Atomic layer deposited coatings to significantly stabilize anodes for Li ion batteries: effects of coating thickness and the size of anode particles†

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A study of the effect of thickness of alumina coating on the electrochemical performances of various sizes of SnO2 electrodes has been systematically studied in this paper. It is found that the different volume changes in various sizes of SnO2 electrodes can be suppressed by optimized thickness of Al2O3 coating layers, with a range from less than 1 nm to up to 3 nm deposited by atomic layer deposition (ALD), which have significant impact on the electrochemical behaviour of the composites. The well-defined and optimized Al2O3 layer could not only relieve mechanical degradation and improve cycling stability, but also form an artificial solid electrolyte interphase (SEI) layer to prevent the chemical reaction between SnO2 and the electrolyte, leading to improved electrochemical performances compared with bare SnO2 electrodes.

Introduction

With the demand for alternative energy sources to replace conventional fossil fuels, lithium ion batteries (LIB) have been widely studied in recent years and are regarded as some of the most promising candidates.1,2 More and more interest in LIB is focused on enhancing the lithium storage capability to satisfy the requirements of large-scale applications, such as electrical grids, hybrid electrical vehicles and full electrical vehicles.3,4 The state-of-the-art LIB has limitations including safety concerns, high cost and low energy density. Such issues could be overcome by exploiting new types of electrode materials and attempting various electrode composites.5–8

Much research has concentrated on Sn-based anodes, originating from its attractive features including large reserves, environmental friendliness, low operating potential level and high lithium storage capability, which is more than twice of that of commercial graphite (e.g. 784 mA h g–1 for SnO2, 992 mA h g–1 for Sn).9,10 However, starting from the work of Idota,11 more than a decade of research effort has been devoted to improving the cycling stability that remains hampered by volume variation (>300%) and the accompanying serious pulverization of electrodes, the undesired accumulation of a thick solid electrolyte interphase (SEI) layer, and the falling off of Sn-based materials. Among the approaches used to overcome these challenges, designing nanostructured Sn-based composites is regarded as one of the most effective strategies. Various Sn-based nanostructures and related composites, including tubular SnO2/C nanotubes,12 SnO2 nanosheets,13–15 hollow SnO2,16–18 and SnO2/C nanostructures,19 SnO2 nanowire/C arrays,20 SnO2 nanowire/C arrays,20 SnO2/graphene,21 Sn/graphene,22 SnO2/Co3O4/C,23 and SnO2/SiC/graphene nanocomposites,24 have been proposed and improved long life cycling and rate performances have been obtained. However, nanostructured electrodes possess a large amount of irreversible SEI due to the large contact area with electrolyte, resulting in low initial coulombic efficiency. Also, the mechanical and chemical degradation of the SEI will cause a vicious cycle, resulting in the depletion of the electrolyte and the waste of electrodes.

Surface modification of electrodes, especially surface coating on active materials, has been proved as an effective route to stabilize the SEI layer. Moreover, it could maintain the mechanical integrity of the whole electrode. A desired coating layer should be ionically conductive to facilitate charge transfer, while being mechanically and electrochemically stable to continuously prohibit the direct contact between electrolyte and electrodes. Meanwhile, the coating layer should be controlled in a limited amount to maximize the whole capacity of the composites. Recently, atomic layer deposition (ALD) has attracted great interest as a novel technique and a suitable
approach for application in LIB because of its excellent capability to realize conformal coating of thin films in the scale of atomic layers.22 The interest for LIB applications in our group is using ALD to synthesize various coatings23 on cathodes and anodes, synthesize anode materials24,25 and solid-state electrolytes. Work from other groups has also demonstrated that enhanced electrochemical performance was achieved using ALD coatings of metal oxides for cathodes, such as LiCoO2,26,29 LiNi0.5Mn1.5O4,30,31 and LiMn2O4.32–34 Dillon and coworkers demonstrated the success of MoO3 electrodes with an Al2O3 coating.35 Xiao et al. and Huang et al. reported the multifunctional effect of Al2O3 on Si thin film and patterned Si electrodes with improved current efficiency. Jung et al. found that a whole battery (separator, cathode and anode) with Al2O3 coating could endure extremely severe conditions, such as high voltage over 4.5 V.36 However, to the best of our knowledge, few studies have been focused on ALD coatings on promising SnO2-based anodes. Herein, we report a systematic study of the effect of the thickness of Al2O3 coating on the electrochemical behaviours of SnO2 electrodes. To set up a simple but detailed model, electrodes composed of SnO2 with three different sizes were chosen as references and compared with the Al2O3 coated electrodes. It was found that a well-defined and optimized Al2O3 coating could mitigate the mechanical and chemical degradation of the SEI layer and the electrodes, leading to improved electrochemical behaviour compared with pure SnO2 electrodes.

**Experimental methods**

**Synthesis of SnO2 nanoparticles**

In a typical synthesis of SnO2 nanoparticles, 2 mmol SnCl4 was dissolved in 10 mL water and vigorously stirred for 30 min to obtain a clear solution. Then the transparent solution was transferred to a 20 mL high pressure microwave-assisted Teflon-lined autoclave (Anton Paar Synthesos 3000). The solution was subsequently heated to 120 °C and kept at this temperature for 20 min. After cooling to room temperature, the obtained samples were rinsed with large amounts of distilled water and ethanol. The as-obtained products were collected after a final drying at 100 °C overnight for use in the next step. To get three different sizes of SnO2 nanoparticles, the products were annealed in a tube furnace at different temperatures for 2 h (400 °C for SnO2-A, 600 °C for SnO2-B and 900 °C for SnO2-C, respectively).

**Synthesis of ALD-Al2O3 coated SnO2 electrodes**

The working electrodes were composed of the SnO2 nanomaterials (SnO2-A, SnO2-B or SnO2-C), conductive carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 8 : 1 : 1. The slurry obtained with N-methylpyrrolidinone (NMP) solvent was uniformly cast on a copper foil and dried overnight at 120 °C under vacuum. The as-prepared electrodes were ready for ALD coating without further treatment. ALD-Al2O3 was coated directly on the SnO2 electrodes in an ALD reactor (Savannah 100, Cambridge Nanotechnology Inc., USA) using trimethylaluminum (TMA) as the Al precursor and H2O as the oxidizer. The deposition temperature was set at 100 °C. Different numbers of ALD cycles (2, 5 and 20 cycles) were used to get different thicknesses of coating layer. The coated electrodes were applied for LIB testing without further treatment.

**Characterization**

Products were characterized by X-ray diffraction (XRD, Rigaku RU-200BVH with a Co Kz source (λ = 1.7892 Å)), field-emission scanning electron microscopy (FE-SEM, Hitachi 4800S), transmission electron microscopy (TEM, Hitachi H-7000), high-resolution transmission electron microscopy (HRTEM, JEOL 2010 FESEM microscope), and energy dispersive spectroscopy (EDX). X-ray absorption near edge structure (XANES) experiments on the Al K edge and the Al L3,2 edge were conducted on the undulator Spherical Grating Monochromator (SGM) beamline and the variable line spacing plane grating monochromator (VLS PGM) beamline at the Canadian Light Source (CLS), located at the University of Saskatchewan in Saskatoon. Sn K edge XANES and extended X-ray absorption fine structure (EXAFS) data were obtained at the X-ray Science Division (XSD)/Pacific Northwest Consortium (PNC) at Sector 20 of the Advanced Photon Source located in the Argonne National Laboratory, and were recorded in fluorescence mode.

**Electrochemical measurements**

The electrochemical experiments were conducted using two electrode coin cells (2032) using pure lithium metal sheets as the counter electrode and polypropylene film as the separator assembled inside an argon-filled glove box (O2 < 1 ppm). The electrolyte was 1.0 M LiPF6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) solvent (1 : 1 in volume). The profiles of galvanostatic charging and discharging curves were collected on a computer controlled Arbin BT-2000 battery tester system with a cut-off voltage window of 0.01 to 3 V (vs. Li+/ Li). Cyclic voltammetry (CV) measurements were conducted on an electrochemical workstation (Potentiostat/Galvanostat/EIS (VMP3)) at a scanning rate of 0.1 mV s⁻¹ in a voltage range of 0.01–3.0 V (vs. Li+/Li). Electrochemical impedance spectroscopy (EIS) measurements were conducted by applying an AC voltage of 5 mV amplitude in the frequency range from 0.01 to 100 kHz at 0.7 V of the 10th discharge cycle.

**Results and discussion**

The SnO2 nanoparticles were synthesized by a microwave-assisted hydrothermal method through the hydrolysis of SnCl4 in aqueous solution at 120 °C for 20 min, followed by annealing at a selected temperature in air for 2 h. For distinction, the samples are denoted as SnO2-A (annealed at 400 °C), SnO2-B (annealed at 600 °C) and SnO2-C (annealed at 900 °C). Then, an ALD coating of Al2O3 was directly applied on the electrodes composed of the SnO2 nanomaterials. Al2O3 layers with different thicknesses were obtained by alternate pulses of Al(CH3)3 and water with 2, 5 and 20 ALD cycles at 100 °C, in a Savannah 100 ALD system. The Al2O3-coated SnO2 electrodes...
thus obtained were used without further treatment and are henceforth denoted as $x$-SnO$_2$-A, $x$-SnO$_2$-B and $x$-SnO$_2$-C ($x = 2, 5, 20$ for 2, 5 and 20 ALD cycles, respectively).

Fig. 1a compares the XRD patterns of different sized SnO$_2$ with and without Al$_2$O$_3$ coating, in which all the intense peaks match well with those of rutile SnO$_2$ (JCPDS no: 41-1445), indicating that crystallized SnO$_2$ is successfully synthesized without detectable impurities. Further closer examination shows that the XRD pattern of SnO$_2$-C is stronger and sharper than those of SnO$_2$-B and SnO$_2$-A, indicating that the grain size in this sample is bigger. Based on calculation using Scherrer’s equation from the strongest peak, average particle sizes of 4.1, 8.8 and 25.8 nm are obtained for SnO$_2$-A, SnO$_2$-B and SnO$_2$-C, respectively. It should be noted that no peaks for the Al$_2$O$_3$ phase were observed in any of the Al$_2$O$_3$-coated SnO$_2$ samples, which is due to its amorphous structure, considering that the ALD deposited Al$_2$O$_3$ was obtained at 100 °C. Fig. S1a† displays the energy dispersive X-ray (EDX) spectrum of 20-SnO$_2$-C. The appearance of the Al signal conclusively illustrates that Al element is successfully introduced into SnO$_2$ composites. To identify the chemical states of Al, X-ray absorption near edge structure (XANES) was conducted at the Al K edge for the 20-SnO$_2$-C electrode. As depicted in Fig. 1b, the Al K edge spectrum of the 20-SnO$_2$-C electrode is similar to that of standard $x$-Al$_2$O$_3$, indicating the formation of Al$_2$O$_3$ after the ALD process. Compared with standard Al$_2$O$_3$, which exhibits two resolved peaks centered at 1567 and 1571 eV, the spectrum of 20-SnO$_2$-C shows fewer features, with only one broad peak located at 1570 eV, confirming its amorphous state. The XANES results demonstrate that amorphous Al$_2$O$_3$ was successfully coated on the SnO$_2$ anodes.

The morphologies of SnO$_2$ and the Al$_2$O$_3$ coating layer were examined using TEM, as shown in Fig. 2. Three different sizes of SnO$_2$ nanoparticles with average diameters of 3 nm, 10 nm and 25 nm are unambiguously shown in Fig. 2a–c, respectively. Fig. S1b to S1d† depict the SEM images of the different sized SnO$_2$, where spherical nanoparticles exhibit a uniform size distribution. Higher temperature annealing will facilitate the growth rate of crystallites, leading to a bigger particle size. Meanwhile, all particles show high crystallinity with clean surfaces, as demonstrated by the clear lattice fringes of the HRTEM images. The morphologies of the 2-SnO$_2$-C, 5-SnO$_2$-C and 20-SnO$_2$-C composites are shown in Fig. 2d–f. For 2-SnO$_2$-C, the Al$_2$O$_3$ coating layer is hard to observe because of the thickness (too thin), as it was formed by only 2 ALD cycles. After 5 cycles, it is evident that a conformal Al$_2$O$_3$ layer is successfully coated on the surface of the SnO$_2$ particles, which presents a distinct contrast under electron spectroscopy compared to that of the crystallized SnO$_2$. With the increase of the number of ALD cycles from 5 to 20, the thickness of the Al$_2$O$_3$ layer increased from ~0.8 nm to ~3.1 nm, illustrating that the thickness of Al$_2$O$_3$ could be precisely tuned by the number of ALD cycles. The Al$_2$O$_3$ shell displays no crystalline features in either sample, which is consistent with the XANES result. A uniform Al$_2$O$_3$ coating layer with similar thickness could also be found for 20-SnO$_2$-A and 20-SnO$_2$-B electrodes, as revealed in Fig. S2.† EDX mapping (Fig. S3†) of 20-SnO$_2$-A further confirms the homogeneous distribution of Al element, while the carbon signal comes from the conductive carbon black applied for preparation of the electrodes. Al$_2$O$_3$ could be homogeneously deposited on different sized SnO$_2$ electrodes using the ALD technique, which is critical for optimal electrochemical behaviour.
The electrochemical performances of the obtained Al₂O₃-coated electrodes and their uncoated counterparts are compared in Fig. 3. Cyclic performances were measured in a voltage window from 0.01 to 3 V with a current density of 50 mA g⁻¹. The rate performances were recorded at various current densities of 50 up to 1000 mA g⁻¹, and then reversed back to 50 mA g⁻¹. As presented in Fig. 3a and b, SnO₂-A delivers an initial discharge capacity of 1951 mA h g⁻¹ and stabilizes from the 20th cycle, retaining 530 mA h g⁻¹ in the 60th cycle. It should be noted that since the particle size of SnO₂-A is small enough (3 nm) and below the critical size, the stress and strain caused by volume change is not serious and thus stable discharge and charge capacities were obtained. For the Al₂O₃-coated samples with various numbers of ALD coating cycles, all samples still exhibit stable cycling performance, but their specific capacities are obviously different. The 2-SnO₂-A and 5-SnO₂-A samples exhibit increased capacities of 883 mA h g⁻¹ and 612 mA h g⁻¹ in the 60th cycle, respectively, while the 20-cycle-coated sample maintains a decreased capacity of 420 mA h g⁻¹. Noting that the Al₂O₃ layer is thin but conformally coated on SnO₂ in 2-SnO₂-A and 5-SnO₂-A, the coated Al₂O₃ could effectively inhibit the direct contact between SnO₂ and the electrolyte, reducing the amount of SEI which is unstable and easily degraded mechanically, and avoiding the consumption of active materials thus leading to increased capacities. For 20-SnO₂-A, the coating thickness is comparable to the size of the SnO₂ particles, as depicted in Fig. S2a. Since bare electrodes already display a steady cycling performance, a thicker Al₂O₃ coating layer could only result in a lower capacity further formation of a large amount of SEI, but more importantly, it can effectively absorb the strain and stress, providing a cushioning effect. For the 10 nm sized SnO₂-B, the 5 cycle ALD coating layer is not robust enough to endure the expansion/contraction of SnO₂-B during cycling very well. Thus 2-SnO₂-B shows poorer cycling performance than 5-SnO₂-B and 20-SnO₂-B. Similar phenomena could also be observed for the rate performances of different ALD coated electrodes, where the 2-SnO₂-B sample also exhibits fast decay of performance at high rates. In contrast, for the 5-SnO₂-B and 20-SnO₂-B composites, the coating layer could not only prevent the formation of a large amount of SEI, but more importantly, it can effectively absorb the strain and stress, providing a cushioning effect. For the pure SnO₂-C electrode, indicating that the coating layer from 2 or 5 cycles of ALD is not robust enough to endure the expansion/contraction of SnO₂-C during prolonged cycling. Similarly, the rate performance profiles further confirmed the increased stabilities for ALD-coated samples due to the protection from the outer Al₂O₃ layer. Fig. S5† presents the first three CV curves of SnO₂-C and 20-SnO₂-C. The shape of the CV curves for the coated electrodes is quite similar to that for the pure SnO₂-C electrode, indicating that the coating layer has no effect on the reaction mechanism of SnO₂ with lithium. The reduction peak at 0.78 V can be attributed to Li insertion into SnO₂, accompanied by the phase transformation of SnO₂ to Sn and Li₂O. The second pronounced reduction peak at

![Image](49x99 to 285x355)

Fig. 3 (a, c, and e) Cycling performances (at 50 mA g⁻¹) and (b, d, and f) rate performances (at 50 mA g⁻¹ to 1000 mA g⁻¹) of Al₂O₃-coated and non-coated SnO₂ samples: (a and b) SnO₂-A series; (c and d) SnO₂-B series; (e and f) SnO₂-C series.
around 0.25 V can be ascribed to the alloying of lithium with Sn to form Li$_x$Sn.

For the anodic scan, the peaks located at ~0.52 V correspond to the dealloying of Li$_x$Sn. It can be seen that for the 20-SnO$_2$-C sample, the oxidation peaks at 0.53 V decreased less than those of the pure SnO$_2$-C electrode, indicating the improved stability due to the coating layer. Xiao$^{*}$ et al. also reported that Al$_2$O$_3$ could react with lithium ions and the electrolyte to form an artificial solid electrolyte interphase layer, thus improving the ionic conductivity, which is favourable for high rate performance and enhanced current efficiency. As shown in Fig. S6,$^{+}$ compared with the uncoated SnO$_2$ samples, all Al$_2$O$_3$-coated SnO$_2$ samples exhibit improved current efficiency, especially in the first ten cycles, benefitting from the Al$_2$O$_3$ layer which forms an artificial ionically conductive SEI layer and prevents the mechanical and electrochemical degradation of the electrodes. The thickest coating exhibits the best coulombic efficiency due to its more robust framework and highly ionic conductive channels. Fig. S7$^{+}$ exhibits the electrochemical impedance spectroscopy for pure SnO$_2$-C and 20-SnO$_2$-C electrodes, conducted at 0.7 V in the 10th discharge cycle. It is evident that the diameter of the semicircle for 20-SnO$_2$-C is much smaller compared with that of pure SnO$_2$ upon cycling, indicating the lower impedance value due to the ALD-alumina coating. The enhanced ionic conductivity in the composites should be attributed to the artificial ionically conductive SEI layer mentioned above, which facilitates Li$^+$ alloying and dealloying into the anodes.

In order to examine the morphology evolution of the SnO$_2$ particles after cycling, HRTEM was performed, as shown in Fig. 4. For the pure SnO$_2$-A electrode shown in Fig. 4a, patches of blurry SEI film can be observed, as indicated by the arrows. Some crystallites can also be found, however, the size of the particles became irregular due to pulverization and they tend to aggregate to form bigger particles (as indicated by the circles). It is believed that the pulverization of SnO$_2$ will produce new fresh surface, which leads upon contact with the electrolyte to the formation of more and more SEI (marked by arrows) and consumption of the active materials. Conversely, after cycling, the 2-SnO$_2$-A electrode still maintains its original morphology without obvious change of particle size, as depicted in Fig. 4b. A careful examination illustrates that a thin layer appeared on the outside of the nanoparticles (as depicted by the dotted lines), which is absent in the original 2-SnO$_2$-A particles before cycling. The thin layer seen here should be ascribed to the artificial SEI layer formed by the reaction of Al$_2$O$_3$ with the electrolyte or lithium ions.$^{*}$ This artificial SEI layer is ionically conductive and could mitigate the pulverization of the SnO$_2$ core, inhibit the formation of undesired SEI between SnO$_2$ and the electrolyte and result in excellent electrochemical behavior. Similar to that reported recently by Hu et al.,$^{*}$ improved cycling behavior and safety are also realized through the reduction of SEI thickness by using high concentration electrolyte. For the bare SnO$_2$-C electrode after cycling, the SnO$_2$ particles were pulverized into small particles without crystalline features, as shown in Fig. 4c. Also, a thick SEI film of around 6.8 nm accumulated at the surface of small particles (as indicated by the arrow) through the reaction of the electrolyte with the continuously emerging fresh surface of SnO$_2$-C due to the pulverization. The unstable and non-uniformly covered SEI film could deteriorate the cycling performances of the electrodes. In contrast, for the cycled 20-SnO$_2$-C electrodes shown in Fig. 4d, the spherical particles are still well maintained under the protection of the outer shell which expands a little compared with that before cycling. The swollen shell may be due to the reaction of lithium ions or electrolyte with Al$_2$O$_3$ to form an ionically conductive SEI layer with an average thickness of around 3.8 nm. More importantly, the SnO$_2$ core without pulverization showed that the highly stable artificial SEI layer could effectively buffer the stress and strain upon cycling. Elemental mapping was further performed on the 20-SnO$_2$-C electrode after 60 cycles, as shown in Fig. S8.$^+$ The distribution of Al is still homogeneous in the electrode after cycling, along with the F signal, illustrating that the artificial SEI is tightly attached to the inside core and the integrity of the electrode is well maintained. Fig. 4e shows the schematic representation of ALD-coated and bare SnO$_2$ electrodes during cycling, where the coating layer could form an artificial SEI layer to effectively inhibit the detrimental reaction between SnO$_2$ and the electrolyte. As a result, improved cycling performance and rate performances were obtained for the optimal ALD-coated SnO$_2$ electrodes.

![Figure 4](image-url)
To reveal the local chemistry environment variation of the SnO$_2$ electrodes behind their different electrochemical performances, Sn K edge XANES was performed on the 2 cycle ALD-coated and non-coated SnO$_2$-A electrodes before and after cycling. As shown in Fig. 5, it can be seen that the spectrum of 2-SnO$_2$-A overlapped well with that of pure SnO$_2$-A, illustrating that the deposition of Al$_2$O$_3$ did not affect the local symmetry and chemical states of SnO$_2$. After 60 cycles, the spectrum of the SnO$_2$-A electrodes became broader with a slight shift of the white line towards lower energy, indicating a more disordered structure with reduced valence states. More intriguingly, for 2-SnO$_2$-A after cycling, the line shape is identical to that of the 2-SnO$_2$-A, illustrating that the outer Al$_2$O$_3$ shell could effectively protect the integrity and crystallinity of the core SnO$_2$. Fig. 5b shows the Fourier transform magnitudes of the Sn K edge Extended X-ray Absorption Fine Structure (EXAFS) spectra. All four samples exhibit similar spectral features except for the different magnitudes, illustrating the different average coordination numbers of Sn and hence the disorder among them. It is found that the magnitude of the Sn-O nearest neighbour distance decreases a little after coating with Al$_2$O$_3$, indicating that the outer Al$_2$O$_3$ shell may affect the ordered arrangement of the SnO$_2$ particles. For bare SnO$_2$-A after cycling, the magnitudes decreased considerably, demonstrating an increase of the disorder inside the crystallite and a decrease of the crystallite size, which is in accordance with the HRTEM results. However, for 2-SnO$_2$-A after cycling, the decrease of magnitude is not significant, indicating that both the crystallinity and the size of the crystallites are well maintained by the coating layer.

We further conducted Al L$_{3,2}$ edge XANES experiments on the 20-SnO$_2$-C electrodes before and after cycling to reveal the electronic structure variation. XANES spectra of two major components, the LiAlO$_2$ and AlF$_3$ in the artificial SEI layer as reported by Xiao et al. are also given for comparison, as shown in Fig. 6. It can be clearly seen that after cycling, the Al L edge XANES for 20-SnO$_2$-C is quite different compared with that before cycling, as seen in the peak positions and intensities. The two features located at c and d correspond to the amorphous Al$_2$O$_3$, which is in accordance with our previous results, indicating a six-fold coordination. After cycling, the spectra became broader, with peak a shifted to lower energy, indicating a phase transition induced by the lithium and fluoride ions. Closer observation demonstrates that it shows similar features to that of LiAlO$_2$ in the first peak (a and a1) and mixed features of LiAlO$_2$ and AlF$_3$ in the following shoulder (b, b1, and b2). It should be noted that the Al L-edge spectrum (2p electrons to 3d or 3s) is sensitive to Al coordination number and the surrounding atoms. Also, the artificial SEI layer presented here is amorphous and quite thin (only a few nanometers), which leads to a broader and more irregular spectrum. Thus, XANES spectra provide spectroscopic evidence that an artificial SEI layer is formed after the lithiation/delithiation process, with a major composition of ionic conductive LiAlO$_2$ and AlF$_3$. The ALD-Al$_2$O$_3$ coating layer helps to maintain the size and structure of the SnO$_2$ electrodes and facilitates charge transfer at the interface, resulting in more stable electrochemical behaviour compared with the pristine electrodes.

**Conclusions**

In summary, a controlled Al$_2$O$_3$ layer has been successfully coated on different sizes of SnO$_2$ particles using the ALD technique. As demonstrated by the HRTEM results and the synchrotron radiation spectra, well-defined and optimized Al$_2$O$_3$ coating layers could maintain the integrity of the electrodes by suppressing the volume change to improve the cycling performances. It could also function as an artificial ionic conductive SEI layer and inhibit direct contact between SnO$_2$ and the electrolyte to increase the rate capability and the coulombic efficiency. This work opens up a path for studying the connection between the coating layer and the inner active electrodes, and will inspire future applications of the ALD technique in electrodes for lithium ion batteries.

**Notes and references**


![Fig. 5](image-url) (a) XANES of Sn K edge spectrum and (b) Fourier-transformed magnitudes of Sn K edge k$^2$-weighted EXAFS spectra for 2 cycle ALD-coated and bare SnO$_2$ electrodes, before and after cycling.

![Fig. 6](image-url) Al L$_{3,2}$-edge XANES of AlF$_3$, LiAlO$_2$ and the 20-SnO$_2$-C electrode before and after cycling.


