4.5 V. The oxidation reaction is suspected to be due to the decomposition of the LPON electrolyte/organic-electrode interface. Recent investigations on the LiPON/Li-metal interface have revealed the interfacial phenolate and Li-phosphate layers.[20] Such decomposition layers (R_{series}) of ~1 μA h cm^{-2} are also observed in the present cells and in control measurements, we conclude that during the oxidation both the Li$^+$ ions of each quinone molecule are involved. Whether the process is fully reversible, cannot be concluded based on the present data. However, the cell is also found to operate at room temperature without any loss during cycling.[21] Also in this study, more parasitic analysis of the cells using XRR revealed that upon cycling, the *in situ*-formed Li-layer penetrates into the i_nQ layer and the LPON electrolyte layer affects the porosity of the i_nQ. In previous work the effect of such deposits have been attributed to reactions with O_2/H_2O traces present in the glove-box atmosphere. We found that the amount of the deposits depends on the number and on the duration of the charge-discharge cycles and is also dependent on the measurement date (Fig. S5(a)–S5(c)†).

The full capacity is found to be the most interesting feature. As shown in Fig. 2(a), at a rate-/cell-current of 1 μA cm^{-2} the capacity follows the theoretical line only up to 10 nm-thick i_nQ layers. From 15 nm up to 40 nm, the integrated charge associated with the anodic ($Q_{ox,peak}$) corresponds to 0.4 mA h cm^{-2} μm^{-1}. The corresponding voltammograms are shown in Fig. S4(b).† The peak-potential 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 with ΔE_{peak} of 0.3 V. The asymmetry is suspected to be affected by the lower Li$^+$ ion diffusion rate in the i_nQ layer. Increasing the thickness up to 40 nm increases this area as is seen in the symmetric increase in the peak-separation and peak-broadening typical to a kinetically limited redox reaction (Fig. S6(c)†). The charge-discharge curves for the 40 nm-thick i_nQ layer are presented in Fig. S6(a).† The constant current charge/discharge curves, where at a current density of 5 μA cm^{-2} the capacity increases linearly only up to the 20 nm-thick i_nQ layer, and a charge capacity of 0.4 mA h cm^{-2} μm^{-1} is obtained. Moreover, 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 was also tested at current densities between 5 and 5000 μA cm^{-2} (Fig. S6(b)†). The results show that the electrolyte allows for high operation voltages in comparison to aqueous electrolytes and the voltage remains stable throughout the discharge, measured by the potential drop at the end of discharge. When the current density is 10 μA cm^{-2}, the 20 nm-thick i_nQ layer has an energy density of 1.35 μW h cm^{-2} μm^{-1} obtained and even at 5000 μA cm^{-2} one third of this, i.e. 0.51 μW h cm^{-2} μm^{-1} is still obtained. The corresponding power densities range from 13.5 μW cm^{-2} μm^{-1} at 10 μA cm^{-2} to 5100 μW cm^{-2} μm^{-1} at 5000 μA cm^{-2} as presented in the Ragone plot (Fig. 3(c)). The energy-power densities of the 40 nm-thick i_nQ layer are presented in Fig. S6(d).† The results are in good agreement with the previous reports on the electrochemical activity of bulk quinone materials.[1–3]

Fig. 3 (a) Integrated capacity corresponding to the redox peaks of the solid-state cells as a function of i_nQ layer thickness. The experimental values follow the theoretical line only up to 10 nm-thick i_nQ layers. (b) Discharge voltage curves with current density ranging from 2 μA cm^{-2} (approximately 2 kC *vs.* 500 μA cm^{-2} (~500 kC *vs.* i_nQ layer thickness of 15 nm. (c and d) Cyclic voltammograms between 3 and 4.5 V at 100–10 000 mV s^{-1} (c) and the corresponding anodic peak potentials (d) with 15 nm-thick i_nQ layer. The inset in (c) highlights the cathodic peak for the scan rates between 2 and 20 mV s^{-1} whereas the inset in (d) shows the redox peak separation as a function of the scan rate.

Up to the i_nQ layer thickness of 15 nm the rate-performance is excellent. The discharge voltage profiles measured at current rates from 5 000 μA cm^{-2} are shown in Fig. 3(b). Even at 5000 μA cm^{-2} cell-current 70% of the initial full theoretical capacity for a 15 nm-thick i_nQ layer), a discharge capacity of 0.7 mA h cm^{-2} μm^{-1} and Fig. 4(a) is obtained. Moreover, 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 was also tested at current densities between 5 and 5000 μA cm^{-2} (Fig. S6(b)†). The results show that the electrolyte allows for high operation voltages in comparison to aqueous electrolytes and the voltage remains stable throughout the discharge, measured by the potential drop at the end of discharge. When the current density is 10 μA cm^{-2}, the 20 nm-thick i_nQ layer has an energy density of 1.35 μW h cm^{-2} μm^{-1} obtained and even at 5000 μA cm^{-2} one third of this, i.e. 0.51 μW h cm^{-2} μm^{-1} is still obtained. The corresponding power densities range from 13.5 μW cm^{-2} μm^{-1} at 10 μA cm^{-2} to 5100 μW cm^{-2} μm^{-1} at 5000 μA cm^{-2} as presented in the Ragone plot (Fig. 3(c)). The energy-power densities of the 40 nm-thick i_nQ layer are presented in Fig. S6(d).† The results are in good agreement with the previous reports on the electrochemical activity of bulk quinone materials.[1–3]

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Fig. 4 (a) Comparison of the cycling stability of the all-solid-state cells with different anode materials, *in situ*-formed Li (black), germanium (red) and lithium terephthalate (blue). The open diamond-type markers represent the charge/discharge capacity, respectively. For visualization purposes, the data is normalized to the initial discharge capacity. (b) A SEA, and (c) a TEM, image of the i_nQ/Li-terephthalate/Cu/Pt cell.

4. Conclusions

We have presented all-quinone thin-film batteries free of any co-acting 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 discharged state. In the cell-design by the scheme, as the *in situ*-Li anode layer is formed on the cathode-current collector upon the first charge. Despite the insulating nature of conductive additives, this film could be of great benefit in fundamental studies of quinone materials. Most importantly, the work has demonstrated the high-power performance of quinones and indeed the access to the extremely high rate-values of quinones that further benefit from the ultra-thin solid electrolyte layer. Also notable is the fact that quinone-based cells can be manufactured with a high reproducibility. In contrast to many other cell concepts presented here could be an important step towards devices merging the energy density of batteries with the power density of supercapacitors.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

The present work has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013)/ERC Advanced Grant agreement No. 339456 and under the European Union's Horizon 2020 research and innovation Programme/ERC Proof of Concept Grant Agreement No. 749161, and also from the Academy of Finland through the Regular Research Project No. 296705 and the Centre of Excellence Program (2014–2019). We thank Professor Esko Kauppinen for kindly providing the platinum-coated substrates. We Tanna Ruokola is thanked for her assistance with the SEM experiments.

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Footnote

† Electronic supplementary information (ESI) available: Supplementary graphs for initial electrochemical response of the solid-state cells, additional Li-organic thin-film battery configurations and graphs on the effect of using Li and LiPON layer thickness, cell capacity and energy-power density as a function of cell-current. See DOI: 10.1039/C8TA10604C

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