Atomic layer deposition for nanostructured Li-ion batteries

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Atomic layer deposition for nanostructured Li-ion batteries

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Nanostructuring is targeted as a solution to achieve the improvements required for implementing Li-ion batteries in a wide range of applications. These applications range in size from electrical vehicles down to microsystems. Atomic layer deposition (ALD) could be an enabling technology for nanostructured Li-ion batteries as it is capable of depositing ultrathin films (1–100 nm) in complex structures with precise growth control. The potential of ALD is reviewed for three battery concepts that can be distinguished, i.e., particle-based electrodes, 3D-structured electrodes, and 3D all-solid-state microbatteries. It is discussed that a large range of materials can be deposited by ALD and recent demonstrations of battery improvements by ALD are used to exemplify its large potential. © 2012 American Vacuum Society. [DOI: 10.1116/1.3660699]

I. INTRODUCTION

Atomic layer deposition (ALD) is a thin-film deposition technique that can conformally coat surfaces at relatively low temperatures with high-quality thin films (typical range 1–100 nm). ALD has recently been implemented in microelectronics and is being considered for a variety of applications such as solar cells and catalysts. One of the new applications that could benefit from ALD is Li-ion batteries. Although ALD has only recently been considered for use for Li-ion batteries, it has gained interest very rapidly in the last few years. Because of their high energy density, Li-ion batteries are used and designated as energy storage solution for a wide range of applications varying in size from (hybrid) electric vehicles, laptops, mobile phones, down to microsystems. However, continuous improvement of the battery technologies is needed to fulfill ever more stringent requirements such as higher capacity, higher power, and higher cycle-life (cycle-life is typically defined as the number of full charge and discharge cycles a battery can undergo before it reaches 80% of its original capacity). To realize these improvements there is a strong trend in conventional Li-ion batteries toward nanostructuring of the electrode materials, which has been designated as a paradigm shift from bulk to nanomaterial electrodes.1–4

Similarly, for the emerging small thin-film Li-ion batteries such a trend toward nanostructuring can also be observed. For thin-film batteries the capacity per footprint area is limited by the limited thickness of the thin-film device. The film thickness is constrained by low ion and electron diffusion, similar to the constraints in particle size in conventional batteries.5–7 3D structuring of thin-film batteries can increase the storage capacity without increasing film thickness. Therefore, the two previously very different fields of conventional batteries and thin-film batteries come closer together with nanostructuring and as a consequence they encounter, in principle, similar benefits and issues. ALD with its excellent conformality and precise growth control has a high potential to enable new nanostructured designs for battery applications.

In this work the potential of ALD for the synthesis of 3D battery structures is discussed and the investigations of ALD for batteries reported in the literature, to date, are reviewed. First, the basics of Li-ion batteries are explained and three different battery concepts ranging from large size to small size are described. Second, the capability of ALD to deposit various battery materials is described. Finally, the research efforts directly aimed at application and implementation of ALD in batteries are summarized.

II. LI-ION BATTERIES

The basics of Li-ion batteries are explained using the most common battery chemistry, the combination of an LiCoO2 cathode and a graphite anode as shown in Fig. 1. This configuration also facilitates the identification of several limitations of Li-ion batteries. The energy capacity of the battery is determined by the amount of Li that can be stored reversibly in the cathode and the anode, and by the difference in standard redox potential between cathode and anode. In general, the standard redox potential of the electrode redox reaction should be high for the cathode (e.g., 3.7 V versus Li/Li+ for LiCoO2) and low for the anode (e.g.,...
0.1–0.2 V versus Li/Li$^+$ for graphite), leading to a high cell voltage.

The operation of the battery is as follows: during charging (ch), the Co$^{3+}$ in LiCoO$_2$ is oxidized into Co$^{4+}$ and the excess of positive charge is liberated from the electrode in the form of Li$^+$ ions, according to

$$\text{LiCoO}_2 \xrightarrow{\text{ch}} \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-, $$

where the reverse occurs during discharging (d). To prevent irreversible structure changes of the LiCoO$_2$ electrode, not all Li$^+$ ions can be removed. Therefore, in practice, $x$ is not increased above 0.5. During charging, the liberated Li$^+$ ions dissolve into the electrolyte. The electrolyte generally consists of an organic solution such as propylene carbonate, ethylcarbonate, or diethylcarbonate, containing a high concentration of an Li salt (e.g., LiClO$_4$, LiAsF$_6$, or LiPF$_6$) to ensure the ionic conductivity between the two electrodes. Arriving at the other electrode, the Li$^+$ ions are transported into a graphite (C$_6$) electrode and are subsequently reduced according to

$$x\text{Li}^+ + xe^- \xrightarrow{\text{d}} y\text{C}_6,$$

where $z = x/y$ and has a maximum value of 1. During discharging the reverse occurs where Li$^+$ ions are liberated from the graphite electrode and dissolve into the electrolyte. From the overall reaction,

$$\text{LiCoO}_2 + y\text{C}_6 \xrightarrow{\text{ch}} \text{Li}_{1-x}\text{CoO}_2 + y\text{Li}_x\text{C}_6,$$

it is clear that the essence is that Li$^+$ ions are transported from one electrode through the organic electrolyte to the other electrode. While the Li$^+$ ions diffuse through the electrolyte, the electrons go through the charger during charging and through the load to be powered during discharging. A high Li$^+$-ion conductivity is desired for the electrolyte, while it has to be insulating for electrons to prevent self-discharging. Although strictly speaking the terms cathode and anode switch when going from discharging to charging, we use the terms defined during discharging, as is common in the battery literature.

To improve the conventional Li-ion battery with its LiCoO$_2$ and graphite chemistry, new materials are being investigated. Cathode, anode, and electrolyte materials are called active, while current collectors and barrier layers are denoted as passive. Protective layers sometimes have to be conductive to ions and can be denoted as either active or passive. A large amount of effort goes into improving electrode materials. Improvements of the battery in terms of higher capacity and better cycle-life are the main objectives for new electrode materials. A new electrode material also has to fulfill a wide range of other requirements, such as having an optimal redox potential, being conductive to electrons, and being conductive to Li$^+$ ions. Due to the extensive set of requirements, a suitable electrode material is hard to find. Furthermore, a new electrode material often introduces new problems such as extensive volume expansion or phase separation. Candidate electrode materials can be divided into three groups with respect to the storage mechanism, as follows:

1. Insertion: LiCoO$_2$ and graphite fall into this category. These materials typically have fast kinetics and little volume expansion but also a limited storage capacity.
2. Alloying: Metals and semimetals can alloy with Li offering very large capacities. For instance, Si can alloy with Li forming Li$_{11.5}$Si$_4$, which is accompanied by a large increase of the volume, which can be as high as 300%. This large volume expansion typically causes cracking and crumbling of the material, which significantly limits the cycle-life.
3. Conversion: In conversion materials, compounds of the form MX react with Li to form a mixture of M and LiX, where M is typically a transition metal and X an anion such as O or N. For instance, in the case of CoO, the conversion reaction during (dis)charging is

$$\text{CoO} + 2\text{Li}^+ + 2e^- \xrightarrow{\text{ch}} \text{Co} + \text{Li}_2\text{O}.$$
(2) Volume changes without cracking and crumbling of the material. At small feature sizes, stresses due to volume expansion and contraction can be handled more easily, which allows reversible cycling of the electrode material.

(3) Increase in electrode storage capacity due to nanosize effects. Certain storage mechanisms, which are not present in the bulk, can be present on the surface or in distorted near-surface regions, thereby increasing the storage capacity. For instance, bulk anatase-phase TiO$_2$ can host up to 0.5 Li per formula unit while for anatase-phase TiO$_2$ nanoparticles (<40 nm) up to 0.8 Li can be stored per formula unit.

Nanostructuring also leads to some challenges, such as the following:

(1) The very large surface areas present can greatly enhance the decomposition of electrolyte at electrode surfaces, which would lead to a very poor cycle-life.

(2) The porous nanostructure can cause a relatively low density of active material to be present in the battery. This could counteract any expected improvements in storage capacity by using the new material.

(3) The complex nanostructures can be more difficult to synthesize, which would add cost to production.

New synthesis methods are furthermore needed to achieve nanostructuring. ALD, as a powerful technique to deposit thin films, could play a key role in realizing the advantages associated with nanostructuring and also has the potential to assist in overcoming the challenges.

III. CONCEPTS FOR NANOSTRUCTURED LI-ION BATTERIES

A. Particle-based electrodes

Commercial battery electrodes are mostly based on micrometer-sized particles of active material, which are mixed with binder compounds and conductive additives to form the electrode. Figure 2 shows a schematic illustration of a particle-based electrode. In this example, the electrode forms the cathode. The liquid electrolyte penetrates into the porous electrode facilitating the Li$^+$-ion transport, and the binder compounds and conductive additives facilitate the electrical contact with the Al current collector. When going to smaller particle sizes the surface area becomes larger and decomposition of electrolyte, as is observed in the so-called solid electrolyte interphase (SEI) formation, will be greatly enhanced. SEI formation in the case of graphite anodes is actually known to passivate the graphite surface and prevent further electrolyte decomposition. However, with other electrode materials this passivation can be poor or absent and together with the volume changes and the large surface areas, electrolyte decomposition can lead to a very poor cycle-life. At nanosize dimensions, electrolyte decomposition could even be a problem with fairly stable cathode materials like LiFePO$_4$.

Surface modification of the particles, for instance by applying a passivating or protective film, has been designated as the most convenient way to reduce electrolyte decomposition. Because of the low thickness, ultrathin films have higher Li$^+$ and electron conductivities compared to thicker coatings. Furthermore, surface coatings can improve reliability and reversibility of cathode materials in the high voltage range, increasing their usable voltage range and thereby increasing the effective energy density.

The possibilities for ALD with respect to particle-based electrodes lies in depositing protective or conductive layers on the particles. A thin conductive layer can be used to improve electronic performance since many electrode materials are semiconductors or insulators. Since ALD provides excellent conformality the amount of inactive material in the form of protective or conductive layers can be kept to a minimum.

B. 3D-structured electrodes

In 3D-structured electrodes, the electrode is specifically designed such that diffusion paths in the materials are short and that the transport of electrons and Li$^+$ ions is improved. Figure 3 shows an example of such a structure where nanowires of Al serve as current collector and allow for easy transport of electrons to the active material deposited on the nanowire. Li$^+$-ion transport is facilitated by the open structure in which the electrolyte can penetrate easily. Another example of such a structure would be cathode or anode nanowires grown on a current collector in which a high electron conductivity in the nanowire direction allows for effective transport of electrons. Nonconductive 3D-nanostructured templates can also be used on which both the current collector and the electrode material are deposited as thin films.
Although the particle-based electrode can in principle also be considered as a 3D-structured electrode, a 3D-structured electrode is defined in this work as an electrode with not just a decrease in feature size (to alleviate problems with ionic conductivity or volume expansion), but also with a structure that allows for easy transport of the electrons and Li\(^+\) ions. For 3D-structured electrodes the area in contact with the electrolyte is high and anode or cathode materials should be in a safe voltage range to prevent electrolyte decomposition, similar to particle-based electrodes. In other cases a protective layer is needed. For instance, an Si nanowire electrode suffers from excessive SEI formation.\(^{19}\)

The opportunities for ALD in this case lie also in the deposition of protective layers similar to the case of particle-based electrodes. For example, for Si thin films it has been shown that coating the Si with a solid-state electrolyte (i.e., LiPON) greatly increases the battery cycle-life and prevents excessive SEI formation.\(^{7,10,20}\) The electrode material itself and the current collector can also be deposited by ALD. An ALD-deposited current collector provides a solution in case the 3D-structured template used is not sufficiently conductive.

### C. 3D all-solid-state microbatteries

For microbatteries the challenge is to achieve a high energy density at small sizes. Packaging methods for liquid electrolytes do not scale well to small device sizes, and consequently the designs for microbatteries are typically fully solid state. Since also the electrolyte is a solid-state material, electrolyte decomposition issues are greatly reduced and the battery cycle-life is extended significantly. All-solid-state batteries consist of thin films that are limited in thickness due to the low ion and electron diffusion in the materials compared to batteries using liquid electrolyte. In this case, 3D structuring has the potential to increase storage capacity without deteriorating the power capability. 3D all-solid-state microbatteries can be considered either as the full-solid-state evolution from the 3D-structured electrode or as 3D structuring applied to planar thin-film batteries. A large variety of possible implementations of 3D all-solid-state microbatteries can be considered.\(^{5,6,21}\) These implementations could, for instance, be composed of interdigitated plates, of arrays of rods, or of a so-called sponge geometry, which is a more disordered 3D structure.\(^{5,6,21}\)

For maximum compatibility with microsystem technology, Notten \textit{et al.} proposed a System-in-Package (SiP) solution.\(^{7}\) In this solution, a 3D topology with a typical aspect ratio of 10 is etched into an Si substrate in which the battery stack is deposited. SiP provides a flexible and convenient way of integrating multiple functionalities in a single package. Besides energy storage, which is discussed in this work, other functionalities can be integrated in a single package in the so-called More-than-Moore approach (e.g., logic, sensors, communication, and energy scavenging). The preferred substrate for SiP is silicon, since silicon gives high compatibility between SiP solutions and the ability to use standard microsystem technologies.\(^{22}\) The concept proposed by Notten \textit{et al.} is depicted in Fig. 4. As the battery storage capacity scales with the battery area, 3D structuring using the depth of the substrate is used to greatly reduce the required footprint area on the substrate. Figure 4 also shows a cross section of a generalized battery configuration. In this stack, the electrolyte in the middle separates the electrodes (anode and cathode), which in turn are both connected to the electrical circuit by current collectors. The battery structure needs to be isolated from the environment with an encapsulation layer,\(^{23}\) and from the silicon substrate with an Li-diffusion-barrier layer. The choice between having the anode or the

![Fig. 3. (Color online) Schematic representation of a 3D-structured electrode. The structure allows for both easy transport of electrolyte via the open electrode structure and easy transport of electrons by means of, for instance, Al nanowires used as current collector. In this particular example the nanowires are coated with the active electrode material.](image)

![Fig. 4. (Color online) Schematic representation of a 3D all-solid-state microbattery. A 3D structure is etched in an Si substrate to increase the storage capacity per footprint area. The thin-film battery materials are deposited in the 3D structure to form the battery stack. The stack consists of current collectors (with barrier layers) as well as of top and bottom electrodes and solid electrolyte.](image)
cathode as the bottom electrode depends on the compatibility of the different processing steps to synthesize the stack (e.g., the maximum temperature allowed during the deposition of the individual layers).

Since all layers have to be deposited as thin films in 3D topologies, ALD is in principle a good candidate for all materials. In addition to the materials already discussed for the 3D-structured electrodes, the other materials that need to be deposited by ALD in this case are the solid-state electrolyte and also the current collector and the barrier layers (not considering the example in Sec. III B of using an inactive template). Furthermore, the deposition of encapsulation layers by ALD can be considered.

IV. ALD FOR BATTERY MATERIALS

A wide range of materials have been demonstrated by ALD. To deposit a certain material by ALD a combination of precursor and reactant leading to a self-limiting surface chemistry has to be found. Typically, ALD is a two-step process with the first step involving exposure of the surface to the vapor of a metalorganic or metal-halide precursor and in the second step exposure of the surface to a reactant. The reactant typically induces an exchange or removal of the ligands from the adsorbed precursor to obtain the desired material. A well-known example is the deposition of Al₂O₃ from AlMe₃ and H₂O. Material compounds for most of the elements in the periodic table have been deposited by ALD.²⁴,²⁵ Mostly, compounds containing two elements have been reported. However, in principle, ALD processes can be easily combined by alternating cycles for different materials to make more complex materials or film structures.

It is illustrative to address which materials that can potentially be applied in batteries are difficult to deposit by ALD. Single elements are typically quite difficult to deposit by ALD and for many of such materials no processes have been reported at all. Si, an interesting anode material,²⁶ is known to be very challenging by ALD. Typically, Cu, good ALD processes for this material.²⁷ No processes are known for carbon films are also missing, although some processes have been reported at all. Si, an interesting anode material,²⁷ is known to be very challenging by ALD. For Cu, good ALD processes are also missing, although some processes have been reported for this material.²⁸ No processes are known for carbon films such as graphite. On the other hand, polymer films and other organic compounds can be synthesized by molecular layer deposition (MLD). MLD is a kind of ALD equivalent for depositing organic films through self-limiting surface reactions.²⁹ For certain functionalities, the materials need to have a specific crystalline phase. To increase the range in material compositions, crystalline phases, and film properties attainable under the conditions allowed by the application, energy-enhanced ALD processes such as plasma-assisted ALD can be used.³⁰ In plasma-assisted ALD the second step in the process involves a plasma as reactant which extends the range of operating conditions that can be used for deposition.

The ability to conformally coat complex 3D structures such as collections of particles or nanowires is one of the strengths of ALD. Conformal deposition can be achieved for (nearly) ideal ALD chemistries as long as the precursor and reactant exposures are high enough. The question whether the time to reach saturation of the ALD reactions is practical depends on the precursor diffusion into the 3D structure and on the precursor and reactant surface chemistry. Conformal deposition can also be more difficult for plasma-assisted ALD processes.²⁹

Although the growth per cycle of ALD is on the order of 0.1 nm, cost-effective processes have been proven and ALD has been implemented and is being implemented in a variety of applications. To this end, batch and inline deposition tools are available. Although ALD is typically envisioned for very thin films (~10 nm), industrial use of thicker films (~1 μm) deposited in batch tools has been demonstrated.³⁰ Inline deposition tools using spatial ALD also have recently received a lot of attention and deposition rates of 1.2 nm/s have been demonstrated.³¹

In the following, candidate materials for application in Li-ion batteries are discussed as well as their ability to be deposited by ALD. A wide range of materials can be considered and several of them have been discussed by Oudenhoven et al. in a recent review on 3D all-solid-state microbatteries.²¹ The most interesting for ALD are those materials for which the ALD processes are relatively straightforward and which perform well at small thickness. Reports of materials deposited by ALD that have been tested in battery-related device structures will be discussed in Sec. V.

Protective layers: Al₂O₃ is often considered as a protective layer for electrode materials in contact with electrolyte. Protective layers can be used to reduce electrolyte decomposition on the surface of the electrode and dissolution of electrode material into the electrolyte. Protective layers should not react with Li in the potential range used and should be sufficiently conductive to Li⁺ ions. Extremely thin layers are sometimes applied (as will be shown in Sec. V), which indicates that the positive effect might not be because of a closed Al₂O₃ layer, but because of a change in the surface properties through surface engineering.

Current collectors: Current collectors and conductive barrier layers should not react with Li in the potential range used. Since Li can be highly mobile, a barrier layer can be required to prevent loss of Li from the battery structure through the current collector. For instance, a barrier layer can be required at the anode side where the electrochemical potential can cause dissolution of Li in the current collector as most metals allow dissolution of Li at low voltages (0 V versus Li/Li⁺). When a thin Cu film is used as anode current collector a protective overlayer is necessary to keep the Li in the battery stack.³² Thin sputtered TiN and TaN films have been shown to be both good current collectors and Li barriers.³³ Dissolution of Li into the current collector is not such a problem at the cathode side due to the higher voltage (>3 V versus Li/Li⁺), but here the current collector has to be especially stable against oxidation. Pt and other noble metals can be used, and also Al is often used for Li-ion batteries. The Al directly in contact with the cathode material oxidizes, which protects the Al from further oxidation. Cu and Al are difficult to deposit by ALD, but TiN, TaN, and Pt are quite common ALD materials.³⁴–³⁷

Electrode materials: Cathode materials are generally intercalation materials and contain Li when in the discharged
state (Li-ion batteries are generally produced in the discharged state). Li metal oxides and phosphates such as LiCoO$_2$ and LiFePO$_4$ are typically used. Recently, the first ALD processes of Li compounds were reported in the literature.$^{38,39}$ ALD of phosphate-containing materials has not been extensively investigated, but Putkonen et al. demonstrated the deposition of CaPO thin films by ALD.$^{40}$ Furthermore, an ALD process for LiFePO$_4$ was presented,$^{41}$ and an ALD process for LiCoO$_2$ was reported.$^{42}$

For the anode, mainly intercalation and conversion materials are of interest to be deposited by ALD. For intercalation materials, TiO$_2$ is a well-known candidate, and for conversion materials a wide range of metal oxides can be deposited by ALD. Single-element materials such as Si are difficult to deposit by ALD, making these materials, for which alloying is the storage mechanism, not a proper choice in this respect.

Typically, the thickness of the cathode and the anode layer differs considerably. The thicknesses of these two layers in a battery are matched to have the same capacity, i.e., during charging the anode has to take up all the Li released by the cathode and vice versa during discharging. The large difference in thickness is caused by the generally much lower storage capacity of cathode materials. LiCoO$_2$ can, for instance, reversibly (de)insert 0.5 Li per LiCoO$_2$ unit while Si has been reported to be able to reversibly (de)insert 3.75 Li per Si atom.$^{20}$ This difference in capacity density is also reflected in the volumetric storage capacities of 706 and 8303 mA h cm$^{-3}$ for LiCoO$_2$ and Si, respectively.$^{10,43}$

Solid-state electrolytes: The electrolyte has to be sufficiently thick to provide enough electrical insulation, while it should be sufficiently thin to provide acceptable conduction of Li$^+$ ions. Typically in thin-film batteries, thicknesses in the range of 500–2000 nm are used for the electrolyte.$^{7,44}$ However, the usage of thin (10–20 nm poly(p-phenylene oxide) films as electrolyte in porous 3D batteries has been demonstrated.$^6$ In thin-film capacitors, energy is stored by storing charge in conductive films separated by a thin insulating layer. Dielectric layers with a thickness in the order of 10 nm are sufficient to prevent short-circuiting in these capacitors.$^{45}$ This suggests that, in principle, also much thinner inorganic electrolyte layers should be possible, while maintaining sufficient insulation. Also, nanolaminate techniques such as those used in thin-film capacitor structures$^{46}$ could be used to combine sufficient ionic conductivity with good insulating properties. Note that, since the electrolyte has a large area due to the 3D structuring, the current density will be lower and, therefore, the requirements on the ionic conductivity will be lower as well.$^{51,47,48}$ Similarly, the demands on the electrical insulating properties become more stringent, as the large area can lead to an unacceptably high electron current through the electrolyte even when the electron conductivity per unit area is relatively low, which would lead to a high self-discharge.

For the main candidates for the electrolyte material, i.e., Li$_3$PO$_4$ and LiPON, the deposition of the phosphate component (PO$_4$) can be a challenge, as already mentioned. Nevertheless, an ALD process for Li$_3$PO$_4$ has been recently presented.$^{49}$ LiLaTiO$_3$ (LLT) also has been suggested as an electrolyte material, but this material has been reported to have high electrical conductivity, causing short-circuit issues.$^{50}$ Because of the small thickness envisioned for ALD deposited films an extremely low electrical conductivity is required. Therefore, LiLaTiO$_3$ deposited by ALD is probably not suitable as an electrolyte unless the material properties can be greatly improved. To this end, LiAlO$_2$ has been suggested as a possible interlayer between the anode and the electrolyte. LiAlO$_2$ is a known electrolyte material and has a low ionic conductivity.$^{51}$ An ALD process for Li,Al,Si,O, a very similar compound, has also been presented recently.$^{52}$

V. APPLICATION AND IMPLEMENTATION

To date, not many ALD deposited materials have been tested in Li-ion battery related device structures (e.g., electrochemical half cells). In the following, only the ALD materials tested in such structures are discussed. The discussions are grouped per battery concept. An overview of the materials is given in Table I. Note that although a particular material might be tested with a certain battery concept in mind, the results can often be generalized to other battery concepts.

A. Particle-based electrodes

The benefit of ALD deposited films was for the first time demonstrated for TiN coatings on Li$_4$Ti$_5$O$_12$ powder aimed at improving interparticle electrical conductivity.$^{53}$ Although TiN is a known barrier material, the film in this study was reported to be noncontinuous and only 6 nm thick; consequently the film does not cause problems with Li$^+$-ion diffusion. Recently, there has been a lot of interest in coating cathode and anode particles by ALD with a protective layer of Al$_2$O$_3$. Improved stability by depositing Al$_2$O$_3$ on LiCoO$_2$ particles has been demonstrated,$^{54-56}$ as well as for depositing Al$_2$O$_3$ on the cathode material LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$.$^{57}$ Depositing Al$_2$O$_3$ on natural graphite particles was also shown to improve the cycle-life.$^{58}$ Figure 5(a) shows the effect of Al$_2$O$_3$ coatings by ALD on the electrochemical performance of natural graphite (NG) composite electrodes.$^{58}$ Three electrodes were coated by five ALD cycles of AlMe$_3$ (TMA) and H$_2$O and their performance was compared with the performance of a bare electrode. The ALD cycles were either carried out directly on the electrode, directly on the electrode after an NO$_2$ treatment to improve surface nucleation, or on the NG powder before composing the electrode. Both electrodes which were coated by ALD after being composed show a clear improvement. The electrode where the particles were coated beforehand shows, however, an accelerated decrease in capacity resulting in a poor cycle-life. Figure 5(b) shows a schematic representation of electron transport for the NG composite electrodes coated by ALD. Due to the poor electrical conductivity of Al$_2$O$_3$, direct coating of the composed electrodes gives better performance than coating the particles beforehand. In the latter case, the electrode particles are basically isolated from the conductive additives by the Al$_2$O$_3$ film. Depositing Al$_2$O$_3$ on MoO$_3$ particles was also shown to improve the cycle-life.$^{59}$ This improvement is remarkable because MoO$_3$ is a conversion type material.
with high volume expansion during charging and therefore the Al₂O₃ coating is expected to break apart. The improvement is expected to be mostly caused by a stronger attachment of the MoO₃ particles to the conductive additives due to the coating which reduces detachment during the volume changes. Similarly, anodes composed of Fe₃O₄ nanoparticles confined in mesocellular carbon foam showed improved cycle-life after coating by Al₂O₃.₆₀

Besides using ALD for conductive or protective layers, ALD of Al₂O₃ has also been used to investigate the voltage hysteresis for SiCO as anode material in which a small upward shift in voltage by 50 mV was observed during charging.₆¹ ALD has furthermore been demonstrated to assist in making composite nanoparticles. Electrodes were made composed of nanoparticles of a metal-oxide graphene nanosheet composite. The metal-oxide graphene nanosheet composite was made by using an SnO₂ ALD process on graphene nanosheet powder.₆²

B. 3D-structured electrodes

To date, only ALD of TiO₂ has been demonstrated for the 3D-structured electrode concept of Li-ion batteries. TiO₂ is used as anode electrode material and has the advantage of having a relatively high redox potential, alleviating problems with electrolyte decomposition. Kim et al. reported on the deposition of a 15 nm TiO₂ film by ALD on a peptide assembly. The peptide assembly was removed by a high temperature step at 400°C, which also crystallized the TiO₂ to the anatase phase.₆₃ The resulting hollow TiO₂ nanonetwork had a higher storage capacity and rate capability than TiO₂ nanopowder electrodes as indicated in Fig. 6. The higher storage was attributed to a nanosize effect. Bulk anatase-phase TiO₂ can host up to 0.5 Li per formula unit while for anatase-phase TiO₂ nanoparticles (<40 nm) up to 0.8 Li can be stored per formula unit.₁₅ The nanosize effect is most prominent in the TiO₂ nanonetwork. The higher rate capability, as indicated by the high capacity at high C rates, can be explained by the network, which enhances electron transport, and the high surface area with low film thickness, which enhances Li⁺-ion transport. Similarly, Gerasopoulos et al. coated Ni plated biological scaffolds with TiO₂ using ALD,₆₄ and Cheah et al. coated Al nanowires with TiO₂ using ALD.₆₅ They both found a high capacity and high rate capability.

Electrode materials with electrochemical potentials at which electrolyte decomposition would be a problem can also be considered. To allow for the use of such materials, the materials have to be coated with an ALD electrolyte or protective layer, as has been demonstrated for particle-based electrodes of MoO₃ particles coated with Al₂O₃ described in the previous section.

<table>
<thead>
<tr>
<th>Battery concept</th>
<th>ALD deposited material</th>
<th>Purpose</th>
<th>Type of Material</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>Particle based</td>
<td>Al₂O₃</td>
<td>Protective layer</td>
<td>Passive/Electrolyte</td>
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<td></td>
<td>TiN</td>
<td>Conductive layer</td>
<td>Passive</td>
<td>53</td>
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<tr>
<td>3D structured</td>
<td>TiO₂</td>
<td>Anode</td>
<td>Intercalation</td>
<td>63–65</td>
</tr>
<tr>
<td></td>
<td>V₂O₅</td>
<td>Cathode/anode</td>
<td>Intercalation</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>LiCoO₂</td>
<td>Cathode</td>
<td>Intercalation</td>
<td>42</td>
</tr>
<tr>
<td>3D all-solid-state microbattery</td>
<td>Co₃O₄</td>
<td>Anode</td>
<td>Conversion</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>TiN and TaN</td>
<td>Barrier/layer/anode current collector</td>
<td>Passive</td>
<td>20, 35, 67</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>Cathode current collector</td>
<td>Passive</td>
<td>68</td>
</tr>
</tbody>
</table>

FIG. 5. (Color online) (a) Comparison of the electrochemical performance of several prepared NG composite electrodes. Three electrodes coated with five ALD cycles of AlMe₃ (TMA) and H₂O were compared with a bare electrode. The ALD cycles were either performed directly on the electrode, directly on the electrode after an NO₂ treatment, or on the NG powder before composing the electrode. Galvanostatic charge–discharge cycles were performed at 50°C between 0.005 and 1.500 V at 0.1 C rate for the first two cycles and at 0.5 C rate for the subsequent cycles. A C rate of 1 C indicates that the full electrode is (dis)charged in 1 h, for a C rate of 2 C (dis)charging takes 0.5 h. (b) Schematic representation of electron transport in NG composite electrodes coated by ALD. The NG powder was either coated before composing the electrode or after composing the electrode. Reprinted from Ref. 58 with permission from John Wiley and Sons.
C. 3D all-solid-state microbatteries

For this battery concept mostly passive materials have been investigated so far, namely TiN as anode current collector and Li-diffusion-barrier layer, and Pt as cathode current collector. Remote plasma ALD was used to deposit TiN and TaN. It was found that particularly ALD TiN showed excellent Li-diffusion-barrier properties. The Li-diffusion-barrier properties of the ALD TiN were clearly better than those for sputtered TiN. The latter had a weaker and different preferential growth orientation than the ALD material, i.e., (111) vs (200), respectively. Although a strong orientation is often related to columnar growth, which can provide fast diffusion paths, this difference in orientation direction possibly explains the difference in performance, since the (200) orientation plane has a lower surface energy than the (111) orientation plane. A long-term test revealed that a TiN barrier layer with 20 nm thickness can survive more than 6000 charge–discharge cycles, demonstrating its excellent barrier properties.

ALD TiN deposited in pores with an aspect ratio of 20 was shown to result in a working barrier layer and current collector. In this study, pores with various aspect ratios were coated by ALD TiN and LPCVD Si as anode material and cycled electrochemically afterwards. Figure 7 shows SEM images of pores with an aspect ratio of 10 [Fig. 7(a)] and 20 [Fig. 7(b)]. Although the deposition was not fully conformal, i.e., 67% conformality for aspect ratio 10 and 33% conformality for aspect ratio 20, the TiN film was thick enough to serve as Li barrier and current collector.

Another passive material tested for microbatteries and deposited by ALD is Pt. In 3D microbatteries, the Pt current collector will be either deposited on the cathode layer when the cathode is the top electrode or on the substrate material when the cathode is the bottom electrode (Fig. 4). Only the case where the cathode serves as bottom electrode was investigated and in this case the adhesion of the Pt, which is generally poor, was significantly improved using an H2 plasma treatment and a TiO2 adhesion layer. This procedure resulted in good adhesion of the Pt as the samples passed multiple scotch-tape tests. Furthermore, the conformality was shown to be sufficient for application in the 3D all-solid-state microbatteries.

Very few ALD deposited active materials have been demonstrated for 3D microbatteries so far. Thin films of ALD V2O5 were shown to be good cathode materials. V2O5 films annealed at 400°C were reported to offer excellent electrochemical stability and cyclability for Li+-ion (de)insertion between 3 and 3.8 V. Furthermore, it was demonstrated that ALD deposited Co3O4 is a good thin-film anode candidate material. A good cycle-life and a high capacity were obtained in electrochemical tests. Recently, Donders et al. demonstrated electrochemical activity for ALD deposited LiCoO2. Although deposition by ALD of other Li-containing materials has been reported (see Sec. IV), LiCoO2 is, to the best of our knowledge, the first active Li-containing material that has been tested in an Li-ion battery related device structure. Such tests, for the current and an extended set of ALD materials, will be essential to fully assess the possibilities of using ALD for Li-ion batteries.
VI. CONCLUSION

Nanostructuring of battery materials is very promising in terms of improving Li-ion batteries as is required for many emerging battery applications. To enable or facilitate nanostructuring, ALD can be used for a variety of battery concepts. In this work, three battery concepts were described, i.e., particle-based, 3D-structured, and 3D all-solid-state microbattery. Demonstrator experiments for all three battery concepts in which ALD was used were reported on. Despite various challenges, the possibility of depositing lithium and phosphate compounds together with the wide range of other compounds that can be synthesized by ALD should enable an almost all-ALD-deposited battery. Moreover, this wide range of materials together with the demonstrator experiments carried out express the large potential ALD has in improving battery structures for future applications.

ACKNOWLEDGMENT

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