SnO_2_ Anode Surface Passivation by Atomic Layer Deposited HfO_2 Improves Li-Ion Battery Performance

Nulati Yesibolati, Muhammad Shahid, Wei Chen, M. N. Hedhili, M. C. Reuter, F. M. Ross, and H. N. Alshareef*

For the first time, it is demonstrated that nanoscale HfO_2 surface passivation layers formed by atomic layer deposition (ALD) significantly improve the performance of Li ion batteries with SnO_2-based anodes. Specifically, the measured battery capacity at a current density of 150 mAg\(^{-1}\) after 100 cycles is 548 and 853 mAhg\(^{-1}\) for the uncoated and HfO_2-coated anodes, respectively. Material analysis reveals that the HfO_2 layers are amorphous in nature and conformably coat the SnO_2-based anodes. In addition, the analysis reveals that ALD HfO_2 not only protects the SnO_2-based anodes from irreversible reactions with the electrolyte and buffers its volume change, but also chemically interacts with the SnO_2 anodes to increase battery capacity, despite the fact that HfO_2 is itself electrochemically inactive. The amorphous nature of HfO_2 is an important factor in explaining its behavior, as it still allows sufficient Li diffusion for an efficient anode lithiation/delithiation process to occur, leading to higher battery capacity.

1. Introduction

Lithium ion batteries (LIBs) are considered to be one of the most promising energy storage technologies for hybrid electric or plug-in hybrid electric vehicles.\(^{[1]}\) In conventional LIBs, graphite and lithium metal oxides are used as anode and cathode materials, respectively. The inherent properties of the electrode materials play a significant role in determining the overall performance of LIBs. The capacity of commercial graphite, which operates by forming intercalation compounds LiC\(_6\), is limited to 350 mAhg\(^{-1}\), an insufficient value for electric vehicle applications.\(^{[2]}\) Hence, other materials have been investigated to improve the performance of LIBs. Metal oxides like SnO_2,\(^{[3]}\) MoO_3,\(^{[4]}\) Mn_3O_4,\(^{[5]}\) and Fe_3O_4\(^{[6]}\) are considered as promising materials due to their large theoretical capacities, environmental friendliness, and natural abundance. Among them, SnO_2 has a theoretical capacity of 782 mAhg\(^{-1}\), which is twice that of graphite,\(^{[3a]}\) and a voltage plateu around 0.5 V, which reduces the potential safety problems associated with metallic lithium deposition on the host anode during high current discharge and charge.\(^{[3]}\) Unfortunately, SnO_2 is plagued by a large volume change (300%) induced by the alloying reaction, resulting in cracking, crumbling and delamination of the active materials from the current collector, which affects the batteries’ cycling stability. Moreover, agglomeration of SnO_2 nanoparticles reduces the number of active Li\(^+\) sites, and creates more severe mechanical stress during electrochemical cycling. Volume change and agglomeration are therefore the two most serious issues that hinder the development of SnO_2 anode for high performance LIBs.\(^{[3,7]}\)

One of the most studied approaches to eliminate these issues is to reduce the SnO_2 size to nanoscale in order to reduce the volume change and shorten the lithium ion diffusion pathways.\(^{[7]}\) Another approach is to use porous...
or hollow SnO\textsubscript{2} to accommodate the volume change and improve the diffusion kinetics of lithium ions and cycle life of LIBs\textsuperscript{[3b,7h,7i]}. Furthermore, homogeneously dispersing SnO\textsubscript{2} nanoparticles in a carbon matrix is attractive not only for reducing the agglomeration, but also for accommodating volume change and increasing conductivity\textsuperscript{[78]}. For example, SnO\textsubscript{2}-carbon nanotubes\textsuperscript{[74]} SnO\textsubscript{2}-porous carbons\textsuperscript{[7c,7d]} and SnO\textsubscript{2}-graphene composites\textsuperscript{[7e,7f]} have shown improved lithium storage properties. Previous studies have mainly focused on improving electrical conductivity and relaxing the internal stress of SnO\textsubscript{2} associated with lithium insertion/extraction. However, widely dispersed SnO\textsubscript{2} nanoparticles on carbon materials are prone to disintegrate and break away during lithiation/delithiation\textsuperscript{[7a,7b]} due to the high surface-to-volume ratio and high surface energy of nanomaterials, reactions such as formation of the solid electrolyte interface (SEI) layer may be enhanced also\textsuperscript{[8]} The first irreversible reaction between SnO\textsubscript{2} and lithium ions will produce Li\textsubscript{2}O\textsuperscript{[9]} which accumulates on the electrode surface and results in a substantial first cycle irreversible capacity loss by consuming the active lithium and forming the SEI layer. Hence, surface passivation of the anode is necessary to alleviate both mechanical and chemical degradation of the SnO\textsubscript{2}, but it must not significantly hinder Li diffusion. Various processes, such as the sol-gel method\textsuperscript{[10]} and chemical vapor deposition\textsuperscript{[11]} have been developed to create surface passivation layers on the active electrode materials in LIBs to improve the electrochemical performance. Recently, Su \textit{et al.} reported that carbon-coated SnO\textsubscript{2}/graphene and Fe\textsubscript{3}O\textsubscript{4}/graphene anodes were able to maintain their capacity without apparent loss in the first 100 cycles\textsuperscript{[12]} Wang \textit{et al.} also improved the cycle performance of their LIBs by coating 1–2 nm thick polydopamine on SnO\textsubscript{2}/reduced graphite oxide (rGO) electrodes\textsuperscript{[13]}. In these two studies, graphene was used as a carbon-based matrix to support the SnO\textsubscript{2} nanoparticles, and thin layer carbon was coated over the active anode material by utilizing wet chemical reactions. Although electrochemical performance was improved, wet chemical reactions lack control over surface coverage, thickness, and uniformity, and are difficult to implement widely in many applications.

On the other hand, atomic layer deposition (ALD) can effectively apply thin and conformal coatings on complex high-surface-area anodes using sequential, self-limiting surface reactions\textsuperscript{[14]}. Furthermore, the thickness of ALD coatings can easily be tailored at the atomic level\textsuperscript{[15]} ALD has already been used to deposit surface coatings on battery electrodes or active powders, and the electrochemical performances have been improved. Issac \textit{et al.} reported that coating LiCoO\textsubscript{2} with an ultrathin ALD Al\textsubscript{2}O\textsubscript{3} film enhanced the reversible capacity to 250% even at a high current density (7.8 C)\textsuperscript{[16]}. Jung \textit{et al.}, reported that inactive metal oxide coatings on graphite and LiCoO\textsubscript{2} cathodes using ALD have significantly improved both long-term durability and safety of LIBs\textsuperscript{[17]} Nanolayers of Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} coatings were applied to Li\textsubscript{12}Ni\textsubscript{13}Mn\textsubscript{6}Co\textsubscript{13}O\textsubscript{4} high voltage cathode material. The nanolayers could address the capacity fading\textsuperscript{[18]}. ALD has been applied to anode materials. In the case of nanosize MoO\textsubscript{3}, the cycle stability was improved after Al\textsubscript{2}O\textsubscript{3} coating by ALD\textsuperscript{[19]}, Recently, the Mitlin’s group reported that conformably ALD TiO\textsubscript{2}, TiN and Al\textsubscript{2}O\textsubscript{3} coated silicon nanowires demonstrated enhanced cycling stability and columbic efficiency\textsuperscript{[20]} Ti nanoparticles have also been coated with ALD Al\textsubscript{2}O\textsubscript{3} and used in sodium ion battery by Hu’s group\textsuperscript{[21]} They emphasized that the ALD coated oxide, like ion-conductive nanoglue, robustly anchors the SnNP anode to the substrate during charging/discharging which is a key to improved battery performance. Another exceptional benefit of ALD is that the thin film coatings could be directly deposited on composite electrodes without disturbing the electrode morphology\textsuperscript{[16–22]}. Herein, we demonstrate, for the first time, functional LIBs with ALD HfO\textsubscript{2} surface passivation of SnO\textsubscript{2}/rGO anodes, resulting in a 56% increase in battery capacity as compared to pristine SnO\textsubscript{2}-based anodes.

2. Results and Discussion

2.1. Material and Electrode Characterization

Anode materials were synthesized, structurally and chemically characterized, assembled in 2032 coin cells and electrochemically characterized as described in the methods section. Herein, we compare the performance of two anode materials: nanoscale SnO\textsubscript{2} on rGO with and without ALD HfO\textsubscript{2} coating.

Powder XRD and Raman data from the GO, rGO, SnO\textsubscript{2}/rGO powder are shown in Figure 1(a) and 1(b). Due to the insertion of oxygenated groups and H\textsubscript{2}O molecules, GO shows a diffraction peak at 2θ = 10.0° with an interlayer thickness of 4.43 Å, which corresponds to the (002) reflection of stacked GO sheets. Chemical reduction of GO to rGO leads to broadening and shifting of the XRD peak to around 24.6°. The interlayer distance changes to 3.72 Å after reduction. The peaks labeled in “∗” in GO and rGO XRD pattern originate from sample holders. The XRD pattern of SnO\textsubscript{2}/ rGO can be indexed to the rutile SnO\textsubscript{2} structure (JCPDS No. 41-1445). The (110) peak of SnO\textsubscript{2} overlaps with rGO (002) as indexed with an arrow in SnO\textsubscript{2}/rGO XRD pattern. The SnO\textsubscript{2} nanoparticle size was estimated to be 5–20 nm from the Scherrer formula (see Methods). GO, rGO, SnO\textsubscript{2}/rGO powder were further characterized with Raman spectroscopy. Raman spectroscopy shows (Figure 1(b)) three characteristic peaks at 465 cm\textsuperscript{−1}, 620 cm\textsuperscript{−1}, and 774 cm\textsuperscript{−1}, which can be assigned to the E\textsubscript{g}, A\textsubscript{1g}, and B\textsubscript{2g} active modes of SnO\textsubscript{2}, respectively\textsuperscript{[22]}. Specifically, E\textsubscript{g} can be assigned to the vibration of oxygen atoms in the oxygen plane, while A\textsubscript{1g} and B\textsubscript{2g} are induced by the expansion and contraction vibration mode of the Sn–O bonds. The graphitic G band can be assigned to the first-order scattering of the E\textsubscript{2g} mode of sp\textsuperscript{2} carbon domains\textsuperscript{[24]}. For GO, the G band is located at 1601 cm\textsuperscript{−1}, while for the rGO, it moves to 1596 cm\textsuperscript{−1}, which is close to the value of pristine graphite. This result confirms the reduction of GO during the hydrothermal process. The D band (∼1358 cm\textsuperscript{−1}) is related to a breathing mode of k-point phonons of A\textsubscript{1g} symmetry, which is an indication of disorder originating from defects in the form of vacancies and the size of the in-plane sp\textsuperscript{2} domain\textsuperscript{[25]} The intensity ratio of D to G bands (I\textsubscript{D}/I\textsubscript{G})
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is an indication of the quantity of defects, where a low \( I_D / I_G \) ratio corresponds to a small defect density. Compared with GO, rGO has a lower \( I_D / I_G \) ratio, indicating an increase in the average size of the \( sp^2 \) domains during reduction of GO in the EG solvent.\(^{[26]} \) The surface area was measured using the BET method. It is 342.9 m\(^2\)g\(^{-1}\). The isotherms were characterized as type IV with hysteresis loops in the relative pressure region between 0.4 and 1.0 according to the International Union of Pure and Applied Chemistry (IUPAC) classification (Figure S1).

Figure 1(c) shows an SEM image of the SnO₂/rGO powder, which indicates the formation of a disordered porous carbon network. In Figure 1(d), TEM imaging shows a uniform, densely packed dispersion of SnO₂ nanoparticles with diameter of 5–20 nm on the rGO network, which is consistent with the calculated results obtained from XRD results. The HR-TEM image (inset picture in Figure d) shows that SnO₂ nanoparticles are surrounded by layers of rGO, and layers of graphene structure could be detected. The rGO sheets are expected to facilitate the electron transfer and their high mechanical flexibility is likely to buffer the stress from the volume change of isolated SnO₂ nanoparticles during lithiation.

TGA analysis of the composite anodes was conducted in air and was used to deduce the amount of SnO₂ in the composite (Figure S1. Supporting information). The mass loss in the TGA plot around 100 °C can be attributed to the removal of absorbed water. The mass loss around 200 °C can be attributed to the decomposition of oxygen functional groups. However, for the SnO₂/rGO composite anodes, this peak is small indicating the efficient removal of oxygen functional groups after GO reduction.\(^{[27]} \) The mass loss between 300 and 900 °C can be attributed to carbon oxidation. Thus the composition of the SnO₂/rGO nanocomposite based on TGA is estimated to be 65.5 wt% SnO₂ and 34.5 wt% rGO.

We evaluated the effect of ALD oxide coating by performing ALD on the fabricated SnO₂/rGO electrode directly, rather than on the anode powder prior to electrode assembly.\(^{[16, 17, 19]} \) Figure 2(a) shows a SEM cross-sectional image of the (SnO₂/rGO)-HfO₂ 6 ALD cycles electrode including a copper foil substrate. It is clear that, the electrode is highly porous. Energy dispersive X-ray spectroscopy (EDS) was applied to obtain Hf and other elemental analysis data in the electrodes. Six regions were analyzed from top of electrode to bottom with EDS as shown in Figure 2a. Figure 2c is a plot of the weight fraction of Hf/Sn as a function of the EDS depth profile in the electrode. It is clear that, the Hf content remains relatively constant throughout the (SnO₂/rGO)-HfO₂ 6 ALD cycles electrode (regions 1–6). This shows that ALD precursors can diffuse through the porous electrodes to deposit a conformal film in the torturous path of the entire electrode structure. Figure 2d is the EDS data from region 3, and the peak at 1.64 KeV can be indexed to Hf.\(^{[28]} \) Furthermore, comparison of the HRTEM images of the bare SnO₂/rGO (Figure 1d, inset picture) and the HfO₂ ALD coated SnO₂/rGO (figure 2b, a sample with 20 ALD cycles of HfO₂ deposition) also strongly supports conformal ultrathin coating.

Figure 1. Materials Characterization: (a) XRD pattern of SnO₂/rGO, rGO and GO. (b) Raman spectra of SnO₂/rGO, rGO and GO. (c) SEM of SnO₂/rGO and (d) TEM images showing the SnO₂/rGO at different magnifications.
2.2. Electrochemical Performance of the SnO$_2$/rGO and (SnO$_2$/rGO)-HfO$_2$ electrodes

The cycling performance of SnO$_2$/rGO and (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles electrodes are shown in Figure 3(a). Several observations can be found. The first cycle delivered a specific discharge capacity of 1796 mAhg$^{-1}$ for SnO$_2$/rGO electrode, and 1989 mAhg$^{-1}$ for the (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles electrode. The corresponding initial coulombic efficiencies were 53.6%, and 61.7%, respectively (see Table 1 for details). Furthermore, discharge/charge capacity results at different cycle numbers (using a current density of 150 mAg$^{-1}$) indicate that after 100 discharge/charge cycles, the (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles electrode exhibits 56% improvement in capacity (853 mAhg$^{-1}$), compared to the uncoated SnO$_2$/rGO (Table 1). In addition, the reversible specific capacity decreases to a low value then gradually increases, as has been reported.[29] The decay of reversible capacity during the first 45 cycles could be related to the pulverization of original SnO$_2$ and in situ formation of Sn nanoparticles during electrochemical cycles, which lead to the loss of electrical connectivity.[30] Moreover, it has been reported that structural reorganization of the rGO may also contribute to the capacity fading.[31] During the cycling, the size of Sn nanoparticles becomes smaller which could assist the reaction.[32] The conversion reactions SnO$_2$+4Li$^+$+4e$^-$→2Li$_2$O+Sn becomes possible, which is usually reported as irreversible.[33] From the charge/discharge plots of SnO$_2$/rGO electrode, Figure 3(b) at different cycles, the capacity above 1.0 V indeed increased indicating the irreversible reactions happening during the long-term cycling. It is very possible that the increasing electrochemical reactivity results in the increase of reversible capacity of SnO$_2$/rGO after 45 cycles. Furthermore, evaluations of rate abilities of the electrodes are shown in Figure 3(c). At various current densities from 150 to 1500 mAg$^{-1}$, the electrodes exhibited good rate abilities. At a high current density of 1500 mAg$^{-1}$, the (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles electrode is shown to retain higher reversible capacity (500 mAhg$^{-1}$) compared to uncoated SnO$_2$/rGO electrode which is 370 mAhg$^{-1}$.

The detailed electrochemical processes taking place in these electrodes with respect to lithiation/delithiation were further investigated using cyclic voltammetry (CV). Figure 4 shows the CV data obtained at a scan rate of 0.2 mVs$^{-1}$ in the potential window of 3.0 V to 5 mV. The CV curves show typical SnO$_2$ peaks both in the cathodic and anodic reactions. These CV results match well with those obtained from the charge/discharge curves. In addition, no new peaks are observed for the HfO$_2$ coated electrode. With ALD surface coating effect on SnO$_2$ anode performance clearly demonstrated, we carried out a series of experiments to help understand this effect. 200 ALD cycles of HfO$_2$ was deposited directly on the surface of copper foil without anything and CV was conducted to investigate its electrochemical activity. As shown in Figure 5a, a flat line is found when the same vertical scale is used to compare with previous SnO$_2$/rGO and (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles electrodes’ CV results. No obvious contribution to current density could be
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confirmed. However, close inspection shows several peaks could be observed, but the current density is low. Hence, we could confirm that HfO$_2$ has no capacity contributions to our system. Furthermore, new devices were prepared with thicker HfO$_2$ ALD oxides (20 ALD cycles) deposited on the same SnO$_2$/rGO anodes. Cycle performances of (SnO$_2$/rGO)-HfO$_2$ 20 ALD cycles and SnO$_2$/rGO electrodes at 150 mAg$^{-1}$ current density are shown in the Supporting Information (Figure S2). It can be seen that, after 100 charge/discharge cycles, the 20 ALD cycles HfO$_2$ coated anode still outperforms the uncoated anodes. Specifically, the anode passivated with 20 ALD HfO$_2$ cycles shows a capacity of 762 mAhg$^{-1}$, which is 28% higher than the uncoated electrode. However, it is interesting to note that the SnO$_2$/rGO anodes passivated with 20 ALD cycles HfO$_2$ show lower capacity compared to anodes passivated with only 6 ALD cycles of HfO$_2$. The results suggest that the Li diffusion rate from electrolyte to the surface of rGO/SnO$_2$ is decreasing with increasing HfO$_2$ layer thickness, which is an important consideration for explaining the overall effect of surface passivation by HfO$_2$.

In addition, AC impedance measurements were performed on different anodes in an attempt to further understand the effect of HfO$_2$ coating on SnO$_2$. Figure 5(a) shows the Nyquist plots of SnO$_2$/rGO and (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles electrodes before and after the electrochemical tests. In SnO$_2$/rGO electrodes, the typical characteristics of the Nyquist plots are one semicircle in the high frequency range and a straight line in the low frequency range. In contrast the (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles electrodes have an extra small semi-circle in the highest frequency (Figure 5(b), 5(c)), which could be assigned to the artificial thin film of HfO$_2$.\[34\] Hence, the equivalent circuit models of the SnO$_2$/rGO and (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles electrodes are shown in Figure 5(d), 5(e), respectively, to represent the internal resistances of the test batteries according to literature:\[35\] $R_e$ is the electrolyte resistance; $R_t$ is the resistance of the surface film formed on the electrodes after HfO$_2$ deposition, which is not present in the SnO$_2$/rGO electrode; $R_{ct}$ is charge-transfer resistance; $Z_w$ is the Warburg impedance\[36\] related to the lithium ions diffusion into the bulk electrodes and, the CPE represents the constant phase element. The

Table 1. Capacity parameters of SnO$_2$/rGO, and (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles electrodes.

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<tr>
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<th>Initial Discharge Capacity/ mAhg$^{-1}$</th>
<th>Initial Charge Capacity/ mAhg$^{-1}$</th>
<th>Initial Coloumbic efficiency /%</th>
<th>Capacity after 100 cycle / mAhg$^{-1}$</th>
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<tr>
<td>SnO$_2$/rGO</td>
<td>1796</td>
<td>963</td>
<td>53.6</td>
<td>548</td>
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<tr>
<td>(SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles</td>
<td>1989</td>
<td>1227</td>
<td>61.7</td>
<td>853</td>
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</table>
fitted impedance parameters (ZsimWin software) are listed in Table 2. Before cycling, $R_c$ is essentially the same for both the electrodes (Figure 5(b)). The magnitude of the $R_c$ term decreased after ALD coatings (Figure 5(a)), possibly because ALD coated HfO$_2$ modified the surface of SnO$_2$/rGO electrode. After three electrochemical cycles, there are no large changes in $R_c$ either for SnO$_2$/rGO or the (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles electrodes (Figure 5(b), 5(c) and Table 2). $R_{ct}$ becomes smaller in both electrodes; indicating an increased electric conductivity resulting from irreversible lithium reactions. In (SnO$_2$/rGO)-HfO$_2$ 6-cycles electrodes, $R_c$ increases slightly after 3 electrochemical cycles, this could be attributed to the surface film formation during the electrochemical cycles.[37] All these results confirm that HfO$_2$ ALD thin films can preserve the high ion conductivity of the composite electrode and thus greatly enhance the rapid lithium insertion/extraction, resulting in significant improvement in the electrochemical performance over uncoated SnO$_2$/rGO electrode.

Besides electrochemical testing and SEM/TEM analysis, XPS analysis was also performed on the anodes to determine the possible factors that lead to the observed difference in device performance after ALD HfO$_2$ coating. Figure 6 shows high resolution XPS spectra of the Hf 4f core level from electrodes coated with ALD HfO$_2$ with different thicknesses (6 ALD cycles and 20 ALD cycles), before and after one discharge/charge cycle. The Hf 4f core level was fitted using one doublet (Hf 4f$_{5/2}$-Hf 4f$_{7/2}$) with a fixed area ratio equal to 3:4 and doublet separation of 1.7 eV. The binding energy (BE) of Hf 4f$_{7/2}$ in the as deposited HfO$_2$ films is 0.75 eV higher for the 6 cycle (Figure 6(a)) than for the 20 cycles HfO$_2$ ALD thin film. There are literature reports that the ALD thickness of HfO$_2$ can affect its binding energy.[38] which is the same observation as in our samples. The origin of such shift in binding energy is generally attributed to factors such as charge transfer effect, the presence of electric fields, environmental charge density, and hybridization. Among these, charge transfer is regarded as a dominant mechanism. According to the charge transfer mechanism, removing an electron from the valence orbital increases the core electron’s potential and results in a chemical binding energy shift.[39] Therefore, it is likely that the Hf 4f$_{7/2}$ peak shift (BE = 0.75 eV) for the sample with 6 ALD cycles of HfO$_2$ comes from an enhanced charge transfer from Hf to Sn. One expects that Hf, which has a Pauling electronegativity of 1.3, would donate charge to Sn, which has a Pauling electronegativity of 1.9, and this should result in a substantial shift toward higher binding energy for the Hf 4f core level. For the thicker HfO$_2$ film (20 cycles), we expect the measured Hf intensity to be dominated by the signal from the top surface of the film, where charge transfer to Sn is less prominent. Hence the BE of Hf 4f$_{7/2}$ (20 cycle HfO$_2$) before electrochemical testing (Figure 6(b)) is 17.26 eV and corresponds to HfO$_2$.[23a] Interestingly, after one discharge/charge cycle, the Hf 4f showed a 0.65 eV decrease in BE for the 6 ALD cycle sample (Figure 6(a), 6(c)), and only 0.15 eV for 20 ALD cycles (Figure 6(b), 6(d)). Apparently, the 6 ALD cycles HfO$_2$ is thin enough that the whole film may be involved in the charge transfer process from Hf to Sn. This is not the case for the thicker 20 ALD cycles HfO$_2$ film since only a small portion of the film is involved in the charge transfer process with the Sn-containing anode.

Figure 4. Cyclic voltammetry measurements of (a) SnO$_2$/rGO and (b) (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles anodes at 1$^{st}$, 2$^{nd}$ and 10$^{th}$ cycle with a scan rate of 0.2 mVs$^{-1}$ between 3.0 V and 5 mV. (c) CV of HfO$_2$ 200 ALD cycles electrode directly on copper foil, inset figure is the scaled data.
An additional experiment was also performed to determine if the HfO₂ effect is specific to our SnO₂/rGO anodes. We performed surface passivation of commercial SnO₂ nanoparticles (as opposed to our own hydrothermally produced SnO₂ nanoparticles) using HfO₂, and used the coated nanoparticles as the anode material in a Li ion battery, prepared using the same procedure described in the methods section. Up to 200 ALD cycles of HfO₂ were deposited on the commercial SnO₂ anode, and the electrochemical performance was still improved over SnO₂ anodes, Figure 7a. The CV curves indicate that the SnO₂ anodic/cathodic peak intensities increased after HfO₂ coating, and that there are no alien peaks detected in the CV curves. It appears that even 200 cycles of ALD HfO₂ do not block the lithium diffusion.

More importantly, depositing HfO₂ by ALD on only rGO anodes, without SnO₂ nanoparticles, shows no performance improvement over uncoated rGO electrode, Figure 7b. This result suggests that HfO₂ itself does not behave as active anode material; instead, it seems to enhance the SnO₂ electrode performance, possibly through a charge transfer process, while not limiting the Li diffusion due to its amorphous nature.

To summarize so far, our data indicate that (1) HfO₂ itself does not contribute to the electrode capacity, Figure 4 and Figure 7 (2) ALD HfO₂ coatings improve the performance of SnO₂ anodes irrespective of the SnO₂ fabrication procedure or morphology (commercial vs hydrothermally prepared, Figure 7a, and (3) even after 200 cycles HfO₂ coating by ALD, the battery performance is still better than the SnO₂ without HfO₂ coating. We believe that the weak dependence of battery performance on ALD HfO₂ thickness is a result of the amorphous nature of the HfO₂ film, which does not substantially hinder lithium ion diffusion, but protects SnO₂ from severe interaction with the electrolyte. The AC impedance also shows that R_{ct} becomes the smaller in the case of HfO₂, suggesting that the ion conductivity of the electrode has been improved. We conclude that the electrochemical performance is improved after coating HfO₂ by both a charge transfer process and by the minimal impact of

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<th>Before/After 3 cycles</th>
<th>R_e/ohm</th>
<th>R_f/ohm</th>
<th>R_{ct}/ohm</th>
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<tr>
<td>SnO₂/rGO</td>
<td>2.4/2.7</td>
<td>NA</td>
<td>166.1/91.7</td>
</tr>
<tr>
<td>(SnO₂/rGO)-HfO₂ 6 ALD cycles</td>
<td>2.3/2.7</td>
<td>1.5/3.6</td>
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Figure 5. Impedance analysis of the assembled devices: (a) Nyquist plots of SnO₂/rGO and (SnO₂/rGO)-HfO₂ 6 ALD cycles electrode before cycling and after 3 charge/discharge cycles performed by applying a wave with an amplitude of 5 mV over the frequency range 1000 kHz to 0.01Hz. (b) and (c) are Nyquist plots at high frequency for the same devices; (d) and (e) are the Randles equivalent circuit for SnO₂/rGO and (SnO₂/rGO)-HfO₂ 6 ALD cycles electrode/electrolyte interface, respectively.
amorphous HfO$_2$ on the diffusion of Li, particularly for the thin HfO$_2$ films. When HfO$_2$ films are thin (6 ALD cycles), Li HfO$_2$ appears to interact with the SnO$_2$ anodes, an interaction that possibly involves a charge transfer process, leading to more stable SnO$_2$ and better lithiation performance.

3. Conclusion

In conclusion, we have shown that the surface passivation of SnO$_2$-based anodes by atomic layer deposition of HfO$_2$ significantly enhances the performance of Li ion batteries. The results indicate that HfO$_2$ protects the SnO$_2$-based anode from irreversible reactions with the electrolyte, and buffers its volume change during lithiation/delithiation, as evidenced by the improved performance compared to the un-passivated SnO$_2$. The amorphous nature of the ALD HfO$_2$ films allows efficient diffusion of the lithium ions, even with thick HfO$_2$ passivation layers. XPS analysis suggests that an interaction takes place between Hf and Sn, a process which apparently enhances the lithiation reaction for the HfO$_2$ coated SnO$_2$-based anodes.

4. Experimental Section

Material Synthesis: Graphite Oxide (GO) was synthesized from natural graphite powder by a modified Hummer’s method.$^{[40]}$ SnO$_2$ nanoparticles supported by reduced graphene oxide (SnO$_2$/rGO) were prepared by a one-step hydrothermal process, using tin salts in an ethylene glycol solution containing GO. In a typical experiment, SnCl$_4$·5H$_2$O and GO with weight ratio of 1:1 (a ratio optimized according to the electrochemical performance of the resulting material) were suspended into ethylene glycol, and ultrasonicated for 1h. The resulting dark brown solution was transferred to a Teflon autoclave and heated to 210 °C for 12 h in an oven. After cooling to room temperature, the product was washed and centrifuged with acetone and ethanol four times, and the resultant black product was dried at 70 °C in air to obtain the desired SnO$_2$/rGO powder.

Material Characterization: The SnO$_2$/rGO powder was characterized using a powder X-ray diffraction (XRD) system (Bruker, D8 ADVANCE) with Cu Kα radiation ($\lambda = 0.15406$ nm) at a scanning speed of 2°/min. The SnO$_2$ nanoparticle size was estimated using the Scherrer formula, $D = (0.89\lambda)/\beta\cos \theta$, where $\lambda$ is the wavelength, $\beta$ is the peak full width at half-maximum (FWHM) in radians, and $\theta$ is the Bragg angle. Raman spectroscopic analysis

![Figure 6](image1.png)  
**Figure 6.** High-resolution XPS spectra of Hf 4f core level obtained from (SnO$_2$/rGO)-HfO$_2$ 6 ALD cycles electrode (a) before and (c) after one charge/discharge cycle; Similar spectra for 20 ALD cycles HfO$_2$ are shown (b) before and (d) after one charge/discharge cycle

![Figure 7](image2.png)  
**Figure 7.** a) Cyclic Voltammetry of commercial powder SnO$_2$ (SnO$_2$ CP) and SnO$_2$ CP-HfO$_2$ 200 ALD cycles electrode at a scan rate of 0.1 mVs$^{-1}$. b) Cyclic Voltammetry of rGO and rGO/HfO$_2$ 200 ALD cycles at a scan rate of 0.1 mVs$^{-1}$ between the voltage 3.0 V and 0.005 V
was carried out using a LabRam Aramis Raman spectrometer with He–Ne laser having an excitation wavelength of 633 nm. Thermogravimetric analysis (TGA) was performed using a TG 209 F1 Iris system at a heating rate of 5 °C/min in air. The surface morphology and microstructure of the samples were investigated by scanning electron microscopy (SEM, FEI Helios Nanolab), and transmission electron microscopy (TEM, FEI CM30) measurements. XPS analysis was carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source (hν = 1486.6 eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of ~10−9 mbar. The high-resolution spectra were collected at fixed analyzer pass energy of 20 eV.

**Fabrication of Electrodes:** The working electrodes were prepared by mixing the active material (SnO2/rGO) with Acetylene Black (MTI, Inc.), poly(vinylidene fluoride) (PVDF, MTI Inc) in a weight ratio of 75:10:15 in N-methyl-2-pyrrolidone (NMP, MTI) to form a slurry. This slurry was uniformly pasted on a copper foil (MTI, Inc.) using a scraper, and dried at 70 °C for 12 h in air.

**ALD Growth of Hafnium Oxide:** HfO2 ultrathin films were directly deposited on the prepared electrodes at 180 °C (Cambridge Nano Tech Savannah). The HfO2 ALD reaction sequence was: 1) N2 dose to 20 psi; 2) H2O dose for 0.015 sec; 3) H2O reaction time 10sec; 4) Tetakis (dimethylamino) hafnium (Hf(NMe2)4) dose to 0.2 sec; 5) Hf(NMe2)4 reaction time 15 sec. This sequence constitutes one cycle of ALD HfO2. The growth rate per cycle is 1.01Å/cycle at these conditions.

**Electrochemical Measurements:** Electrochemical measurements were carried out in 2032 coin-type (MTI) half-cell devices using a VMP3 electrochemical analyzer (Biologic Inc.). The working electrodes were SnO2/rGO and (SnO2/rGO)-HfO2. Average testing was performed using a VMP3 electrochemical analyzer (Biologic Inc.). The working electrodes were SnO2/rGO and (SnO2/rGO)-HfO2. Average testing was performed using a VMP3 electrochemical analyzer (Biologic Inc.).

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**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.


