Author's Accepted Manuscript

Atomic Layer Deposition of SnO₂ on MXene for Li-Ion Battery Anodes

Bilal Ahmed, Dalaver H. Anjum, Yury Gogotsi, Husam N. Alshareef

PII: S2211-2855(17)30121-0
DOI: <http://dx.doi.org/10.1016/j.nanoen.2017.02.043>
Reference: NANOEN1819

To appear in: *Nano Energy*

Received date: 3 January 2017
Revised date: 15 February 2017
Accepted date: 22 February 2017

Cite this article as: Bilal Ahmed, Dalaver H. Anjum, Yury Gogotsi and Husam N. Alshareef, Atomic Layer Deposition of SnO₂ on MXene for Li-Ion Battery Anodes, *Nano Energy*, <http://dx.doi.org/10.1016/j.nanoen.2017.02.043>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Atomic Layer Deposition of SnO₂ on MXene for Li-Ion Battery Anodes

Bilal Ahmed¹, Dalaver H. Anjum¹, Yury Gogotsi², Husam N. Alshareef^{1*}

¹*King Abdullah University of Science and Technology (KAUST), Materials Science and Engineering, Thuwal, 23955–6900, Saudi Arabia*

²*Department of Materials Science and Engineering, and A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, PA 19104, USA*

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

Abstract

In this report, we show that oxide battery anodes can be grown on two-dimensional titanium carbide sheets (MXenes) by atomic layer deposition. Using this approach, we have fabricated a composite SnO₂/MXene anode for Li-ion battery applications. The SnO₂/MXene anode exploits the high Li-ion capacity offered by SnO₂, while maintaining the structural and mechanical integrity by the conductive MXene platform. The atomic layer deposition (ALD) conditions used to deposit SnO₂ on MXene terminated with oxygen, fluorine, and hydroxyl-groups were found to be critical for preventing MXene degradation during ALD. We demonstrate that SnO₂/MXene electrodes exhibit excellent electrochemical performance as Li-ion battery anodes, where conductive MXene sheets act to buffer the volume changes associated with lithiation and delithiation of SnO₂. The cyclic performance of the anodes is further improved by depositing a very thin passivation layer of HfO₂, in the same ALD reactor, on the SnO₂/MXene anode. This is shown by high-resolution transmission electron microscopy to also improve the structural integrity of SnO₂ anode during cycling. The HfO₂ coated SnO₂/MXene electrodes demonstrate a stable specific capacity of 843 mAh/g when used as Li-ion battery anodes.

Graphical abstract

Keywords: MXene, Ti_3C_2 , SnO_2 , anode, lithium ion battery, ALD

1. Introduction

Li-ion batteries have matured from a technology for powering portable electronic devices to grid energy storage and many other applications. Nevertheless, opportunities to improve battery performance, especially through exploring new classes of layered materials, including oxides, sulfides, and transition metal carbides, need to be further explored.[1-3] Two-dimensional (2D) materials offer gallery space for shuttling metal ions while impressively sustaining volumetric changes, which could lead to the improved storage capacity and excellent cycling stability.[4] Optimization of the battery performance of 2D materials requires tailoring

the surface chemistry while enabling the intercalation of metal ions to enhance the charge storage capacity and operational voltage window.

To this end, MXenes, which are a large family of 2D transition metal carbides, nitrides, and carbonitrides are an attractive option.[5, 6] They are represented by the general formula of $M_{n+1}X_nT_x$, where ‘M’ represents an early transition metal, ‘X’ represents either carbon, nitrogen or both and $n = 1, 2$ or 3 , and T_x indicates the surface functional groups, such as $-OH$, $=O$ or $-F$. [5, 6] These surface functionalities provide hydrophilicity, which is good for use with aqueous electrolytes, but may be detrimental for non-aqueous electrolytes. The surface structure and chemistry govern the metal ions adsorption and intercalation to achieve optimal storage capacity and operating potential windows. Therefore, chemical treatment or decoration of MXene surfaces can be used to improve their electrochemical performance in organic electrolytes.

MXenes, such as Ti_3C_2 , have been reported to exhibit metallic conductivity, negative surface charge in solutions, and high hydrophilicity.[5, 7] Due to their high electrical conductivity and 2D structure, MXenes have been studied as electrode materials in supercapacitors,[8] Li[9-11] and Na[12, 13] ion batteries, electrochemical sensors,[14, 15] electromagnetic interference shielding[16] and water purification[17] applications.

Ti_3C_2 is one of the most studied MXene phases because of the well-established etch chemistry involved and the detailed theoretical studies.[18, 19] Furthermore, its large volumetric capacitance has made it an attractive candidate for supercapacitors electrodes [8, 20, 21] and as anode material for Li ion batteries.[22, 23] For instance, based on density functional theory calculations, Tang et al. predicted the theoretical capacity of bare Ti_3C_2 for Li intercalation to be 320 mAh/g and it can be doubled as a double-layer of Li atoms is formed between MXene

sheets.[24] However, in reality, the presence of functional groups, such as $-F$ or $-OH$, on MXene surface, limits the Li^+ ion capacity such that the measured actual capacities were only about 130 mAh/g for $Ti_3C_2F_2$ and 67 mAh/g for $Ti_3C_2(OH)_2$. [25, 26] On the experimental front, HF-etched Ti_3C_2 powder showed a specific capacity of 123.6 mAh/g at a 1C rate.[22] However, delaminated, etched and assembled with nanotubes $Ti_3C_2T_x$ showed the capacity exceeding 700 mAh/g, showing a potential of MXene to deliver good performance if a proper electrode design is applied.[27]

Few research groups have aimed to exploit the surface chemistry of MXenes to enhance Li^+ ion storage by either decorating the MXene surface with metal ions[28] or by producing *in-situ* TiO_2 on the MXene surface.[10, 29] For example, Naguib et al. performed flash oxidation of Ti_3C_2 MXene, which formed TiO_2 nanocrystals on thin sheets of disordered graphitic carbon with a specific capacity of 220 mAh/g at a C/18 rate.[29] Ahmed et al. reported that H_2O_2 -assisted room-temperature oxidation of Ti_2C MXene results in the formation of anatase TiO_2 on the MXene surface with a specific capacity of 389 mAh/g at a C/3.7 rate.[10] Recently, Luo *et al.* decorated the negatively charged MXene surface with Sn^{4+} ions by a facile polyvinylpyrrolidone (PVP)-assisted liquid-phase immersion method. The prepared composite showed improved specific capacity up to 544 mAh/g and good cyclic performance.[28] Tin oxide was also used for pillaring Ti_3C_2 layers in Li-ion capacitors.[28] However, gas phase deposition of oxides onto MXenes has never been reported.

Atomic layer deposition (ALD) has been widely used in the electronics industry to deposit uniform and conformal coatings with excellent thickness control.[30] Recently, ALD has been used to improve battery technology either by creating 3D electrode nanostructures or by

modifying the electrode/electrolyte interface.[31-33] The sequential layer-by-layer ALD at the atomic scale facilitates the production of finely tuned nanostructures with controlled properties.

Coating the MXene surface with oxides by chemical methods, such as hydrothermal, may not be the best choice because MXenes are prone to oxidation and structural degradation in harsh chemical environments, such as supercritical water.[29, 34] For instance, hydrothermal treatment of $\text{Ti}_3\text{C}_2\text{T}_x$ has caused formation of TiO_2 and free carbon on the MXene surface.[29] Therefore, we used a low-temperature atomic layer deposition (ALD) process to conformally deposit oxides on the MXene sheets. In our anode design, SnO_2 -coated MXene was prepared to combine the high theoretical capacity of SnO_2 with the structural stability and high electronic conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ to stabilize the anode during the charge/discharge process. The second aspect of our electrode design was to further improve the stability of the SnO_2 /MXene anode by coating it with a conformal thin passivation layer of inactive HfO_2 in the same ALD reactor, which we previously showed can act as artificial solid-electrolyte interphase (SEI) layer in Li-ion batteries.[31, 35, 36] The proposed electrode design strategy indeed led to MXene-supported anode architectures with high capacity and cycling stability.

2. Experimental

Material Synthesis and Characterization: Commercially available Ti_2AlC powders (Kanthal, Sweden) and TiC (Sigma Aldrich) were mixed in a 1:1 molar ratio, ball milled for 24 h, and sintered at 1350 °C for 2.5 h under argon flow. The resulting loosely held compact powder was crushed and sieved to obtain Ti_3AlC_2 powder with particles of < 38 μm . Ti_3C_2 MXene was prepared by HF etching of Al from the MAX phase.[6] In a typical etching protocol, 2 g of MAX phase powder was added to 20 mL of 48% HF (Sigma Aldrich) and stirred for 18 h at room temperature. The resulting solution was washed several times with deionized water to remove the

acid (until the solution reached a pH value of 6) and bath sonicated to obtain exfoliated Ti_3C_2 MXene sheets. The resulting MXene sheets consist of few-layer and multilayer stacks. The MXene powder was collected by vacuum filtration, dried in a vacuum oven at 70 °C overnight, and stored in a vacuum desiccator for further experiments.

The X-ray diffraction patterns of MXene and oxide-coated MXene anodes were measured using a powder X-ray diffractometer (XRD, Bruker, D8 ADVANCE) with Cu K_α radiation ($\lambda = 0.15406$ nm). The surface morphology and microstructure of MXene samples were characterized with field-emission scanning electron microscopy (FESEM, Nova NanoSEM from FEI) and transmission electron microscopy (TEM) (Titan G² 80-300 ST, FEI). The TEM samples were prepared by scratching SnO_2 /MXene powders off Cu-foil and dispersing it in ethanol.

Atomic Layer Deposition of SnO_2 and HfO_2 : The ALD coating of SnO_2 and HfO_2 was directly performed on MXene layers deposited on a Cu foil. The MXene layer was prepared by mixing the MXene powder with acetylene black (MTI, Inc.) and poly(vinylidene fluoride) (PVDF, MTI Inc.), in a weight ratio of 80:10:10, in NMP solvent. The prepared slurry was uniformly pasted on a copper foil using a doctor blade to coat thickness up to 100 μm (MTI, Inc.) and dried at 80 °C for 24 h under vacuum conditions. The MXene-coated Cu foil was placed in ALD chamber for SnO_2 and HfO_2 deposition and mass of active material was measured afterwards (1–2 mg/cm^2). This mass was used to calculate current densities and specific capacities.

SnO_2 deposition was carried out at two temperatures (150 °C or 200 °C) in a Cambridge Nanotech Savannah ALD reactor. A typical process cycle at 150 °C comprised the following steps: 1) a constant N_2 dose at 20 psi, 2) a dose of Sn precursor (Tetrakis(diethylamido)tin(IV)) dose for 0.5 sec, 3) a Sn precursor reaction time of 30 sec, 4) an O_3 oxidant dose for 0.2 sec, and

5) an oxidant reaction time of 15 sec for a deposition rate of 0.1 nm per cycle. A typical cycle at 200 °C involved the same precursors, but the reaction times were adjusted to obtain comparable thickness of SnO₂ on MXene sheets. Similarly, ultrathin films of HfO₂ were deposited on the prepared SnO₂/MXene electrodes at 180 °C. The HfO₂ ALD reaction sequence comprised the following steps: 1) a constant N₂ dose at 20 psi; 2) an H₂O dose for 0.015 s; 3) an H₂O reaction time for 10 s; 4) a dose of precursor (Tetrakis (dimethylamino) hafnium (Hf(NMe₂)₄)) for 0.2 s, and 5) an Hf(NMe₂)₄ reaction time of 15 sec for a growth rate of 0.1 nm per cycle.

Electrochemical Testing. To assess the electrochemical performance, 2032 coin-type (MTI, Inc.) half-cell devices were fabricated. SnO₂/MXene served as the working electrode, lithium foil served as the counter and reference electrode, and Celgard 3501 microporous membrane separated the anode and cathode compartments. 1M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by weight) was used as electrolyte. The cells were assembled in an argon-filled glove box (MBRAUN) with the concentrations of O₂ and H₂O < 0.5 ppm. The electrochemical performance of the assembled cells was measured at different current densities (100–1000 mA/g) in the voltage window from 0.01 to 3.0 V vs. Li⁺/Li (unless otherwise specified) using an Arbin battery tester (Arbin BT-2143-11U, College Station, TX, USA). Cyclic voltammetry was performed to examine the reduction and oxidation peaks in the voltage range of 0.01 – 3.0 V (V vs. Li/Li⁺) at a scan rate of 0.2 mV/s using VMP3 Biologic potentiostat (Biologic, France). The electrical impedance spectra (EIS) were measured by applying a sine wave with an amplitude of 5.0 mV over the frequencies 1000 kHz to 0.1 Hz.

3. Results and Discussion

The as-prepared MXene sheets were used for SnO₂ deposition by hydrothermal synthesis on as-exfoliated MXene sheets, and by sputtering or ALD process on MXene films coated on Cu-foil substrates. The schematic illustration of three different processes along with resulting effects on MXene sheets is presented in Figure 1. Hydrothermal synthesis resulted in the formation of SnO₂ particles on distorted MXene sheets, due to high temperature, pressure and aqueous environment, which can modify the MXene (see supporting information, Figure S1). Sputter-deposited SnO₂ films partially covered the MXene sheets, mainly the accessible outer surface and not the interlayer space, however Ti₃C₂ MXene retained its structure and morphology (see supporting information, Figure S1) due to the non-conformal nature of the sputtering process. The ALD process produced conformal SnO₂ films that completely covered the MXene surface.

The XRD patterns of as-prepared Ti₃AlC₂ and HF-etched Ti₃C₂T_x are shown in Figure 2a. A small amount of titanium carbide (TiC) was found as secondary phase of the as-synthesized Ti₃AlC₂ powder. The XRD pattern of the as-prepared Ti₃AlC₂ was indexed with JCPDS card no. 52-0875. HF etching resulted in a significant loss of crystallinity and structural distortion, which is indicated by the weakening of XRD peaks. Most importantly, due to the exfoliation process, the (002) peak ($2\theta \approx 10^\circ$) shifted to the lower angle and broadened as compared to its original location in the Ti₃AlC₂ phase, which indicates an increase in the *c*-lattice parameter and less regular spacing between the Ti₃C₂ layers after Al removal.. Typically, Ti₃AlC₂ has a *c*-lattice parameter of 18.58 Å, which increased to 19.96 Å after HF etching. Thus, d-spacing values of Ti₃AlC₂ and Ti₃C₂T_x were 0.929 and 0.997 nm, respectively. Note that the space available between a pair of MXene sheets can act as a 2D gallery for shuttling electrolyte ions[6] The SEM image from a typical flake of Ti₃C₂T_x presented in Figure 2b illustrates successful exfoliation,

where sheets are separated and exhibit an accordion-like structure. We used $\text{Ti}_3\text{C}_2\text{T}_x$, which consisted of single-layer and multilayer flakes, without further delamination for ALD of oxides because we wanted to use the inter-flake separation to ensure uniform SnO_2 coverage on the MXene surfaces. The low-magnification TEM image of $\text{Ti}_3\text{C}_2\text{T}_x$ and the corresponding selected-area electron diffraction (SAED) pattern (Figure 2c) clearly show the flake-like nature of the nanosheets after exfoliation. The SAED pattern of $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits the hexagonal symmetry of the carbide layers inherited from Ti_3AlC_2 . Moreover, fast Fourier transform (FFT) filtered high-resolution TEM image (Figure 2d) shows the hexagonal arrangement at the atomic scale, indicating removal of the Al layers and exfoliation. This MXene powder was used for further experiments in this study.

As mentioned earlier, to use MXene sheets as support for SnO_2 anodes, we needed to ensure that the MXene remains stable in the synthesis environment.[29, 34] For instance, when we tried to decorate MXene surface with SnO_2 nanoparticles by hydrothermal synthesis, XRD confirmed degradation of MXene (Figure S1a) - the (002) MXene peak disappeared and only SnO_2 peaks were observed. We attribute these changes to the high temperature (180 °C) and pressure used in the hydrothermal process of SnO_2 . This observation is consistent with previous reports of the hydrothermal treatment of MXene, which resulted in the formation of TiO_2 nanoparticles on the MXene surface.[29] Figure S1b shows a typical SEM image of a hydrothermally synthesized $\text{SnO}_2/\text{MXene}$ anode, where the SnO_2 particles appear on distorted MXene flakes. For similar reasons, other techniques that involve the use of strong oxidizing agents that can degrade MXene cannot be used. In this scenario, physical vapor deposition techniques, such as magnetron sputtering, may seem like a viable option for coating SnO_2 onto MXenes, but they lack the conformity needed to uniformly coat the complex layered

arrangement of MXene sheets. Although we find that the MXene phase remains stable during the sputtering process (XRD pattern in Figure S1a), sputtered SnO_2 does not conformally coat the MXene sheets and is only deposited on the outermost MXene flakes (inter-flake space remains uncoated).

For atomic layer deposition of SnO_2 on any given substrate, the substrate surface must be hydrophilic to attach $-\text{O}$ or $-\text{OH}$ functional groups onto the surface of the substrate. These functional groups are normally chemically attached to the substrate by flowing an oxidant (ozone or water vapor) in the exposure step of the ALD process at high temperature. To prevent MXene oxidation from the ozone or water vapor exposure, we exploited the already present (from the etching process) functional groups ($-\text{O}$ or $-\text{OH}$) on the MXene surface [26, 37], and the first exposure step in our ALD process used Sn precursor (Tetrakis(diethylamido)tin(IV) rather than oxidant (water vapor or ozone). To study the effect of the chemistry of the first exposure step used in the ALD process on MXene stability, we compared XRD patterns of MXenes after SnO_2 deposition in two cases. In one case, SnO_2 deposition on MXene was done using oxidant (water vapor or ozone) in the first exposure step, and in the second case using Sn precursor in the first exposure step. When ozone was used for the first exposure step at 200 °C, the MXene was oxidized, as reflected by the disappearance of (002) peak (Figure S1c), and the MXene flakes were ruptured, as can be seen in Figure S1d. In contrast, when Sn precursor was introduced in the first ALD exposure step, the MXene structure remained intact. Hence, the presence of functional groups (OH or O) on MXene surface after the aqueous acidic etching process is actually beneficial for SnO_2 growth by ALD.[26, 37] Hence, the “Sn precursor first” approach was used for all subsequent SnO_2 growth studies.

SnO₂ layers of various thickness were grown by ALD on MXene sheets at 150 °C and 200 °C. The precursor and oxidant exposure times as well as the purge times were adjusted such that the growth rate remained constant at 0.1 nm per cycle (see Experimental for details). SnO₂ layers of 5 – 50 nm thickness were deposited on MXene sheets and studied as anode materials for Li ion batteries. Two thicknesses (10 nm and 50 nm) were chosen for detailed electrochemical characterization and the results are discussed in the remaining portion of this manuscript. Images from HRTEM analysis show 50-nm SnO₂-coated MXene anodes deposited at 150 °C (Figure 3a) and 200 °C (Figure 3b) using Sn precursor in the first purge. These images show that the layered and stacked nature of MXene flakes was preserved during SnO₂ deposition, and the corresponding SAED patterns confirm this via the presence of hexagonal crystal structures. Furthermore, the SAED pattern of 50-nm SnO₂-coated MXene sheets prepared at 150 °C (inset of Fig. 3a) showed no significant contribution to the diffraction pattern, indicating that amorphous SnO₂ had formed on the MXene surface. However, at 200 °C, a ring pattern is visible (inset of Fig.3b), indicating the formation of crystalline SnO₂. At the same time, the MXene structure was preserved at the atomic and microscopic scales. This is a result of two factors (1) the extremely slow heating rate (1 °C/minute) prevented MXenes flakes from rupturing, and (2) using Sn precursor during the first cycle of the ALD process, which protected the MXene flakes from unwanted oxidation. XRD confirms these findings (Figure S2) and a (211) peak from SnO₂-coated MXene flakes was observed after deposition at 200 °C.

SEM images show the microstructure of 50-nm SnO₂/MXene electrodes prepared at 150 °C (Figure S2c) and 200 °C (Figure S2d) and confirm that the layered nature of MXene was preserved after ALD at both temperatures. To illustrate the distribution of SnO₂ on MXene sheets, an RGB plot of a Fourier-filtered HRTEM image is shown in Figure 3c. It clearly

demonstrates the presence of SnO_2 crystallites on MXene. Furthermore, Figure 3d shows a STEM image illustrating the preserved layered structure of the MXene after ALD. The HRTEM image without Fourier filtering and the corresponding images with fast Fourier transform (FFT) and with applied filters are given in Figure S3. The inset in Figure 3d shows the EDS line scans for Sn and Ti, which clearly indicate the presence of uniform Sn layers and a low content of Ti between the flakes.

The electrochemical performance of SnO_2 -coated MXene was evaluated using half-cell Li ion batteries (Li foil as the counter electrode). Figure 4a shows the cyclic voltammetry (CV) curves of as-prepared MXene, along with SnO_2 /MXene composite electrodes measured at a scan rate of 0.2 mV/s in the voltage range of 0.01–3.00 V (vs. Li/Li^+). The shape of the CV curves for as-prepared MXene and SnO_2 -coated MXene anodes is similar to those reported in the literature.[22, 28] In the first cathodic scan of the as-prepared MXene electrode, three large and two small cathodic peaks were observed at 1.39, 1.18, 0.78, 0.50, and 0.01 V, respectively. The broad peaks at 1.39 and 0.78 V disappear in subsequent cycles, which can be attributed to the formation of an SEI and trapping of Li^+ ions between MXene sheets.[28] Note that HF-etched MXene is terminated with hydroxyl or fluorine groups and Li ions may interact with these functional groups, resulting in a large first-cycle irreversibility.[22, 37] The third large peak at 0.01 V, corresponds to the lithiation of carbon present in the anode material.[28] During the anodic scan, two distinct anodic peaks at 1.00 and 0.85 V were observed, corresponding to the removal of Li ions from MXene sheets.[9, 28] With subsequent cycling, these two peaks merge and form one broader peak centered at 0.90 V. SnO_2 /MXene anode behaved differently depending on the thickness of the SnO_2 layer. For instance, with a 10-nm-thick SnO_2 layer (Figure 4a), the combined effect of MXene and SnO_2 can be seen in the CV curves, while the

SnO₂ dominated the electrochemical performance of samples with a 50-nm-thick SnO₂ coating. For SnO₂/MXene electrodes, a large reduction peak below 1.00 V corresponds to the formation of SEI and reduction of SnO₂ with Li⁺ ions, as its intensity significantly decreases during subsequent cycles.[38] The reduction reaction of SnO₂ with Li⁺ ions can be described by the following equation[39]:

The more prominent peak between 0.01 – 0.50 V corresponds to the formation of Li_xSn alloy.[40] This alloying/dealloying reaction is highly reversible, providing a major contribution to lithium storage capacity and can be described by the following equation ($0 \leq x \leq 4.4$)[39]:

In the anodic scan, three distinct peaks appear at 0.50, 0.80, and 1.00 V. The latter two peaks (0.80 and 1.00 V) correspond to the removal of Li⁺ ions from MXene sheets, while the first peak corresponds to the electrochemical oxidation of Sn.[39] The peak at 1.25 V (more visible in the 5th CV cycle, Figure S4) corresponds to the reversible reaction of Li⁺ ions with SnO₂. When the thickness of the SnO₂ layer is increased from 10 to 50 nm, both alloying/dealloying reactions of Li⁺ ions with Sn and redox reactions of SnO₂ become more significant.[28, 38] The first five CV cycles of all samples are separately plotted in Figure S4, where it can be readily observed that alloying/dealloying reactions are highly reversible, while oxidation/reduction reactions of SnO₂ are only partially reversible. This partial reversibility of SnO₂ plays a major role in the poor cyclic performance of conventional SnO₂-based anodes.

The galvanostatic charge/discharge (specific capacity vs. voltage) curves measured at 100 mA/g in the voltage range of 0.01–3.00 V (vs. Li/Li⁺) are shown in Figure 4b. The first-cycle discharge and charge capacities of as-prepared MXene were 351 and 182 mAh/g, respectively, which correspond to a Coulombic efficiency of 51%. The voltage plateau and slope of the charge/discharge curves are consistent with the observations made from the CV curves. For SnO₂/MXene composite anodes, a 10-nm-thick SnO₂ layer (ALD @ 200 °C) shows first cycle discharge and charge capacities of 1024 and 583 mAh/g, which correspond to a Coulombic efficiency of 56%. For a 50-nm-thick SnO₂ layer prepared under the same conditions (ALD @ 200 °C), the first discharge and charge capacities of 1463 and 1041 mAh/g were obtained, respectively. The charge capacity achieved in this case was higher than the theoretical capacity of SnO₂ (782 mAh/g), which may be due to the extremely small nanocrystals of SnO₂ achieved by ALD.[41] Ideally, this effect should be seen with a 10-nm-thick SnO₂ coating on MXene, but the calculation for specific capacity is based on the total mass of the coated MXene electrode, which accounts for the combined capacities of SnO₂ and MXene. The performance parameters, including specific capacity, Coulombic efficiency, and capacity retention are summarized in Table S1.

The cyclic performance of SnO₂-coated MXene anodes was assessed at various current densities, ranging from 100 to 1000 mA/g. The comparison of cyclic performance at 500 mA/g is given in Figure 4c. The as-prepared MXene delivered a first-cycle discharge capacity of 260 mAh/g and showed a stable capacity of 109 mAh/g after 50 cycles. The SnO₂/MXene anode (10-nm-thick SnO₂ layer) showed a first-cycle discharge capacity of 736 mAh/g and delivered a stable capacity of 258 mAh/g after 50 cycles. We hypothesize that this stable cyclic performance is a result of the layered MXene structure, which accommodates volumetric changes during the

charge/discharge process. To test this hypothesis, we deposited a 10-nm-thick layer of SnO₂ on bare Cu foil (without MXene). Without support from MXene, the capacity quickly faded, and after the 50th cycle, a discharge capacity of 77 mAh/g was obtained (Figure S5). Moreover, the SnO₂-only electrode had a specific capacity of 168 mAh/g, which is mainly due to the non-conductive nature of SnO₂ films which causes the specific capacity to decrease quickly. Previous reports showed that ALD prepared SnO₂-only anode on stainless steel substrate retained 11% of its initial capacity because of detachment of active material from substrate due to large volumetric changes.[38] Therefore, in addition to structural support, MXene provides a conductive 3D network (in contrast to the flat surface of the Cu foil) to the deposited SnO₂ layer, which resulted in higher specific capacity of SnO₂/MXene electrodes (696 mAh/g). Furthermore, when the thickness of SnO₂ layer was increased to 50 nm, the SnO₂-coated MXene anode showed high charge/discharge capacities during initial cycles, but the capacity faded quickly and specific capacities of 239 and 451 mAh/g were achieved after deposition at 150 °C and 200 °C, respectively. Although, the achieved specific capacity was four times higher than for as-prepared MXene (109 mAh/g) and two times higher than for the 10-nm-thick SnO₂ layer coated MXene composite electrode (178 mAh/g); the 50-nm-thick coating of SnO₂ on MXene (ALD @ 200 °C) showed a capacity retention of 50% (calculated based on 2nd cycle discharge capacity). This capacity fade indicates that with increasing SnO₂ layer thickness, the MXene sheets can no longer accommodate the larger volumetric changes of SnO₂ electrodes. Hence, it appears that an optimal SnO₂ thickness exists for a given loading of MXene. Another important observation is that electrodes prepared at 200 °C, showed more stable behavior than those prepared at 150 °C (Figure S6). We attribute this to a higher crystallinity after ALD at 200°C. The 10-nm-thick

coating of SnO₂ on MXene (ALD @ 200 °C) resulted in a specific capacity of 258 mAh/g at the 50th cycle, which corresponds to a capacity retention of 59.5 %.

To further improve the cyclic stability of SnO₂-coated MXene electrodes with thick SnO₂ layers, we used an ALD process that was recently shown to significantly stabilize Li-ion battery anodes.[35, 36] This process involves deposition of a thin layer of HfO₂ at the anode/electrolyte interface, which helps in preserving the structure of the anode materials when large volumetric changes occur.[31, 35, 36] Moreover, HfO₂ does not take part in the electrochemical process, as evidenced by the CV curves of HfO₂ (200 ALD cycles) on bare Cu-foil (Figure S7). Furthermore, the thin amorphous HfO₂ film does not hinder Li⁺ and Na⁺ ions diffusion.[42] Therefore, we aimed to improve the cyclic performance of SnO₂/MXene anodes by depositing a thin layer of HfO₂ on SnO₂/MXene electrodes. SnO₂ and HfO₂ were sequentially deposited on the MXene by ALD to create a dual-oxide on MXene composite electrodes. The electrochemically inactive nature of HfO₂ can be also seen from the CV curves of the HfO₂ coated SnO₂/MXene anodes (Figure S7). These anodes were cycled in a voltage range of 0.01 – 3.00 V (vs. Li/Li⁺) and delivered a specific capacity of 843 mAh/g at the 50th cycle, which corresponds to a capacity retention of 92%. Note that this specific capacity was achieved at 500 mA/g, and will be even higher at lower current densities. Recall that in the absence of HfO₂, SnO₂-coated MXene electrodes delivered a specific capacity of 451 mAh/g at the same current density after the 50th cycle, which corresponds to a capacity retention of 50% (based on the 2nd cycle discharge capacity). Moreover, the cyclic performance of bare SnO₂/MXene electrodes is much less stable than that of HfO₂ coated SnO₂/MXene composites anodes. We compared our results with the published data and summarized the comparison in Table S2, where we

demonstrate that the performance of the first-generation oxide/MXene anodes is comparable to the advanced Sn-C based compositions.

In addition, EIS was carried out to assess the effect of the HfO₂ layer on the performance of SnO₂/MXene composite anodes. The EIS plots for SnO₂/MXene anodes with and without HfO₂ are presented in Figure 4d. The typical Nyquist plots at OCV can be fitted with Randles circuit[43], where bulk resistance of battery components (electrolyte, electrodes, and the separator) is indicated by R_b , charge transfer resistance by R_{ct} , and double-layer capacitance by C_{dl} . A combination of the interfacial diffusion resistance of Li⁺ ions across the anode/electrolyte interface is given by Warburg impedance (W) and corresponds to a straight sloping line in the low frequency region of the Nyquist plots. The semicircle in the mid-frequency region shows the combined effect of R_{ct} and C_{dl} , and it can be readily observed that charge transfer resistance of the dual-oxide-coated MXene electrode is smaller than that of the single-oxide-coated MXene electrode. Lower values of R_{ct} correspond to faster reaction kinetics and the EIS suggests that the presence of an ultrathin HfO₂ layer at the anode/electrolyte interface decreases the overall charge transfer resistance. This result suggests that the presence of an electrochemically inactive HfO₂ layer at the anode/electrolyte interface does not hinder Li⁺ diffusion, which is consistent with the observations from the CV and galvanostatic charge/discharge tests.[35, 42]

To understand the role of HfO₂, we conducted *ex-situ* TEM analysis of SnO₂/MXene and HfO₂ coated SnO₂/MXene anodes (Figure 5). The capacity retention was found to be directly related to the nature of the reversibility of stepwise Li⁺ ions reaction with SnO₂ during the charge/discharge.[35] The alloying/dealloying reaction of metallic Sn is highly reversible. However, the conversion reaction of SnO₂ with the formation of intermediate SnO is partially reversible and results in distortion of the crystal structure.[38] Therefore, it is reasonable to

expect that the crystal structure of the $\text{SnO}_2/\text{MXene}$ electrode without HfO_2 could be more prone to degradation during the charge/discharge process. TEM analysis provided evidence for this phenomenon as can be concluded by comparing SAED patterns of both electrodes with and without the HfO_2 layer, after 50 charge/discharge cycles (Figure 5). The dot-pattern corresponding to crystalline SnO_2 (shown earlier in Figure 3b) disappeared after cycling of $\text{SnO}_2/\text{MXene}$ anodes, suggesting that SnO_2 was transformed to amorphous SnO_x (Figure 5c). In contrast, the HfO_2 coated $\text{SnO}_2/\text{MXene}$ electrode showed that the crystallinity of SnO_2 was preserved after the charge/discharge process (Figure 5f). The *ex-situ* SEM images showing lamellar structure of $\text{SnO}_2/\text{MXene}$ with and with HfO_2 coating after cycling are presented in Figure S8. The SEM images show that bare $\text{SnO}_2/\text{MXene}$ electrode gets distorted after cycling, while the HfO_2 -coated electrodes retain their original microstructure. In agreement with previous studies on MXene in Li-ion batteries,[10, 28, 29] both $\text{SnO}_2/\text{MXene}$ and HfO_2 coated $\text{SnO}_2/\text{MXene}$ anodes, retained MXene's hexagonal structure after cycling.

4. Conclusions

In summary, we have demonstrated that MXene-supported SnO_2 anodes deposited by atomic layer deposition can be stabilized during cycling of Li-ion batteries. In addition, we discovered that the MXene surface functional groups protect it from harmful oxidation from the oxidants typically used in ALD at high temperatures. The $\text{SnO}_2/\text{MXene}$ electrode composite design provides a high capacity thanks to conversion reaction of SnO_2 , while MXene sheets provide a conductive network that accommodates the large volume changes that occur in SnO_2 during the battery charge/discharge process. The $\text{SnO}_2/\text{MXene}$ electrode performance can be further

improved by depositing a very thin HfO_2 passivation layer on top of SnO_2 , in the same ALD reactor. The HfO_2 layer, though inactive, slows down the reaction of SnO_2 with the electrolyte, and preserves the SnO_2 crystalline structure during cycling. The HfO_2 coated $\text{SnO}_2/\text{MXene}$ anodes exhibit a stable specific capacity of 843 mAh/g. This first report of ALD of oxide on a MXene opens up alternate avenues to improve the cycling stability of SnO_2 and other conversion anodes.

Supporting Information

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

Acknowledgements

Research reported in this publication is supported by funding from King Abdullah University of Science and Technology (KAUST). The authors thank Mrinal Hota and Narendra Kurra for their support, and Heno Hwang for the design of schematic illustrations.

References

- [1] Y. Gogotsi, ACS Nano, 8 (2014) 5369-5371.
- [2] D. Deng, Energy Science & Engineering, 3 (2015) 385-418.
- [3] M.R. Lukatskaya, B. Dunn, Y. Gogotsi, Nature Communications, 7 (2016) 12647.
- [4] M. Naguib, Y. Gogotsi, Acc Chem Res, 48 (2015) 128-135.

- [5] M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M.W. Barsoum, *ACS Nano*, 6 (2012) 1322-1331.
- [6] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M.W. Barsoum, *Adv Mater*, 23 (2011) 4248-4253.
- [7] M. Ghidui, M.R. Lukatskaya, M.Q. Zhao, Y. Gogotsi, M.W. Barsoum, *Nature*, 516 (2014) 78-81.
- [8] M.R. Lukatskaya, O. Mashtalir, C.E. Ren, Y. Dall'Agnese, P. Rozier, P.L. Taberna, M. Naguib, P. Simon, M.W. Barsoum, Y. Gogotsi, *Science*, 341 (2013) 1502-1505.
- [9] M. Naguib, J. Come, B. Dyatkin, V. Presser, P.L. Taberna, P. Simon, M.W. Barsoum, Y. Gogotsi, *Electrochem Commun*, 16 (2012) 61-64.
- [10] B. Ahmed, D.H. Anjum, M.N. Hedhili, Y. Gogotsi, H.N. Alshareef, *Nanoscale*, 8 (2016) 7580-7587.
- [11] S.J. Kim, M. Naguib, M. Zhao, C. Zhang, H.-T. Jung, M.W. Barsoum, Y. Gogotsi, *Electrochim Acta*, 163 (2015) 246-251.
- [12] S. Kajiyama, L. Szabova, K. Sodeyama, H. Iinuma, R. Morita, K. Gotoh, Y. Tateyama, M. Okubo, A. Yamada, *ACS Nano*, 10 (2016) 3334-3341.
- [13] X. Wang, S. Kajiyama, H. Iinuma, E. Hosono, S. Oro, I. Moriguchi, M. Okubo, A. Yamada, *Nat Commun*, 6 (2015) 6544.
- [14] X.F. Yu, Y.C. Li, J.B. Cheng, Z.B. Liu, Q.Z. Li, W.Z. Li, X. Yang, B. Xiao, *ACS Appl Mater Interfaces*, 7 (2015) 13707-13713.
- [15] H. Liu, C.Y. Duan, C.H. Yang, W.Q. Shen, F. Wang, Z.F. Zhu, *Sensor Actuat B-Chem*, 218 (2015) 60-66.

- [16] F. Shahzad, M. Alhabeb, C.B. Hatter, B. Anasori, S. Man Hong, C.M. Koo, Y. Gogotsi, *Science*, 353 (2016) 1137-1140.
- [17] K. Rasool, M. Helal, A. Ali, C.E. Ren, Y. Gogotsi, K.A. Mahmoud, *ACS Nano*, 10 (2016) 3674-3684.
- [18] C. Eames, M.S. Islam, *Journal of the American Chemical Society*, 136 (2014) 16270-16276.
- [19] M. Khazaei, M. Arai, T. Sasaki, C.-Y. Chung, N.S. Venkataramanan, M. Estili, Y. Sakka, Y. Kawazoe, *Advanced Functional Materials*, 23 (2013) 2185-2192.
- [20] M. Hu, Z. Li, H. Zhang, T. Hu, C. Zhang, Z. Wu, X. Wang, *Chem Commun (Camb)*, 51 (2015) 13531-13533.
- [21] Z. Lin, D. Barbara, P.-L. Taberna, K.L. Van Aken, B. Anasori, Y. Gogotsi, P. Simon, *Journal of Power Sources*, (2016).
- [22] D.D. Sun, M.S. Wang, Z.Y. Li, G.X. Fan, L.Z. Fan, A.G. Zhou, *Electrochem Commun*, 47 (2014) 80-83.
- [23] O. Mashtalir, M. Naguib, V.N. Mochalin, Y. Dall'Agnese, M. Heon, M.W. Barsoum, Y. Gogotsi, *Nat. Commun.*, 4 (2013) 1716.
- [24] Y. Xie, M. Naguib, V.N. Mochalin, M.W. Barsoum, Y. Gogotsi, X. Yu, K.-W. Nam, X.-Q. Yang, A.I. Kolesnikov, P.R.C. Kent, *Journal of the American Chemical Society*, 136 (2014) 6385-6394.
- [25] Q. Tang, Z. Zhou, P. Shen, *J Am Chem Soc*, 134 (2012) 16909-16916.
- [26] B. Anasori, M.R. Lukatskaya, Y. Gogotsi, *Nature Reviews Materials*, 2 (2017) 16098.
- [27] C.E. Ren, M.-Q. Zhao, T. Makaryan, J. Halim, M. Boota, S. Kota, B. Anasori, M.W. Barsoum, Y. Gogotsi, *Chemelectrochem*, 3 (2016) 689-693.

- [28] J. Luo, X. Tao, J. Zhang, Y. Xia, H. Huang, L. Zhang, Y. Gan, C. Liang, W. Zhang, *ACS Nano*, 10 (2016) 2491-2499.
- [29] M. Naguib, O. Mashtalir, M.R. Lukatskaya, B. Dyatkin, C. Zhang, V. Presser, Y. Gogotsi, M.W. Barsoum, *Chem Commun (Camb)*, 50 (2014) 7420-7423.
- [30] S.M. George, *Chemical Reviews*, 110 (2010) 111-131.
- [31] B. Ahmed, C. Xia, H.N. Alshareef, *Nano Today*, 11 (2016) 250-271.
- [32] X. Chen, H. Zhu, Y.-C. Chen, Y. Shang, A. Cao, L. Hu, G.W. Rubloff, *ACS Nano*, 6 (2012) 7948-7955.
- [33] A. Kohandehghan, P. Kalisvaart, K. Cui, M. Kupsta, E. Memarzadeh, D. Mitlin, *Journal of Materials Chemistry A*, 1 (2013) 12850-12861.
- [34] R.B. Rakhi, B. Ahmed, M.N. Hedhili, D.H. Anjum, H.N. Alshareef, *Chem Mater*, 27 (2015) 5314-5323.
- [35] B. Ahmed, D.H. Anjum, M.N. Hedhili, H.N. Alshareef, *Small*, 11 (2015) 4341-4350.
- [36] B. Ahmed, M. Shahid, D.H. Nagaraju, D.H. Anjum, M.N. Hedhili, H.N. Alshareef, *ACS Appl Mater Interfaces*, 7 (2015) 13154-13163.
- [37] M.A. Hope, A.C. Forse, K.J. Griffith, M.R. Lukatskaya, M. Ghidui, Y. Gogotsi, C.P. Grey, *Phys Chem Chem Phys*, 18 (2016) 5099-5102.
- [38] V. Aravindan, K.B. Jinesh, R.R. Prabhakar, V.S. Kale, S. Madhavi, *Nano Energy*, 2 (2013) 720-725.
- [39] Y. Jiang, T. Yuan, W. Sun, M. Yan, *Acs Applied Materials & Interfaces*, 4 (2012) 6216-6220.
- [40] C. Guan, X. Wang, Q. Zhang, Z. Fan, H. Zhang, H.J. Fan, *Nano Letters*, 14 (2014) 4852-4858.

- [41] K. Zhao, L. Zhang, R. Xia, Y. Dong, W. Xu, C. Niu, L. He, M. Yan, L. Qu, L. Mai, *Small*, 12 (2016) 588-594.
- [42] N. Yesibolati, M. Shahid, W. Chen, M.N. Hedhili, M.C. Reuter, F.M. Ross, H.N. Alshareef, *Small*, 10 (2014) 2849-2858.
- [43] S.S. Zhang, K. Xu, T.R. Jow, *Electrochim Acta*, 49 (2004) 1057-1061.

Figure 1: Schematic illustration of the various methods used for SnO₂ deposition on Ti₃C₂ MXene sheets, including hydrothermal synthesis, sputtering, and atomic layer deposition (ALD). Atomistic view of exfoliated MXene sheets is shown on the left, the stack of exfoliated MXene sheets is in the middle, and MXene hybrid electrodes after SnO₂ deposition are on the right.

Figure 2: Characterization of as-prepared HF-etched Ti_3C_2 MXene: (A) XRD patterns of Ti_3AlC_2 and Ti_3C_2 ; (B) typical SEM image of HF-etched Ti_3C_2 MXene; (C) TEM image of HF-etched few-layer Ti_3C_2 MXene, inset shows the SAED pattern; and (D) Fourier-filtered HRTEM image showing the hexagonal atomic arrangement of HF-etched Ti_3C_2 MXene.

Figure 3: TEM analysis of MXene sheets coated with a 50-nm-thick layer of SnO₂: low-magnification TEM image and SAED pattern for ALD (A) @ 150 °C and (B) @ 200 °C; (C) a Fourier-filtered high-resolution RGB image for ALD @ 200 °C, showing the presence of two phases and (D) a STEM image along with the EDS line-scan for ALD @ 150 °C showing the conformal SnO₂ coating.

Figure 4: Electrochemical characterization of Ti_3C_2 MXene electrode architectures with varying ALD cycles and temperatures. Comparison of (A) first cycle of cyclic voltammograms at 0.2 mV/s (B) First cycle charge/discharge curves at 100 mA/g (C) cyclic performance over 50 cycles at 500 mA/g and (D) typical Nyquist plots of $\text{SnO}_2/\text{MXene}$ electrode and HfO_2 coated $\text{SnO}_2/\text{MXene}$ electrodes; the inset shows a close-up in the medium- and high-frequency regions and the Randles circuit.

Figure 5: TEM analysis after electrochemical testing: low magnification (A, D), high resolution (B, E) TEM images and SAED pattern (C, F) of MXene without (A-C) and with (D-F) a HfO_2 coating on electrodes with a 50-nm-thick layer of SnO_2 (ALD @ 200 °C). The SAED patterns were taken from regions marked in (A) and (B).

Highlights

- Gas phase oxide growth on MXene surface by ALD
- $\text{SnO}_2/\text{MXene}$ anode shows high capacity and cyclic performance
- Surface functional groups present on MXene surface assist in ALD process
- Presence of surface passivation layer (HfO_2) by ALD further improves cyclic performance of $\text{SnO}_2/\text{MXene}$ anodes