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Complete List of Authors:	Zhang, Jizhen; Deakin University, IFM Kong, Na; Deakin University Hegh, Dylan; Deakin University Usman, Ken; Deakin University Guan, Guangwu; Deakin University Qin, Si (Alex); Deakin University Jurewicz, Izabela; University of Surrey, Physics Yang, Wenrong; Deakin University Faculty of Science Engineering and Built Environment, School of Life and Environmental Sciences Razal, Joselito; Deakin University, Institute for Frontier Materials

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Freezing Titanium Carbide (MXenes) Aqueous Dispersions for Ultra-long-term Storage

Jizhen Zhang,^{†,||} Na Kong,^{‡,||} Dylan Hegh,[†] Ken Aldren S. Usman,[†] Guangwu Guan,[†] Si Qin,[†]
Izabela Jurewicz,[§] Wenrong Yang,[‡] Joselito M. Razal^{†,*}

[†]Institute for Frontier Materials, Deakin University, Geelong, VIC 3216, Australia.

[‡]School of Life and Environmental Sciences, Deakin University, Geelong, VIC 3216, Australia

[§]Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom.

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ABSTRACT

Two-dimensional titanium carbide ($\text{Ti}_3\text{C}_2\text{T}_x$), or MXene, is a new nanomaterial that has attracted increasing interest due to its metallic conductivity, good solution processability, and excellent energy storage performance. However, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes suffer from degradation through oxidation due to prolonged exposure to oxygenated water. Preventing the occurrence of oxidation i.e. the formation of TiO_2 particles, was found to be the crucial to maintain MXene quality. In present work, we found that freezing aqueous MXene dispersions at low-temperature can

effectively prevents the formation of TiO_2 nanoparticles at the flake edge, which is known as the early stage of oxidation. The $\text{Ti}_3\text{C}_2\text{T}_x$ flakes in frozen dispersion remains consistent in morphology and elemental composition for over 650 days, compared with freshly synthesized MXene; which in contrast, exhibits flake edge degradation within two days when stored at room temperature. This result suggests that freezing MXene dispersion dramatically postpones the oxidation of MXene flakes and the stored MXene dispersion can be treated as freshly prepared MXene. This work not only fundamentally fulfilled the study on temperature dependence of MXene oxidation, but has also demonstrated a simple method to extend the shelf life of MXene aqueous dispersion to years, which will be a cornerstone for large scale production of MXene and ultimately benefit the research on MXenes.

1. INTRODUCTION

MXenes are a new class of 2D nanomaterials that have emerged from a large family of transition metal carbides, nitrides and carbonitrides denoted by the general formula $\text{M}_{n+1}\text{X}_n\text{T}_x$ ($n = 1-4$), where M is an early transition metal group, X is carbon and/or nitrogen, and T_x is surface terminal groups ($-\text{OH}$, $-\text{O}-$, and/or $-\text{F}$).¹⁻² MXenes combine 2D conductive carbide layers with a hydrophilic, primarily hydroxyl-terminated surface.³⁻⁷ To date, close to 30 MXenes have been successfully synthesized including $\text{Ti}_3\text{C}_2\text{T}_x$, Ti_2CT_x , and $\text{Nb}_4\text{C}_3\text{T}_x$.⁸⁻⁹ Of the various MXenes, $\text{Ti}_3\text{C}_2\text{T}_x$ is of particular interest, exhibiting the highest capacitance ($\sim 1500 \text{ F cm}^{-3}$) in supercapacitors¹⁰ and possessing excellent high metallic conductivity ($\sim 15000 \text{ S cm}^{-1}$).¹¹

Despite the promise of MXenes, one notorious limitation to their widespread implementation is the poor oxidation resistance of MXene flakes in aerated aqueous media, leading to rapid degradation into titanium dioxide (TiO_2).^{5-6, 12-13} By summarizing previous studies, as shown in

Figure 1a, the MXene oxidation process can be divided into three stages: firstly (I) the formation of TiO_2 at the MXene flake edge;^{12, 14-15} followed by (II) expansion of the TiO_2 particles from the edge of MXene flake to surface whilst the carbon layer is retained;¹⁶⁻¹⁷ and finally (III) the carbon layers are etched by hydroxyl radicals generated by the surrounding TiO_2 and the MXene flakes is fully converted to amorphous TiO_2 .^{12, 18} As a consequence of the oxidation of MXenes, both the electrical conductivity and passivation of the reactive interface are impaired, decreasing the energy storage performance. Thus, maintaining the intact of MXene flakes is a critical demand for the application that requires aqueous solutions of MXene, such as filtration films,¹⁹ wet-spinning fibers,²⁰ hydrogel/aerogel preparation,²¹⁻²² and aqueous-based supercapacitors.²³

Investigations into the preservation of MXene flakes have demonstrated that the oxidation rate was influenced by the surrounding media,^{13, 24} and it can be slowed down by using organic solvents,^{18, 24} air-free water,¹² antioxidant,²⁵ or polymer media.¹³ For example, both Seyedin et al.¹⁸ and Maleski et al.²⁴ have reported that using organic solvents, such as dimethyl sulfoxide, ethanol, and N-methyl-pyrrolidone, to replacing water can extend the shelf time of $\text{Ti}_3\text{C}_2\text{T}_x$ to over 30 days. Green et al.²⁵ found that adding sodium L-ascorbate enables $\text{Ti}_3\text{C}_2\text{T}_x$ flakes to retain their colloidal stability in water for 21 days. These approaches, however, only reported on short-term (~30 days) storage of MXenes; additionally, retention of organic solvents and additives in MXene films or fibers leads to a gradual decrease in electrical conductivity with time.²⁶⁻²⁸ Moreover, repeated centrifugation to transfer across MXene sheets into organic solvents, is laborious and a batch process that takes several hours to complete. This process inevitably increases the exposure time of MXene to water and air allowing edge oxidation to occur. Traditionally, the most efficient approach for long-term storage of MXene has been regarded as a powder or film under vacuum as since it is isolated from water and air. However, film and powder requires the assistance of

intercalating agents and sonication for re-dispersion in water, which both decreases the flake size and significantly lowers the yield of single-layer MXene.²⁹ Therefore, long-term (years) storage of MXenes as an aqueous dispersion without any additives while preventing the oxidation is regarded as ideal; however, this has proven challenging.^{13, 30}

Figure 1. (a) Schematically illustration of the oxidation process of single $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes in dispersion. Photos of the aqueous MXene dispersion (0.5 mg mL^{-1}) (b) stored at room temperature (RT, $\sim 25^\circ\text{C}$) over 30 days, (c) incubated in an oven at 90°C for 0, 6 and 12 hours, and (d) stored at -20°C for 250 and 650 days. (e) Color fading of MXene dispersions stored at different temperatures as a function of storing time, in which the data point was obtained by digital analysis of the photograph of MXene dispersions using Image J. The background is a dark green step-wedge linearly changed from R:G:B = 4:4:4 (bottom) to R:G:B = 247:247:247 (top), which

works as the y-axis. The error bar is derived from the variation of colors at different positions of the dispersion in the photographs.

Low-temperature preservation is a common strategy to prevent the degradation of biological materials and is widely used in food preservation, biochemical research and medical surgery.³¹⁻³⁴ Recently, Chae et al. demonstrated that the oxidation of MXene can be significantly delayed by storing at -80°C, with the stored MXene showing similar gas response behavior compared with pristine MXene.³⁵ However, for wider applicability, a simple and readily available method are still required. Herein, we found that decreasing the storage temperature of aqueous MXene dispersions to -20 °C can successfully prolong its shelf-life from tens of days to nearly two years. This temperature can be readily achieved by commonly used freezers in most lab environments. Detailed characterization of the frozen MXene dispersion shows that frozen flakes have intact clean flake edges and high electrical properties compared with the freshly made dispersion. Moreover, it is observed that TiO₂ nanoparticles formed at the edge of MXene flakes hinder the close stacking of flakes, which is also responsible for the decrease in conductivity and mechanical properties of MXene films. These findings provide a simple method for storing Ti₃C₂T_x, which may also apply to other MXenes, and it potentially benefits future large-scale synthesis and further MXene studies.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Ti₃C₂T_x dispersions. Ti₃C₂T_x was synthesized by a wet-etching process using an etching solution, containing 0.8 g lithium fluoride (LiF, 99 %, Sigma-Aldrich Pty Ltd) and 10 ml of 9 M hydrochloric acid (HCl). Then, 0.5 g of Ti₃AlC₂ powder (MAX phase, <40 µm particle size, Carbon-Ukraine) was slowly added to the etchant and the reaction incubated at room

temperature for 24h. The acidic dispersion was washed with deionized (DI) water through several rounds of centrifugation at 3500 rpm until the pH of the suspension was close to 6, using a Centrifuge-5810R (Eppendorf AG, Germany), with decantation of the supernatant after each cycle. The single-layer delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ was collected in the supernatant from multilayer MXene and unreacted MAX phase by further centrifugation at 1500 rpm for 30 min. The as-synthesized dark green supernatant containing single layer $\text{Ti}_3\text{C}_2\text{T}_x$ flakes was labeled as “Fresh MXene”.

2.2. Oxidation study on MXene dispersions. The MXene dispersion (0.5 mg mL^{-1}) was sealed into 4 mL vials with 3 mL of dispersion and 1 mL of air. The vials were then stored at 90°C , room temperature (RT, 25°C), 4°C and -20°C . For the samples stored at -20°C , the vials that contain $\text{Ti}_3\text{C}_2\text{T}_x$ dispersions were wrapped with aluminum foil and placed directly in a conventional freezer without liquid nitrogen treatment. The dispersion stored at RT for two days was labeled as “RT-2” and the frozen sample at -20°C for 650 days was defined as “Frozen-650”, in which the number represents the days of storage. The -20°C sample was thawed to room temperature by placing it on a bench for 2 h. After equilibration to room temperature, the dispersion was used for further characterization.

2.3. Characterization. Field emission scanning electron microscope (FESEM) (Zeiss SUPRA 55-VP) was conducted to study the fiber morphology and the cross-section of the LC MXene fibers. Transmission electron microscopy (TEM) characterization was employed on a JEM-2100 to study exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ layer. The X-ray diffraction (XRD) patterns of the fibers were obtained with a powder diffractometer (Rigaku SmartLab, Tokyo, Japan) using $\text{Cu K}\alpha$ radiation (40 kV, 30 mA) with an X-ray wavelength of (λ) $1.54 \text{ \AA}$ at a 2θ scan step of 0.02° from $3-70^\circ$ with a scan time of 14 seconds/step. Dynamic light scattering (DLS) was performed by Zetasizer Nano ZS, Malvern Instruments to measure the size distribution of MXene flakes. DLS measurements were repeated

for five measurements from each sample. The electrical conductivity of the MXene films was measured using a four-point probe set-up (Ossila Ltd.) with uniform 1 mm probe spacing. The mechanical properties of MXene films were measured using a universal tensile testing system (Instron 30 kN Tensile Tester) with a 5 N load cell. Film samples were fixed between the grips with the gap length of 5 mm and stress and strain data were recorded at an extension rate of 0.5 mm min⁻¹.

2.4. Electrochemical test of MXene electrodes. Electrochemistry tests were performed using a three-electrode configuration with carbon rod and Ag/AgCl (3.5 M KCl) electrode as counter and reference electrodes, respectively. H₂SO₄ (1 M) solution was used as electrolyte. The working electrode was prepared by drop-casting 3 µL of Ti₃C₂T_x dispersion on a glassy carbon electrode (diameter of 3 mm). The electrode was then coated with Nafion® 117 solution (~5 wt.%, ~2 µL) to prevent the thin MXene film from peeling off. After drying under vacuum at RT for 2 h, MXene electrodes were tested using a Biologic SP-300 electrochemical station at room temperature. EIS measurements were carried out at an open circuit potential by applying an alternating-current voltage with an amplitude of 10 mV in a frequency range of 10 mHz to 1 MHz. The long-term cyclic stability test was performed using CV at 50 mV s⁻¹ for 10,000 cycles. The values of gravimetric capacitance (C, F g⁻¹) of the electrodes were estimated from:

$$C = \frac{\int I dU}{M \nu \Delta U}$$

where I is the current (A), ν is the potential scan rate (V s⁻¹), ΔU is the potential window (V), and M is the mass of MXene loaded on the electrode, respectively.

3. RESULTS AND DISCUSSION

3.1. Synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene dispersion. $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes (from here on referred to as “MXene”) were synthesized from the Ti_3AlC_2 precursor (0.5 g) by selective etching of the aluminum layer using a mixture of LiF (0.8 g) and HCl (9 M, 10 mL) at room temperature (RT, $\sim 25^\circ\text{C}$) for 24 h. The subsequent intercalation of water and Li ions within the negatively charged surface resulted in a volume increase during washing with ultra-pure water indicates the self-delamination of multi-layered MXene to few/single layers. Delamination and the removal of the aluminum was confirmed by the down-shifting of the (002) peak and a disappearance of aluminum peak at 2θ of 39° on X-ray diffraction (XRD) spectra (Figure S1a). The dispersed, or as-synthesized, MXene suspension was dark green in color and the flakes exhibited an average hydrodynamic diameter of ~ 500 nm (Figure S1b). These dispersions, referred to as “Fresh MXene” were subsequently stored under various conditions to study their rate of degradation.

Compared with previous studies on MXene oxidation stability,^{12, 14, 18} we synthesized MXene using a higher molar ratio of LiF and Ti_3AlC_2 (12:1 vs. 7.5:1) and a lower etching temperature (RT vs. 35°C). Etching Ti_3AlC_2 in the presence of a high LiF molar ratio is known to produce readily-delaminated MXene without further sonication.^{14, 36} Delamination and/or re-dispersion of MXene with the aid of sonication has been found to cause flake damage and induce oxidation, resulting in lower conductivity.^{18, 37-38} Likewise, elevated etching temperature also promotes MXene oxidation.^{16, 39} It is noteworthy that the frozen MXene dispersion employed in this study allowed us to eliminate the initial oxidation of MXene caused by both sonication and heating.

To assess the difference of this synthetic variation with previously published MXene oxidation studies,^{12, 14, 18} a dispersion (0.5 mg mL^{-1}) was monitored at room temperature. Oxidation of the MXene dispersion resulted in fading of the solution color from black, or translucent greenish at very low concentrations, to cloudy white upon full MXene oxidation, due to the formation of TiO_2

crystals at the edges and surface of MXene flakes (Figure 1a).¹² Although the color of MXene dispersions depend on MXene concentration, color change is typically the proxy used to indicate the oxidation of MXene flakes, as such the same concentration of MXene was used.^{12, 18} Fading can be easily observed as early as the second day (RT-2) and continues until the dispersion turns completely white by day 30 (RT-30) (Figure 1b). Oxidation of MXene is indicated by color fading and solution stability was observed to be similar with previous reports on MXene oxidation that used different etching conditions.^{12, 40}

3.2. Temperature dependence of MXene oxidation rate in aqueous dispersion. To study the temperature dependence of MXene oxidation rate, the as-synthesized MXene dispersions were stored at temperatures from -20 °C, 4 °C, 25°C and 90 °C. -20 °C was selected as the lowest temperature in our study, which was the readily reached temperature of a general laboratory freezer, aiming to demonstrate the wide applicability of this storage method. The color changes of all samples were plotted on a dark green step-wedge (Figure 1e). MXene dispersions exhibited reduced stability with increasing temperature from 30 days at 20 °C, (Figure 1b) to less than 24 hours at 90 °C (Figure 1c). In contrast, there was no change in color when the as-synthesized MXene dispersion was frozen at -20 °C, even after 650 days (Frozen-650, Figure 1d). For the MXene dispersion stored at 4 °C, we observed a significant delay in color change, however oxidation still occurred within 30 days. Those observation suggest that the rate of oxidation increases with temperature. Though irreversible, the rate of oxidation could then be slowed down by lowering the temperature.¹² From the color changes, freezing the MXene dispersion seems to be the best approach for long term storage of MXene.

Figure 2. Morphology and structural characterization of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes. TEM images of (a) Fresh MXene, (b) Frozen-650, and (c) RT-2 samples. AFM images of (d) Fresh MXene, (e) Frozen-650, and (f) RT-2 samples. Bottom represents the thickness data along the green lines indicated in figures. The red arrow indicates the TiO_2 particles at the edge of MXene flakes.

To investigate the effect of freezing on the oxidation degree of MXene flakes, the morphology changes of MXene flakes taken from Fresh MXene, Frozen-650, and RT-2 were assessed through transmission electron microscopy (TEM) and atomic force microscopy (AFM) studies. Figure 2a and 2b show that both Fresh MXene and Frozen-650 exhibited a clean surface at the edge of the MXene flakes. For RT-2, small black dots were observed, indicating the formation of nanoparticles at the edge of MXene flakes, suggesting Stage I oxidation^{12, 14} (Figure 2c). The AFM micrographs of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes in Fresh MXene show flake thicknesses of ~ 1.9 nm, indicating the synthesis of

single layer MXene flakes.^{14, 41} $\text{Ti}_3\text{C}_2\text{T}_x$ flakes stored after two days at normal laboratory condition (RT-2) exhibited a significant increase in thickness (~ 4 nm) at the flake edge while in contrast the Frozen-650 sample showed flakes with clean surfaces (Figure 2b and c), indicating that freezing prevents the formation of TiO_2 particles. The DLS data shows a size distribution around 90-100 nm which were consistent with TEM and AFM images in which small MXene flakes with sizes around 100 nm could be observed.

To study the changes in the elemental composition of MXene flakes after storage, X-ray photoelectron spectroscopy (XPS) analysis was performed. High resolution XPS spectra of MXene at varying storage conditions were fitted into Ti 2p, C 1s and O 1s core levels (Figure 3). The peak corresponding to the Ti 2p core level was fitted to four doublets of Ti $2p_{3/2}$ and Ti $2p_{1/2}$, namely Ti-C $2p_{3/2}$, Ti-C $2p_{1/2}$, Ti(II) $2p_{3/2}$, Ti(II) $2p_{1/2}$, Ti(III) $2p_{3/2}$, Ti(III) $2p_{1/2}$, Ti(IV) $2p_{3/2}$ and Ti(IV) $2p_{1/2}$ located at $\sim 454.9, 460.8, 455.9, 461.9, 457.6, 462.9$ eV, 458.5 eV and 464.1 eV, respectively (Figure 3a, d and g). The C 1s core was fitted to four peaks of C-Ti (281.8 eV), C-Ti-O (282.0 eV), C-C (284.4 eV) and C-O (286.0 eV). The O 1s core was assigned to C-Ti-OH 1s, C-Ti-Ox and O-Ti-O 1s located at $\sim 532.7, 529.6$ and 530.6 eV, respectively (Figure 3c, f and i). Fitted peaks of the Ti 2p, C 1s and O 1s core levels were all comparable to the previously reported XPS spectra of MXene in existing literature.⁴²⁻⁴⁵ Fresh MXene and Frozen-650 showed very similar shape in the Ti 2p region while the Ti-O $2p_{3/2}$ peak exhibited a slight increase in RT-2 spectra, suggesting the formation of TiO_2 nanoparticles during Stage I oxidation. The C 1s spectra of all samples showed neglectable change, suggesting the carbon layer in MXene is not decomposed at early stage of oxidation. Furthermore, the O 1s spectra were relatively similar between Fresh MXene and Frozen-650 samples, whereas the RT-2 showed dramatic increase in the ratio between O-Ti-

O 1s and C-Ti-OH 1s peaks (Figure 3), suggesting that the frozen sample retains its elemental composition even after storing for ~2 years while oxidation occurs within two days for room temperature MXene.

Figure 3. High resolution Ti 2p, C 1s and O 1s XPS spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ films prepared from (a-c) Fresh MXene, (d-f) Frozen-650 and (g-i) RT-2 dispersions.

3.3. Effect of storing conditions on film properties. Free-standing MXene films of similar thicknesses (3.6 to 3.8 μm) were prepared using vacuum-assisted filtration. All films (Fresh MXene, Frozen-650, and RT-2) showed good flexibility (Figure S2), suggesting the early stage

oxidation, such as that observed in RT-2 dispersions, has negligible effect on the processability using the vacuum assisted filtration method. Quantitative assessment of the mechanical properties of the films revealed that the tensile strength of RT-2 film (49.4 ± 3.1 MPa) is half of that of Fresh MXene film (84.2 ± 3.7 MPa) and Frozen-650 film (80.9 ± 4.3 MPa). The Young's Modulus also decreased from 4.9 ± 0.6 GPa (Fresh MXene film) and 4.2 ± 0.4 GPa (Frozen-650 film) to 2.5 ± 0.2 GPa for RT-2 film (Figure 4a). The electrical conductivity of these films (Figure 4b) showed that the films composed of Frozen-650 and Fresh MXene have higher conductivity of 5608 ± 302 S cm⁻¹ and 5480 ± 285 S cm⁻¹, compared to the RT-2 film (4347 ± 217 S cm⁻¹). These results suggest that the electrical conductivity of MXene films prepared from RT-2 dispersion were significantly compromised, whereas Frozen-650 has almost the same performance compared to that of Fresh MXene.

To understand the stacking structure of MXene flakes in films, XRD spectra and morphology were assessed. Based from the XRD spectra of vacuum filtered films of Fresh MXene, Frozen-650, and RT-2 (Figure 4c), all films showed the same peak position for (002) peak $\sim 6.9^\circ$, attributing to lamellar layer spacing of 1.2 nm. The full width at half maximum (FWHM) of this (002) peak for Fresh MXene and Frozen-650 are 0.62° and 0.65° , respectively, while the FWHM increased to 1.25° for RT-2 film. According to Scherrer's equation, the increase in FWHM indicates that MXene flakes in the RT-2 film has irregular orientation and the increased intensity at low 2 theta indicates larger d-spacing between MXene flakes. Considering the formation of TiO₂ particles at the edges of flakes, it can be an important reason for the decrease of conductivity and mechanical strength of RT-2 film. The SEM micrographs of the cross-section of MXene films at the same magnification revealed that Fresh MXene and Frozen-650 films exhibit close stacking of the MXene along the film plane, while RT-2 film shows loose packing with small particles between

MXene flakes (Figure 4d-f). These small particles can be attributed to TiO_2 , as suggested by Energy Dispersive X-ray (EDX) data on MXene films showing slightly increased oxygen content from 16.6 wt.% for Fresh MXene film to 18.6 wt.% for RT-2 film (Figure S3). Due to the increased layer spacing, RT-2 film showed a lower density of 3.2 g cm^{-3} compared to that of Fresh MXene (3.4 g cm^{-3}). We proposed the following structural models of $\text{Ti}_3\text{C}_2\text{T}_x$ films prepared using fresh $\text{Ti}_3\text{C}_2\text{T}_x$ and oxidized RT-2 dispersions. Fresh MXene flakes possess a uniformly smooth flat surface, and forms closely stacked layers when filtered into a film. In contrast, RT-2 samples with protruding TiO_2 particles along the flake edge form relatively loosely stacked layers in films, due to TiO_2 induced voids during the filtration process, leading to an increase in film thickness and decrease in packing density, which is one of the reasons for the reduction of both electrical conductivity and mechanical strength.

Figure 4. (a) The tensile-strain curves, (b) current-voltage (I-V) curves, (c) XRD spectra of MXene films produced from Fresh MXene, Frozen-650, and RT-2 dispersions. Scanning electron microscopy (SEM) photos of the cross-section of Ti₃C₂T_x films prepared using (d) Fresh MXene, (e) Frozen-650, and (f) RT-2 dispersions. Red arrows in (f) indicate the particles between MXene flakes. The structural models of Ti₃C₂T_x films prepared using (g) Fresh MXene and (h) RT-2 dispersions. The white TiO₂ particles on Ti₃C₂T_x flakes working as spacers that increased the layer distance.

3.4. Electrochemical properties. To understand the electrochemical properties of Fresh MXene, RT-2 and Frozen-650 films, thin MXene films were prepared on glassy carbon electrodes

and then assembled into a three-electrode test system in 1M of sulfuric acid electrolyte, using carbon rod and Ag/AgCl electrode as counter and reference electrodes, respectively. All MXene electrodes show wide operation window of -0.7 V to 0.2 V, which is in agreement with previous works.¹⁰ Figure 5a-c show that all samples have the same curve shapes at low scan rate of 10 mV s⁻¹ with a peak at ~ -0.37 V, which can be attributed to the intercalation/de-intercalation of H⁺ and surface redox reactions.⁴⁶⁻⁴⁷ For Fresh MXene and Frozen-650 films, the position of the peak current at 2 V s⁻¹ shifted slightly to -0.24 V and -0.21 V, respectively. However, at scan rate of 2 V s⁻¹ the RT-2 electrode shows a significant shift to -0.05 V. The RT-2 peak shift indicates the electrode has slower charge transfer rate than Fresh MXene and Frozen-650 electrodes. By integrating the area under the cyclic voltammetry (CV) curves, the specific capacitance changes of Fresh MXene, Frozen-650 and RT-2 electrodes were calculated as shown in Figure 5d. All electrodes showed the similar specific capacitance of ~ 375 F g⁻¹ at low scan rate of 10 mV s⁻¹. This result suggests that the early stage of oxidation has negligible impact on the electrode performance at low scan rate. The Frozen-650 shows the same changes in capacitance from ~ 375 F g⁻¹ at 10 mV s⁻¹ to ~ 154 F g⁻¹ at 10 V s⁻¹, indicating the capacitance performance of Frozen-650 is as good as Fresh MXene. Otherwise, the specific capacitance of RT-2 sample dropped from 374 F g⁻¹ at 10 mV s⁻¹ to ~ 81 F g⁻¹ at 10 V s⁻¹, which showed the rate performance is inhibited by MXene that has undergone Stage I oxidation.

Figure 5. Cyclic voltammetry (CV) curves of (a) Fresh MXene, (b) Frozen-650 and (c) RT-2 electrodes in 1M sulfuric acid electrolyte at scan rates of 10 mV s⁻¹ to 1000 mV s⁻¹. (d) The changes of specific capacitance of electrodes as function of scan rate. (e) The Nyquist Plots of electrochemical impedance spectroscopy (EIS) data on above films. (f) Capacitance retention of Fresh MXene, Frozen-650 and RT-2 electrodes cycling at CV scan rate of 50 mV s⁻¹.

To further understand the differences in the electrochemical properties of the fabricated films, we used electrochemical impedance spectroscopy (EIS) to study the above electrodes. The RT-2 film shows significant increase in the ohmic resistance (R_s), which is in consistent with the reduced electrical conductivity due to oxidation (Figure 5e). The semi-circle in the high frequency region for RT-2, which corresponds to charge-transfer resistance (R_{ct})⁴⁸⁻⁵⁰, becomes larger compared with Fresh MXene and Frozen-650 films. In addition, all samples show quasi-vertical lines at low frequency ranging from around 100 mHz to 1 Hz, which are resulted from their highly capacitive

behaviors. In the intermediate frequency region, the plots with their slope close to 45° , which appeared at 16.3 Hz and 14.7 Hz for the Fresh MXene and Frozen-650 films, respectively, can be attributed to the Warburg resistance originated from the semi-finite diffusion of ions in the electrodes.⁵¹⁻⁵² The observed Warburg frequency region decreased to 2.3 Hz for the RT-2 electrode, which suggests that Stage I oxidation hinders the ions diffusion in MXene electrode. The Fresh MXene and Frozen-650 electrodes exhibited good capacitance retention of 99.1% at a scan rate of 50 mV s^{-1} after 10,000 charging/discharging cycles, while the RT-2 electrode decreased to 98.3 % (Figure 5f). These results demonstrated the good long cycle stability of Frozen-650 electrodes.

Based from the evidences presented in this study, it can be inferred that there are three major reasons for the delay of early-stage oxidation of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes. First, the lowered oxidation reaction rate constant resulted from a decreased storage temperature. Comparing the 4°C and -20°C sample, we found that 4°C is suitable for storing MXene for less than 5 days, but for long-term storage, the liquid water has to be frozen in order to completely delay the oxidation of MXene flakes. Secondly, the ice formed around MXene flakes changed the media from liquid to solid in which ice crystals prevents the growth of TiO_2 nanoparticles.¹³ The solid ice matrix surrounding the MXene flakes isolates said flakes from direct exposure to air. Additionally, the solid ice significantly decreases the diffusion rate of oxygen from the air to the MXene flakes. The third reason is that the amount of dissolved oxygen decreased when the aqueous dispersion was frozen into ice, reducing the contact of MXene flakes to oxygenated water molecules. Also, the solid ice can significantly decrease the diffusion rate of oxygen from air to MXene flakes. The combination of these three factors inhibits oxidation enabling long-term preservation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene dispersions through freezing. The present work revealed that the oxidation rate of MXene is

influenced by temperature, which suggests it may follow the Arrhenius equation. However, more evidence is needed to prove that this is indeed the case and many other factors such as flake size, concentration, etc. need to be investigated to provide fundamental understanding to this Arrhenius-like behavior.

4. CONCLUSION

In this study, the temperature dependence of MXene oxidation in water was evaluated where a method to preserve $\text{Ti}_3\text{C}_2\text{T}_x$ MXene aqueous dispersions through freezing was developed. Assessment of morphology and properties of Fresh MXene, frozen MXene and MXene dispersions stored at room temperature, demonstrated that the TiO_2 nanoparticles had already formed by the second day at room temperature while frozen dispersions showed minimal signs of oxidation. It is noteworthy that the MXene flakes stored by freezing also maintained same flake morphology and physical characteristics, such as electrical conductivity, mechanical properties and energy storage performance even after 650 days of storage. These results demonstrate that freezing MXene dispersions is a simple and effective method to enable long-term storage and transfer of MXene in aqueous dispersion.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

XRD pattern of Ti_3AlC_2 MAX phase and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, photos of folded MXene film, and energy-dispersive X-ray spectroscopy (EDX) analysis of MXene films. (PDF)

AUTHOR INFORMATION

Corresponding Author

Prof. Joselito M. Razal (joselito.razal@deakin.edu.au)

Author Contributions

|| J. Zhang and N. Kong contributed equally to this manuscript. All authors have given approval to the final version of the manuscript.

Notes

There are no conflicts to declare.

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