Surface Modification of MXenes: A Pathway to Improve MXene Electrode Performance in Electrochemical Energy Storage Devices

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ABSTRACT

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Bilal Ahmed

The recent discovery of layered transition metal carbides (MXenes) is one of the most important developments in two-dimensional (2D) materials. Preliminary theoretical and experimental studies suggest a wide range of potential applications for MXenes. The MXenes are prepared by chemically etching ‘A’-layer element from layered ternary metal carbides, nitrides and carbonitrides (MAX phases) through aqueous acid treatment, which results in various surface terminations such as hydroxyl, oxygen or fluorine. It has been found that surface terminations play a critical role in defining MXene properties and affects MXene performance in different applications such as electrochemical energy storage, electromagnetic interference shielding, water purification, sensors and catalysis. Also, the electronic, thermoelectric, structural, plasmonic and optical properties of MXenes largely depend upon surface terminations. Thus, controlling the surface chemistry of MXenes can be an efficient way to improve their properties.

This research mainly aims to perform surface modifications of two commonly studied MXenes; Ti$_2$C and Ti$_3$C$_2$, via chemical, thermal or physical processes to enhance electrochemical energy storage properties. The as-prepared and surface modified MXenes have been studied as electrode materials in Li-ion batteries (LIBs) and supercapacitors (SCs). In pursuit of desirable MXene surface, we have developed an in-situ room temperature oxidation process, which resulted in TiO$_2$/MXene nanocomposite and enhanced Li-ion storage. The idea of making metal oxide and MXene nanocomposites was taken to the next level by combining a high capacity anode
materials – SnO₂ – and MXene. By taking advantage of already existing surface functional groups (–OH), we have developed a composite of SnO₂/MXene by atomic layer deposition (ALD) which showed enhanced capacity and excellent cyclic stability.

Thermal annealing of MXene at elevated temperature under different atmospheres was carried out and detailed surface chemistry was studied to analyze the change in surface functional groups and its effect on electrochemical performance. Also, we could replace surface functional groups with desirable heteroatoms (e.g., nitrogen) by plasma processing and studied their effect on energy storage properties. This work provides an experimental baseline for surface modification of MXene and helps to understand the role of various surface functional groups in MXene electrode electrochemical performance.
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<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>BDEs</td>
<td>Bond dissociation energies</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BN</td>
<td>Boron nitride</td>
</tr>
<tr>
<td>CD</td>
<td>Charge–Discharge</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulphoxide</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrical impedance spectroscopy</td>
</tr>
<tr>
<td>EES</td>
<td>Electrochemical energy storage</td>
</tr>
<tr>
<td>ESR</td>
<td>Equivalent series resistance</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier transform</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric acid</td>
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HRTEM  High-resolution transmission electron Microscopy
LIBs  Li-ion batteries
LiF  Lithium fluoride
Ni-MH  Nickel metal hydride battery
OCV  Open circuit voltage
PTFE  Polytetrafluoroethylene
PVdF  Poly(vinylidene fluoride)
PVP  Polyvinylpyrrolidone
SAED  Selected area electron diffraction
SCs  Supercapacitors
SEI  Solid electrolyte interface
SEM  Scanning Electron Microscopy
SSA  Specific surface area
STEM  Scanning Transmission Electron Microscopy
TEM  Transmission Electron Microscopy
TMDs  Transition metal dichalcogenides
TMOs  Transition metals oxides
XPS  X-ray photoelectron spectroscopy
XRD  X-ray diffraction
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Brief Overview

Fossil fuels have been successful at meeting the world’s energy needs at affordable cost. However, increasing energy demand and fast dwindling fossil resources and their severe environmental issues (global warming) make it imperative that new, sustainable, and clean energy sources are developed. The renewable energy sources such as wind and solar energy are efficient, clean and viable and have shown promise in meeting future energy requirements. However, one of the biggest challenges with these renewable energy sources is that they are intermittent, hence efficient and cost-effective storage technologies to handle intermittent nature of solar or wind energy technology are required.\(^1\) Electrochemical energy storage (EES) is one of the most promising energy storage technologies that can help mitigate the intermittent nature of renewable sources. The EES offer excellent efficiency, low maintenance and clean operability, therefore successful realization in grid-storage and portable devices is possible.\(^2\)\(^3\) The research on EES devices has evolved in multiple directions, but one common theme has always been the development of high capacity and stable electrode materials.\(^4\)\(^5\)\(^6\)\(^7\) For instance, conventional anode material, graphite, for Li-ion batteries (LIBs) offers a specific capacity of 372 mAh/g with excellent stability. On the other hand, silicon provides a specific capacity of 4200 mAh/g with extremely poor cyclic performance.\(^4\)\(^6\) Therefore, to enhance energy density of LIBs, we should enhance the cyclic performance of high capacity anode materials. Similarly, enhancing the specific capacity of materials with stable cyclic performance is another way of approaching high energy density goal.

This thesis focuses on the electrochemical energy storage performance of a newly discovered 2D material, known as MXene. MXene is a large family of 2D transition metal carbides, nitrides and carbonitrides with exciting properties and has
shown promise in a wide range of applications including LIBs and supercapacitors (SCs). This work aims to understand the role of MXene surface chemistry on its electrochemical energy storage properties. Two prominent members of MXene-family, Ti$_2$C and Ti$_3$C$_2$, have been studied in this work, and their surface modification was carried out via chemical, thermal or physical processes to enhance electrochemical energy storage properties. The brief composition of the thesis is given below:

Chapter 1: This chapter includes an introduction to electrochemical energy storage devices (LIBs and SCs) and MXenes synthesis processes. The objectives of this dissertation are also presented at the end of this chapter.

Chapter 2: This chapter describes the surface modification of MXene via chemical oxidation. The electrochemical performance of resulting MXene has been discussed as anode materials for LIBs.

Chapter 3: This chapter describes the preparation of metal oxide/MXene composite (SnO$_2$/Ti$_3$C$_2$) by exploiting existing surface functional groups by atomic layer deposition. The high capacity anode material (SnO$_2$/MXene) with stable performance has been shown demonstrated.

Chapter 4: This chapter includes some of our preliminary results, where based on theoretical studies, we aimed to replace surface functional groups with a desirable heteroatom (e.g., N$_2$) by plasma processing and studied the energy storage properties of resulting MXene as anode material in Li-ion batteries.

Chapter 5: This chapter describes the thermal annealing of MXene at elevated temperature under different atmospheres and changes to its surface chemistry. The
electrochemical performance of MXene treated in various atmospheres has been studied as electrode materials in supercapacitors.

Chapter 6: The conclusions of this dissertation and future research perspective has been discussed in this chapter.
1. Chapter 1: Introduction

In this chapter, a brief introduction of electrochemical energy storage devices, including secondary ion batteries and electrochemical supercapacitors is described. Also, a detailed literature review of two-dimensional MXenes, their synthesis, and role of their surface termination is discussed. The objectives of this dissertation have also been included at the end of this chapter.

1.1 Electrochemical Energy Storage

Electrochemical energy technologies can be classified into two main categories: electrochemical energy conversion devices such as fuel cells and electrolyzers, and electrochemical energy storage devices such as secondary ion batteries and supercapacitors. The underlying principle for these devices is quite simple: conversion of electrical energy into chemical energy and vice versa. In electrochemical energy storage devices, batteries and supercapacitors, the electrical energy are stored in the form of chemical energy of electrode materials (anodes and cathodes), which is released during discharge. The most distinct advantage of electrochemical energy storage is their high energy and power densities, depending on device type, and relatively compact size which makes them suitable for many types of applications.1,3,8

1.2 Secondary Ion Batteries – Importance and Chemistry

Batteries can be divided into two categories; primary batteries and secondary batteries. The primary batteries are used once – cannot be recharged – whereas the secondary batteries can be recharged for an extended number of cycles. The commonly used batteries in electronic devices are secondary batteries, in general, and Li-ion batteries, in particular.
The basic components of a secondary battery include cathode, anode, separator, and electrolyte. The electrodes serve as host-material where oxidation and reduction reactions take place and the electrolyte constitutes a medium in which mobile ions such as Li can move efficiently. The electrons are transferred-in (charging) or transferred-out (discharging) via an external circuit. The schematic diagram of a working Li-ion battery (LIB) is given in Figure 1.1.

The most commonly used electrode materials in LIBs are carbon, as an anode, and lithium cobalt oxide, as a cathode. Lithium salts (LiPF₆ and LiClO₄) dissolved in organic solvents such as ethylene carbonates and diethyl carbonates are used as the electrolyte. Lithium is stored in carbon anode, forming an intercalated compound LiC₆, and migrates towards cathode during the discharge process. Equation 1 explains the chemistry of discharge process occurring at the anode; removal of Li⁺ ions from intercalated compound and migration towards the cathode.

\[ Li_xC_6 \leftrightarrow Li_0C_6 + xLi^+ + xe^- \]

On the other hand, the equilibrium reaction at the cathode, in case of LiCoO₂, is given by the following equation:

\[ Li_0CoO_2 + yLi^+ + ye^- \leftrightarrow Li_yCoO_2 \]

Li-ion batteries have matured as a technology for powering portable electronic devices to grid energy storage a large scale. Nevertheless, opportunities to improve battery performance, especially through exploring new classes of layered materials, including oxides, sulfides, and transition metal carbides, are still needed.⁴,⁶,⁹-¹⁰
1.3 Supercapacitors

Another type of electrochemical energy storage devices is called electrochemical capacitors, which are often referred as supercapacitors (SCs) due to their high capacitance relative to conventional electrostatic capacitors.\textsuperscript{11-12} SCs offer high power density and extended cycle life (> 100000 cycles), but suffer from low energy density compared to LIBs.\textsuperscript{12-13} SCs can be used in electronic devices and power back-up applications. Also, their application in low-emission hybrid electric vehicles is also being considered.\textsuperscript{14}
Like batteries, SCs working principle relies on charge storage in appropriate electrode materials, but unlike batteries, charge storage occurs mainly on the surface of electrodes. Double-layer supercapacitors store charge by ion adsorption on electrode surfaces. Unlike LIBs, where organic electrolytes are used, SCs can use aqueous or organic electrolyte. Carbon is most commonly studied electrode material for SCs due to its high surface area and excellent conductivity but suffers from low relatively capacitance. Other materials such as metal oxides and conducting polymers offer higher capacitance, but suffer from relatively short cycle life.

The charge storage mechanism of SCs can be explained by adsorption and diffusion of charged ions into the porous electrode, which has gained either positive or negative charge due to the applied voltage. The accumulated charge on electrode/electrolyte interface results in the formation of a double layer with extremely small separation, leading to high capacitance. As shown in Figure 1.2, the capacitance of capacitance has a direct relationship with electrode area and inversely related the separation between layers. Therefore, porous carbon has been a good supercapacitor electrode because it offers good conductivity and high surface area, which results in adsorption of a large amount of ions on the carbon surface.
Ragone plot, a plot of energy and power density, is mostly used to assess the performance of electrochemical energy storage devices. A typical Ragone plot for a different type of electrochemical energy storage devices is presented in Figure 1.3.\textsuperscript{17} The researchers in electrochemical energy storage area try to push each device’s performance towards the upper right-hand corner of this plot.\textsuperscript{18} SCs power high power density, while LIBs offer high energy density.
Figure 1.3: Ragone Plot (Specific power against specific energy) showing various electrical energy storage devices.\textsuperscript{17}
1.4 Two-dimensional Materials

Two-dimensional (2D) nanomaterials have grabbed a substantial amount of research focus due to their exciting properties and potential application in wide range of applications. The 2D nature and high-aspect-ratio of 2D materials offer distinct advantages such as direct integration of planar devices and ability to sustain harsh operating conditions (e.g., volumetric changes in electrochemical energy storage devices). The isolation of one-atomic thickness graphite flake, termed as graphene, has revolutionized the 2D materials world and considered as most promising material for a host of applications. The unique 2D nature and fascinating electronic properties of graphene such as half-integer quantum Hall effect, extremely high carrier mobility and ambipolar electric field effect has assisted to understand some of the most important physical phenomena of high-energy physics. Also, the discovery of graphene proved that the set of properties offered by 2D materials is a lot more different than it’s 3D counterpart – graphite – and observation had a transformative effect on research in materials science and technology. The discovery of graphene has encouraged researchers to focus on other graphene-like two-dimensional (2D) materials and now a wide variety of 2D materials, other than graphene, are being researched such as hexagonal boron nitride (BN), transition metal dichalcogenides (TMDs) and transition metal oxides (TMOs).

2D materials such as graphene, TMDs and TMOs are preferred in energy storage devices due to their high surface area to volume ratio. The large surface area of 2D materials provides more active sites for ion adsorption or intercalation. Also, the 2D nature offers a gallery space for ion shuttling during charge/discharge process and open 2D ion transport channels lead to faster ion diffusion as compared to bulk counterparts. Furthermore, in most of the cases, cyclic stability is improved by employing 2D
materials due to their ability to sustain volumetric changes during charge/discharge process. The excellent mechanical properties of 2D materials also offer unique design features such as free-standing electrodes. Therefore, application of 2D materials in energy storage technology is prime research focus and successful implementation can help us realize the goal of high energy and power density devices for future energy needs.

1.5 MXenes

MXene\textsuperscript{27-28} is most recent addition to 2D materials world and, like graphene, it has gained significant research focus due to high conductivity, hydrophilic surface, rich chemistry and large surface area.\textsuperscript{29-33} MXenes, a generic name for early transition metal carbides and carbonitrides, offers a fascinating array of electronic, electrochemical, optical, mechanical and thermal properties. MXenes are produced\textsuperscript{34} by etching ‘A’ group element from layered ternary metal carbides, nitrides or carbonitrides (MAX phases),\textsuperscript{35} where M represents an early transition metal, A indicates an A-group (III or IV) element, and X represents C and/or N. MAX phases can be represented by general formula of $M_{n+1}AX_n$ ($n=1–3$) and resulting MXenes as $M_{n+1}X_nT_x$, where $T_x$ shows the surface termination resulting from aqueous medium etching hydrofluoric acid (HF) or mixture of lithium fluoride and hydrochloric acid (LiF/HCl).\textsuperscript{29, 34, 36} The schematic illustration of MAX phases and resulting MXene is presented in Figure 1.4 and a large family of MAX phases consists of more than seventy members. Moreover, The ‘M’, ‘A’ and ‘X’ sites of MAX phases can be alloyed or doped with other elements via solid-solution and resulting MXenes are either double-ordered MXenes (Mo$_2$TiC from Mo$_2$TiAlC$_2$)\textsuperscript{37} or site-deficient MXene (Mo$_{1.33}$C from (Mo$_{2/3}$Sc$_{1/3}$)$_2$AlC)\textsuperscript{38}. 

Figure 1.4: Schematic Illustration of MAX and MXene Phases

Various compositions of MXenes with different etching protocols and post-etch processing have been investigated in number of applications such as Li and Na ion batteries,\textsuperscript{39-46} Li-S batteries,\textsuperscript{47-52} hybrid ion capacitors,\textsuperscript{39, 53-54} conventional\textsuperscript{29-30, 33, 44, 55-57} and micro-supercapacitors,\textsuperscript{58-60} hydrogen storage,\textsuperscript{61} electrochemical sensing,\textsuperscript{62-65} catalysis,\textsuperscript{31, 66-72} water purification,\textsuperscript{73-75} electromagnetic interference shielding\textsuperscript{76-79} and thermoelectrics.\textsuperscript{80-81} As mentioned earlier, the aqueous medium etching in HF or LiF/HCl results in different surface terminations such as fluorine (–F), oxygen (–O), hydroxyl group (–OH), chlorine (–Cl) and lithium (–Li).\textsuperscript{29, 34} Since the discovery of MXene, researchers had known that surface functional groups largely affect the electronic properties of MXene. For instance, in the very first report of MXene synthesis, M. Naguib et al.\textsuperscript{34} predicted, based on density functional theory (DFT) calculations, that the band structure of a bare Ti$_3$C$_2$ resembles a typical semimetal with
a finite density of states at the Fermi level. However, after addition of –F and –OH on Ti$_3$C$_2$ surface, MXene showed semiconducting behavior with a band gap of 0.1 eV and 0.05 eV, respectively. Similarly, Q. Tang et al.$^{82}$ carried out detailed DFT computations to investigate the Li-ion storage capacity of Ti$_3$C$_2$ MXene with –F and –OH terminations. Their results about band structure of MXene as a function of surface terminations are exactly similar to earlier predictions$^{34}$ and they added that Li adsorption on MXene surface is due to the strong coulombic interaction between Li$^+$ ions and (negatively charged) Ti$_3$C$_2$ sheets.$^{82}$ The Li-ion storage capacity for bare-Ti$_3$C$_2$, F-terminated Ti$_3$C$_2$ and OH-terminated Ti$_3$C$_2$ were found to be 320, 130 and 67 mAh/g, respectively. These calculations suggested that surface functionalization should be avoided as much as possible, however, from a practical viewpoint, this is near to impossible. These examples show that surface termination of MXene can affect their electronic and electrochemical properties. Therefore, various research groups have carried out theoretical and experimental studies to understand and engineer MXene’s surface terminations.$^{27-28, 83-85}$

1.6 MXene Synthesis

The most generic approach for MXene synthesis has been first developed by M. Naguib et al.$^{34}$ for Ti$_3$AlC$_2$, where Ti$_3$AlC$_2$ MAX phase powder was immersed in HF solution to attack weak metallic bond between Ti and Al. The MAX phases contain a combination of metallic, ionic and covalent bonds and bond strengths are high.$^{86}$ HF etching selectively removes Al layer from Ti$_3$AlC$_2$ because metallic bond between Ti and Al is weaker than covalent bond present between Ti and C.$^{34, 36}$ The chemical reactions for Al-etching can be presumed as below:$^{28}$

$$M_{n+1}AlX_n + 3HF = AlF_3 + M_{n+1}X_n + 1.5H_2$$
\[ M_{n+1}X_n + 2H_2O = M_{n+1}X_n(OH)_2 + H_2 \]

\[ M_{n+1}X_n + 2HF = M_{n+1}X_nF_2 + H_2 \]

Immersion of MAX phase in HF solution removes ‘Al’ layer and bath sonication can be used to separate MXene sheets (Figure 1.5). This two-step process depends on several factors such as composition of MAX phase, particle size, HF concentration, reaction time and temperature. Figure 1.5 presents the X-ray diffraction analysis for HF-etched Ti\textsubscript{3}AlC\textsubscript{2} with 50 wt. % HF at different temperature and times.\textsuperscript{87} It can be seen that if sufficient time or required temperature has not been provided, incomplete etching process results in a mixture of MXene and parent MAX phase. In case of successful etching, the (0002) peak of MAX phase broadens and shifts towards lower angle, which indicates loss of crystallinity and increase in the c-lattice parameter.\textsuperscript{34, 36} For Ti\textsubscript{2}AlC and Ti\textsubscript{3}AlC\textsubscript{2}, the c-lattice constant changed from 1.36 nm to 1.504 nm and 1.842 nm to 2.051 nm, respectively and yield of HF etching was found to be 60 wt. % and 100 wt. %.\textsuperscript{36} This generic approach has been applied to various other MAX phases such as Ti\textsubscript{2}AlC\textsuperscript{36} (as an example of M\textsubscript{2}AX), Ta\textsubscript{4}AlC\textsubscript{3}\textsuperscript{36} (as an example of M\textsubscript{4}AX\textsubscript{3}), TiNbAlC\textsubscript{3}\textsuperscript{36} (represents M-site doped (MM`)\textsubscript{2}AX), Ti\textsubscript{3}AlCN\textsuperscript{36} (as an example of X-site doped M\textsubscript{3}A(XX`)\textsubscript{2}) and V\textsubscript{2}AlC\textsuperscript{88} (as an example of M\textsubscript{2}AX where M ≠ Ti). The HF concentration of as low as 10 wt. % for Ti\textsubscript{2}AlC and as high as 50 wt. % Ti\textsubscript{3}AlC\textsubscript{2} were used for successful etching. The bath sonication results in an accordion-like structure, as shown in Figure 1.5. The layered structure confirmed the successful exfoliation and energy dispersive X-ray showed the presence of Ti, C, O and F. Which implies that this process results in adsorbed fluorine (–F), oxygen (–O) and hydroxyl (–OH) groups on MXene surface.\textsuperscript{36}
Figure 1.5: (A) Schematic for the exfoliation process of MAX phases and formation of MXenes.\textsuperscript{36} (B-C) XRD patterns attained after etching Ti$_3$AlC$_2$ powders in 50% HF solution (B) at different temperatures for 2 hours and (C) for different times at room temperature.\textsuperscript{87} (D-I) Secondary electron SEM micrographs for (D) Ti$_3$AlC$_2$ particle before HF treatment, (E) Ti$_3$C$_2$ MXene, (F) Ti$_2$C MXene, (G) Ta$_4$C$_3$ MXene and (H) TiNbC MXene after HF treatment.\textsuperscript{36}
HF-etched MXene can be further processed by intercalation of various ions or organic molecules and individual sheets can be delaminated.\textsuperscript{40} One should note that intercalation and delamination process increases c-lattice parameter and changes MXene’s surface functional groups. For instance, O. Mashtalir et al.\textsuperscript{40} successfully intercalated hydrazine in Ti\textsubscript{3}C\textsubscript{2} MXene sheets and c-lattice parameter increased from 1.95 nm to 2.68 nm. Moreover, dimethyl sulphoxide (DMSO) assisted delamination changed surface functional groups of MXene and resulted in a stable colloidal solution which was used to prepare MXene-‘paper’.\textsuperscript{40}

A relatively safer and better etching process has been reported by M. Ghidiu et al.\textsuperscript{29} where the solution of LiF and hydrochloric acid was used to remove Al-layer from Ti\textsubscript{3}AlC\textsubscript{2}. The etched material absorbs relatively larger amounts of water and swells, which helps to attain clay-like structure. The mild nature of LiF/HCl mixture (as compared to HF) resulted in larger flakes and intercalated water assisted in absorbing more water by facile shearing. The MXene prepared by this method is way too conductive than HF-etched MXene (1500 S/cm) and delivered volumetric capacitance of 900 F/cm\textsuperscript{3} with excellent cyclic performance and rate capability.\textsuperscript{29} The flakes prepared by this method has typical surface terminations (–F, –O and –OH) as well as intercalated water, adsorbed Li and Cl.

It has also been reported that small changes in etching protocols led to major differences regarding flake quality. A. Lipatov et al.\textsuperscript{89} reported that by changing molar ratio of LiF to Ti\textsubscript{3}AlC\textsubscript{2} and avoiding sonication (Figure 1.6) after etching process results in large flakes with high quality, clean edges and visually defect-free surfaces. The field-effect transistors fabricated by using high-quality MXene showed a field-effect electron mobility of 2.6 ± 0.7 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} and a low resistivity of 2.31 ± 0.57 μΩ·m.
The electrical conductivity of individual flake has been reported as 4600 ± 1100 S/cm. It has also been revealed that Route 1\textsuperscript{89} (Figure 1.6) retained some of the MAX phases, while increasing amount of LiF salt completely transformed MAX phase into MXene. It is worth mentioning here that not only Al, but other A-group elements can be removed from MAX phases by either HF etching of LiF/HCl etching. J. Halim et al.\textsuperscript{90} reported the synthesis of Mo\textsubscript{2}C from Mo\textsubscript{2}Ga\textsubscript{2}C via HF and LiF/HCl etching. The quality of MXene flakes depends upon etchant and delamination process. Furthermore, Q. Tao et al.\textsuperscript{38} reported the targeted removal of Al and Sc from (Mo\textsubscript{2/3}Sc\textsubscript{1/3})\textsubscript{2}AlC and introduced ordered divacancies in Mo\textsubscript{2/3}C MXenes. This Mo\textsubscript{2/3}C MXene delivered higher volumetric capacitance than defect-free Mo\textsubscript{2}C. Furthermore, synthesis of first nitride MXene (Ti\textsubscript{4}N\textsubscript{3}) has been reported by etching Al-layer from Ti\textsubscript{3}AlN\textsubscript{3} via molten salt reaction at high temperature (550 °C). The etched and delaminated Ti\textsubscript{4}N\textsubscript{3} was terminated by –F, –O and –OH.\textsuperscript{91} An overview of the synthesis process, presented in this section, confirms that all the MXene produced so-far has a combination of surface functional groups. The most common among these surface termination are –F, –O and –OH but in some cases, Li and Cl can also be present. Moreover, the vacancies or defects present on the surface of MXene flake also act as a surface functional group and can affect MXene’s performance. Surface terminations, oxidation and defects depend upon etchant type and etching conditions.
Figure 1.6: Synthesis and electron microscopy characterization of Ti$_3$C$_2$T$_x$ flakes produced by different routes. A) Summary of Routes 1 and 2 and schematic structures of Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_x$. B) SEM and C) TEM images of Ti$_3$C$_2$T$_x$ flakes produced using Route 1. D) SEM and E) TEM images of Ti$_3$C$_2$T$_x$ flakes synthesized using Route 2. Small panels in (C) and (E) show HR TEM images and SAED patterns of monolayer 2D crystals of Ti$_3$C$_2$T$_x$. F) Schematic showing synthesis and delamination of Mo$_2$CT$_x$. 
Furthermore, theoretical studies have also been carried out to understand the exfoliation kinetics of MAX phases and properties of bare or surface terminated MXenes. Similar to the experimental front, where MXene synthesis and utilization in wide range of applications has been demonstrated, theoretical models to understand the reaction kinetics between MAX phase and HF, which governs the exfoliation process and surface functionalization, have been studied. P. Srivastava et al. has reported, based on DFT calculations, the exfoliation mechanism of Ti$_3$C$_2$ MXene from Ti$_3$AlC$_2$ when reacted with HF. The exfoliation process initiates due to the HF dissociation and adsorption of H and F on edges on Ti atoms. These initial surface terminations (–H and –F) increases interlayer spacing which facilitates HF induction in MAX phase structure. These calculations also demonstrated the formation of AlF$_3$ and H$_2$, as shown in equations 1–3. The same group has studied the transformation mechanism of Nb$_4$AlC$_3$ MAX phase into MXene by applying common etchants such as HF and LiF. When bond dissociation energies (BDEs) were compared for various vulnerable bonds, it has been shown the HF etching and Li insertion cannot result in pristine (bare) MXene due to strong H adsorption on MXene surface. Calculated Gibbs free energy of F-terminated and OH-terminated MXene showed that values are negative and close, which proves the random surface functionalization of MXene. The results also suggested that HF etching should be carried out at mild conditions to avoid degradation, which is consistent with experimental results presented earlier.

The theoretical study of MXene properties is also well explored and provides the basis for a wide range of applications. I.R. Shein et al. reported the structural, electronic and magnetic properties of two dimensional Ti$_{n+1}$C$_n$ and Ti$_{n+1}$N$_n$ (n=1–3) using ab initio simulations and predicted the trends in interatomic bonding and relative stability. The stability analysis based on cohesive and formation energies revealed the
relative stability of 2D metal carbides and nitrides largely depends upon thickness (increase in $n$) and metal nitrides are less stable than carbide counterparts. The same study also predicted that density of near-Fermi states increases 2.5 to 4.5 times as compared to parent MAX phase due to redistribution of Ti 3d states, which gives these metal carbides and nitrides a metallic character. Electronic and optical properties of 2D metal carbides and nitrides have also been studied using DFT calculations. Dielectric function, energy-loss function, reflectivity and absorption spectra were obtained and it has been predicted that metallic character of titanium nitrides MXenes is stronger than carbide counterparts due to an extra electron in nitrogen atom compared to carbon.

From an applications viewpoint, bare Ti$_2$C$^{96}$ and Sc$_2$C$^{97}$ MXene have been investigated as hydrogen storage materials by using first-principles total energy pseudopotential calculations. The results confirmed hydrogen storage at different sites on the Ti$_2$C layer and maximum hydrogen storage capacity was found to be 8.6 wt. %. Three different hydrogen storage modes were also identified: chemisorption (1.7 wt. %), physisorption (3.4 wt. %) and Kubas-type binding (3.4 wt. %). Fe$_2$C$^{98}$ and Cr$_3$C$_2$$^{99}$ have also been investigated by using DFT calculations and found to be metallic and ferromagnetic, which encourage their utilization in spintronic applications. Also, structural, thermal, electronic and mechanical properties of Mo$_2$C$^{100}$ MXene has been investigated as well. These studies, investigated MXene in its pure form, without any surface functionalization, and shed light on intrinsic properties of bare MXene. However, MXene synthesis without surface functional groups is not possible with existing etching methods. Therefore several groups have studied the MXene properties in the presence of different surface functional groups.$^{82, 101-117}$ A schematic illustration of commonly found surface functional groups is presented in Figure 1.7 for M$_3$X$_2$T$_x$ MXene.
Q. Ting el al. \cite{Ting2017} has employed DFT computations to explore the electronic and electrochemical properties of Ti$_3$C$_2$ in its bare and fluorinated and hydroxylated form. Like the previous report,\cite{Wang2016} they also observed that bare MXene shows metal-like behavior, whereas the MXene terminated with –F and –OH shows semiconducting nature with a small band gap. Li adsorbs on the surface of Ti$_3$C$_2$ MXene via coulomb interaction without distorting the structure of host material. Also, the bare MXene demonstrated higher theoretical capacity, as compared to surface terminated MXenes due to the lower energy barrier. Authors argued that presence of F and OH on MXene surface hindered Li$^+$ ion adsorption and reduced Li-ion capacity.
F. Li et al.\textsuperscript{118} explored another MXene, Cr$_3$C$_2$, by DFT computations as a cathode material for lithium and non-lithium ion batteries. The Cr$_3$C$_2$ MXene demonstrated excellent electronic conductivity and a low diffusion barrier to Li$^+$ ions. They also predicted high operating voltage (>2 V), which makes it a desirable candidate for cathode materials for Li, Na and Ca ion batteries. Another study\textsuperscript{115} also explored the potential of using Ti$_3$C$_2$ MXene in different battery systems (Li, Na, K and Ca batteries) by first-principles DFT calculations. The ionic radii have been reported to have a strong correlation with binding energy and dictate the coverage, thus define the maximum capacity for Li$^+$ ions. The calculated values of theoretical capacities for Li, Na, K, and Ca on Ti$_3$C$_2$ are 447.8, 351.8, 191.8, and 319.8 mAh/g, respectively.\textsuperscript{115} The role of surface terminations has been discussed and it has been suggested that surface terminations should be avoided as much as possible to attain maximum capacity in secondary ion battery systems.
1.7 Objectives

This dissertation mainly focuses on the enhancement of electrochemical properties of MXene by understanding and exploiting the existence of surface functional groups and surface oxides. The electrochemical performance of LIBs and SCs using MXene electrodes has been assessed using the following strategies:

The preparation of *in-situ* metal oxide (TiO$_2$) on MXene surface was carried out by a room-temperature, solution-based process, which resulted in the nanocrystalline composite of TiO$_2$/MXene. The resulting TiO$_2$/MXene served as an excellent anode material regarding capacity, stability and rate capability for Li-ion batteries.

The presence of –O and –OH surface functional groups on MXene surface was exploited to deposit another metal oxide on MXene surface via atomic layer deposition (ALD). The ALD process resulted in uniform and conformal coating of MXene flakes and the resulting SnO$_2$/MXene anode showed enhanced battery performance with excellent cyclic stability.

The nature of surface functional groups on MXene has been studied by a variety of methods and post-etching processing has been carried out to enhance the performance of surface modified MXenes in SCs and LIBs. The post-etch processing was either thermal, heat treatment in different ambient, or a combination of the chemical and physical process, i.e. plasma treatment in reactive and inert environments.
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2. Chapter 2: H₂O₂ Assisted Room Temperature Oxidation of Ti₂C MXene for Li-ion Battery Anodes

2.1 Summary

Herein we demonstrate that a prominent member of MXene family, Ti₂C, undergoes surface oxidation at room temperature when treated with hydrogen peroxide (H₂O₂). The H₂O₂ treatment results in opening up of MXene sheets and formation of TiO₂ nanocrystals on their surface, which is evidenced by high surface area of H₂O₂ treated MXene and X-ray diffraction (XRD) analysis. We show that the reaction time and amount of hydrogen peroxide used are the limiting factors, which determine the morphology and composition of the final product. Furthermore, it is shown that the performance of H₂O₂ treated MXene as anode material in Li-ion batteries (LIBs) was significantly improved compared to as-prepared MXenes. For instance, after 50 charge/discharge cycles, specific discharge capacities of 389 mAh/g, 337 mAh/g and 297 mAh/g were obtained for H₂O₂ treated MXene at current densities of 100 mA/g, 500 mA/g and 1000 mA/g, respectively. In addition, when tested at a very high current density, such as 5000 mA/g, the H₂O₂ treated MXene showed a specific capacity of 150 mAh/g and excellent rate capability. These results clearly demonstrate that H₂O₂ treatment of Ti₂C MXene improves MXene properties in energy storage application, such as Li-ion batteries or capacitors.

2.2 Introduction and Background

Typically, the exfoliated MXene sheets are terminated by –OH, -O and/or –F functional groups (marked as Tₓ) due to aqueous HF treatment and their formula is written as Ti₂CTₓ or Ti₃C₂Tₓ.¹ Furthermore, it has been reported that band gap of these materials can be finely tuned by changing the nature of functional groups.¹ Also, based on density functional theory (DFT) studies, it has been predicted that bare MXene
sheets have a higher theoretical capacity in Li-ion batteries than terminated ones. In recent reports, heat treatment has been reported as an efficient way to alter the surface chemistry of MXene sheets. Rakhi et al. reported that heating Ti$_2$CT$_x$ in different atmospheres significantly improves its capacitive performance. Naguib et al. reported that flash oxidation of Ti$_3$C$_2$T$_x$ MXene in air results in growth of nanocrystalline TiO$_2$ on disordered graphitic carbon sheets. The resulting TiO$_2$/C composite showed promising performance when tested as anode material in LIBs. In situ transmission electron microscopy (TEM) revealed that either anatase or rutile nanocrystals of TiO$_2$ can be formed by controlling time, temperature and heating rate. In addition, hydrothermal treatment of Ti$_3$C$_2$T$_x$ resulted in a hybrid TiO$_2$/Ti$_3$C$_2$ structure with an enhanced photocatalytic activity. The amount of produced TiO$_2$ depended on temperature and time of hydrothermal treatment.

In this study, we aimed to alter the surface chemistry of Ti$_2$CT$_x$ MXene by a simple and scalable room-temperature oxidation in hydrogen peroxide (H$_2$O$_2$) solution. It resulted in the formation of TiO$_2$ nanocrystals on the surface of MXene sheets, which significantly improved the performance of the anode material in Li-ion battery anodes. The schematic of H$_2$O$_2$ assisted room temperature oxidation of MXene flakes is given in Figure 2.1.
2.3 Experimental Section

Chemical exfoliation of commercially available Ti$_2$AlC (~325 mesh, Maxthal 211, Kanthal, Sweden) resulted in 2D titanium carbide (Ti$_2$CT$_x$) nanosheets. The exfoliation procedure was the same as reported elsewhere; Ti$_2$AlC powder was immersed in 10% HF for 10 h at room temperature. The resulting suspension was washed with DI water and filtered to obtain 2D Ti$_2$CT$_x$ powder and dried at 60 °C for 24 hrs under vacuum. The as-prepared MXene powder was allowed to react with H$_2$O$_2$ solutions of different concentrations for different times. In a typical reaction, 0.5 grams of Ti$_2$CT$_x$ powder was immersed in 50 mL of water under constant magnetic stirring and 5 mL of 30 wt. % H$_2$O$_2$ was added afterwards. The H$_2$O$_2$ treated MXene powder was washed several times with DI water and dried under vacuum for 24 hours before further experiments.

The as-prepared and H$_2$O$_2$ treated MXene powders were characterized by using a powder X-ray diffractometer (XRD, Bruker, D8 ADVANCE) with Cu K$_\alpha$ radiation ($\lambda = 0.15406$ nm). Raman spectroscopy was carried out using a LabRam Aramis Raman
spectrometer with a diode-pumped solid-state blue laser having an excitation wavelength of 473 nm. XPS studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source ($h\nu=1486.6$ eV) operating at 150 W, a multichannel plate and a delay line detector under a vacuum of $1\approx10^{-9}$ mbar. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively and quantified using empirically derived relative sensitivity factors provided by Kratos analytical. Samples were mounted in floating mode to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the C 1s peak of (C-C, C-H) bond, which was set at 284.8 eV. The data were analyzed with commercially available software, CasaXPS. The surface morphology and microstructure of as-prepared and H$_2$O$_2$ treated MXene powders were characterized with a field emission scanning electron microscope (FESEM, Nova NanoSEM from FEI), and a TEM (Titan G$^2$ 80-300 ST, FEI). Surface area and pore size distribution measurement was carried out by using nitrogen as adsorbent at liquid nitrogen temperature (ASAP 2420, Micromeritics) and samples were degassed at 150 °C for 12 hours before analysis.

The working electrodes were prepared by mixing the active material ($H_2O_2$ treated MXene powder) with acetylene black (MTI, Inc.) and poly(vinylidene fluoride) (PVDF, MTI Inc) in a weight ratio of 80:10:10. The prepared slurry was uniformly pasted on a copper foil (MTI, Inc.) and dried at 80 °C for 24 hrs under vacuum. The average mass of active material after drying is $\approx 0.75$ mg/cm$^2$. To assess the electrochemical performance, 2032 coin–type (MTI, Inc.) half–cell devices were fabricated. The $H_2O_2$ treated MXene powder, pasted on copper foil, served as a working electrode, Lithium foil was used as counter electrode and Celgard 3501 micro porous membrane has used a separator. 1 M LiPF$_6$ 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 (100–5000 mA/g) in the 0.005–3.00 V range. Cyclic voltammetry was performed to examine the reduction and oxidation peaks in the voltage range of 0.005 – 2.8 V (V vs. Li/Li⁺) at a scan rate of 0.2 mV/s.

2.4 Results and Discussions

Three different samples will be discussed in this chapter: 1) As-prepared Ti₂CTₓ, 2) Ti₂CTₓ treated in H₂O₂ for 5 minutes and 3) Ti₂CTₓ treated in H₂O₂ for 5 hours. Figure 2.2a shows the XRD patterns of as-prepared and H₂O₂ treated (5 minutes) powders. It can be readily observed that (0002) peak of Ti₂AlC MAX phase shifts towards lower angles in the as-prepared Ti₂CTₓ, which indicates the removal of Al and increase of the c lattice parameter.² Also, the (0002) peak, mentioned as MXene peak, broadens as compared to the sharper parent phase peak which corresponds to the decreasing structural order.² However small amount of residual Ti₂AlC remained ion the Ti₂CTₓ powder. The XRD spectrum of H₂O₂ treated MXene powder shows the presence of anatase (TiO₂). A sharp peak at 2θ ≈ 25° corresponds to (101) plane of anatase TiO₂ (JCPDS card no. 00–021−1272).⁴ Despite the formation of anatase, the (0002) peak of MXene phase is also present, which indicates that the resulting product is mainly MXene phase. Figure 2.2b shows the Raman spectra of as-prepared MXene and H₂O₂ treated MXene (immersion time ≈ 5 minutes) powders. The H₂O₂ treated MXene powder showed a major peak around 150 cm⁻¹, which corresponds to the anatase.⁵,⁹ The other three Raman bands (≈ 250, 400 and 600 cm⁻¹) represent the vibration modes which can be assigned to nonstoichiometric titanium carbide.¹⁰ Furthermore, it can be observed that after H₂O₂ treatment the Raman band centered at
400 cm\(^{-1}\) shifted towards higher wavelengths, which can be attributed to the layers emaciation.\(^4\) As previously reported, the decrease in layer thickness shifts the band position to a higher energy due to slight hardening of the bonds.\(^4\) Another interesting observation in Raman spectra is the absence of D and G bands after H\(_2\)O\(_2\) treatment. In previous reports, when flash oxidation of MXene powder\(^5\) was carried out, the final product was nanocrystalline TiO\(_2\) supported on disordered carbon sheets due to an insufficient amount of oxygen or oxidation time to oxidize carbon. However, in this case, the absence of D and G bands indicates that our final product is nanocrystalline TiO\(_2\) supported on MXene (Ti\(_2\)CT\(_x\)) sheets. The chemical reaction of MXene oxidation in H\(_2\)O\(_2\) can be written as follow:

\[
aT\text{Ti}_2\text{CT}_x + H_2O_2 \rightarrow b\text{TiO}_2 + (1-b)\text{Ti}_2\text{CT}_x + CO_y
\]

Figure 2.2: Characterization of as-prepared and H\(_2\)O\(_2\) treated MXene powder (immersion time \(\approx 5\) minutes): (a) XRD patterns (b) Raman spectra and (c) SEM image of a typical H\(_2\)O\(_2\) treated MXene flake.
When Ti$_2$CT$_x$ powder is immersed in the H$_2$O$_2$ solution, it oxidizes to form TiO$_2$ and emits CO/CO$_2$. The nitrogen adsorption/desorption isotherms of the as-prepared and H$_2$O$_2$ treated MXene powders are shown in. The specific surface area (SSA) values were calculated by using Brunauer–Emmett–Teller (BET) model, where the as-prepared MXene powder showed the SSA of $\approx 12.6$ m$^2$/g, while H$_2$O$_2$ treated MXene powder exhibited an increase in SSA to 58 m$^2$/g (Figure 2.3). This fivefold increase in SSA values can be explained by the formation of TiO$_2$ nanoparticles and opening/swelling of the layers after H$_2$O$_2$ treatment. Figure 2.2c shows the SEM image of H$_2$O$_2$ treated MXene where layers are being opened up and TiO$_2$ formation on their surface is initiated. The XRD and Raman results presented earlier also support this conclusion.

![Figure 2.3: Nitrogen adsorption-desorption isotherms of as-prepared Ti$_2$CT$_x$ and H$_2$O$_2$ treated MXene (immersion time $\approx 5$ minutes)](image-url)
XPS investigations were performed to characterize the chemical composition of prepared powder and to determine the oxidation state of titanium (Ti). The detailed survey spectrum for the as-prepared MXene powder shows the presence of Ti, fluorine (F), oxygen (O), and carbon (C) (Figure 2.4A).

Figure 2.4: XPS survey spectrum of (A) as-prepared Ti$_2$CT$_x$, (B) H$_2$O$_2$ treated Ti$_2$CT$_x$ (immersion time ≈ 5 minutes) and (C) H$_2$O$_2$ treated MXene (immersion time ≈ 5 hours)

High-resolution XPS spectra of Ti 2p and C 1s core levels from the same sample are shown in Figure 2.5a and Figure 2.5b, respectively. The Ti 2p core level was fitted with four doublets (Ti 2p $2p_{3/2}$ – Ti $2p_{1/2}$) with a fixed area ratio equal to 2:1 and doublet separation of 5.7 eV. The Ti 2p$_{3/2}$ components were located at 454.4 eV, 455.9 eV, 457.4 eV and 458.6 eV, respectively. The Ti 2p$_{3/2}$ component centered at 458.6 eV is associated with Ti ions with a formal valence $4^+$, while the peak at lower binding energy 457.4 eV is associated with Ti ions with reduced charge state (TiO$_{2-x}$). The Ti 2p$_{3/2}$ component centered at 454.4 eV corresponds to Ti-C bond. The Ti 2p$_{3/2}$ component centered at 455.9 eV can be assigned to the Ti-X peak in Ti$_2$CT$_x$ (a combination of a sub-stoichiometric TiC$_x$ ($x<1$) and to titanium oxycarbides TiC$_x$O$_y$.

The C 1s core level was fitted using six components located at 281.0 eV, 282.1 eV, 284.1, 284.8 eV, 286.3, 288.0 and 288.9 corresponding to C-Ti, C-Ti-O, C=C (sp$^2$), C-C/C-H (sp$^3$), C-O, C=O and (O=C=O and C-F) bonds, respectively. The survey spectrum for H$_2$O$_2$ treated MXene powder (immersion time ≈ 5 minutes) shows
the presence of Ti, F, O and C (Figure 2.4B). High-resolution XPS spectra of Ti 2p and C 1s core levels have been obtained and presented in Figure 2.5c and Figure 2.5d, respectively. The same fitting parameters were used to deconvolute the Ti 2p and C 1s core levels as in Figure 2a and 2b. It can be readily observed that there was a substantial decrease in the intensity of Ti 2p\textsubscript{3/2} components at 454.4 eV, 455.9 eV and 457.4 eV for the Ti 2p spectrum accompanied with a decrease in the intensity of the C 1s component at 281.1 eV for the C 1s spectrum. This indicates that TiO\textsubscript{2} was formed at the expense of Ti\textsubscript{2}C and the ratio of titanium carbides and titanium oxycarbides to TiO\textsubscript{2} was 0.25.

Similarly, the detailed XPS spectrum for H\textsubscript{2}O\textsubscript{2} treated MXene powder (immersion time \(\approx\) 5 hours) also shows the presence of Ti, F, O and C (Figure 2.4C). High-resolution XPS spectra of Ti 2p and C 1s core levels are presented in Figure 2.5e and Figure 2.5f, respectively. The Ti 2p core level was fitted with two doublets (Ti 2p\textsubscript{3/2} – Ti 2p\textsubscript{1/2}) with a fixed area ratio equal to 2:1 and doublet separation of 5.7 eV. The Ti 2p\textsubscript{3/2} components were located at 456.6 eV and 458.8 eV respectively. The dominant Ti 2p\textsubscript{3/2} component centered at 458.8 eV is associated with Ti\textsuperscript{4+} ions, while the peak at lower binding energy 456.6 eV is associated with Ti\textsuperscript{3+} ions.\textsuperscript{11} Interestingly, this sample didn’t indicate the presence of any titanium carbides and oxycarbides. This result was confirmed by the high-resolution XPS spectrum of C 1s core level and presented in Figure 2.5f. The C 1s core level was fitted using four components located at 284.8 eV, 286.4, 288.0 and 288.9 corresponding to C-C/ C-H, C-O, C=O and (O-C=O and C-F) bonds, respectively. The absence of Ti-C bonds (which were expected to be observed at around 281 eV) is evident. These results demonstrate that with the extended reaction time, Ti\textsubscript{2}C is completely converted into TiO\textsubscript{2}.
Figure 2.5: High-resolution Ti 2p and C 1s XPS spectra: (a, b) as-prepared MXene, (c–d) H$_2$O$_2$ treated MXene ($\approx$ 5 minutes) and (e–f) H$_2$O$_2$ treated MXene ($\approx$ 5 hours)
The morphology and microstructure of as-prepared and H$_2$O$_2$ treated MXene powders were investigated using TEM. Figure 2.6a shows a relatively low magnification TEM micrograph of as-prepared MXene powder. The stacked, layered and flake-like nature of MXene sheets can be readily observed. Figure 2.6b presents the high-resolution (HR) TEM image, which shows the lattice planes of MXene and some surface defects. Similar type of defects has been reported for functionalized graphene$^{21}$ and it has been proposed that these defects might act as nucleation sites for metal oxide formation.$^{22-23}$ This idea supports our previously mentioned hypothesis that when MXene powder is placed in the H$_2$O$_2$ environment, TiO$_2$ growth is observed on the surface of MXene sheets with its nucleation starting at defects. The selected area electron diffraction (SAED) of as-prepared MXene sample, presented in Figure 2.6c, shows the hexagonal symmetry of the structure. It can be concluded that the MXene powder retained the crystallinity and symmetry of parent phase – Ti$_2$AlC.$^{1,8}$

Figure 2.6d and Figure 2.6e show the TEM images of H$_2$O$_2$ treated MXene powder (immersion time ≈ 5 minutes). The flake-like MXene morphology can be seen in Figure 2.6d; however, when observed at a high magnification, the TiO$_2$ nanocrystals are found to be nucleated on the surface of MXene sheets. This is a clear evidence of TiO$_2$ growth on MXene sheets which is also supported by SAED pattern, presented in Figure 2.6f. The SAED pattern consists of two distinct phases; MXene phase, which is evidenced by the hexagonal symmetry, and anatase TiO$_2$ which is confirmed by the appearance of diffraction rings. It should be noted that the sample prepared under the same conditions was used for electrochemical characterization. However, as mentioned earlier, there are two parameters which determine the growth rate of TiO$_2$ in H$_2$O$_2$; the amount of H$_2$O$_2$ and the reaction time. Figure 2.6g and Figure 2.6h presents the TEM
and HRTEM images of an H$_2$O$_2$ treated sample with prolonged immersion time ($\approx$5 hours).

It can be readily observed that almost 100% MXene is converted into a TiO$_2$ phase, in agreement with our XPS data presented in Figure 2.5e and Figure 2.5f. The size (20–100 nm) and shape of TiO$_2$ nanoparticles can be seen from Figure 2.6g. The HRTEM image and SAED pattern confirmed the presence of pure anatase TiO$_2$ phase. Based on HRTEM and SAED results, it can be concluded that room temperature oxidation of Ti$_2$CT$_x$ with H$_2$O$_2$ produces a hybrid structure of TiO$_2$ and Ti$_2$C.

Figure 2.6: Low- and high-magnification TEM images, and SAED patterns: (a–c) as-prepared MXene, (d–f) H$_2$O$_2$ treated MXene ($\approx$ 5 minutes) and (g–i) H$_2$O$_2$ treated MXene ($\approx$ 5 hours).
To assess the potential of using H$_2$O$_2$ treated MXene in Li–ion batteries (LIBs), we studied its electrochemical behavior with respect to Li$^+$ ion insertion and extraction. The cyclic voltammetry (CV) study of as-prepared MXene and H$_2$O$_2$ treated MXene (immersion time ≈ 5 minutes) electrodes was performed in the potential window of 5.0 mV to 2.8 V, at the scan rate of 0.2 mV/s and measured current–voltage (I–V) curves are presented in Figure 2.7a. The CV scan for as-prepared MXene matches with the previously published data,$^{24-25}$ where two distinct oxidation and reduction peaks were observed on charging/discharging. Interestingly, the CV scan for H$_2$O$_2$ treated MXene is not entirely different from the as-prepared MXene, except the higher values of obtained current which, in turn, indicates a higher capacity. In addition, typical oxidation and reduction peaks for TiO$_2$ were not observed, which implies that the major capacity contribution is still coming from Ti$_2$CT$\chi$. Thus, the observed increase in specific capacity after H$_2$O$_2$ treatment is mainly due to opening of layer spacing and improved accessibility of MXene surface to Li ions. When the CV scan was initiated from open circuit voltage (OCV), four distinct peaks were observed at ≈1.75 V, ≈1.30 V, ≈0.95 V and ≈0.60 V (vs. Li/Li$^+$). Two peaks among these are irreversible and do not appear in the succeeding cycles. The presence of irreversible peaks can be assigned to the formation of solid electrolyte interface (SEI) and/or reaction with the electrode material.$^{25}$ The broad oxidation and reduction peaks imply that lithium is stored over a larger voltage range which makes it a better candidate for Li ion capacitors.$^{24}$
Figure 2.7: Electrochemical characterization of as-prepared and H$_2$O$_2$ treated MXenes (immersion time ≈5 minutes): (a) CV curves, (b) galvanostatic charge/discharge curves for H$_2$O$_2$ treated MXene, (c) cyclic performance at 100 mA/g (C/3.5), 500 mA/g and 1000 mA/g (solid symbols - H$_2$O$_2$ treated MXene; hollow symbols - as-prepared MXene) and (d) rate-ability assessment of H$_2$O$_2$ treated MXene (≈ 5 min) at different current densities.

The galvanostatic charge/discharge curves at current densities 100 mA/g (C/3.5), 200 mA/g (C/1.75), 300 mA/g, 400 mA/g, 500 mA/g and 1000 mA/g (Figure 2.7b) show similar voltage plateaus (the C-rates were calculated based on theoretical capacity of Ti$_2$CO$_2$ ≈ 350 mAh/g). These data are consistent with the observations made using CV scans. The cyclic performance of H$_2$O$_2$ treated MXene at three different current densities has been measured and presented in Figure 2.7c. The first discharge capacity was measured as 1015 mAh/g, 826 mAh/g and 681 mAh/g at 100 mA/g, 500 mA/g and 1000 mA/g, respectively. The second discharge capacity values were 507 mAh/g, 429 mAh/g and 384 mAh/g at 100 mA/g, 500 mA/g and 1000 mA/g, respectively. Again, the irreversible capacity loss could be attributed to the formation of SEI layer or reaction of Li ions with –F and –OH groups on the surface of
After 50 cycles, the observed specific capacity was 389 mAh/g, 337 mAh/g and 297 mAh/g at 100 mA/g, 500 mA/g and 1000 mA/g, respectively. These values are almost two times higher when compared with the specific capacity of as-prepared MXene at similar current densities, presented in the same figure (hollow symbols). The most probable reason is the formation of TiO$_2$ nanoparticles and improved accessibility of MXene surface after H$_2$O$_2$ treatment. At this stage, we won’t assign this high specific capacity to the presence of TiO$_2$ because we have not observed its contribution towards capacity in CV scans or charge/discharge curves. One should note that the previously published literature also suggests that whenever surface area of MXene was increased either by delamination$^{27-28}$ or flash oxidation,$^5$ the specific capacity increased tremendously. Furthermore, the observed specific capacity of oxidized Ti$_2$CT$_x$ allows it to compete with the graphite anodes and suggests that partial oxidation of MXenes, which holds promise for increasing their capacity, is a valuable route for practical applications in energy storage devices.

Besides this promising gravimetric capacity and cyclic performance, H$_2$O$_2$ treated Ti$_2$CT$_x$ demonstrated excellent performance at current densities as high as 1000–5000 mA/g. After being cycled at 5000 mA/g, the cell was retested at 1000 mA/g, showed the specific capacity of 280 mAh/g at the 1000th cycle (compared to 297 mAh/g after the 50th cycle), indicating excellent rate performance of oxidized Ti$_2$CT$_x$. This ability of handle high current densities makes Ti$_2$CT$_x$ a suitable candidate for Li ion capacitors.

2.5 Conclusions

We have demonstrated that H$_2$O$_2$ treatment is a scalable and cost effective room temperature method to produce TiO$_2$/Ti$_2$C hybrid materials. The presence of TiO$_2$ was observed by XRD, Raman, XPS and HRTEM. The MXene powder treated in H$_2$O$_2$ for
5 min showed the fivefold increase in specific surface area, as compared to as-prepared MXene powder. In addition, when H$_2$O$_2$ treated MXene powder was tested as anode in Li ion batteries, it showed a significantly improved performance. The excellent battery performance is mainly attributed to the higher surface area accessible to Li ions, which comes from the opening/swelling of MXene layers due to the H$_2$O$_2$ treatment and titania formation. Furthermore, the high rate performance and excellent cycle life make partially oxidized MXene a viable candidate for Li ion capacitors.

REFERENCES


3. Chapter 3: Atomic Layer Deposition of SnO$_2$ on MXene for Li-Ion Battery Anodes

3.1 Summary

In this project, 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 SnO$_2$/MXene anode for Li-ion battery applications. The SnO$_2$/MXene anode exploits the high Li-ion capacity offered by SnO$_2$, while maintaining the structural and mechanical integrity by the conductive MXene platform. The atomic layer deposition (ALD) conditions used to deposit SnO$_2$ on MXene terminated with oxygen, fluorine, and hydroxyl-groups were found to be critical for preventing MXene degradation during ALD. We demonstrate that SnO$_2$/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 SnO$_2$. The cyclic performance of the anodes is further improved by depositing a very thin passivation layer of HfO$_2$, in the same ALD reactor, on the SnO$_2$/MXene anode. This is shown by high-resolution transmission electron microscopy to also improve the structural integrity of SnO$_2$ anode during cycling. The HfO$_2$ coated SnO$_2$/MXene electrodes demonstrate a stable specific capacity of 843 mAh/g when used as Li-ion battery anodes.

3.2 Introduction and Background

MXenes, such as Ti$_3$C$_2$, have been reported to exhibit metallic conductivity, negative surface charge in solutions, and high hydrophilicity.$^{1-2}$ Due to their high electrical conductivity and 2D structure, MXenes have been studied as electrode materials in supercapacitors,$^3$ Li$^{+6}$ and Na$^{+8}$ ion batteries, electrochemical sensors,$^9-10$ electromagnetic interference shielding$^{11}$ and water purification$^{12}$ applications.
Ti$_3$C$_2$ is one of the most studied MXene phases because of the well-established etch chemistry involved and the detailed theoretical studies. Furthermore, its large volumetric capacitance has made it an attractive candidate for supercapacitors electrodes and as anode material for Li ion batteries. For instance, based on density functional theory calculations, Tang et al. predicted the theoretical capacity of bare Ti$_3$C$_2$ 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. 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$_3$C$_2$F$_2$ and 67 mAh/g for Ti$_3$C$_2$(OH)$_2$. On the experimental front, HF-etched Ti$_3$C$_2$ powder showed a specific capacity of 123.6 mAh/g at a 1C rate. However, delaminated, etched and assembled with nanotubes Ti$_3$C$_2$Tx showed the capacity exceeding 700 mAh/g, showing a potential of MXene to deliver good performance if a proper electrode design is applied.

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 or by producing in-situ TiO$_2$ on the MXene surface. For example, Naguib et al. performed flash oxidation of Ti$_3$C$_2$ 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. Ahmed et al. reported that H$_2$O$_2$-assisted room-temperature oxidation of Ti$_2$C 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. 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. Tin oxide was also used for pillaring
Ti$_3$C$_2$ layers in Li-ion capacitors.\textsuperscript{24} 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.\textsuperscript{26} Recently, ALD has been used to improve battery technology either by creating 3D electrode nanostructures or by modifying the electrode/electrolyte interface.\textsuperscript{27-29} 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.\textsuperscript{25,30} For instance, hydrothermal treatment of Ti$_3$C$_2$Tx has caused formation of TiO$_2$ and free carbon on the MXene surface.\textsuperscript{25} 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 Ti$_3$C$_2$Tx 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.\textsuperscript{31} The proposed electrode design strategy indeed led to MXene-supported anode architectures with high capacity and cycling stability.
3.3 Experimental Section

Commercially available Ti$_2$AlC 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$_3$AlC$_2$ powder with particles of < 38 μm. Ti$_3$C$_2$ MXene was prepared by HF etching of Al from the MAX phase. 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$_3$C$_2$ 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 ºC 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 Kα radiation (λ = 0.15406 nm). The surface morphology and microstructure of the 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.

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\textsubscript{2} and HfO\textsubscript{2} deposition and mass of active material was measured afterwards (1–2 mg/cm\textsuperscript{2}). This mass was used to calculate current densities and specific capacities.

SnO\textsubscript{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\textsubscript{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\textsubscript{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 SnO\textsubscript{2} on MXene sheets. Similarly, ultrathin films of HfO\textsubscript{2} were deposited on the prepared SnO\textsubscript{2}/MXene electrodes at 180 °C. The HfO\textsubscript{2} ALD reaction sequence comprised the following steps: 1) a constant N\textsubscript{2} dose at 20 psi; 2) an H\textsubscript{2}O dose for 0.015 s; 3) an H\textsubscript{2}O reaction time for 10 s; 4) a dose of precursor (Tetrakis (dimethylamino) hafnium (Hf(NMe\textsubscript{2})\textsubscript{4})) for 0.2 s, and 5) an Hf(NMe\textsubscript{2})\textsubscript{4} reaction time of 15 sec for a growth rate of 0.1 nm per cycle.

To assess the electrochemical performance, 2032 coin–type (MTI, Inc.) half–cell devices were fabricated. SnO\textsubscript{2}/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 LiPF\textsubscript{6} 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 O\textsubscript{2} and H\textsubscript{2}O < 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.

3.4 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 3.1.

Figure 3.1: 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.
Hydrothermal synthesis resulted in the formation of SnO$_2$ particles on distorted MXene sheets, due to high temperature, pressure and aqueous environment, which can modify the MXene. The XRD and corresponding SEM images of SnO$_2$ deposited on MXene by hydrothermal and sputtering are presented in Figure 3.2. Sputter-deposited SnO$_2$ films partially covered the MXene sheets, mainly the accessible outer surface and not the interlayer space, however Ti$_3$C$_2$ MXene retained its structure and morphology (Figure 3.2) due to the non-conformal nature of the sputtering process. The ALD process produced conformal SnO$_2$ films that completely covered the MXene surface.

Figure 3.2: Material characterization: (A) XRD patterns of as-prepared Ti$_3$C$_2$ MXene and SnO$_2$-coated MXene prepared by hydrothermal synthesis and magnetron sputtering, (B) typical SEM image of the SnO$_2$-coated MXene electrode after hydrothermal reaction, (C) XRD patterns of ALD SnO$_2$-coated MXenes with different purging schemes and (D) SEM image from a typical region when ozone was used for the first purge.
Figure 3.3: Material characterization: XRD patterns and SEM images of as-prepared MXene and SnO$_2$-coated MXene anodes processed at (A, C) 150 °C and (B, D) 200 °C.

The XRD patterns of as-prepared Ti$_3$AlC$_2$ and HF-etched Ti$_3$C$_2$T$_x$ are shown in Figure 3.4a. A small amount of titanium carbide (TiC) was found as secondary phase of the as-synthesized Ti$_3$AlC$_2$ powder. The XRD pattern of the as-prepared Ti$_3$AlC$_2$ 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 (2θ ≈ 10°) shifted to the lower angle and broadened as compared to its original location in the Ti$_3$AlC$_2$ phase, which indicates an increase in the c-lattice parameter and less regular spacing between the Ti$_3$C$_2$ layers after Al removal. Typically, Ti$_3$AlC$_2$ has a c-lattice parameter of 18.58 Å, which increased to 19.96 Å after HF etching. Thus, d-spacing values of Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_x$ 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. The SEM image from a typical flake of Ti$_3$C$_2$Tx presented in Figure 3.4b illustrates successful exfoliation, where sheets are separated and exhibit an accordion-like structure. We used Ti$_3$C$_2$Tx, 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 surface.

Figure 3.4: Characterization of as-prepared HF-etched Ti$_3$C$_2$ MXene: (A) XRD patterns of Ti$_3$AlC$_2$ and Ti$_3$C$_2$; (B) typical SEM image of HF-etched Ti$_3$C$_2$ MXene; (C) TEM image of HF-etched few-layer Ti$_3$C$_2$ MXene, inset shows the SAED pattern; and (D) Fourier-filtered HRTEM image showing the hexagonal atomic arrangement of HF-etched Ti$_3$C$_2$ MXene.
The low-magnification TEM image of Ti$_3$C$_2$T$_x$ and the corresponding selected-area electron diffraction (SAED) pattern (Figure 3.4c) clearly show the flake-like nature of the nanosheets after exfoliation. The SAED pattern of Ti$_3$C$_2$T$_x$ exhibits the hexagonal symmetry of the carbide layers inherited from Ti$_3$AlC$_2$. Moreover, fast Fourier transform (FFT) filtered high-resolution TEM image (Figure 3.4d) 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. For instance, when we tried to decorate MXene surface with SnO$_2$ nanoparticles by hydrothermal synthesis, XRD confirmed degradation of MXene (Figure 3.2a) - 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. Figure 3.2b shows a typical SEM image of a hydrothermally synthesized SnO$_2$/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 3.2a), 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 SnO₂ on any given substrate, the substrate surface must be hydrophilic to attach –O or –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 (–O or –OH) on the MXene surface²¹,³³, 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 SnO₂ deposition in two cases. In one case, SnO₂ 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 3.2c), and the MXene flakes were ruptured, as can be seen in Figure 3.2d. 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 SnO₂ growth by ALD.²¹,³³ Hence, the “Sn precursor first” approach was used for all subsequent SnO₂ 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 section 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 SnO$_2$-coated MXene anodes deposited at 150 °C (Figure 3.5a) and 200 °C (Figure 3.5b) using Sn precursor in the first purge. These images show that the layered and stacked nature of MXene flakes was preserved during SnO$_2$ deposition, and the corresponding SAED patterns confirm this via the presence of hexagonal crystal structures. Furthermore, the SAED pattern of 50-nm SnO$_2$-coated MXene sheets prepared at 150 °C (inset of Figure 3.5a) showed no significant contribution to the diffraction pattern, indicating that amorphous SnO$_2$ had formed on the MXene surface. However, at 200 °C, a ring pattern is visible (inset of Figure 3.5b), indicating the formation of crystalline SnO$_2$. 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 3.3) and a (211) peak from SnO$_2$-coated MXene flakes was observed after deposition at 200 °C.
Figure 3.5: TEM analysis of MXene sheets coated with a 50-nm-thick layer of SnO$_2$: 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 SnO$_2$ coating.

SEM images show the microstructure of 50-nm SnO$_2$/MXene electrodes prepared at 150 °C (Figure 3.3c) and 200 °C (Figure 3.3d) and confirm that the layered nature of MXene was preserved after ALD at both temperatures. To illustrate the distribution of SnO$_2$ on MXene sheets, an RGB plot of a Fourier-filtered HRTEM image is shown in Figure 3.5c. 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 3.6. The inset in Figure 3.5d 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.

**Figure 3.6:** TEM analysis: (A) HRTEM image of Ti$_3$C$_2$ MXene coated with a 50 nm thick layer of SnO$_2$, (B) corresponding FFT pattern and mask for FFT filtering for (C) Ti$_3$C$_2$ MXene and (D) SnO$_2$.

The electrochemical performance of SnO$_2$-coated MXene was evaluated using half-cell Li ion batteries (Li foil as the counter electrode). Figure 3.7a 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.\textsuperscript{18, 24} 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.\textsuperscript{24} 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.\textsuperscript{18, 33} The third large peak
at 0.01 V, corresponds to the lithiation of carbon present in the anode material. 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. 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 3.7a), the combined effect of MXene and SnO$_2$ can be seen in the CV curves, while the SnO$_2$ dominated the electrochemical performance of samples with a 50-nm-thick SnO$_2$ coating. For SnO$_2$/MXene electrodes, a large reduction peak below 1.00 V corresponds to the formation of SEI and reduction of SnO$_2$ with Li$^+$ ions, as its intensity significantly decreases during subsequent cycles. The reduction reaction of SnO$_2$ with Li$^+$ ions can be described by the following equation:

$$\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Sn(0)} + 2\text{Li}_2\text{O}$$

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

$$\text{Sn} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Sn}$$

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. The peak at 1.25 V (more visible in the 5th CV cycle, Figure 3.8) corresponds to the reversible reaction of Li$^+$ ions with SnO$_2$. When the thickness of the SnO$_2$ layer is increased from 10 to 50 nm, both alloying/dealloying reactions of Li$^+$ ions with Sn and
redox reactions of SnO$_2$ become more significant.$^{24,34}$ The first five CV cycles of all samples are separately plotted in Figure 3.8, where it can be readily observed that alloying/dealloying reactions are highly reversible, while oxidation/reduction reactions of SnO$_2$ are only partially reversible. This partial reversibility of SnO$_2$ plays a major role in the poor cyclic performance of conventional SnO$_2$-based anodes.

Figure 3.7: Electrochemical characterization of Ti$_3$C$_2$ 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 SnO$_2$/MXene electrode and HfO$_2$ coated SnO$_2$/MXene electrodes; the inset shows a close-up in the medium- and high-frequency regions and the Randles circuit.

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 3.7b. 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.37 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.

Figure 3.8: Electrochemical characterization: CV curves for Ti₃C₂ MXene coated with (A) a 10-nm-thick layer of SnO₂ @ 150 °C, (B) a 50-nm-thick layer of SnO₂ @ 150 °C, (C) a 10–nm-thick layer of SnO₂ @ 200 °C, and (D) a 50-nm-thick layer of SnO₂ @ 200 °C
The cyclic performance of SnO$_2$-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 3.7c. 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 SnO$_2$/MXene anode (10-nm-thick SnO$_2$ 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 SnO$_2$ on bare Cu foil (without MXene). Without support from MXene, the capacity quickly faded, and after the 50$^{th}$ cycle, a discharge capacity of 77 mAh/g was obtained. Moreover, the SnO$_2$-only electrode had a specific capacity of 168 mAh/g, which is mainly due to the non-conductive nature of SnO$_2$ films which causes the specific capacity to decrease quickly. Previous reports showed that ALD prepared SnO$_2$-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. 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 SnO$_2$ layer, which resulted in higher specific capacity of SnO$_2$/MXene electrodes (696 mAh/g). Furthermore, when the thickness of SnO$_2$ layer was increased to 50 nm, the SnO$_2$-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 SnO$_2$ layer coated MXene composite electrode (178 mAh/g); the 50-
nm-thick coating of SnO$_2$ on MXene (ALD @ 200 °C) showed a capacity retention of 50% (calculated based on 2$^{nd}$ cycle discharge capacity). This capacity fade indicates that with increasing SnO$_2$ layer thickness, the MXene sheets can no longer accommodate the larger volumetric changes of SnO$_2$ electrodes. Hence, it appears that an optimal SnO$_2$ 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 3.9). We attribute this to a higher crystallinity after ALD at 200°C. The 10-nm-thick coating of SnO$_2$ on MXene (ALD @ 200 °C) resulted in a specific capacity of 258 mAh/g at the 50$^{th}$ cycle, which corresponds to a capacity retention of 59.5 %.

Figure 3.9: Cyclic performance of SnO$_2$/MXene hybrid electrodes at 500 mA/g; ALD @ 150 °C

To further improve the cyclic stability of SnO$_2$-coated MXene electrodes with thick SnO$_2$ layers, we used an ALD process that was recently shown to significantly stabilize Li-ion battery anodes. This process involves deposition of a thin layer of HfO$_2$ at the anode/electrolyte interface, which helps in preserving the structure of the anode materials when large volumetric changes occur.$^{27, 31, 38}$ Moreover, HfO$_2$ does not take
part in the electrochemical process, as evidenced by the CV curves of HfO$_2$ (200 ALD cycles) on bare Cu-foil (Figure 3.10). Furthermore, the thin amorphous HfO$_2$ film does not hinder Li$^+$ and Na$^+$ ions diffusion$^{39}$. Therefore, we aimed to improve the cyclic performance of SnO$_2$/MXene anodes by depositing a thin layer of HfO$_2$ on SnO$_2$/MXene electrodes. SnO$_2$ and HfO$_2$ were sequentially deposited on the MXene by ALD to create a dual-oxide on MXene composite electrodes. The electrochemically inactive nature of HfO$_2$ can be also seen from the CV curves of the HfO$_2$ coated SnO$_2$/MXene anodes (Figure 3.10). 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 50$^{th}$ 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 HfO$_2$, SnO$_2$-coated MXene electrodes delivered a specific capacity of 451 mAh/g at the same current density after the 50$^{th}$ cycle, which corresponds to a capacity retention of 50% (based on the 2$^{nd}$ cycle discharge capacity) (Figure 3.7). Moreover, the cyclic performance of bare SnO$_2$/MXene electrodes is much less stable than that of HfO$_2$ coated SnO$_2$/MXene composites anodes. We demonstrate that the performance of the first-generation oxide/MXene anodes is comparable to the advanced Sn-C based compositions.
Figure 3.10: Electrochemical Characterization: CV curves for dual-oxide coated MXene electrodes processed at (A) 150 °C and (B) 200 °C. (C-D) CV curves of ALD of HfO$_2$ on bare Cu foil to assess the electrochemical activity of HfO$_2$, where D has been plotted on the same scale as SnO$_2$/MXene (y-axis) to show that the contribution from HfO$_2$ was negligible.

In addition, EIS was carried out to assess the effect of the HfO$_2$ layer on the performance of SnO$_2$/MXene composite anodes. The EIS plots for SnO$_2$/MXene anodes with and without HfO$_2$ are presented in Figure 3.7d. The typical Nyquist plots at OCV can be fitted with Randles circuit$^{40}$, 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 HfO$_2$ layer at the anode/electrolyte interface decreases the overall charge transfer resistance. This result suggests that the presence of an electrochemically inactive HfO$_2$ 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.$^{38-39}$

To understand the role of HfO$_2$, we conducted *ex-situ* TEM analysis of SnO$_2$/MXene and HfO$_2$ coated SnO$_2$/MXene anodes (Figure 3.11). The capacity retention was found to be directly related to the nature of the reversibility of stepwise Li$^+$ ions reaction with SnO$_2$ during the charge/discharge.$^{38}$ The alloying/dealloying reaction of metallic Sn is highly reversible. However, the conversion reaction of SnO$_2$ with the formation of intermediate SnO is partially reversible and results in distortion of the crystal structure.$^{34}$ Therefore, it is reasonable to expect that the crystal structure of the SnO$_2$/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 3.11). The dot-pattern corresponding to crystalline SnO$_2$ (shown earlier in Figure 3.5b) disappeared after cycling of SnO$_2$/MXene anodes, suggesting that SnO$_2$ was transformed to amorphous SnO$_x$ (Figure 3.11). In contrast, the HfO$_2$ coated SnO$_2$/MXene electrode showed that the crystallinity of SnO$_2$ was preserved after the charge/discharge process (Figure 3.11f).
Figure 3.11: 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).

The *ex-situ* SEM images showing lamellar structure of SnO$_2$/MXene with and with HfO$_2$ coating after cycling are presented in Figure 3.12. The SEM images show that bare SnO$_2$/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, both SnO$_2$/MXene and HfO$_2$ coated SnO$_2$/MXene anodes, retained MXene’s hexagonal structure after cycling.
3.5 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 SnO$_2$/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 SnO$_2$/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 SnO$_2$/MXene anodes exhibit a stable specific capacity of 843 mAh/g. This first report of ALD of oxide on MXene opens up alternate avenues to improve the cycling stability of SnO$_2$ and other conversion anodes.
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4. Chapter 4: Plasma-Assisted Surface Modification of Ti$_3$C$_2$ MXene Enhances Li ion Storage

4.1 Summary

Herein we demonstrate that Li$^+$ ion uptake by Ti$_3$C$_2$ MXene can be significantly enhanced using plasma-based modification of MXene surface chemistry. Four different atmospheres, inert (Ar), inert-reducing (Ar/H$_2$), reactive (N$_2$), and reactive-reducing (N$_2$/H$_2$) were used and their effects on the structural, surface, and electrochemical characteristics of Ti$_3$C$_2$ MXene were explored. We show that the plasma process modified the surface of Ti$_3$C$_2$ in various ways, including replacing -F functional groups with N, reducing surface oxidation, and increasing interlayer spacing, thus opening MXene structure and facilitating Li$^+$ ion intercalation between the MXene sheets. After 100 charge/discharge cycles, specific discharge capacities of 141, 192, 200, 236 and 269 mAh/g were obtained for MXenes treated in Ar, Ar/H$_2$, N$_2$, and N$_2$/H$_2$-plasma environments, respectively. The N$_2$/H$_2$-treated MXene showed a specific capacity of 151 mAh/g at higher current density (1000 mA/g) and stability up to 450 cycles. These results demonstrate that Li ion storage capacity of as-prepared Ti$_3$C$_2$ MXene can be nearly doubled using the N$_2$/H$_2$ plasma process.

4.2 Introduction and Background

The surface functional groups play critical role in determining the electronic properties of MXenes such as band gap, which can be tuned by changing the surface functional groups.$^1$ For instance, it has been postulated that –OH and –F terminated Ti$_3$C$_2$ show semiconducting behavior with band gaps of 0.05 eV and 0.1 eV, respectively, while bare Ti$_3$C$_2$ exhibits metallic character.$^2$ In addition, the surface functional groups may dictate the application of MXene in energy storage devices such
as Li and Na ion batteries. For instance, density functional theory (DFT) studies confirmed that bare MXene (Ti$_3$C$_2$) can store five times more Li$^+$ ions than fluorine terminated MXene (Ti$_3$C$_2$F$_2$) because surface functional groups blocks the Li$^+$ access. However, it is worth mentioning that MXene preparation via wet chemical etching method makes preparation of bare MXene impossible. Hence, the research direction on MXenes has been focused on two main themes, including exploiting surface functional groups to form composite structures, or modifying the surface functionality to tune the electrochemical and electronic properties of MXenes.

On the other hand, the presence of these surface functional groups can be exploited for some applications. For instance, we have reported that presence of –OH functional groups on the surface of Ti$_3$C$_2$ MXene facilitates the fabrication of SnO$_2$/MXene structure by atomic layer deposition (ALD). The resulting composite showed excellent Li$^+$ ion storage and cyclic performance. Similarly, the negatively charged MXene sheets were used to prepare Sn$^{4+}$/MXene composites by facile polyvinylpyrrolidone (PVP)-assisted liquid-phase immersion method. The prepared composite showed improved specific capacity up to 544 mAh/g with good cyclic performance.

The surface chemistry of MXene has also been altered by heat treatment or wet chemical processing. Heat treatment at elevated temperature resulted in conversion of Ti$_3$C$_2$ MXene into TiO$_2$/C comoposite. Hydrothermal treatment of MXene phases resulted in formation of TiO$_2$ on MXene surfaces. H$_2$O$_2$-assisted room temperature oxidation of Ti$_2$C MXene has been reported, and the resulting TiO$_2$/MXene composite delivered specific capacity of 389 mAh/g at a C/3.7 rate. Rakhi et al. reported the thermal treatment of Ti$_2$CT$_x$ MXene in various environments.
and studied their capacitive performance. The study showed that MXene annealed in N₂/H₂ atmosphere exhibited the best pseudocapacitive performance, a result that mainly attributed to the reducing nature of N₂/H₂ atmosphere, which could mitigate MXene surface oxidation.

To the best of our knowledge, there have not been any reports on using plasma to modify the surface chemistry of MXenes and its influence on Li ion battery performance. Thus, in this work, we first carried out plasma treatment of MXenes to identify proper plasma process parameters to minimize changes to MXene structure and surface oxidation; then we systematically studied plasma gas atmospheres to modify the surface chemistry of MXenes. Our results indicate that Li ion storage capacity of as-prepared MXene can be nearly doubled using certain plasma surface modification process, and that our results are in good agreement with the DFT predictions.

4.3 Experimental Procedure

Commercial grade Ti₂AlC powder was obtained from Kanthal, Sweden and TiC from Sigma Aldrich. The Ti₂AlC and TiC powders were mixed in 1:1 molar ratio and ball milled for 24 h. The mixture was sintered at 1350 °C for 2.5 h under constant argon flow to avoid oxidation. The sintered powder was collected, crushed and sieved to obtain Ti₃AlC₂ powder (< 38 μm). The preparation of Ti₃C₂ MXene through HF treatment was carried out using the same protocol as reported elsewhere. In a typical reaction, 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 washing with deionized water was continued till the solution reached a pH value of 6 (complete removal of acid), and bath sonication in water was carried out to obtain exfoliated Ti₃C₂ MXene sheets. Few-layer and multilayer stacks of MXene sheets were collected by vacuum filtration, dried in a
vacuum oven at 70 ºC overnight, and stored in a vacuum desiccator for further experiments. The X-ray diffraction (XRD) patterns of as-prepared MXene and plasma treated MXene powders were measured using a powder X-ray diffractometer (XRD, Bruker, D8 ADVANCE) with Cu Kα radiation (λ = 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 CT, FEI). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra DLD spectrometer with Al Kα radiation and C 1s peak (284.4 eV) was used to calibrate the XPS spectra.

All density functional theory calculations were performed based on the projector augmented wave method as implemented in Vienna Ab-initio Simulation Package. The exchange-correlation potential and the long-range interlayer interaction are described by the generalized gradient approximation of Perdew, Burke and Ernzerhof and DFT-D3 correction. 2x2x1 supercells are built to investigate the lithiation processes, together with a vacuum layer of 15 Å thickness to avoid artificial interaction between periodic images. A 6x6x1 k-mesh is employed for the Brillouin zone integrations. The cut-off energy of plane-wave is set to 500 eV and the energy of the self-consistent calculations converges to 10⁻⁶ eV. The residual forces on the atoms have declined to less than 0.01 eV/A.

Plasma treatment was carried out in a commercial plasma-enhanced chemical vapor deposition (PECVD) system using four different atmospheres: inert (Ar), inert-reducing (Ar/H₂), reactive (N₂) and reactive-reducing (N₂/H₂). As the MXene powder cannot be directly placed in the plasma chamber, we used a blade coating process to
deposit MXene slurry containing conductive additive and poly(vinylidene fluoride) (PVDF, MTI Inc.) binder on Cu foil. The MXene-covered Cu foil was placed in the PECVD system, followed by plasma treatment at varying temperature (100, 250 and 500 °C), plasma power (50, 100 and 250 W) and reaction time (15, 30 and 60 minutes). The optimal conditions for the plasma treatment process parameters were determined based on the structural and electrochemical properties of the resulting MXene anodes.

2032 coin–type (MTI, Inc.) half–cell devices were used to assess the electrochemical performance of plasma-treated MXene. As-prepared and plasma treated Ti3C2 MXene were used as the working electrodes, lithium foil served as the counter and reference electrode, and Celgard 3501 microporous membrane was used as separator to avoid physical contact between anode and cathode terminals. 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 2.5 V vs. Li+/Li 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 – 2.5 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.

4.4 Results and Discussions

Density functional theory (DFT) calculations were carried out to study the impact of various MXene surface functional groups on Li ion storage. The surface
functional groups inherited from the etching medium (HF) \(^{14}\) (such as –O and –F) or plasma-treatments (such as –N) were simulated as surface terminations on MXene, and the theoretical Li\(^+\) ion storage capacities were calculated. Figure 4.1 shows the structure of Ti\(_3\)C\(_2\) MXene sheets with different functional groups and their calculated Li\(^+\) ion storage capacity. As mentioned earlier, bare Ti\(_3\)C\(_2\) MXene offers the highest theoretical capacity for Li\(^+\) ion intercalation, however preparation of bare Ti\(_3\)C\(_2\) MXene without functional groups is practically impossible.\(^{21-22}\) The calculated Li\(^+\) ion storage capacity for bare Ti\(_3\)C\(_2\) MXene is 319.8 mAh/g, which is comparable to commercially used graphite.\(^{23}\) On the other hand, –F terminated MXene surface reduces the theoretical Li\(^+\) storage capacity to 65.2 mAh/g, with 0.5 Li atoms per unit cell. Meanwhile, –O terminated MXene surface gives a theoretical Li\(^+\) ion storage capacity of 268.5 mAh/g with 2 Li\(^+\) ions per unit cell. It is worth mentioning here that, experimentally, most MXene surfaces are terminated with both –F and –O functional groups. Therefore, the experimentally measured capacities for Ti\(_3\)C\(_2\) MXene fall between the theoretical capacities of –F terminated MXene and –O terminated MXene. We have reported that as-prepared Ti\(_3\)C\(_2\) MXene gives a specific capacity of 109 mAh/g after 50\(^{th}\) charge/discharge cycle at high current density (500 mA/g).\(^3\) Most interestingly, when Ti\(_3\)C\(_2\) MXene surface is terminated with nitrogen (–N) functional group, the theoretical Li\(^+\) ion storage capacity increased from 65.2 to 274.1 mAh/g. This theoretical prediction encouraged us to devise experimental strategies to partially or completely replace common functional groups on MXene surface (e.g., –F and –O) with –N.
Figure 4.1: Schematic illustration of Ti$_3$C$_2$ MXene with different surface functional groups (A) bare Ti$_3$C$_2$ MXene, (B) F terminated Ti$_3$C$_2$ MXene – Ti$_3$C$_2$F$_2$, (C) O terminated Ti$_3$C$_2$ MXene – Ti$_3$C$_2$O$_2$ and (D) N terminated Ti$_3$C$_2$ MXene – Ti$_3$C$_2$N$_2$. Li$^+$ ion adsorption was studied using DFT to calculate theoretical Li$^+$ ion storage capacities.

One strategy that seemed to work well is to expose MXene surface to N and H-containing plasma environments. Unlike solution treatment$^{4,24}$ or post etching heat treatment,$^{14,25-27}$ this process is both physical and reactive in nature. Plasmas typically consist of ions or radicals that are energetic and highly reactive. Previously, we have shown that thermal annealing of Ti$_3$C$_2$ in reactive-reducing environment (in N$_2$/H$_2$) improves supercapacitor performance by preventing surface oxidation of MXene.$^{14}$ Therefore, we have chosen N$_2$/H$_2$ plasma as a starting gas mixture to assess the effect of plasma process parameters (power, time, temperature) on the morphological,
structural, and electrochemical characteristics of Ti$_3$C$_2$ MXene. The effect of plasma power, plasma process temperature, and plasma exposure time was systematically varied and the resulting Ti$_3$C$_2$ anodes thoroughly evaluated by SEM, TEM, and electrochemical analysis to determine optimum plasma parameters that we should to tune the MXene surface functional groups without damaging it. Figure 4.2 shows SEM images of as-prepared MXene (inset in Figure 4.2-A) and N$_2$/H$_2$ plasma-treated MXene at different plasma exposure times, chamber temperatures, and plasma powers.

Figure 4.2: SEM images of as-prepared MXene and plasma-treated MXene in N$_2$/H$_2$ gas mixture at different plasma process conditions: Plasma time series: (A) 30 minutes, (B) 60 minutes, and (C) 90 minutes; Plasma power series: (D) 50 W, (E) 100 W, and (F) 250 W; Process temperature series: (G) 100 °C, (H) 250 °C, and (I) 500 °C. The inset in A shows the as-prepared MXene. Scale bar corresponds to 1 µm. These images show that the 50W, 60 min, 100°C process produces the least change in MXene surface morphology.
It can be readily observed that increasing plasma exposure time, plasma power and process temperature leads to morphological distortion of MXene. SEM images of as-prepared MXene (inset Figure 4.2-A) has a clean surface with accordion-like structure. However, nano-crystallites of TiO_2 and TiO_x were observed on the surface of MXene sheets after plasma treatment. Severe conditions such as highest power (250 W), highest temperature (500 °C) and maximum plasma exposure time (90 minutes) results in almost complete distortion of 2D sheet-like MXene morphology and converts into TiO_2. Figure 4.3 shows TEM images and selected area electron diffraction patterns of the N_2/H_2 treated MXene samples run at different plasma powers, reaction time and process temperatures. The TEM images clearly reveal that plasma power of 250 W, reaction time of 90 minutes and process temperature of 500 °C, distort the MXene structure. The SAED pattern shows the hexagonal symmetry of MXene structure and its gradual conversion into TiO_2 at higher power, longer time and higher temperatures. The combination of TEM SAED patterns (Figure 4.3) and SEM images (Figure 4.2) was used to identify the plasma conditions that resulted in least amount of morphological changes and least amount of surface oxidation. In addition to these SEM and TEM studies, we also studied the electrochemical performance of LIBs by galvanostatic charge-discharge testing at a current density of 100 mA/g. Figure 4.4 shows the specific capacity vs. cycle number curves for as-prepared MXene and plasma treated MXene sample at the same plasma process conditions used in Figure 4.3 and Figure 4.2. The maximum specific capacity at 100th cycle was considered as selection criterion for the plasma process conditions and based on these results we identified that the optimum plasma conditions. We have achieved a specific capacity of 269 mAh/g at given plasma conditions: plasma power: 100 W, process temperature: 100 °C and process time: 30 mints.
Figure 4.3: TEM images and SAED patterns of plasma treated MXene in N\textsubscript{2}/H\textsubscript{2} environment at different plasma powers: (A) 50 W, (B) 100 W and (C) 250 W, different plasma exposure times: (C) 30 minutes, (D) 60 minutes, and (E) 90 minutes; and different process temperatures: (G) 100 °C, (H) 250 °C, and (I) 500 °C. Scale bar corresponds to 50 nm and 5 1/\text{nm} in TEM images and insets, respectively.

These conditions do not distort MXene layered morphology or severely oxidized its surface. With these conditions identified, we have studied the impact of four different plasma atmospheres, namely, inert (Ar), inert-reducing (Ar/H\textsubscript{2}), reactive (N\textsubscript{2}) and reactive-reducing (N\textsubscript{2}/H\textsubscript{2}) on surface modification and electrochemical performance. As mentioned earlier, hydrogen (H\textsubscript{2}) gas was used to create more reducing environment to avoid surface oxidation of MXene during plasma treatment.\textsuperscript{14}
Figure 4.4: The effect of plasma conditions on electrochemical performance of Li ion battery anodes: (A) reaction time, (B) plasma power and (C) plasma temperature.

We found out that plasma treatment ambient has profound effect on the structure of Ti$_3$C$_2$ MXene as evidenced from the XRD patterns of as-prepared MXene, Ar-treated MXene, Ar/H$_2$-treated MXene, N$_2$-treated MXene and N$_2$/H$_2$-treated MXenes, which are shown in Figure 4.5a. The peaks at $2\theta \approx 43^\circ$ and $51^\circ$ correspond to the Cu-foil substrate and serve as internal standard to observe the downshifting of (0002) peak. The zoom-in region from $2\theta \approx 5 – 15^\circ$ is presented in Figure 4.5b from which it can be readily observed that plasma treatment results in further downshifting of (0002) peak. This indicates the opening of MXene layers and suggests that electrochemical performance should be improved after plasma treatment. The increase in interlayer spacing is more profound in case of N$_2$/H$_2$-treated MXene which we surmise is due to the adsorption of –N functional groups on surface of MXene sheets. One should also note that the (0002) peak of MXene changes after plasma treatment. The (0002) peak appears to be made from three distinct peaks, which are indicated by vertical lines in Figure 4.5b, after plasma exposure. This effect indicates that the plasma process does not modify the MXene electrode to the same extent l) throughout its thickness (~ 150 µm). The outermost surface layer of the MXene electrodes appear to have shifted the most due to plasma treatment and resultant increase in interlayer spacing. The interlayer spacing of intermediate layers shows small shift and the deepest layers (in the 150 um electrode), seem to have maintained the same interlayer spacing as before the plasma treatment.
Figure 4.5: (A) X-ray diffraction patterns of as-prepared and plasma treated MXene samples in different gas environments. (B) zoom-in region in lower angle range. TEM and HRTEM analysis contains low magnification image, high resolution image and SAED patterns: (C, D) N\textsubscript{2}-treated Ti\textsubscript{3}C\textsubscript{2} MXene and (E-F) N\textsubscript{2}/H\textsubscript{2}-treated Ti\textsubscript{3}C\textsubscript{2} MXene.
Furthermore, we carried out TEM analysis to study the effect of different plasma environments on MXene morphology and structure. The low-magnification image and SAED patterns are shown in Figure 4.5(c-f) for MXene and MXene treated in different ambient. The TEM images show that the flake-like nature of MXene remained intact after plasma treatment, while the SAED results exhibited the hexagonal symmetry that is signature of MXene phase. The low-magnification TEM image of N₂-treated Ti₃C₂ MXene is presented in Figure 4.5e, and clearly shows the flake-like nature of MXene. It appears that the N₂ plasma treatment results in surface oxidation of Ti₃C₂ MXene as confirmed by corresponding selected-area electron diffraction (SAED) pattern shown in Figure 4.5e (inset) along with high resolution transmission electron microscope (HRTEM) image. Though, hexagonal pattern in SAED indicates that MXene phase remained intact during plasma treatment, the appearance of circular ring and dot pattern shows some sort of surface oxidation, presumably formation of TiOₓ.⁴,²⁸-²⁹ On the other hand, when reactive-reducing plasma environment (N₂/H₂ plasma) was used, a relatively clean SAED pattern was observed with distinct hexagonal dot pattern (Figure 4.5e inset), suggesting that negligible MXene oxidation is observed when H₂ is present in the plasma.

XPS investigations were performed to characterize the chemical composition, surface oxidation and surface functional groups of as-prepared MXene and plasma-treated MXene electrodes. The detailed XPS survey spectrum for the as-prepared and plasma treated MXene samples (Ar-treated, Ar/H₂-treated, N₂-treated and N₂/H₂-treated MXenes) are shown in Figure 4.6. The overview of XPS indicates the presence of Ti, fluorine (F), oxygen (O), carbon (C) and nitrogen (N).
Figure 4.6: The survey scan showing XPS spectra of as-prepared MXene and plasma treated MXene samples

As discussed later in this manuscript, N$_2$/H$_2$-treated MXenes showed optimum electrochemical performance; the high-resolution XPS spectra of that sample showing Ti 2p, C 1s, O 1s, F 1s and N1s core levels are shown in Figure 4.7a–e. The Ti 2p core level was fitted with two doublets (Ti 2p 3/2–Ti 2p 1/2) with a fixed area ratio equal to 2 : 1 and a doublet separation of 5.6 eV. The Ti 2p$_{3/2}$ components were located at 456.4 eV and 459.5 eV, respectively. The Ti 2p$_{3/2}$ component centered at 459.5 eV is associated with Ti ions with a formal valence of $4^+$ and indicates the presence of surface oxide.$^4$ The Ti 2p$_{3/2}$ component centered at 456.4 eV corresponds to the Ti–C bond.$^4$, $^{31-33}$ The C 1s core level was fitted using two components located at 284.8 eV and 288.0 eV corresponding to the C–C (sp$^2$) and C–O bonds, respectively.$^{33-34}$ Similarly, the O 1s spectrum can be fitted with two different regions, indicating the presence of oxygen either as surface functional group or in surface TiO$_2$.$^{35}$ The F 1s spectrum was also fitted with two main regions, indicating the sources of fluorine.$^{33}$ It is either coming from wet
chemical etching as surface functional groups, or it is present in the poly(vinylidene fluoride) (PVDF) binder. The N 1s spectrum showed in Figure 4.7e indicates successful incorporation of nitrogen on the surface of MXene sheets. The weight percentages of Ti, C, O, F and N are summarized in the bar chart in Figure 4.7f. The weight percentage of Ti seems to drop after plasma treatment but it should be noted that XPS is a surface sensitive technique and, as mentioned earlier, MXene surface can be partially oxidize during the plasma treatment process. In case of Ar-treated and Ar/H₂-treated MXene samples, the weight percentage of Ti was found to be 2.3 and 3.1 wt. %, which should be compared with 6.2 wt. % in as-prepared MXene sample. This result indicates that reducing atmosphere (Ar/H₂) helps in preventing surface oxidation. Similarly, the N₂/H₂-treated MXene sample has 6.4 wt. % of Ti, which indicates that instead of surface oxidation, an adsorbed layer of –N has been introduced on MXene surface. The weight percentage of O has also the same trend. The maximum oxidation occurred in case of Ar-treated MXene sample (46.01 wt. %). On the other hand, reducing and reactive (N₂/H₂ plasma) environment helps in preventing surface oxidation. The removal of –F surface functional groups was also evidenced in this bar chart (Figure 4.7f). The as-prepared MXene sample contained 23.7 wt. % of F (combination of F coming from HF treatment and PVDF binder) and after plasma treatment it got reduced to 3 – 9 wt. % in different atmospheres. Based on XPS analysis, it can be concluded that plasma treatment does not destroy MXene sheets (Ti–C bond remained intact), but surface oxidation can occur during plasma treatment. However such oxidation can be significantly reduced by introducing H₂ in the plasma process. Further, surface functional groups such as –F can be removed and replaced by plasma treatment.
Figure 4.7: High resolution XPS analysis of N$_2$/H$_2$-treated Ti$_3$C$_2$ MXenes: (A) Ti 2p, (B) C 1s, (C) O 1s, (D) F 1s, and (E) N 1s. Bar chart showing elemental composition of plasma-treated MXene in different atmospheres (F).

The electrochemical performance of plasma treated MXene was evaluated using half-cell Li ion batteries (with Li foil as the counter electrode). Figure 4.8a shows the cyclic performance, deduced from galvanostatic charge/discharge testing, of as-prepared MXene and plasma-treated MXene anodes at current density of 100 mA/g. The as-prepared MXene delivered a first-cycle discharge capacity of 238 mAh/g and
showed a stable capacity of 140 mAh/g after 100 cycles. However, the specific capacity was substantially improved after plasma treatment. The first cycle discharge capacities after Ar-treated, Ar/H₂-treated, N₂-treated and N₂/H₂-treated MXenes were found to be 618, 624, 634 and 753 mAh/g, respectively. This first cycle columbic efficiencies of Ar-treated, Ar/H₂-treated, N₂-treated, and N₂/H₂-treated MXenes were 54%, 54%, 63% and 61%, respectively. This first cycle efficiency is much lower than the as-prepared MXene (93%), which indicates that surface functionalities have been drastically changed after plasma treatment because first cycle efficiency mainly depends upon the formation of solid electrolyte interface (SEI) and electrolyte decomposition.\textsuperscript{36-37} The higher first cycle efficiencies of as-prepared MXene are usually considered as a positive point in practical perspective despite the low capacities. The plasma treated MXene anodes also exhibited excellent cyclic performance. The Ar-treated, Ar/H₂-treated, N₂-treated and N₂/H₂-treated MXene anodes delivered specific capacities of 191, 200, 235 and 269 mAh/g after 100\textsuperscript{th} cycle.

We also studied the cyclic performance of N₂/H₂-treated MXene at various current densities and the results are presented in Figure 4.8b. Even at high current density (1000 mA/g), N₂/H₂-treated MXene electrode delivered specific capacity of 151 mAh/g after 100\textsuperscript{th} cycle. The specific capacity of N₂/H₂-treated MXene electrode (269 mAh/g) at 100 mA/g almost reaches the theoretical limit of –O and –N functional groups (268.5 and 274.1 mAh/g, respectively). The better performance of N₂/H₂-treated MXene electrode can be attributed to (1) opening of MXene layers, (2) preventing surface oxidation by introducing reducing environment (H₂ gas) into the plasma process, and (3) replacing -F with –N on MXene surface.
Figure 4.8: Electrochemical characterization of as-prepared MXene and plasma treated MXene electrodes in Li+ ion batteries: (A) cyclic performance at 100 mA/g, (B) cyclic performance of N\textsubscript{2}/H\textsubscript{2}-treated Ti\textsubscript{3}C\textsubscript{2} MXene electrodes at various current densities, (C) CV curves for N\textsubscript{2}/H\textsubscript{2}-treated Ti\textsubscript{3}C\textsubscript{2} MXene, (D) EIS spectra of as-prepared MXene and N\textsubscript{2}/H\textsubscript{2}-treated Ti\textsubscript{3}C\textsubscript{2} MXene electrodes and (E) cyclic performance of N\textsubscript{2}/H\textsubscript{2}-treated Ti\textsubscript{3}C\textsubscript{2} MXene at 100 mA/g.
The cyclic voltammetry (CV) curves of N$_2$/H$_2$-treated MXene electrode was measured at scan rate of 0.2 mV/s in the voltage range of 0.01–2.50 V (vs. Li/Li$^+$). In the first cathodic scan of the N$_2$/H$_2$-treated MXene electrode, three large and two small cathodic peaks were observed at 1.42, 0.89, 0.57, 0.33, and 0.01 V, respectively. The broad peaks at 1.42 and 0.89 V disappear in subsequent cycles, which can be attributed to the formation of SEI layer and to trapping of Li$^+$ ions between MXene sheets. The number of peaks in cathodic scan are the similar to as-prepared MXene reported elsewhere, but peak positions are shifted. This is likely because Li$^+$ ion interaction barrier is quite sensitive to the type of functional group present on MXene surface. Finally, the large peak at 0.01 V vs. Li/Li$^+$ can be attributed to carbon lithiation present as conductive additive in electrode.

The Anodic scan of N$_2$/H$_2$-treated MXene shows two distinct anodic peaks at 1.03 and 0.82 V vs. Li/Li$^+$ which indicates the removal of Li ions from MXene sheets. The proposed redox reaction can be written like this:

$$Ti_3C_2N_2 + yLi^+ + ye^- \leftrightarrow Li_yTi_3C_2N_2$$

The excellent electrochemical performance of N$_2$/H$_2$ plasma treated MXene samples can be attributed to the increased interlayer spacing (evidenced by downshifting of (0002) XRD peak) and replacing –F functional groups with –N functional groups on MXene surface. Nitrogen doping on graphene has reported to enhance electrochemical performance and proposed mechanisms for performance improvement include the pseudocapacitive behavior of N6 and N5 groups at basal plane edges as well as enhancement of electrical conductivity. To assess the effect of plasma treatment on electrical charge transfer behavior of MXene electrodes, electrical impedance spectroscopy (EIS) analysis was carried out before and after N$_2$/H$_2$ plasma treatment.
The EIS plots for as-prepared and N$_2$/H$_2$-treated MXene are presented in Figure 4.8d. The typical Nyquist plots at OCV can be fitted with Randles circuit, where bulk resistance of battery components (electrolyte, electrodes, and the separator) is indicated by $R_b$, and 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 MXene electrode after N$_2$/H$_2$ plasma treatment is smaller than that of the as-prepared MXene electrode. Lower values of $R_{ct}$ correspond to faster reaction kinetics and the EIS suggests that the presence of –N functional group at the anode/electrolyte interface reduces the overall charge transfer resistance. Based on these results it can be concluded that the presence –N improves the electrical conductivity, which enables faster charge transfer rates which is good for higher power applications.

4.5 Conclusions

We have demonstrated for the first time that plasma modification of MXene surface can have significant impact on their Li ion storage capacity. We have studied the effect of plasma gas composition on structural, morphological and electrochemical behavior of plasma-treated Ti$_3$C$_2$ MXene anodes for Li ion batteries. The N$_2$/H$_2$ plasma process modified the MXenes in various ways, including, increasing interlayer spacing, reducing surface oxidation, and replacing -F functional groups with N. These modifications nearly doubled the Li storage capacity and significantly improved the charge transfer resistance compared to the as-prepared MXene. This is the first report
on replacement of surface functional groups by plasma treatment, and opens up a new way to improve MXene properties by engineering surface functional groups.

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Chapter 5: Effect of Post-Etch Annealing Gas Composition on the Structural and Electrochemical Properties of Ti$_2$CT$_x$ MXene Electrodes for Supercapacitor Applications

5.1 Summary

Two-dimensional Ti$_2$CT$_x$ MXene nanosheets were prepared by the selective etching of Al layer from Ti$_2$AlC MAX phase using HF treatment. The MXene sheets retained the hexagonal symmetry of the parent Ti$_2$AlC MAX phase. Effect of the postetch annealing ambient (Ar, N$_2$, N$_2$/H$_2$, and air) on the structure and electrochemical properties of the MXene nanosheets was investigated in detail. After annealing in air, the MXene sheets exhibited variations in structure, morphology, and electrochemical properties as compared to HF treated MAX phase. In contrast, samples annealed in Ar, N$_2$, and N$_2$/H$_2$ ambient retained their original morphology. However, a significant improvement in the supercapacitor performance is observed upon heat treatment in Ar, N$_2$, and N$_2$/H$_2$ atmospheres. When used in symmetric two-electrode configuration, the MXene sample annealed in N$_2$/H$_2$ atmosphere exhibited the best capacitive performance with specific capacitance value (51 F/g at 1A/g) and high rate performance (86%). This improvement in the electrochemical performance of annealed samples is attributed to highest carbon content, and lowest fluorine content on the surface of the sample upon annealing, while retaining the original two-dimensional layered morphology and providing maximum access of aqueous electrolyte to the electrodes.

5.2 Introduction and Background

The structure and properties of MXenes can be modulated by different chemical treatments, resulting in either surface oxidation or surface modifications.\textsuperscript{1,2} The MXene layers obtained by the selective etching of the MAX phases are usually terminated with either −OH or −F or a combination of both. Hence, they can be represented as M$_{n+1}$X$_n$T$_x$, where T stands for the surface termination. In 2012, on the basis of density functional theory computations, Q. Tang and P. Shen reported that dramatic improvement in the theoretical Li-ion specific capacity
of Ti$_3$C$_2$ MXenes can be achieved by the removal of F groups from the surfaces.\textsuperscript{3} It has also been widely reported that 2D materials like graphene exhibit exceptional sensitivity to their environment. In a recent report, Li et al.\textsuperscript{4} stated that heat treatment is an efficient way to eliminate the surface groups on MXenes and tune their properties. It is of great importance to understand how heating in different ambient influences the morphology, structure, and electrochemical properties of MXenes to modulate the structure and properties of MXenes by proper heat treatment processes for various applications. Herein, we aimed to explored the influence of post-etch annealing ambient on the supercapacitive performance of MXenes. We chose the lightest MXene, Ti$_3$CT, as the representative (as no reports are available on its supercapacitive performance in aqueous electrolytes) and conducted detailed experimental studies on its structural and energy storage properties upon heat treatment in different ambient gases.

5.3 Experimental Procedure

Two-dimensional (2D) titanium carbide nanosheets were synthesized by exfoliation of commercially available Ti$_2$AlC (MAXTHAL 211) powders following similar procedure reported by Naguib et al.\textsuperscript{5} The as-prepared Ti$_2$AlC powders were immersed in 10% HF for 10 h at room temperature. The resulting suspension was washed with deionized water several times and then filtered to get 2D titanium carbide nanosheets (MXenes). The as-prepared MXenes were then annealed at 500 K, in air, Ar, N$_2$, and N$_2$/H$_2$ atmosphere for 2 h.

Phase structures of MXene nanosheets were characterized by a powder X-ray diffraction system (XRD, Bruker, D8 ADVANCE) equipped with Cu K$_\alpha$ radiation ($\lambda = 0.15406$ nm). Raman spectroscopic measurements were carried out at both room temperature and 100 K using a Lab Ram Aramis Raman spectrometer with a He–Ne laser having an excitation wavelength of 633 nm. Chemical compositions of the samples were further analyzed using high-resolution X-ray photoelectron spectroscopy (XPS). XPS studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K$_\alpha$ X-ray source ($hv = 1486.6$ eV) operating at 150 W, a multichannel plate and delay line detector under a vacuum
of 1–10⁻⁹ mbar. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively, and quantified using empirically derived relative sensitivity factors provided by Kratos Analytical. Samples were mounted in floating mode to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the C 1s peak of (C–C, C–H) bond, which was set at 284.8 eV. The data were analyzed with commercially available software, CasaXPS. Brunauer–Emmett–Teller (BET) surface area of the samples was determined using surface area and porosimetry system “Micromeritics” (ASAP 2420) at 77 K. Before measurements, the samples were dried at 70 °C for 10 h in a vacuum oven and then degassed at 150 °C for 12 h until the vacuum was less than 2 μm Hg. The surface morphology and microstructure of the samples were investigated by scanning electron microscopy (SEM, FEI Helios NanoLab) and transmission electron microscopy (TEM, FEI Titan).

Electrochemical measurements were carried out in symmetric two-electrode configurations using Model 660D electrochemical workstation (CH Instruments). Supercapacitor electrodes of 1.13 cm² area were prepared using HF treated MAX phase powder and MXene samples annealed at Ar, N₂, N₂/H₂, and air by the following procedure. The MXene powder was mixed with polytetrafluoroethylene (PTFE) binder and Acetylene Black, which was added to create a conductive network in between the MXene sheets, in a mass ratio of 90:5:5 and dispersed in ethanol. The resulting mixture was homogenized by ultra-sonication and coated onto the conductive carbon cloth (ELAT, Nuvant Systems Inc.) substrate, which was followed by drying at 80 °C for 12 h in a vacuum oven. Each electrode contained ~4 mg of MXene. Two symmetric electrodes, separated by a thin polymer separator (Celgard 3501) in 30 wt % KOH aqueous electrolyte, were sandwiched in a coin cell (CR2032, MTI). Average thickness of active materials in the electrodes was ~28 μm.

The electrochemical properties of the supercapacitor electrodes were studied by cyclic voltammetry (CV), galvanostatic charge–discharge (CD), and electrochemical impedance spectroscopy (EIS). The CV measurements were conducted in a voltage window between 0 and
0.7 V at a wide range of scan rates, ranging from 5 mV/s to 5 V/s. The CD measurements were also carried out in the same voltage window under a wide range of current densities, from 1–40 A/g. The EIS was performed in the frequency range from 100 kHz to 10 mHz at open circuit voltage by applying a 5 mV signal. All these electrochemical measurements were carried out at room temperature. Specific capacitance ($C_{sp}$) of symmetric supercapacitors was calculated from the cyclic voltammograms and CD curves according to given equations:

$$C_{sp} = \frac{2i}{fm}$$

where “$i$” is average cathodic current of CV loop, and “$f$” corresponds to the scan rate.

$$C_{sp} = \frac{2}{m} \times \frac{I}{\Delta V/\Delta t}$$

where “$I$” is the constant current for CD, and $\Delta V/\Delta t$ is the slope of the discharge curve. “$m$” represents the mass of MXene in one electrode.

5.4 Results and Discussion

The XRD patterns of the as-received powder of Ti$_2$AlC MAX phase and the exfoliated titanium carbide MXene obtained after HF treatment are shown in Figure 5.1, panel a(i) and (ii), respectively. The hexagonal Ti$_2$AlC MAX phase powders (JCPDS card no. 00–029–0095) contain small amounts of Ti$_3$AlC$_2$ (JCPDS card no. 52–0875) as a secondary phase. Considerable loss in crystallinity and structural order is observed in the XRD pattern of the sample after HF treatment. The (002) peak in the MAX phase is broadened and shifted to a lower 2θ value after HF treatment, indicating larger d-spacing in the HF treated sample. The (004) peak of Ti$_3$AlC$_2$ (secondary phase) also got shifted to a lower angle after HF treatment. XRD patterns of HF treated samples annealed at 250 °C at different ambients are shown in Figure 5.1, panel a(iii–vi). Samples annealed under Ar, N$_2$, and N$_2$/H$_2$ atmosphere exhibit patterns similar to that of un-annealed HF treated MAX
phase (Figure 5.1a(ii)). All these samples contain a small amount of anatase TiO$_2$, which was produced by the local heat generated during HF treatment of MAX phase. The XRD pattern of the air annealed sample clearly shows the complete conversion of the MXene to anatase TiO$_2$ (JCPDS card no. 00–021–1272) with some graphitic carbon. To identify the influence of the annealing atmosphere on the d spacing of the MXene samples, the shift in the (002) peak position is carefully analyzed by repeating the XRD measurements in a smaller range of 2θ with smaller step size and longer data acquisition time than in Figure 5.1, panel a, and the results are shown in Figure 5.1, panel b. Because of the insertion of hydroxyl or flouride groups, the (002) diffraction peak of HF treated sample appears at 2θ = 11.89° with an interlayer spacing of 7.43 Å. The (002) reflections from samples annealed at Ar, N$_2$, and N$_2$/H$_2$ shift to lower 2θ values of 11.82°, 11.84°, and 11.79°, respectively. The corresponding inter-planar distances are 7.48, 7.47, and 7.50 Å, respectively. This clearly indicates that the interlayer spacing of MXenes increases upon heat treatment in different ambient. The interlayer spacing of N$_2$–H$_2$ is larger than that of Ar or N$_2$ annealed samples, suggesting removal of more functional groups from the sample. Analysis of these broad peaks indicates the poor order and multilayer character of MXene sheets. Figure 5.1c shows the Raman spectra of the HF treated MAX phase (Ti$_2$CT$_x$-HF) sample before and after annealing under different gas ambients. Air annealed sample shows a major peak centered at 150 cm$^{-1}$ corresponding to anataseTiO$_2$, the intensity of which has been significantly reduced in all the other samples. They exhibit three broad Raman peaks centered nearly around 250, 410, and 610 cm$^{-1}$, which can be attributed to the vibrations from nonstoichiometric titanium carbide.$^6$ Further insight into intramolecular interactions in the materials can be obtained from Raman spectroscopy measurements conducted under low temperature. Figure 5.1, panel d shows the low-temperature
Raman spectra of HF treated sample and that of MXene samples annealed under Ar, N₂, and N₂/H₂ atmospheres. As compared to the HF treated sample, the band centered around 610 cm⁻¹ shifts to higher energy for all annealed samples. It has been reported that for layered materials, as the layer thickness decreases, the band position shifts to higher energy representing a slight hardening of the bonds as the layer thickness decreases. Henceforth, the low-temperature Raman spectra indicate a slight thinning of layers in the annealed samples, leading to larger interplanar distance.

Figure 5.1: (a) XRD pattern of MAX phase and different MXene samples; (b) XRD pattern of HF treated MAX phase and Ar, N₂, and N₂/H₂ annealed MXene samples over a small range of 2θ from 10.5–13.5°. Raman spectra of MAX phase and different MXene samples measured at (c) room temperature and (d) at low temperature (100 K).

XPS investigations were performed to characterize the chemical composition of the surface of the powdered samples and to determine the oxidation state of titanium. Survey spectrum for the powdered sample (Ti₂CTₓ_HF) shows that Ti, F, O, and C elements are detected (Figure 5.2). Figure 5.2, panels b and c, respectively, show the survey spectrum of air annealed and N₂/H₂ annealed MXene samples. The same elements have been detected with different concentrations for all the powdered samples.
Figure 5.2: XPS survey spectra of (a) HF treated MAX Phase, (b) MXene sample annealed in air, and (b) MXene sample annealed in N\text sub{2}/H\text sub{2} atmosphere.

The results of atomic concentrations of Ti, F, O, and C elements, calculated from XPS, on the surface of the powdered samples indicate that the sample annealed in N\text sub{2}/H\text sub{2} atmosphere has the highest carbon concentration and lowest fluorine concentration. High-resolution XPS spectra of Ti 2p and C 1s core levels of HF treated sample, and air and N\text sub{2}/H\text sub{2} annealed samples are shown in Figure 5.3, panels a, b, and c, respectively. The Ti 2p core level is fitted with four doublets (Ti 2p\text sub{3/2} – Ti 2p\text sub{1/2}) with a fixed area ratio equal to 2:1 and doublet separation of 5.7 eV. The Ti 2p\text sub{3/2} components were located at 454.5, 455.9, 457.4, and 458.8 eV, respectively. The dominant Ti 2p\text sub{3/2} component centered at 458.8 eV is associated with Ti ions with a formal valence 4+, while the peak at lower binding energy 457.4 eV is associated with Ti ions with reduced charge state (Ti\text sub{x}O\text sub{y}). The Ti 2p\text sub{3/2} component centered at 454.5 eV corresponds to Ti–C bond.\textsuperscript{8-10} This component is absent in the case of air annealed sample. The Ti 2p\text sub{3/2} component centered at 455.9 eV can be assigned to Ti–X peak (a combination of a substoichiometric TiC\textsubscript{x} (x < 1) and to titanium oxy carbides TiC\textsubscript{x}O\textsubscript{y}).\textsuperscript{8} The C 1s core level of HF treated sample and N\textsubscript{2}/H\textsubscript{2} annealed samples (Figure 5.3d,f) are fitted using six components located at 281.2, 282.1, 284.8, 286.4, 287.9, and 288.9 eV corresponding to C–Ti,\textsuperscript{8,11} C–Ti–O, C–C/C–H, C–O, C═O,\textsuperscript{12-13} and (O–C═O and C–F) bonds,\textsuperscript{13-14} respectively. The components corresponding to C–Ti and C–Ti–O were absent in the high-resolution C 1s spectra of the air annealed sample (Figure 5.3e).
High-resolution Ti 2p and C 1s spectra of all the other samples are similar to HF treated sample, with a difference in concentration for different components. XPS studies confirm that upon heat treatment in air, MXene sample gets converted into carbon and TiO$_2$, and samples annealed under Ar, N$_2$, and N$_2$/H$_2$ atmosphere retain the initial chemical structure.

The nitrogen adsorption and desorption isotherms of the as-received Ti$_2$AlC MAX phase powder, exfoliated Ti$_2$CT$_x$ MXene obtained after HF treatment, and MXene samples annealed at different ambients are shown in Figure 5.4, panel a. The BET surface area values calculated for MAX phase and HF treated samples are, respectively, 2.24 and 21.05 m$^2$/g. The tremendous increase in the surface area of the HF treated sample indicates the successful exfoliation upon the selective etching. The respective BET surface area values of MXene samples annealed at 500 °C in Ar, N$_2$, N$_2$/H$_2$, and air are 21.17, 22.44, 23.89, and 27.45 m$^2$/g. All the annealed samples exhibit distinct hysteresis loops in the range of 0.45–1.0 $P/P_0$, which suggests the presence of a mesoporous structure. BET surface area values obtained for the MXene samples in the present study agree well with the available literature.\textsuperscript{15}
Figure 5.3: High-resolution Ti 2p spectra of (a) HF treated MAX phase, (b) air annealed MXene, and (c) N$_2$/H$_2$ annealed MXene; high-resolution C 1s spectra of (d) HF treated MAX phase, (e) air annealed MXene, and (f) N$_2$/H$_2$ annealed MXene.

MXene samples annealed in Ar, N$_2$, and N$_2$/H$_2$ atmosphere exhibit higher surface areas as compared to the HF treated sample, which may be due to the increase in the interplanar distance upon annealing. The pore size distributions of the samples calculated by desorption isotherms using Barret–Joyner–Halenda (BJH) method are shown in Figure 5.4, panel b. BJH desorption cumulative volumes of pores between
1.70–300.00 nm diameter for the MAX phase, HF treated sample, and the MXene samples annealed at Ar, N₂, N₂/H₂, and air ambients are 0.0136, 0.0474, 0.0511, 0.0547, 0.0634, and 0.0930 cm³/g, respectively.

Figure 5.4: (a) Nitrogen adsorption and desorption isotherms and (b) pore size distributions of different MXene samples.

SEM images of HF treated MAX phase and MXene samples annealed in N₂/H₂ and air are shown in Figure 5.5, panels a, b, and c, respectively. It is evident from that the HF treatment results in the removal of the Al layer from the Ti₂AlC MAX phase, resulting in stacked MXene sheets resembling exfoliated graphite. Some blisters are observed on the edges and surfaces of the exfoliated nanosheets, which may be due to the bubbles liberated due to the release of H₂ gas during the HF treatment of the MAX phase. There is no visible change in the morphology of MXene samples after heat treatment in Ar, N₂, or N₂/H₂ atmosphere. However, the sample annealed in air (Figure 5.5c) undergoes a complete change in its morphology, and it consists of nanosheets composed of numerous TiO₂ nanocrystals on thin graphitic nanosheets similar to the ones reported by Naguib et al.²
Figure 5.5: SEM images of (a) HF treated MAX phase and MXene samples annealed in (b) N₂/H₂ atmosphere and (c) air.

TEM and HRTEM analyses were used to investigate the microstructure of MXene nanosheets in detail. TEM images of HF treated MAX phase nanosheets and those of MXenes annealed in Ar, N₂, and N₂/H₂ atmosphere are shown in Figure 5.6, panels a, b, c, and d, respectively. Stacked multilayer nature of MXene sheets is evident from Figure 5.6, panels a and b. The individual MXene sheets are found to be extremely thin and transparent. These sheets have many nanometer-sized holes similar to those reported for functionalized graphene.

HRTEM images of etched MXene nanosheets in N₂/H₂ annealed MXene sample are shown in Figure 5.7, panels a and b. The lattice resolved HRTEM image of a single exfoliated MXene sheet with the corresponding FFT pattern is shown in Figure 5.7, panel c. Selected area diffraction (SAED) pattern (Figure 5.7d) of the MXene sheets demonstrates that the MXene sheets retain the hexagonal symmetry and crystallinity of the basal planes of the parent Ti₂AlC MAX phase. There is one reflection peak corresponding to TiO₂, which was produced by the local heat developed at the time of etching of the MAX phase.
Figure 5.6: TEM images of (a) HF treated MAX phase and MXene samples annealed in (b) Ar, (c) N\textsubscript{2}, and (d) N\textsubscript{2}/H\textsubscript{2} atmosphere.

Energy-dispersive spectrometer (EDS) elemental mapping was employed to study the spatial distribution of the elements Ti, C, and O in MXene samples. Figure 5.8 shows the results obtained for HF treated MAX phase and N\textsubscript{2}/H\textsubscript{2} annealed MXene samples, respectively. The elemental mapping of O showing the spatial distribution of oxygen in nanosheet and N\textsubscript{2}/H\textsubscript{2} annealed sample indicates that oxygen is present mainly at the edges of the MXene sheet.
Figure 5.7: (a,b) HRTEM images of etched MXene flakes; (c) lattice resolved HRTEM image (inset shows corresponding FFT pattern); and (d) SAED patterns of MXene sample annealed in N$_2$/H$_2$ atmosphere.

MXene sample annealed in air undergoes a complete transformation in its microstructure and morphology, as evident from the TEM and HRTEM images shown in Figure 5.9. TEM image shown in Figure 5.9a, indicates that the sample contains nanocrystals and thin nanosheets. HRTEM image of the nanocrystals and their corresponding SAED pattern are shown in Figure 5.9 c and e, respectively. The SAED pattern indicates the polycrystalline structure of the sample. SAED pattern can be indexed to the body-centered tetragonal anatase TiO$_2$ crystal structure using circular Hough diffraction analysis.$^{17}$ SAED pattern (Figure 5.9f) corresponding to the TEM
images of the nano-flakes (Figure 5.9d) can be indexed to graphitic carbon. The TEM results agree well with the XRD and Raman spectroscopy results.

Figure 5.8: Elemental mapping of (a) HF treated MAX Phase and (b) MXene sample annealed in N$_2$/H$_2$ atmosphere.

Figure 5.9: (a–d) TEM images of MXene sample annealed in air (panels b and c show nanocrystalline TiO$_2$ particles, and panel d shows graphitic carbon); SAED pattern of (e) nanocrystalline TiO$_2$ and (f) graphitic carbon.
Symmetric button cell supercapacitors were fabricated using electrodes based on HF treated MAX phase and MXene samples annealed under Ar, N$_2$, N$_2$/H$_2$, and air atmosphere, and the electrochemical measurements were conducted to investigate the possible influence of the annealing ambient on the electrochemical performance. Figure 5.10, panels a–e, respectively, show CV loops obtained for symmetric button cell supercapacitors based on HF treated MAX phase and MXene samples annealed under Ar, N$_2$, N$_2$/H$_2$, and air atmosphere at different scan rates of 5, 10, 20, 50, and 100 mV/s in a fixed potential range of 0–0.7 V. All the test cells except the one based on air annealed sample retain nearly rectangular CV loops, up to a scan rate of 100 mV/s, which are characteristics for supercapacitors with excellent capacitance behavior and low contact resistance. The deviation from supercapacitive behavior of the supercapacitor based on air annealed sample (Figure 5.10) as compared to other samples can be attributed to the pseudocapacitive behavior of the nanocrystalline TiO$_2$ particles.

A comparison of CV loops of symmetric supercapacitors based on HF treated MAX phase and MXene samples annealed under Ar, N$_2$, N$_2$/H$_2$, and air atmosphere at a scan rate of 20 mV/s is shown in Figure 5.11a. For the same mass loading, the CV curves show different areas indicating different levels of stored charge. The CV loops specific capacitances of 4.2, 28.1, 39.7, 47.4, and 2.4 F/g, respectively, are obtained for the HF treated MAX phase and MXene samples annealed at Ar, N$_2$, N$_2$/H$_2$, and air atmosphere. Figure 5.11b shows the comparison of galvanostatic CD curves for the samples at a constant current density of 1 A/g. The constant current CD curves of all the devices are nearly triangular, with reduced internal resistance at the beginning of the discharge curve. The reduction in internal resistance may be attributable to the excellent contact of the active materials to the conducting carbon cloth substrate.
Supercapacitor based on exfoliated (HF treated) MAX phase exhibited a small specific capacitance value of 4.9 F/g.

Figure 5.10: Cyclic voltammograms of symmetric supercapacitors based on (a) HF treated MAX phase and MXene samples annealed in (b) Ar, (c) N₂, (d) N₂/H₂, and (e) air atmosphere at different scan rates.
A tremendous improvement in the supercapacitive performance is obtained by annealing in Ar, N\textsubscript{2}, and N\textsubscript{2}/H\textsubscript{2} atmosphere. The specific capacitance values for the supercapacitors based on samples annealed under Ar, N\textsubscript{2}, and N\textsubscript{2}/H\textsubscript{2} ambients are, respectively, 36.9, 42.8, and 50.5 F/g. Variations in specific capacitances of symmetric supercapacitors with increase in scan rate and current density are shown in Figure 5.11 c and d, respectively. At lower scan rates (below 20 mV/s)/current densities (below 5 A/g), the specific capacitance decreases with the increase in scan rate/current density, and after that the specific capacitance tends to stabilize. At lower scan rate/discharge current density, electrolyte ions can penetrate into the inner structure of the entire electrode giving rise to the maximum capacitive performance. For 2D materials like MXene, it has been reported that the spontaneous intercalation of cation from the aqueous electrolyte solutions makes an important contribution to the total specific capacitance.

The intercalation phenomena readily takes place in basic electrolytes like KOH, used in the present study.\textsuperscript{18} Among the different supercapacitors, symmetric supercapacitor based on MXene sample annealed under N\textsubscript{2}/H\textsubscript{2} atmosphere exhibited the best supercapacitive performance with a maximum specific capacitance of 51 F/g at a scan rate of 5 mV/s. The rate performance calculated at a very high current density of 40 A/g for the different supercapacitor devices based on for the HF treated MAX phase and MXene samples annealed under Ar, N\textsubscript{2}, N\textsubscript{2}/H\textsubscript{2}, and air atmosphere are 64\%, 69\%, 80\%, 86\% and 35\%. Air annealed MXene sample, which underwent complete structural and morphological transformation, exhibited the poorest supercapacitive performance. Figure 5.11 e presents the Ragone plot (power density vs energy density) of the different symmetric supercapacitors test cells. The energy (\textit{E}) and power
densities \((P)\) for the supercapacitors were calculated from CD curves at different current densities using following equations:

\[
E = \frac{1}{2} C_{sp} \Delta V^2 \quad \text{and} \quad P = E/\Delta t
\]

At a constant power density of 20 kW/kg, the energy densities obtained for supercapacitors based on HF treated sample and MXene samples annealed at Ar, N\(_2\), N\(_2\)/H\(_2\), and air atmosphere are 0.211, 1.811, 2.375, 2.988, and 0.089 Wh/kg, respectively. At a low power density of 0.7 kW/kg, the energy densities reach as high as 0.335, 2.511, 2.913, 3.437, and 0.209 Wh/kg, respectively, for the test cells. From the analysis of Ragone plot, it is evident that MXene sample annealed under N\(_2\)/H\(_2\) atmosphere works as a very promising electrochemical double-layer capacitor (EDLC) electrode material. In comparison with all other MXene samples, N\(_2\)/H\(_2\) annealed sample maintains high power density without much reduction in energy density. Cyclic stability curves for symmetric supercapacitors at a constant current density of 1 A/g are illustrated in Figure 5.11f. At the end of 6000 cycles, supercapacitors based on HF treated MAX phase and MXene samples annealed under Ar, N\(_2\), N\(_2\)/H\(_2\), and air atmosphere retain, respectively, 87%, 94%, 92%, 93%, and 86% of their maximum capacitance.
Figure 5.11: (a) Comparison of cyclic voltammograms of MXene samples at a scan rate of 20 mV/s. (b) Comparison of galvanostatic CD curves of MXene samples at a constant current density of 1 A/g. Specific capacitances of MXene samples at different (c) scan rates and (d) current densities. (e) Ragone plot (power density vs energy density) of MXene based symmetric supercapacitors. The energy densities and power densities were derived from the CD curves at different current densities. (f) Cycling performance of supercapacitors based on different MXene samples at a constant current density of 10 A/g (6000 CD cycles).
Figure 5.12, panel a shows the experimental EIS spectra (Nyquist plot) for symmetric supercapacitors based on HF treated sample and MXene samples annealed under Ar, N\(_2\), N\(_2\)/H\(_2\), and air atmosphere. The impedance spectra can be divided into two regions by the so-called knee frequency, with a semicircle arc in the high-frequency region and a straight line in the low-frequency region. The real axis intercept at high-frequency corresponds to the uncompensated resistance of the bulk electrolyte solution (\(R_s\)), and it is also known as the equivalent series resistance (ESR). The magnitude of ESR obtained from the x-intercept of the Nyquist plot for supercapacitors based on HF treated MAX phase and MXene samples annealed under Ar, N\(_2\), N\(_2\)/H\(_2\), and air atmosphere are 1.23, 1.01, 1.08, 1.03, and 1.10 Ω, respectively. These lower values indicate consistent interfacial contact between the active materials and the carbon substrates. The diameter of the semicircle in the high frequency range gives the value of charge transfer resistance (\(R_{ct}\)). \(R_{ct}\) is a surface property of the porous electrode, which is related to the electroactive surface area. It is a combination of electrolyte accessible area and electrical conductivity of the electrode material. The larger the electroactive surface area, the lower the charge transfer resistance. The line in the low-frequency region making an angle 45° with the real axis is the Warburg line, which is a result of the frequency dependence of ion diffusion in the electrolyte to the electrode interface. Figure 5.12b presents the frequency response of specific capacitance obtained from EIS measurements of supercapacitors based on HF treated MAX phase and MXene samples annealed at Ar, N\(_2\), N\(_2\)/H\(_2\), and air atmosphere. The instrument’s (CHI 660D) limitations in the EIS measurements result in the steps on the frequency plots. The capacitance values were obtained from given equation:

\[ C = -1/2\pi fZ'' \]
Here, $C$ is the cell capacitance, $f$ is the frequency, and $Z''$ is the imaginary part of impedance. When the frequency increases, the capacitance of all samples decreases. At a frequency of 1 Hz, the capacitors retain nearly half of its maximum capacitance (@ 0.01 Hz). At high frequency region above 1000 Hz, the supercapacitors behave like a pure resistance.

![Figure 5.12: (a) Nyquist plots and (b) specific capacitance variation as a function of frequency for supercapacitors based on MXene samples.](image)

From the present study, it is evident that the annealing ambient plays a crucial role in tuning the structure, morphology, and capacitive performance of 2D Ti$_2$CT$_x$ MXene nanosheets. Annealing in air transforms MXenes to TiO$_2$ nanoparticles and graphitic carbon and brings down the capacitive performance. The maximum carbon content ensures high conductivity of the electrode and improves the supercapacitor performance. Moreover, the reduction in the concentration of fluoride ion brings improvement in the specific capacitance.

### 5.5 Conclusions

In summary, we have demonstrated that post-etch annealing ambient of 2D Ti$_2$CT$_x$ MXenes plays a significant role in tuning their structure, surface termination, and electrochemical properties. Annealing in air results in transformation of MXene to TiO$_2$ nanoparticles and graphitic carbon. The MXene sample annealed in
$N_2/H_2$ atmosphere exhibited best performance with specific capacitance values of 51 F/g at 1A/g, high rate performance (86%) (Current densities ranging from 1–40 A/g), and excellent cycling stability (93% after 6000 CD cycles) when used in symmetric two-electrode configuration. This improvement in the performance was attributed to highest carbon content and lowest fluorine content on the surface of the sample upon annealing, while retaining the original 2D layered morphology, and providing maximum access of aqueous electrolyte to the electrodes.

REFERENCES


6. Chapter 6: Conclusions and Perspective

Herein, I summarize the main conclusions of my dissertation and provide my perspective on future research directions.

As predicted by theoretical studies and confirmed by experimental work, the properties of MXene are highly dependent on surface chemistry. Therefore, aiming to exploit the presence of surface functional groups (as discussed in Chapter 2 and Chapter 3 of this thesis) or varying surface chemistry by post-etch thermal, chemical or physical process (Chapter 4 and 5) are two main research directions that we carried out in this work.

The room-temperature oxidation of Ti$_2$C MXene by hydrogen peroxide (H$_2$O$_2$) provides an efficient route for preparation of in-situ oxide on MXene surface. The prepared TiO$_2$/MXene nano-composite showed significantly improved electrochemical performance in Li ion batteries. The enhanced electrochemical performance can be ascribed to larger surface area accessible to Li ions, which comes from the opening/swelling of MXene layers due to the H$_2$O$_2$ treatment and titania formation. Furthermore, the high rate performance and excellent cycle life make partially oxidized MXene a viable candidate for Li ion capacitors.

The ex-situ oxide formation on MXene surface has two fundamental problems; distortion of MXene during processing and an uneven or partial coverage. We have overcome this problem by exploiting the presence of surface functional groups and utilizing atomic layer deposition. The oxide selected for this study was SnO$_2$ due to its high capacity in Li ion batteries and poor stability. Three different deposition methods; hydrothermal processing, sputtering and atomic layer deposition has been compared. The ALD of SnO$_2$ requires a surface with –O ligands and we exploited the presence of
--O and –OH functional groups coming from solution process to deposit ALD SnO₂ without ozone purge, thus avoiding MXene’s distortion. We have demonstrated that MXene-supported SnO₂ anodes deposited by ALD can be stabilized during cycling of Li-ion batteries. The SnO₂/MXene electrode composite design provides a high capacity thanks to conversion reaction of SnO₂, while MXene sheets provide a conductive network that accommodates the large volume changes that occur in SnO₂ during the battery charge/discharge process. The SnO₂/MXene electrode performance can be further improved by depositing a very thin HfO₂ passivation layer on top of SnO₂, in the same ALD reactor. The HfO₂ layer, though inactive, slows down the reaction of SnO₂ with the electrolyte, and preserves the SnO₂ crystalline structure during cycling. The HfO₂ coated SnO₂/MXene anodes exhibit a stable specific capacity of 843 mAh/g.

The second approach adopted to alter the surface chemistry of MXene was post-etch processing via thermal or physical methods. We have studied the effect of annealing MXene in various ambients and carried out detailed surface spectroscopy to resolve the concentration of surface functional groups. We demonstrate that post-etch annealing plays significant role in tuning MXene structure, surface chemistry and electrochemical performance. Air annealing results in oxidation of MXene to TiO₂ and graphitic carbon, whereas annealing in controlled atmosphere retained the morphology and crystal structure of MXene. The electrochemical performance of annealed MXene was studied as electrode material in supercapacitors. We have also employed a physical process to remove surface functional groups from MXene. The plasma modification of MXene surface can have significant impact on their Li ion storage capacity. We have studied the effect of plasma gas composition on structural, morphological and electrochemical behavior of plasma-treated Ti₃C₂ MXene anodes for Li ion batteries. The N₂/H₂ plasma process modified the MXenes in various ways, including, increasing
interlayer spacing, reducing surface oxidation, and replacing -F functional groups with N. These modifications nearly doubled the Li storage capacity and significantly improved the charge transfer resistance compared to the as-prepared MXene. This is the first report on replacement of surface functional groups by plasma treatment, and opens up a new way to improve MXene properties by engineering surface functional groups.

In general, we demonstrate that the fine tuning of MXene’s surface chemistry should be carried out for enhanced electrochemical performance. However, we have observed couple of fundamental issues hindering MXene’s application in practical battery systems. In most of the conducted electrochemical studies, the CV and charge/discharge curves showed that the MXene electrode exhibit substantial first cycle capacity drop, corresponding to a poor 1st cycle columbic efficiency. This phenomenon can be mainly attributed to the formation of undesirable SEI layer formation by consumption of Li-ions and, from practical viewpoint, it should be avoided to because unlike half-cells configuration, we have limited amount of Li-ions in Li-containing cathode. Though, the formation of a thin layer of SEI is essential for safety and long-term performance of Li-ion batteries, a thicker SEI layer along with high capacity drop in 1st cycle consumes major portion of Li-ions.

The second major issue with MXene electrode in Li-ion batteries is the absence of a specific voltage plateau in charge/discharge curves. Unlike, graphite and silicon, where Li+ are intercalated/deintercalated at a specific voltage (0.1 vs. Li/Li+ in case of carbon), the MXene exhibits a sloping voltage vs. specific capacity curves. This indicates the insertion of Li+ ions over the whole voltage range for Li-ion batteries. This type of charge storage mechanism is desirable in hybrid ion capacitors but should be avoided in Li-ion batteries. Recently, we have found out that variation in etching
chemistry can result in appearance of voltage plateau in CV and charge/discharge curves. Further research in this direction should be carried out to understand the role of surface chemistry and surface functional groups on charge storage mechanism of MXene electrode.

In view of these results, future research directions should focus on developing MXene with desired surface chemistries during the etching process or changing surface chemistry via post-etch processing. In addition, the role of specific surface functional groups in electrochemical charge storage mechanism should be explained by using in-situ and ex-situ characterization. If MXene’s are to be used in Li-ion batteries, the first cycle columbic efficiency should be improved by either improving MXene’s surface chemistry or modifying anode/electrolyte interface. The interface modification can be carried out by creating an artificial SEI layer on MXene electrode, which does not hinder the Li$^+$ ion diffusion and stop the undesirable reactions.
List of Publications

1. B. Ahmed, D. H. Anjum, M. N. Hedhili, and H. N. Alshareef, \( \text{H}_2\text{O}_2 \) assisted room temperature oxidation of \( \text{Ti}_2\text{C} \) MXene for Li-ion battery anodes, *Nanoscale*, 2016, 8, 7580-7587


toward High Rate Durable Li Ion Battery Anodes, *ACS Applied Materials and Interfaces*, 2015, 7 (24), pp 13154–13163