Article

Surface Passivation of MoO₃ Nanorods by Atomic Layer Deposition Towards High Rate Durable Li Ion Battery AnodesBilal Ahmed, Muhammad Shahid, D. H. Nagaraju, Dalaver
H. Anjum, Mohamed N. Hedhili, and Husam N. AlshareefACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.5b03395 • Publication Date (Web): 03 Jun 2015Downloaded from <http://pubs.acs.org> on June 8, 2015**Just Accepted**

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications
High quality. High impact.

ACS Applied Materials & Interfaces is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036
Published by American Chemical Society. Copyright © American Chemical Society.
However, no copyright claim is made to original U.S. Government works, or works
produced by employees of any Commonwealth realm Crown government in the course
of their duties.

Surface Passivation of MoO₃ Nanorods by Atomic Layer Deposition towards High Rate Durable Li Ion Battery Anodes

B. Ahmed, Muhammad Shahid, D. H. Nagaraju, D. H. Anjum , Mohamed N. Hedhili and H. N. Alshareef*

Materials Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955–6900, Saudi Arabia

* Corresponding author: husam.alshareef@kaust.edu.sa

Abstract

We demonstrate an effective strategy to overcome the degradation of MoO₃ nanorod anodes in Lithium (Li) ion batteries at high rate cycling. This is achieved by conformal nanoscale surface passivation of the MoO₃ nanorods by HfO₂ using atomic layer deposition (ALD). At high current density such as 1500 mA/g, the specific capacity of HfO₂ coated MoO₃ electrodes is 68% higher than bare MoO₃ electrodes after 50 charge/discharge cycles. After 50 charge/discharge cycles, HfO₂ coated MoO₃ electrodes exhibited specific capacity of 657 mAh/g, on the other hand, bare MoO₃ showed only 460 mAh/g. Furthermore, we observed that HfO₂ coated MoO₃ electrodes tend to stabilize faster than bare MoO₃ electrodes because nanoscale HfO₂ layer prevents structural degradation of MoO₃ nanorods. Additionally, the growth temperature of MoO₃ nanorods and the effect of HfO₂ layer thickness was studied and found to be important parameters for optimum battery performance. The growth temperature defines the microstructural features and HfO₂ layer thickness defines the diffusion coefficient of Li-ions through the passivation layer to the active material. Furthermore, *ex-situ* HRTEM, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and X-ray diffraction was carried out to explain the capacity retention mechanism after HfO₂ coating.

Keywords: MoO₃, Atomic layer deposition (ALD), Anode, Lithium ion battery, TEM

1. Introduction

Lithium ion batteries (LIBs) have been successfully commercialized in small power sources such as portable electronics and power tools because of their high energy density and stable cyclic performance.¹ Recently, LIBs are being extensively researched for large scale applications such as electric vehicles, hybrid vehicles and power backups, which require both high energy and high power densities. However, lower specific power density (the ability to charge/discharge at very high rates) hinders their application in large scale energy storage. Therefore, a great deal of research effort has been focused on development of LIBs with high energy and high power densities.

Graphite is most widely used anode material in commercially available LIBs but due to its low theoretical capacity (~ 372 mAh/g) it cannot meet the growing demand of high capacity energy storage system.² Thus, a lot of research effort has been made to discover new materials for Lithium (Li) storage with high capacity, rate capability, cycling stability and safety to replace the widely used graphitic anode material.

One-dimensional (1D) nanostructures such as nanowires, nanobelts and nanorods showed great promise in energy storage applications due to large surface-to-volume ratio which increases the electrode-electrolyte contact area.³⁻⁴ Furthermore, 1D materials act as efficient electron transport pathway and sustain volumetric expansion because of Li intercalation/deintercalation during charge/discharge process.⁵⁻⁶ Consequently, one dimensional LiMn_2O_4 ,⁵ V_2O_5 ,⁶ TiO_2 ,⁷ $\text{Li}_{0.88}[\text{Li}_{0.18}\text{Co}_{0.33}\text{Mn}_{0.49}]\text{O}_2$,⁸ $\text{Li}_{0.44}\text{MnO}_2$,⁹ Fe_3O_4 ,¹⁰ and $\text{Sn}_{78}\text{Ge}_{22}@\text{carbon}$ ¹¹ nanowires have shown improved rate performances in energy storage devices. Recently, a vast amount of research focus has been devoted on 1D nanostructured transition metal oxides (TMOs) because

of their unique morphology and high theoretical capacity.¹²⁻¹³ Among them, Molybdenum trioxide (MoO_3) is considered as an attractive anode material for LIBs because of its superior theoretical specific capacity ($\sim 1117 \text{ mAh/g}$).¹⁴ MoO_3 was investigated during the early stage of lithium battery research as Li^+ insertion compound because of its stable layered structure which can host intercalated Li^+ ions.¹⁵ In terms of crystal structure, MoO_3 exists in three different forms; orthorhombic ($\alpha\text{-MoO}_3$), monoclinic ($\beta\text{-MoO}_3$) and hexagonal (h-MoO_3). Thermodynamically, $\alpha\text{-MoO}_3$ is the most stable phase and its anisotropic layered structure makes it a suitable candidate for LIBs.¹⁵ The crystal structure of $\alpha\text{-MoO}_3$ can be explained as double layers in [010] direction and each layer consists of two sub-layers by sharing MoO_6 octahedrons along the [100] and [001] directions.¹⁶ The schematic illustration of unit cell and layered structure of $\alpha\text{-MoO}_3$ is given in Figure 1. However, as an anode material in Li ion batteries, the poor conductivity and large volumetric changes during charge/discharge process limit the application of MoO_3 in LIBs.¹⁷ It has been reported that volumetric expansion in metal oxides can be as high as 100– 250% and due to this drastic volumetric change during intercalation/deintercalation of Li^+ ions, MoO_3 shows poor cyclic stability and capacity fades quickly.¹⁸

The cyclic stability and electrochemical performance of LIBs can be improved by number of approaches. The most common approach is to optimize the nanostructure of active material such as conversion of bulk into nano sized powder, preparation of layered structure or synthesis of 1D morphologies such as nanorods, nanowires or nanobelts.¹⁹⁻²⁰ The deposition of a passivation layer at electrode/electrolyte interface to prevent structural degradation during charge/discharge process is another methodology.²¹ Mostly, surface passivation layers are deposited by sol–gel method²² or chemical vapor deposition technique,²³ however, these techniques lacks the control

over thickness, surface coverage and uniformity of coating. However, precise control over thickness is necessary to obtain optimum battery performance because Li^+ ions have to diffuse through the passivation layer and intercalate or react with active material. Moreover, these solution based methods involve mixing of electrode material with precursor followed by annealing at elevated temperature to form a coating layer. This post-annealing sometimes results in structural degradation of electrode material.

On other hand, a thin and conformal layer with excellent control on growth rate can be deposited by atomic layer deposition (ALD) which uses sequential self-limiting gas/solid reactions.²⁴⁻²⁵ The unique reaction mechanism of ALD offers exclusive advantages such as low temperature process, precise control over thickness and conformal coating even with high aspect ratio 3D structures.²⁵ In LIBs, ALD has been used to fabricate different electrode structures,²⁶⁻³⁶ solid state electrolyte³⁷⁻⁴¹ and modify electrode/electrolyte interface.^{18, 42-56} ALD coating on electrode/electrolyte interface aims to avoid undesirable interfacial reactions which occur between the electrode and liquid electrolyte during charge/discharge process. These interfacial reactions compromise the overall performance of LIBs in terms of cyclic stability and safety. For instance, HF generated on cathode side tends to consume the cathode material and results in poor cyclic performance.⁵⁷ On anode side, ALD coatings mainly deal with the problems arising from the SEI such as decomposition products of liquid electrolytes.⁵⁸ These problems become more consequential in anodes where large volumetric changes occur during charge/discharge process such as tin Oxide (SnO_2) and Silicon (Si).

The ALD layer at anode/electrolyte interface serves as an artificial layer which hinders the formation of SEI layer and improves specific capacity, cyclic performance and columbic efficiency.^{42-43, 50-51} Moreover, the problem of pulverization in different anode materials which

goes under large volumetric changes during charge/discharge process such as Si,⁴⁵⁻⁴⁹ SnO₂,⁵³ Fe₃O₄,⁵⁵ and ZnO⁵⁴ can be reduced by ALD surface coating. In published literature, ALD coating of Al₂O₃,^{18, 42, 44-46, 52-53, 55-56} TiO₂,^{43, 48-49, 54} ZrO₂,⁵¹ TiN^{47, 50} and HfO₂⁵⁹ on anode/electrolyte interface has been reported for different materials such as graphite,⁴²⁻⁴⁴ patterned Si,⁴⁵ Si nanowires,⁴⁷ Si nanotubes,⁴⁹ Si films,⁴⁶ Li₄Ti₅O₁₂,⁵⁰⁻⁵² SnO₂,^{53, 59} ZnO⁵⁴ and Fe₃O₄.⁵⁵ Besides coating material, growth temperature and layer thickness are the most important parameters in defining final device performance. Moreover, there are two approaches for ALD coating; coating on electrode material or coating on prepared electrode and it has been reported that later serves better in terms battery performance and improvement in anode/electrolyte interface.¹⁸ Furthermore, some reports focused to understand the mechanism of performance improvement due to ALD coating layer and various *in-situ* or *ex-situ* analysis techniques such as scanning ion conductance microscopy (SICM), electrical impedance spectroscopy (EIS) and transmission electron microscopy (TEM) have been utilized⁵⁶. However, it is worth mentioning that the capacity retention mechanism varies from system to system and therefore it is of utmost importance to understand that how different electrode materials and interfaces modify with different ALD coating materials.

In this study, we deposited HfO₂ coating by ALD on 1D MoO₃ nanorods to enhance the electrochemical performance and overcome the poor cyclic stability. Two important parameters; the growth temperature of MoO₃ nanorods and HfO₂ thickness were optimized in terms of microstructure of MoO₃ and LIBs performance. This study demonstrates remarkable performance improvement and cyclic stability of HfO₂ coated MoO₃ nanorods. Furthermore, we aimed to understand the underlying capacity retention mechanism after HfO₂ coating by *ex-situ* XRD, Raman spectroscopy, TEM and XPS before and after charge/discharge process.

Previously, we have reported the application of HfO_2 layer on SnO_2 nanospheres where cyclic stability of SnO_2 nanospheres has been improved after HfO_2 coating. This study shows that HfO_2 coating can be an effective way of improving cyclic stability in 1D nanostructured system, as well, and describes the capacity retention mechanism of HfO_2 coating.

2. Experimental Section

2.1 Synthesis of MoO_3 nanorods and characterization

MoO_3 nanorods were synthesized via one-step hydrothermal method. In a typical reaction, a certain amount of ammonium molybdate powder was dissolved in deionized water (DI) under continuous stirring to obtain a clear solution. The pH of the solution was maintained at acidic side by adding diluted hydrochloric acid (HCl) during stirring. After 2 hrs, the mixture was transferred to a Teflon lined stainless steel autoclave. The synthesis was carried out at the temperature range of 90–180 °C for 12 hrs. After the hydrothermal reaction, the autoclave was cooled down to room temperature naturally and a white precipitate was obtained. The resulting white precipitates of the MoO_3 nanorods were washed and filtered with DI water, ethanol, and dried at 80 °C for 12 h in a vacuum oven.

Structural analysis of the samples was performed with the x-ray diffraction system (XRD, Bruker, D8 ADVANCE) using Cu K_α radiation of wavelength 1.5418 Å. Field emission scanning electron microscopy (FESEM, Nova Nano) and transmission electron microscopy (300kV TEM, FEI-CM30) were used to investigate the morphology of the MoO_3 nanorods and HfO_2 coated MoO_3 nanorods. Sample preparation for the TEM analysis was carried out by scrapping gently the top layer of the HfO_2 coated MoO_3 electrode using a sharp stainless blade and collected powder was dispersed in ethanol by sonication for about 5 minutes. The dispersed

solution was drop casted onto the TEM nickel grid and dried. Raman spectroscopic measurements were carried out using a LabRamAramis with a He–Ne laser having an excitation wavelength of 473 nm. XPS analysis was carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of $\sim 10^{-9}$ mbar. The high-resolution spectrums were collected at fixed analyzer pass energy of 20 eV. The binding energy was calibrated by taking the C 1s peak (284.4 eV) as a reference corresponds to Acetylene black carbon before the electrochemical process. After the electrochemical process, the binding energy was calibrated by taking the C 1s peak (285.0 eV) as a reference corresponds to carbon which is present on the electrode surface resulting from the decomposition of ethylene carbonate (EC) and dimethyl carbonate (DMC).

2.2 Electrode fabrication, HfO $_2$ coating and electrochemical characterization

The working electrodes were prepared by mixing the active material, MoO $_3$ nanorods, with methyl cellulose binder (Na-CMC, Sigma Aldrich) and acetylene black (MTI, Inc.) as conductive additive in weight ratio of 70:15:15 in DI water to form a slurry. This slurry was uniformly pasted on a copper foil (MTI, Inc.) using a doctor blade and dried at 90 °C for 24 hrs in vacuum oven. Nanoscale HfO $_2$ layer was deposited on the prepared electrodes at 180 °C using atomic layer deposition system (Cambridge Nanotech Savannah). The HfO $_2$ ALD reaction sequence was; 1) a constant N $_2$ dose at 20 psi; 2) H $_2$ O dose for 0.015 sec; 3) H $_2$ O reaction time 10 sec; 4) Tetrakis (dimethylamino) hafnium (Hf(NMe $_2$) $_4$) dose to 0.2 sec; 5) Hf(NMe $_2$) $_4$ reaction time 15 sec. This sequence constitutes one ALD cycle of HfO $_2$. The growth rate per cycle is 0.10 nm per cycle at these conditions. The active material mass loading of the sample on the copper foil was maintained between 2.5 to 2.7 mg/cm 2 .

Electrochemical measurements were carried out in 2032 coin cells (MTI) using an electrochemical analyzer (VMP3, Biologic, Inc.). The lithium foil was used as the counter and a reference electrode. Celgard 2500 micro porous membranes were used as separators. The organic electrolyte was a mixture of lithium salt and organic solvents. Typically, LiPF_6 was dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, by weight) and a certain amount of electrolyte was used in each experiment. The cells were assembled in an argon-filled glove box with the concentrations of moisture and oxygen below 0.1 ppm. The electrochemical performance of the devices was evaluated at various current densities ranging from 100 mA/g to 1500 mA/g between 0.01 to 3.00 V (vs. Li/Li^+). Cyclic voltammetry was performed to examine the reduction and oxidation peaks between the voltage range of 3.0 V – 0.005 V (vs. Li/Li^+) at a scan rate of 0.2 mV/s. Electrochemical impedance spectroscopy (EIS) was measured by applying a sine wave with an amplitude of 5.0 mV over the frequency range 1000 kHz to 0.01 Hz at open circuit voltage (OCV).

3. Results and Discussions

3.1 Materials Characterization

The hydrothermal reaction to prepare MoO_3 nanorods was carried out at four different temperatures; 90 °C, 120 °C, 150 °C and 180 °C for 12 hours. The morphology of final product was observed by field emission scanning electron microscope (FESEM). Figure 2(a–d) presents FESEM image of MoO_3 nanorods obtained at different growth temperatures. At 90 °C, rod-like structure was achieved with thickness of 700–800 nm but with increasing growth temperature, thicker nanorods gradually split into thinner nanorods. Finally, at 180 °C nanorods with uniform thickness of 100–250 nm and 5–10 μm length were formed. Figure 3(a–b) shows the TEM image

of MoO₃ nanorods synthesized at 180 °C. The lattice spacing of 0.39, in Figure 2b, corresponds to (100) plane of orthorhombic α -MoO₃ structure.¹⁶ The selected area electron diffraction pattern (SAED) recorded from the edge of α -MoO₃ nanorod is presented in inset of Figure 3a. The SAED pattern taken along $\langle 010 \rangle$ zone axis confirms that synthesized MoO₃ powder is single crystal in nature. Furthermore, crystallinity and phase formation was also confirmed by XRD and Raman spectroscopy. Figure 4 presents the XRD pattern of MoO₃ powders synthesized at different temperatures. In this XRD pattern, all diffraction peaks can be readily indexed to orthorhombic α -MoO₃ with JCPDS card number 89-7112. It is well-known that α -MoO₃ has a layered crystal structure that exhibits three strong intensity peaks for the (020), (040) and (060) diffraction planes with 2θ values of 12.3°, 25.6° and 39°, respectively.¹⁶ Similarly, the Raman spectroscopy results, presented in Figure S1, confirm that single phase α -MoO₃ was formed when synthesis was carried out at 180 °C. The spectra display peaks at 159 cm⁻¹, 285 cm⁻¹, 334 cm⁻¹, 823 cm⁻¹, 667 cm⁻¹ and 996 cm⁻¹, all of which are characteristic of Raman bands of MoO₃.

Finally, high resolution transmission electron microscope (HRTEM) imaging of bare MoO₃ and HfO₂ coated MoO₃ nanorods was carried out to observe the uniformity and conformality of nanoscale HfO₂ layer. The HRTEM images of bare MoO₃ and HfO₂ coated MoO₃ are shown in Figure 5(a–d) for 0, 30, 50 and 80 ALD cycles. As mentioned earlier that prime advantage of ALD is to deposit a thin layer with excellent thickness control, one can observe in HRTEM images that obtained thickness of HfO₂ layer is according to ALD processing conditions. It is worth noting that HRTEM images of HfO₂ coated MoO₃ nanorods in Figure 5(b–d) do not show lattice fringes, which confirms that HfO₂ layer is amorphous in nature. The deposition of HfO₂ on the surface of MoO₃ nanorods was confirmed by scanning transmission electron microscopy – energy dispersive spectroscopy (STEM–EDS). The composition of MoO₃ nanorods at the center

and at the edge was examined by STEM-EDS and presented in Figure S2, which clearly indicates that HfO_2 is coated on the surface and MoO_3 nanorods are completely covered by HfO_2 layer.

3.2 Electrochemical Characterization:

The detailed electrochemical behavior of bare MoO_3 and HfO_2 coated MoO_3 (10 ALD cycles) electrodes were investigated by cyclic voltammetry (CV). Figure 6(a–b) shows the CV curves of bare MoO_3 and HfO_2 coated MoO_3 electrodes obtained at a scan rate of 0.2 mV/s in potential window of 0.005 – 3.0 V vs. Li/Li^+ . In Figure 6a, the first CV cycle of bare MoO_3 and HfO_2 coated MoO_3 electrodes is presented. The curves show typical peaks of MoO_3 in the oxidation and reduction reactions. In the first cycle, two peaks at around 2.2 V and 2.6 V correspond to the intercalation/deintercalation of Li^+ ions into the interlayer spacing between the MoO_6 octahedron layers.⁶⁰ Figure 6b presents the second CV cycle of bare MoO_3 and HfO_2 coated MoO_3 electrodes and it can be clearly observed that these peaks disappear in second cycle which can be because of loss of crystalline structure during the charge/discharge process.⁶⁰⁻⁶¹ Relatively weaker peaks at ~ 1.6 V suggest the formation of MoO_2 phase, which indicates that the crystal structure of $\alpha\text{-MoO}_3$ changes during charge/discharge process.⁶² Furthermore, CV curves confirmed that HfO_2 does not take part in electrochemical reaction, as no additional peaks were observed for HfO_2 coated MoO_3 electrodes. This result is in well agreement with the previous report where HfO_2 was deposited on SnO_2 nanoparticles.⁵⁹

Before moving further, the cyclic performance of MoO_3 nanorods synthesized at different temperatures was measured and results are presented in Figure S3. The MoO_3 nanorods synthesized at 180 °C showed higher cyclic stability than the MoO_3 nanorods synthesized at 90

°C, 120 °C and 150 °C. This is due to attainment of high crystallinity and morphology and this result is in good agreement with SEM, XRD and Raman results discussed earlier. The similar effect of crystallinity on battery performance has been reported for other materials as well.⁶³⁻⁶⁴ Afterwards, MoO₃ nanorods synthesized at 180 °C were used for further electrochemical characterization. Furthermore, we have mentioned earlier that HfO₂ does not contribute to the device capacity and remain inactive during electrochemical process but one should note that thickness of HfO₂ layer needs to be finely tuned for optimal battery performance. The thickness of HfO₂ layer limits the rate of Li⁺ ions diffusion through the layer to active material. Therefore, we deposited different thickness of HfO₂ layer by varying number of ALD cycles and results are presented in Figure S4. We found that 1 nm thickness of HfO₂ layer which corresponds to 10 ALD cycles performs better than thicker layers. One should note that 1 nm layer of HfO₂ is optimal compromise between Li⁺ ion diffusion and passivation effect. Hence, cyclic performances of bare MoO₃ and HfO₂ coated MoO₃ electrodes were investigated with this optimized thickness of HfO₂ layer (~ 1 nm).

Figure 7(a–b) shows the charge/discharge profiles for the 1st, 20th and 50th cycles at a current density of 100 mA/g between 0.01–3.0 V vs. Li/Li⁺ for bare MoO₃ and HfO₂ coated MoO₃ electrodes, respectively. The first discharge curve in both bare MoO₃ and HfO₂ coated MoO₃ electrodes showed three distinct voltage plateaus at 2.75 V, 2.35 V and 0.40 V (vs. Li⁺/Li) which reconfirms that HfO₂ is electrochemically inactive. The voltage plateaus at 2.75 V and 2.35 V (vs. Li⁺/Li) has been already reported¹⁵ and corresponds to insertion of Li⁺ ions in MoO₃ structure. Overall, Lithium insertion in MoO₃ takes place in two steps, as given below:

Generally, it is considered that reaction (1) provides reversible capacity, while reaction (2) is responsible for irreversible capacity losses because LiO_2 is primarily irreversible. However, presence of nanosize metallic particles in the system leads to the reversibility of LiO_2 .⁶⁵⁻⁶⁶ Previously, when bulk MoO_3 powders has been applied as anode material in Li ion batteries, only two voltage plateaus are observed ($V > 1.5$)¹⁵ but the charge/discharge curves presented in Figure 7a and 7b show the largest Li^+ ion storage in the voltage < 0.40 V. This effect comes from nanostructure of MoO_3 nanorods and mainly responsible for high specific capacity.⁶⁵ The 1st cycle discharge capacity was found to be 1573 mAh/g and 1728 mAh/g for the bare MoO_3 and HfO_2 coated MoO_3 electrodes, respectively. Almost stable capacity of 1008 mAh/g and 1120 mAh/g was obtained after 50 charge/discharge cycles for the bare MoO_3 and HfO_2 coated MoO_3 electrodes, respectively. The theoretical capacity of MoO_3 is about 1111 mAh/g,¹⁴ however, the availability of large surface area and numerous reaction sites in nanostructured conversion reaction anodes provides higher capacity because they can afford additional surface dominated charge/discharge reactions with extra Li^+ ion adsorption/desorption.⁶⁷⁻⁶⁸

These results indicate that the HfO_2 coated MoO_3 nanorods have higher capacity and better electrochemical stability than bare MoO_3 electrodes. However, the effect of HfO_2 was not significant at low current density (100 mA/g). Therefore, bare MoO_3 and HfO_2 coated MoO_3 electrodes were studied at high current densities such as 1000 mA/g and 1500 mA/g. Figure 8a presents the cyclic performance of bare MoO_3 and HfO_2 coated MoO_3 electrodes measured at high current densities. Interestingly, the effect of HfO_2 layer on capacity retention is more significant at high current densities. For instance, at 1000 mA/g, after 50 charge/discharge cycles, the specific capacities of bare MoO_3 and HfO_2 coated MoO_3 electrodes are recorded as

460 mAh/g and 657 mAh/g, respectively. This is mainly because Li insertion/extraction during charge/discharge process involves large volumetric changes and the fast charge/discharge process would induce large stresses and accelerate capacity degradation.¹⁸ As HfO₂ layer act as passivation layer, therefore its effect is significant in fast charge/discharge process. Additionally, the rate capability of the bare MoO₃ and HfO₂ coated MoO₃ electrodes was studied by subjecting electrodes under different current densities from 100 mA/g to 1500 mA/g and results are presented in Figure 8b. At lower current densities such as 100 mA/g, 200 mA/g and 500 mA/g both bare MoO₃ and HfO₂ coated MoO₃ electrodes showed stable capacity but at higher current densities (1000 mA/g and 1500 mA/g) the effect of HfO₂ became significant. At 1500 mA/g, after 50 charge/discharge cycles, the HfO₂ coated MoO₃ showed the specific capacity of 742 mAh/g while bare MoO₃ showed 534 mAh/g. The results presented in Figure 8a and 8b clearly indicate that HfO₂ coating is an effective way of improving cyclic performance and high rate performance of MoO₃ nanorods. Previously, when ALD coated Al₂O₃ was applied on MoO₃ nanoparticles,¹⁸ specific capacity of 900 mAh/g was observed after 50th cycle. However, in this study, we observed higher capacity after 50th cycle for HfO₂ coated MoO₃ electrode (~ 1120 mAh/g).

3.3 *Ex-situ* analysis

Furthermore, the underlying capacity retention mechanism because of HfO₂ coating was investigated by *ex-situ* XRD, Raman spectroscopy, HRTEM and XPS. The *ex-situ* investigations were carried out on bare MoO₃ and HfO₂ coated MoO₃ electrodes before and after charge/discharge process. Figure S5 shows the XRD spectrums of bare MoO₃ and HfO₂ coated MoO₃ electrodes after 50 charge/discharge cycles. The XRD spectrum of MoO₃ nanorods before charge/discharge process displayed a layered crystalline structure (Figure 4) but the XRD

spectrum of bare MoO_3 after 50 charge/discharge cycles lost the crystalline structure and does not show any characteristic diffraction peaks. The disappearance of high intensity peaks at 12.3° , 36.5° and 40.4° indicates that the MoO_3 structure becomes disordered during charge/discharge process but it does not become completely amorphous. On the other hand, HfO_2 coated MoO_3 electrodes showed relatively more crystallinity after charge/discharge process. Though all of the peaks cannot be indexed as single phase $\alpha\text{-MoO}_3$ but crystallinity retention in HfO_2 coated MoO_3 electrodes is more than bare MoO_3 electrodes. The loss of crystallinity in bare MoO_3 electrodes after cycling has already been reported by other research groups and they reported that it is the prime cause of capacity degradation in MoO_3 systems.⁶⁹ Similarly, the Raman spectrums of as-prepared MoO_3 nanorods (Figure S1) exhibited the characteristic Raman active bands of $\alpha\text{-MoO}_3$ structure. However, after 50 charge/discharge cycles, $\alpha\text{-MoO}_3$ peaks are lost in bare MoO_3 sample (Figure S6). The *ex-situ* XRD and Raman results suggested that HfO_2 coating somewhat slows down the degradation of crystalline structure and acts as barrier to the Li^+ ions during charge/discharge process. Further confirmation of this observation was obtained by *ex-situ* HRTEM measurements along with the selected area electron diffraction (SAED) patterns of bare MoO_3 and HfO_2 coated MoO_3 electrodes after 50 charge/discharge cycles. Figure 9(a–f) shows the low and high magnification images and SAED patterns for bare MoO_3 and HfO_2 coated MoO_3 electrodes after 50 charge/discharge cycles. These results should be compared to Figure 3 where HRTEM image and SAED pattern of as prepared MoO_3 nanorods are presented. It can be readily observed that highly crystalline structure of MoO_3 nanorods is severely degraded in case of bare MoO_3 (Figure 9(a–c)) as evidenced by disappearance of lattice fringes and distortion of SAED pattern. On the other hand, HfO_2 coated MoO_3 electrode showed that crystal structure of MoO_3 is also degraded to some extent but the degree of amorphousness is far less than bare

MoO₃ electrode. This result is in good agreement with our observation in electrochemical data and *ex-situ* XRD and Raman. Based on this, it can be concluded that nanoscale HfO₂ layer passivates anode/electrolyte interface and slows down the structural degradation of electrode material. Moreover, amorphous nature of HfO₂ layer does not entirely block Li⁺ ions diffusion and provides high rate performance.

Furthermore, *ex-situ* XPS analysis was also performed on bare MoO₃ and HfO₂ coated MoO₃ electrodes before and after electrochemical process to determine the possible factors that lead to the observed difference in battery performance after HfO₂ coating. Figure S7 shows the typical XPS survey spectra of bare MoO₃ and HfO₂ coated MoO₃ electrodes before and after one charge/discharge cycle. Figure 10a and 10c shows high resolution XPS spectra of the Hf 4f core level from electrodes coated with 1 nm HfO₂ layer, before and after one charge/discharge cycle. As shown in figure, the HfO₂ coated sample show 4f_{5/2} and 4f_{7/2} peaks from the HfO₂ indicating the presence of HfO₂ on the surface of MoO₃ nanorods. After one charge/discharge cycle, it was observed that the intensity of the HfO₂ peaks decreases sharply and their binding energy (B.E.) shifts. The B.E. of Hf 4f_{7/2} and 4f_{5/2} (in 1 nm HfO₂ layer) before electrochemical testing is at 17.31 eV and 18.98 eV, as shown in Figure 10a, and corresponds to HfO₂.⁷⁰ After one charge/discharge cycle, the B.E. of Hf 4f_{7/2} and Hf 4f_{5/2} decreased to 0.5 eV and 0.38 eV, respectively, as shown in Figure 10c. The shift in binding energy of HfO₂ is attributed to donation of charge from Hf to Mo which rises due to the difference in Pauling electronegativity between the Hf and Mo. This indicates that efficient charge transfer process occurs during the electrochemical process for the HfO₂ coated MoO₃, which may help explain the improved behavior with HfO₂ coating.⁵⁹ The mechanism of charge transfer effect is unknown and requires more detailed *in-situ* studies. In comparison, Figure 10b and 10d show the Mo 3d high–

resolution XPS spectra for the HfO_2 coated MoO_3 nanorods before and after electrochemical process. The XPS spectrums show the $\text{Mo } 3d_{5/2}$ and $\text{Mo } 3d_{3/2}$ peaks are located at 233 and 236 eV, as shown in Figure 10b. This binding energy corresponds to Mo in its highest oxidation state (i.e. Mo^{6+}), indicative of stoichiometric MoO_3 with traces of Mo^{5+} oxidation state at 231.56 eV. After one charge/discharge cycle, XPS spectrum shows no obvious shift in the binding energy of $\text{Mo } 3d_{5/2}$ and $\text{Mo } 3d_{3/2}$, as shown in Figure 10b and 10d. We also observed a peak at 230.4 eV, higher than the expected for Mo^{4+} (~229.5 eV) and lower than expected for Mo^{5+} (231.6). This could be attributed to $\text{Mo}^{+5-\delta}$ due to partial charge transfer from Li^+ to Mo_2O_5 after lithiation process. The appearance of Li 1s peak at B.E. of 55.2 eV after electrochemical process may be attributed to the presence of Li_2CO_3 . The XPS results also confirmed that MoO_3 undergoes structural changes during charge/discharge process and HfO_2 assists the structural preservation.

In summary, we studied the electrochemical performance of bare MoO_3 and HfO_2 coated MoO_3 and demonstrated that 1 nm thin layer of HfO_2 deposited by ALD can significantly increase the cyclic performance of MoO_3 electrodes in Li ion batteries. Moreover, we explained the capacity retention mechanism and role of HfO_2 by *ex-situ* analysis of electrodes before and after charge/discharge process. The proposed capacity retention mechanism has been summarized in Figure 11; where bare MoO_3 nanorods structurally degrades after charge/discharge process and HfO_2 coated MoO_3 nanorods retain crystallinity and stability.

4. Conclusions

In conclusion, $\alpha\text{-MoO}_3$ nanorods has been synthesized by hydrothermal method and applied as anode electrode in LIBs. The cyclic performance of MoO_3 nanorods has been improved by coating of a nanoscale HfO_2 layer by ALD. At high current density, the specific capacity of HfO_2

coated MoO_3 was found to be 68% higher than bare MoO_3 electrodes. Electrochemical measurements reveal that growth temperature of MoO_3 nanorods and optimization of the HfO_2 layer thickness needs to be finely tuned for optimal battery performance. It was observed that effect of HfO_2 presence becomes more significant at high current densities such as 1000 mA/g and 1500 mA/g. This is mainly because charge/discharge process induces large volumetric changes, which results in internal stresses and passivation effect of HfO_2 is clearly observed in case of high rate cycling. Furthermore, the capacity retention mechanism was explained by *ex-situ* HRTEM imaging and spectroscopy; XRD, Raman and XPS. The results showed that charge/discharge process distorts the crystal structure of MoO_3 and presence of HfO_2 layer serves as protective barrier at anode/electrolyte interface. *Ex-situ* analysis clearly showed that HfO_2 assists in crystallinity retention and improves battery performance. These results indicate that HfO_2 coating can be an effective approach of improving cycling performance of MoO_3 nanorods in LIBs.

Acknowledgement

This research was supported by King Abdullah University of Science and Technology (KAUST).

Supporting Information

Raman spectrums of MoO_3 , STEM-EDS, effect of MoO_3 growth temperature on cyclic performance, effect of HfO_2 layer thickness on cyclic performance and *ex-situ* XRD, Raman and XPS results are presented in supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

1. Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D., Challenges in the Development of Advanced Li-Ion Batteries: A Review. *Energy Environ. Sci.* **2011**, *4*, 3243-3262.
2. Tarascon, J. M.; Armand, M., Issues and Challenges Facing Rechargeable Lithium Batteries. *Nature* **2001**, *414*, 359-367.
3. Guo, Y.-G.; Hu, J.-S.; Wan, L.-J., Nanostructured Materials for Electrochemical Energy Conversion and Storage Devices. *Adv. Mater.* **2008**, *20*, 2878-2887.
4. Arico, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J.-M.; van Schalkwijk, W., Nanostructured Materials for Advanced Energy Conversion and Storage Devices. *Nat. Mater.* **2005**, *4*, 366-377.
5. Hosono, E.; Kudo, T.; Honma, I.; Matsuda, H.; Zhou, H., Synthesis of Single Crystalline Spinel LiMn_2O_4 Nanowires for a Lithium Ion Battery with High Power Density. *Nano Lett.* **2009**, *9*, 1045-1051.
6. Chan, C. K.; Peng, H.; Twisten, R. D.; Jarausch, K.; Zhang, X. F.; Cui, Y., Fast, Completely Reversible Li Insertion in Vanadium Pentoxide Nanoribbons. *Nano Lett.* **2007**, *7*, 490-495.
7. Armstrong, G.; Armstrong, A. R.; Bruce, P. G.; Reale, P.; Scrosati, B., $\text{TiO}_2(\text{B})$ Nanowires as an Improved Anode Material for Lithium-Ion Batteries Containing LiFePO_4 or $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathodes and a Polymer Electrolyte. *Adv. Mater.* **2006**, *18*, 2597-2600.
8. Lee, Y.; Kim, M. G.; Cho, J., Layered $\text{Li}_{0.88}[\text{Li}_{0.18}\text{Co}_{0.33}\text{Mn}_{0.49}]\text{O}_2$ Nanowires for Fast and High Capacity Li-Ion Storage Material. *Nano Lett.* **2008**, *8*, 957-961.
9. Hosono, E.; Matsuda, H.; Saito, T.; Kudo, T.; Ichihara, M.; Honma, I.; Zhou, H., Synthesis of Single Crystalline $\text{Li}_{0.44}\text{MnO}_2$ Nanowires with Large Specific Capacity and Good

High Current Density Property for a Positive Electrode of Li Ion Battery. *J. Power Sources* **2010**, *195*, 7098-7101.

10. Taberna, P. L.; Mitra, S.; Poizot, P.; Simon, P.; Tarascon, J. M., High Rate Capabilities Fe₃O₄-Based Cu Nano-Architected Electrodes for Lithium-Ion Battery Applications. *Nat. Mater.* **2006**, *5*, 567-573.

11. Lee, H.; Cho, J., Sn₇₈Ge₂₂@Carbon Core-Shell Nanowires as Fast and High-Capacity Lithium Storage Media. *Nano Lett.* **2007**, *7*, 2638-2641.

12. Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J. M., Nano-Sized Transition-Metal Oxides as Negative-Electrode Materials for Lithium-Ion Batteries. *Nature* **2000**, *407*, 496-499.

13. Ku, J. H.; Jung, Y. S.; Lee, K. T.; Kim, C. H.; Oh, S. M., Thermoelectrochemically Activated MoO₂ Powder Electrode for Lithium Secondary Batteries. *J. Electrochem. Soc.* **2009**, *156*, A688-A693.

14. Li, H.; Balaya, P.; Maier, J., Li-Storage Via Heterogeneous Reaction in Selected Binary Metal Fluorides and Oxides. *J. Electrochem. Soc.* **2004**, *151*, A1878-A1885.

15. Sasidharan, M.; Gunawardhana, N.; Noma, H.; Yoshio, M.; Nakashima, K., Alpha-MoO₃ Hollow Nanospheres as an Anode Material for Li-Ion Batteries. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 642-646.

16. Zhou, L.; Yang, L.; Yuan, P.; Zou, J.; Wu, Y.; Yu, C., α -MoO₃ Nanobelts: A High Performance Cathode Material for Lithium Ion Batteries. *J. Phys. Chem. C* **2010**, *114*, 21868-21872.

17. Leroux, F.; Nazar, L. F., Uptake of Lithium by Layered Molybdenum Oxide and Its Tin Exchanged Derivatives: High Volumetric Capacity Materials. *Solid State Ionics* **2000**, *133*, 37-50.
18. Riley, L. A.; Cavanagh, A. S.; George, S. M.; Jung, Y. S.; Yan, Y.; Lee, S.-H.; Dillon, A. C., Conformal Surface Coatings to Enable High Volume Expansion Li-Ion Anode Materials. *ChemPhysChem* **2010**, *11*, 2124-2130.
19. Demir-Cakan, R.; Hu, Y. S.; Antonietti, M.; Maier, J.; Titirici, M. M., Facile One-Pot Synthesis of Mesoporous SnO₂ Microspheres Via Nanoparticles Assembly and Lithium Storage Properties. *Chem. Mater.* **2008**, *20*, 1227-1229.
20. Lou, X. W.; Wang, Y.; Yuan, C.; Lee, J. Y.; Archer, L. A., Template-Free Synthesis of SnO₂ Hollow Nanostructures with High Lithium Storage Capacity. *Adv. Mater.* **2006**, *18*, 2325-2329.
21. Wang, L.; Wang, D.; Dong, Z.; Zhang, F.; Jin, J., Interface Chemistry Engineering for Stable Cycling of Reduced GO/SnO₂ Nanocomposites for Lithium Ion Battery. *Nano Lett.* **2013**, *13*, 1711-1716.
22. Jeong, G.; Kim, J. H.; Kim, Y. U.; Kim, Y. J., Multifunctional TiO₂ Coating for a SiO Anode in Li-Ion Batteries. *J. Mater. Chem.* **2012**, *22*, 7999-8004.
23. Xiao, J.; Xu, W.; Wang, D. Y.; Choi, D. W.; Wang, W.; Li, X. L.; Graff, G. L.; Liu, J.; Zhang, J. G., Stabilization of Silicon Anode for Li-Ion Batteries. *J. Electrochem. Soc.* **2010**, *157*, A1047-A1051.
24. Miikkulainen, V.; Leskelä, M.; Ritala, M.; Puurunen, R. L., Crystallinity of Inorganic Films Grown by Atomic Layer Deposition: Overview and General Trends. *J. Appl. Phys.* **2013**, *113*, 021301.

25. George, S. M., Atomic Layer Deposition: An Overview. *Chem. Rev.* **2010**, *110*, 111-131.
26. Cheah, S. K.; Perre, E.; Rooth, M.; Fondell, M.; Hårsta, A.; Nyholm, L.; Boman, M.; Gustafsson, T.; Lu, J.; Simon, P.; Edström, K., Self-Supported Three-Dimensional Nanoelectrodes for Microbattery Applications. *Nano Lett.* **2009**, *9*, 3230-3233.
27. Kim, S.-W.; Han, T. H.; Kim, J.; Gwon, H.; Moon, H.-S.; Kang, S.-W.; Kim, S. O.; Kang, K., Fabrication and Electrochemical Characterization of TiO₂ Three-Dimensional Nanonetwork Based on Peptide Assembly. *ACS Nano* **2009**, *3*, 1085-1090.
28. Aravindan, V.; Jinesh, K. B.; Prabhakar, R. R.; Kale, V. S.; Madhavi, S., Atomic Layer Deposited (ALD) SnO₂ Anodes with Exceptional Cycleability for Li-Ion Batteries. *Nano Energy* **2013**, *2*, 720-725.
29. Donders, M. E.; Knoops, H. C. M.; Kessels, W. M. M.; Notten, P. H. L., Co₃O₄ as Anode Material for Thin Film Micro-Batteries Prepared by Remote Plasma Atomic Layer Deposition. *J. Power Sources* **2012**, *203*, 72-77.
30. Meng, X.; Libera, J. A.; Fister, T. T.; Zhou, H.; Hedlund, J. K.; Fenter, P.; Elam, J. W., Atomic Layer Deposition of Gallium Sulfide Films Using Hexakis(Dimethylamido)Digallium and Hydrogen Sulfide. *Chem. Mater.* **2014**, *26*, 1029-1039.
31. Meng, X.; He, K.; Su, D.; Zhang, X.; Sun, C.; Ren, Y.; Wang, H.-H.; Weng, W.; Trahey, L.; Canlas, C. P.; Elam, J. W., Gallium Sulfide–Single-Walled Carbon Nanotube Composites: High-Performance Anodes for Lithium-Ion Batteries. *Adv. Funct. Mater.* **2014**, *24*, 5435-5442.
32. Chen, X.; Zhu, H.; Chen, Y.-C.; Shang, Y.; Cao, A.; Hu, L.; Rubloff, G. W., MWCNT/V₂O₅ Core/Shell Sponge for High Areal Capacity and Power Density Li-Ion Cathodes. *ACS Nano* **2012**, *6*, 7948-7955.

33. Chen, X.; Pomerantseva, E.; Banerjee, P.; Gregorczyk, K.; Ghodssi, R.; Rubloff, G., Ozone-Based Atomic Layer Deposition of Crystalline V_2O_5 Films for High Performance Electrochemical Energy Storage. *Chem. Mater.* **2012**, *24*, 1255-1261.
34. Gandrud, K. B.; Pettersen, A.; Nilsen, O.; Fjellvag, H., High-Performing Iron Phosphate for Enhanced Lithium Ion Solid State Batteries as Grown by Atomic Layer Deposition. *J. Mater. Chem. A* **2013**, *1*, 9054-9059.
35. Donders, M. E.; Arnoldbik, W. M.; Knoops, H. C. M.; Kessels, W. M. M.; Notten, P. H. L., Atomic Layer Deposition of $LiCoO_2$ Thin-Film Electrodes for All-Solid-State Li-Ion Micro-Batteries. *J. Electrochem. Soc.* **2013**, *160*, A3066-A3071.
36. Liu, J.; Banis, M. N.; Sun, Q.; Lushington, A.; Li, R.; Sham, T.-K.; Sun, X., Rational Design of Atomic-Layer-Deposited $LiFePO_4$ as a High-Performance Cathode for Lithium-Ion Batteries. *Adv. Mater.* **2014**, *26*, 6472-6477.
37. Aaltonen, T.; Nilsen, O.; Magrasó, A.; Fjellvåg, H., Atomic Layer Deposition of Li_2O – Al_2O_3 Thin Films. *Chem. Mater.* **2011**, *23*, 4669-4675.
38. Comstock, D. J.; Elam, J. W., Mechanistic Study of Lithium Aluminum Oxide Atomic Layer Deposition. *J. Phys. Chem. C* **2013**, *117*, 1677-1683.
39. Liu, J.; Banis, M. N.; Li, X.; Lushington, A.; Cai, M.; Li, R.; Sham, T.-K.; Sun, X., Atomic Layer Deposition of Lithium Tantalate Solid-State Electrolytes. *J. Phys. Chem. C* **2013**, *117*, 20260-20267.
40. Ostreng, E.; Sonsteby, H. H.; Sajavaara, T.; Nilsen, O.; Fjellvag, H., Atomic Layer Deposition of Ferroelectric $LiNbO_3$. *J. Mater. Chem. C* **2013**, *1*, 4283-4290.

41. Perng, Y.-C.; Cho, J.; Sun, S. Y.; Membreno, D.; Cirigliano, N.; Dunn, B.; Chang, J. P., Synthesis of Ion Conducting LixAl₂O₃ Thin Films by Atomic Layer Deposition. *J. Mater. Chem. A* **2014**, *2*, 9566-9573.
42. Jung, Y. S.; Cavanagh, A. S.; Riley, L. A.; Kang, S.-H.; Dillon, A. C.; Groner, M. D.; George, S. M.; Lee, S.-H., Ultrathin Direct Atomic Layer Deposition on Composite Electrodes for Highly Durable and Safe Li-Ion Batteries. *Adv. Mater.* **2010**, *22*, 2172-2176.
43. Lee, M.-L.; Su, C.-Y.; Lin, Y.-H.; Liao, S.-C.; Chen, J.-M.; Perng, T.-P.; Yeh, J.-W.; Shih, H. C., Atomic Layer Deposition of TiO₂ on Negative Electrode for Lithium Ion Batteries. *J. Power Sources* **2013**, *244*, 410-416.
44. Wang, H.-Y.; Wang, F.-M., Electrochemical Investigation of an Artificial Solid Electrolyte Interface for Improving the Cycle-Ability of Lithium Ion Batteries Using an Atomic Layer Deposition on a Graphite Electrode. *J. Power Sources* **2013**, *233*, 1-5.
45. He, Y.; Yu, X.; Wang, Y.; Li, H.; Huang, X., Alumina-Coated Patterned Amorphous Silicon as the Anode for a Lithium-Ion Battery with High Coulombic Efficiency. *Adv. Mater.* **2011**, *23*, 4938-4941.
46. Xiao, X.; Lu, P.; Ahn, D., Ultrathin Multifunctional Oxide Coatings for Lithium Ion Batteries. *Adv. Mater.* **2011**, *23*, 3911-3915.
47. Kohandehghan, A.; Kalisvaart, P.; Cui, K.; Kupsta, M.; Memarzadeh, E.; Mitlin, D., Silicon Nanowire Lithium-Ion Battery Anodes with ALD Deposited Tin Coatings Demonstrate a Major Improvement in Cycling Performance. *J. Mater. Chem. A* **2013**, *1*, 12850-12861.
48. Memarzadeh Lotfabad, E.; Kalisvaart, P.; Cui, K.; Kohandehghan, A.; Kupsta, M.; Olsen, B.; Mitlin, D., ALD TiO₂ Coated Silicon Nanowires for Lithium Ion Battery Anodes with

Enhanced Cycling Stability and Coulombic Efficiency. *Phys. Chem. Chem. Phys.* **2013**, *15*, 13646-13657.

49. Lotfabad, E. M.; Kalisvaart, P.; Kohandehghan, A.; Cui, K.; Kupsta, M.; Farbod, B.; Mitlin, D., Si Nanotubes ALD Coated with TiO₂, Tin or Al₂O₃ as High Performance Lithium Ion Battery Anodes. *J. Mater. Chem. A* **2014**, *2*, 2504-2516.

50. Snyder, M. Q.; Trebukhova, S. A.; Ravdel, B.; Wheeler, M. C.; DiCarlo, J.; Tripp, C. P.; DeSisto, W. J., Synthesis and Characterization of Atomic Layer Deposited Titanium Nitride Thin Films on Lithium Titanate Spinel Powder as a Lithium-Ion Battery Anode. *J. Power Sources* **2007**, *165*, 379-385.

51. Liu, J.; Li, X.; Cai, M.; Li, R.; Sun, X., Ultrathin Atomic Layer Deposited ZrO₂ Coating to Enhance the Electrochemical Performance of Li₄Ti₅O₁₂ as an Anode Material. *Electrochimica Acta* **2013**, *93*, 195-201.

52. Ahn, D.; Xiao, X., Extended Lithium Titanate Cycling Potential Window with near Zero Capacity Loss. *Electrochem. Commun.* **2011**, *13*, 796-799.

53. Wang, D.; Yang, J.; Liu, J.; Li, X.; Li, R.; Cai, M.; Sham, T.-K.; Sun, X., Atomic Layer Deposited Coatings to Significantly Stabilize Anodes for Li Ion Batteries: Effects of Coating Thickness and the Size of Anode Particles. *J. Mater. Chem. A* **2014**, *2*, 2306-2312.

54. Lee, J.-H.; Hon, M.-H.; Chung, Y.-W.; Leu, I.-C., The Effect of TiO₂ Coating on the Electrochemical Performance of ZnO Nanorod as the Anode Material for Lithium-Ion Battery. *Appl. Phys. A* **2011**, *102*, 545-550.

55. Kang, E.; Jung, Y. S.; Cavanagh, A. S.; Kim, G.-H.; George, S. M.; Dillon, A. C.; Kim, J. K.; Lee, J., Fe₃O₄ Nanoparticles Confined in Mesocellular Carbon Foam for High Performance Anode Materials for Lithium-Ion Batteries. *Adv. Funct. Mater.* **2011**, *21*, 2430-2438.

56. Lipson, A. L.; Puntambekar, K.; Comstock, D. J.; Meng, X.; Geier, M. L.; Elam, J. W.; Hersam, M. C., Nanoscale Investigation of Solid Electrolyte Interphase Inhibition on Li-Ion Battery MnO Electrodes via Atomic Layer Deposition of Al₂O₃. *Chem. Mater.* **2014**, *26*, 935-940.
57. Li, C.; Zhang, H. P.; Fu, L. J.; Liu, H.; Wu, Y. P.; Rahm, E.; Holze, R.; Wu, H. Q., Cathode Materials Modified by Surface Coating for Lithium Ion Batteries. *Electrochimica Acta* **2006**, *51*, 3872-3883.
58. Jian, L.; Xueliang, S., Elegant Design of Electrode and Electrode/Electrolyte Interface in Lithium-Ion Batteries by Atomic Layer Deposition. *Nanotechnology* **2015**, *26*, 024001.
59. Yesibolati, N.; Shahid, M.; Chen, W.; Hedhili, M. N.; Reuter, M. C.; Ross, F. M.; Alshareef, H. N., SnO₂ Anode Surface Passivation by Atomic Layer Deposited HfO₂ Improves Li-Ion Battery Performance. *Small* **2014**, *10*, 2849-2858.
60. Li, W.; Cheng, F.; Tao, Z.; Chen, J., Vapor-Transportation Preparation and Reversible Lithium Intercalation/Deintercalation of α -MoO₃ Microrods. *J. Phys. Chem. B* **2006**, *110*, 119-124.
61. Chen, J. S.; Cheah, Y. L.; Madhavi, S.; Lou, X. W., Fast Synthesis of α -MoO₃ Nanorods with Controlled Aspect Ratios and their Enhanced Lithium Storage Capabilities. *J. Phys. Chem. C* **2010**, *114*, 8675-8678.
62. Sun, Y.; Wang, J.; Zhao, B.; Cai, R.; Ran, R.; Shao, Z., Binder-Free α -MoO₃ Nanobelt Electrode for Lithium-Ion Batteries Utilizing Van Der Waals Forces for Film Formation and Connection with Current Collector. *J. Mater. Chem. A* **2013**, *1*, 4736-4746.

63. Wang, L.; Yu, Y.; Chen, P. C.; Zhang, D. W.; Chen, C. H., Electrospinning Synthesis of C/Fe₃O₄ Composite Nanofibers and their Application for High Performance Lithium-Ion Batteries. *J. Power Sources* **2008**, *183*, 717-723.
64. Jung, Y. S.; Lee, S.; Ahn, D.; Dillon, A. C.; Lee, S.-H., Electrochemical Reactivity of Ball-Milled MoO_{3-y} as Anode Materials for Lithium-Ion Batteries. *J. Power Sources* **2009**, *188*, 286-291.
65. Meduri, P.; Clark, E.; Kim, J. H.; Dayalan, E.; Sumanasekera, G. U.; Sunkara, M. K., MoO_{3-x} Nanowire Arrays as Stable and High-Capacity Anodes for Lithium Ion Batteries. *Nano Lett.* **2012**, *12*, 1784-1788.
66. Meduri, P.; Pendyala, C.; Kumar, V.; Sumanasekera, G. U.; Sunkara, M. K., Hybrid Tin Oxide Nanowires as Stable and High Capacity Anodes for Li-Ion Batteries. *Nano Lett.* **2009**, *9*, 612-616.
67. Dylla, A. G.; Xiao, P.; Henkelman, G.; Stevenson, K. J., Morphological Dependence of Lithium Insertion in Nanocrystalline TiO_{2(β)} Nanoparticles and Nanosheets. *J. Phys. Chem. Lett.* **2012**, *3*, 2015-2019.
68. Hu, Y.-Y.; Liu, Z.; Nam, K.-W.; Borkiewicz, O. J.; Cheng, J.; Hua, X.; Dunstan, M. T.; Yu, X.; Wiaderek, K. M.; Du, L.-S.; Chapman, K. W.; Chupas, P. J.; Yang, X.-Q.; Grey, C. P., Origin of Additional Capacities in Metal Oxide Lithium-Ion Battery Electrodes. *Nat. Mater.* **2013**, *12*, 1130-1136.
69. Lee, S.-H.; Kim, Y.-H.; Deshpande, R.; Parilla, P. A.; Whitney, E.; Gillaspie, D. T.; Jones, K. M.; Mahan, A. H.; Zhang, S.; Dillon, A. C., Reversible Lithium-Ion Insertion in Molybdenum Oxide Nanoparticles. *Adv. Mater.* **2008**, *20*, 3627-3632.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

70. Renault, O.; Samour, D.; Rouchon, D.; Holliger, P.; Papon, A. M.; Blin, D.; Marthon, S.,
Interface Properties of Ultra-Thin HfO₂ Films Grown by Atomic Layer Deposition on SiO₂/Si.
Thin Solid Films **2003**, 428, 190-194.

List of Figures

Figure 1 Schematic illustration of crystal structure of α - MoO_3 : (a) unit cell and (b–c) showing layered nature of MoO_3

Figure 2 FESEM images of MoO_3 hydrothermally synthesized at different temperatures for 12 hours: (a) 90 °C, (b) 120 °C, (c) 150 °C and (d) 180 °C

Figure 3 TEM images of MoO_3 nanorods synthesized at 180 °C: (a) low-magnification image of one MoO_3 nanorod, (inset) corresponding SAED pattern and (b) high resolution TEM image from indicated region

Figure 4 XRD patterns of hydrothermally synthesized MoO_3 at different temperatures for 12 hours

Figure 5 High resolution TEM images of bare MoO_3 and HfO_2 coated MoO_3 powders: (a) 0 ALD cycles, (b) 30 ALD cycles, (c) 50 ALD cycles and (d) 80 ALD cycles

Figure 6 Cyclic voltammograms of bare MoO_3 and 10 ALD HfO_2 coated MoO_3 electrodes: (a) first cycle and (b) second cycle

Figure 7 Charge/discharge curves measured at 100 mA/g: (a) bare MoO_3 and (b) 10 ALD HfO_2 coated MoO_3

Figure 8 Electrochemical characterization: (a) cyclic performance at 1000 mA/g and 1500 mA/g and (b) rate-ability of bare MoO_3 and 10 ALD HfO_2 coated MoO_3 at different current densities

Figure 9 HRTEM analysis after 50 charge/discharge cycles: (a–c) low magnification image, high magnification image and SAED pattern of bare MoO_3 and (d–f) low magnification image, high magnification image and SAED pattern of HfO_2 coated MoO_3 electrodes

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Figure 10 High resolution XPS spectra of Hf 4f core level obtained from HfO₂ coated MoO₃ electrodes: (a) before and (c) after one charge/discharge cycle; Similar spectra for Mo 3d are shown (b) before and (d) after one charge/discharge cycle.

Figure 11 Schematic illustration of the proposed capacity retention mechanism.

Figure 1 Schematic illustration of crystal structure of α - MoO_3 : (a) unit cell and (b–c) showing layered nature of MoO_3

Figure 2 FESEM images of MoO₃ hydrothermally synthesized at different temperatures for 12 hours: (a) 90 °C, (b) 120 °C, (c) 150 °C and (d) 180 °C

Figure 3 TEM images of MoO₃ nanorods synthesized at 180 °C: (a) low-magnification image of one MoO₃ nanorod, (inset) corresponding SAED pattern and (b) high resolution TEM image from indicated region

Figure 4 XRD patterns of hydrothermally synthesized MoO_3 at different temperatures for 12 hours

Figure 5 High resolution TEM images of bare MoO₃ and HfO₂ coated MoO₃ powders: (a) 0 ALD cycles, (b) 30 ALD cycles, (c) 50 ALD cycles and (d) 80 ALD cycles

Figure 6 Cyclic voltammograms of bare MoO₃ and 10 ALD HfO₂ coated MoO₃ electrodes: (a) first cycle and (b) second cycle

Figure 7 Charge/discharge curves measured at 100 mA/g: (a) bare MoO_3 and (b) 10 ALD HfO_2 coated MoO_3

Figure 8 Electrochemical characterization: (a) cyclic performance at 1000 mA/g and 1500 mA/g and (b) rate-ability of bare MoO₃ and 10 ALD HfO₂ coated MoO₃ at different current densities

Figure 9 HRTEM analysis after 50 charge/discharge cycles: (a–c) low magnification image, high magnification image and SAED pattern of bare MoO_3 and (d–f) low magnification image, high magnification image and SAED pattern of HfO_2 coated MoO_3 electrodes

Figure 10 High resolution XPS spectra of Hf 4f core level obtained from HfO₂ coated MoO₃ electrodes: (a) before and (c) after one charge/discharge cycle; Similar spectra for Mo 3d are shown (b) before and (d) after one charge/discharge cycle.

Figure 11 Schematic illustration of the proposed capacity retention mechanism: (left) bare MoO_3 and (right) HfO_2 coated MoO_3 electrodes before and after charge/discharge process

TOC:

(Left) Bare MoO₃ and (Right) HfO₂ coated MoO₃ electrodes before and after charge/discharge process