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High-Power Energy Storage and Stability of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene at Extreme Temperatures

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Abstract

Pseudocapacitors have the potential to achieve high energy and high power density simultaneously, a holy grail for electrochemical energy storage. MXene-based pseudocapacitors achieve higher energy and power densities than carbon-based supercapacitors, but their electrochemical stability and degradation mechanisms under extreme temperatures remain underexplored, limiting their widespread application. Herein, we show that $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes exhibit excellent rate capability in 5 M H_2SO_4 electrolyte from $-40\text{ }^\circ\text{C}$ to $100\text{ }^\circ\text{C}$, delivering 700 F cm^{-3} (200 F g^{-1}) and a capacity of $\sim 80\text{ mAh g}^{-1}$ at a rate of 300C (12-sec charge/discharge time) with over 90% capacitance retention at $70\text{ }^\circ\text{C}$ during floating tests at -0.83 V vs. $\text{Hg/Hg}_2\text{SO}_4$ over a month. By systematically varying electrochemical potential, pH, and temperature, we identify titanium dissolution as the principal degradation pathway in strong acids and establish a direct correlation between titanium loss and capacitance decay. Reducing potential suppresses titanium dissolution, thereby extending electrode lifetime. To rationalize the effects of potential and pH, we constructed computational Pourbaix diagrams for $\text{Ti}_3\text{C}_2\text{T}_x$ at room temperature. The experimentally observed potential- and pH-dependent stability trends are consistent with the predicted thermodynamic stability domains. Our findings position $\text{Ti}_3\text{C}_2\text{T}_x$ as a promising negative-electrode material in protic aqueous electrolytes for high-power aqueous energy storage over a wide temperature range and demonstrate how computational Pourbaix analysis, combined with temperature-dependent degradation measurements, can guide the selection of durable electrode–electrolyte combinations for aqueous electrochemical systems.

Keywords: MXene, pseudocapacitor, stability, energy storage, high power, extreme temperatures

Among all energy storage technologies, electrochemical capacitors exhibit the highest energy efficiency, fastest charge/discharge rates, and longest cycle life ($> 5 \times 10^5$ charge-discharge cycles), making them valuable for applications ranging from buffers and filters in power electronics, regenerative braking in automotive transportation, and low-maintenance power sources for intermittent clean energy to powering the emerging data centers.[1] Pseudocapacitors, which use surface-limited redox reactions to store charge, can simultaneously achieve high energy and power densities.[2] Current state-of-the-art lab-scale pseudocapacitors store up to $\sim 80 \text{ Wh kg}^{-1}$ and deliver $\sim 30 \text{ Wh kg}^{-1}$ at 5 kW kg^{-1} , [3, 4] surpassing both carbon-based supercapacitors and batteries over discharge times in the seconds-to-minutes range. However, despite occupying a unique niche in energy and power density, their progress toward commercialization has been slow. Exploring additional competitive advantages is therefore essential to increase their commercial appeal.

One potential advantage of electrochemical capacitors over batteries is their wide operating temperature range. For example, electrochemical energy storage systems are essential for decarbonizing short-haul aviation.[5] Aircraft operating temperatures reach -61°C when cruising at or above the tropopause and 78°C while parked.[6] This temperature range poses challenges for lithium-ion batteries (LIBs), which experience slower solid-state diffusion and lithium metal plating on graphite anodes below 0°C , and accelerated degradation of organic electrolytes and electrodes above 60°C . [7–10] Alternatively, carbon-based supercapacitors experience reduced performance at low temperatures due to slower electrolyte ion diffusion and undergo accelerated degradation at high temperatures.[11] The temperature range of stable performance of pseudocapacitors remains largely unexplored compared to competing technologies.[12, 13] Pseudocapacitive materials show less mechanical degradation and a longer cyclic life than intercalation battery materials because they do not undergo phase transformations and structural changes.[14] Instead, they may show chemical degradation. For example, pseudocapacitive materials such as birnessite manganese oxide (MnO_2) and ruthenium oxide (RuO_2) undergo transition-metal-ion dissolution similar to that of spinel lithium manganese oxide and lithium iron phosphate.[15–17] By identifying compatible electrolytes, long cycle lives of tens of thousands of cycles have been achieved in MXenes and VN.[18, 19] $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is a promising two-dimensional (2D) material for high-rate and long-cycle-life pseudocapacitive electrochemical storage.[20] High metallic conductivity (2-3 orders of magnitude higher than activated carbon and an order of magnitude above reduced graphene oxide) minimizes energy losses. It may eliminate the need for a current collector, thereby reducing device volume and increasing power/energy density. The 2D nature of MXenes enables the fabrication of thin, flexible energy storage devices for wearable and distributed self-powered sensors that never require battery replacement. For example, an impressive capacitance retention exceeding 90% after half a million cycles in 3 M H_2SO_4 was reported.[18]

Despite many advantages, MXenes can degrade to oxides or hydroxides via hydrolysis and/or oxidation in aqueous environments.[21–24] MXene synthesis, processing, and storage practices strongly affect the lifetime in water or air. The stability of MXenes has been greatly improved through three key advances: removing substitutional oxygen from the carbon layer during MAX phase precursor synthesis,[25–27] reducing vacancy concentration by replacing a harsh HF etchant with an HF/HCl mixture,[28, 29] and minimizing exposure to light and environmental oxygen during storage and usage.[30] Consequently, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene can remain

stable in aqueous suspensions for over 10 months and in solid films for years.[25, 31] Reconciling the difference in reactivity requires recognizing that early-stage and present MXenes, though identically named, behave differently due to differences in purity and defect concentration.[32] For example, due to the lower stability of MXenes produced via older synthesis protocols, many pseudocapacitor studies focused on combining MXenes with other materials to form composites to improve their oxidation resistance and mitigate nanosheet restacking.[33, 34] Although composites yielded modest improvements, less-defective $\text{Ti}_3\text{C}_2\text{T}_x$ alone achieves cyclability comparable to or exceeding that of carbon.[18]

In this work, we examined the high-rate electrochemical energy storage and degradation mechanism of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in sulfuric acid under electrochemical conditions that extend beyond the conventional operating window of aqueous supercapacitors. The $\text{Ti}_3\text{C}_2\text{T}_x$ – sulfuric acid system is one of the most established pseudocapacitive material-electrolyte systems in terms of volumetric capacitance, rate capability, cycle life, and mechanistic understanding. At the same time, 5 M H_2SO_4 provides access to charge storage in a wide temperature range.[35, 36] By combining electrochemical characterization at extreme temperatures, extended electrochemical stability tests at 70 °C, and surface and elemental analyses, we demonstrated the fast charge/discharge of $\text{Ti}_3\text{C}_2\text{T}_x$ from -40 °C to 100 °C and determined how electrochemical potential, pH, and temperature govern the degradation mechanisms of $\text{Ti}_3\text{C}_2\text{T}_x$. We also show that Pourbaix diagrams can be a valuable tool for selecting electrode-electrolyte combinations for aqueous electrochemical energy storage systems.

Electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in a wide temperature range

At -70 °C, the cyclic voltammogram (CV) of 1 – 2.5 μm thick $\text{Ti}_3\text{C}_2\text{T}_x$ films shows minimal electrochemical activity, while at -40 °C and above, $\text{Ti}_3\text{C}_2\text{T}_x$ shows enhanced electrochemical activity from proton intercalation within the layers, with an electrochemical non-faradaic double-layer region at higher potentials (> -0.3 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) and a faradaic redox-active region at lower potentials (< -0.3 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$, **Fig. 1a** and Supplementary Figs. 1–3).[37] As temperature increases, the double-layer capacitance stays at ~ 500 F cm^{-2} , and the kinetics of faradaic charge storage improve as indicated by sharper anodic and cathodic redox peaks and a smaller potential difference between them. The electrochemical window at higher temperatures was narrowed to prevent the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) due to increased water activity.[38] While the low-temperature limit, -70 °C, is dictated by the ion-diffusion kinetics in the electrolyte, the high-temperature limit, 100 °C, is dictated by the vapor pressure (and thus boiling point) of the electrolyte. $\text{Ti}_3\text{C}_2\text{T}_x$ MXene shows no compromise in electrochemical performance at 100 °C during the measurement. At -40 °C and above, at an industry-relevant rate of 300C or 12-second galvanostatic charge/discharge of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (**Fig. 1b** and Supplementary Figs. 4–6) shows anodic volumetric capacitance of 920 ± 82 F cm^{-3} (gravimetric capacitance of 242 ± 18 F g^{-1} and specific capacity of 82 ± 10 mAh g^{-1}) between 0 and 100 °C, which dropped to 735 ± 13 F cm^{-3} (199 ± 4 F g^{-1} and 83 ± 3 mAh g^{-1}) between -40 and -10 °C, and then diminished significantly below -40 °C. Despite reduced electrochemical windows at higher temperatures, $\text{Ti}_3\text{C}_2\text{T}_x$ shows similar capacity due to improved kinetics and higher capacitance due to reduced double-layer contribution. $\text{Ti}_3\text{C}_2\text{T}_x$ MXene also demonstrated

decent rate capability between -40 and 100 °C, as shown in Fig. 1c. Capacitance at 100 mV s⁻¹ (sub-minute charge/discharge) was able to retain 70-80% of the capacitance at 1 mV s⁻¹ (over 20-minute charge/discharge) between -40 and 10 °C, and improved to above 90% at temperatures above 30 °C. However, the low-rate capacitance decreases with increasing temperature due to a reduced electrochemical window.

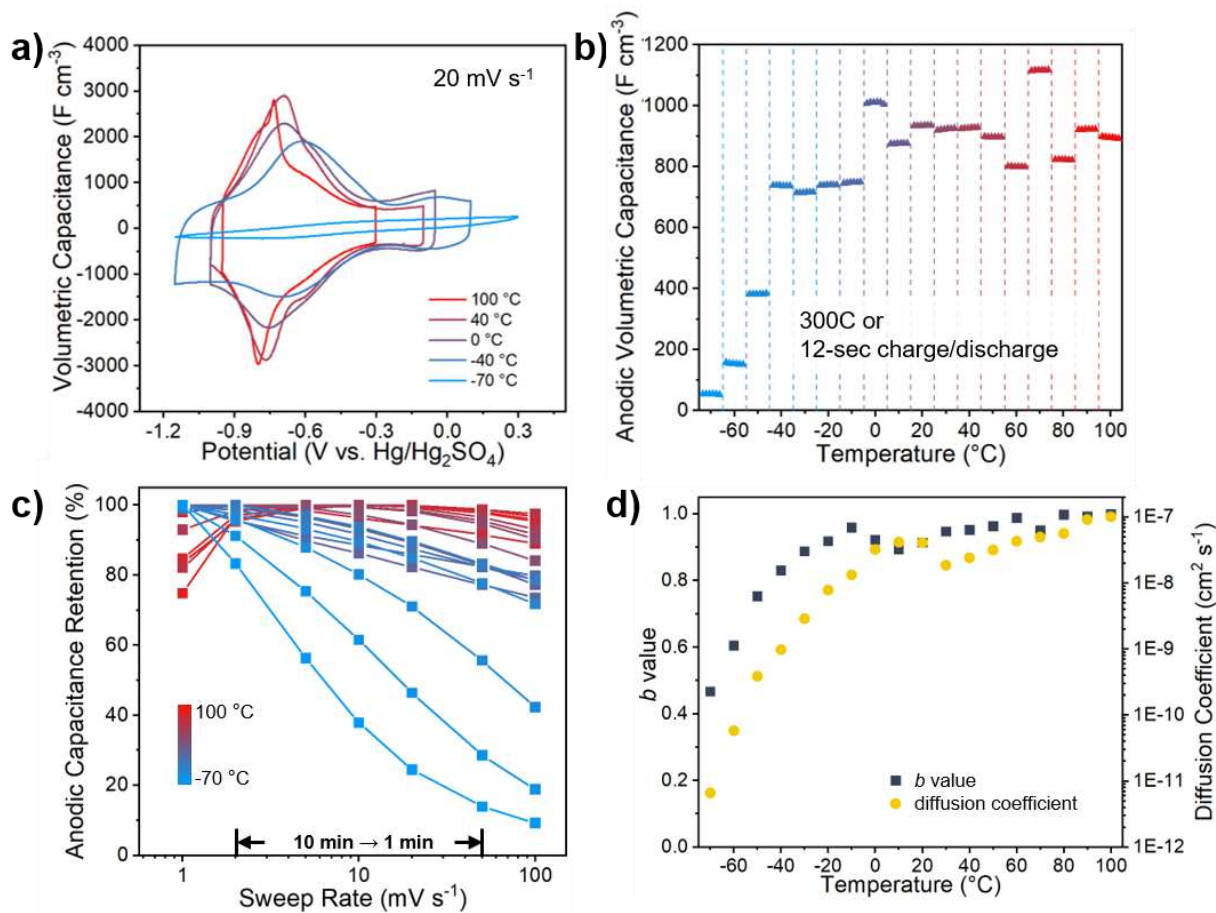


Fig. 1 | Electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes in 5 M H_2SO_4 from -70 °C to 100 °C. (a) Selected cyclic voltammograms at 20 mV s⁻¹, with the complete data presented in Supplementary Figs. 1–3. **(b)** Anodic volumetric temperature performance by galvanostatic charge/discharge test at a rate of 300C (12-sec charge/discharge). **(c)** Anodic capacitance retention by cyclic voltammetry from 1 to 100 mV s⁻¹. **(d)** b value and proton diffusion coefficient at 10 mHz.

To understand the kinetic limitations in the system, we calculated the b -value from CVs and the proton diffusion coefficient from electrochemical impedance spectroscopy (EIS) (Fig. 1d and Supplementary Figs. 7 and 8). The b -value provides insight into the kinetic limitations, with 0.5 indicating diffusion-limited processes and 1 indicating reaction-limited processes.[39] From -70 °C to -10 °C, there is a transition from diffusion-limited to reaction-limited, which is further supported by a concomitant increase in the diffusion coefficient by three orders of magnitude. Above -10 °C, the proton diffusion coefficient is on the order of 10⁻⁸ cm² s⁻¹, consistent with the literature.[40] Given that proton and electron transport in MXene varies linearly from -70 °C to 100 °C and the proton diffusion coefficient in H_2SO_4 aqueous solution is significantly higher in

this temperature range,[41, 42] the observed diffusion limitation is likely due to freezing of the saturated K_2SO_4 solution in the reference electrode (freezing point $-1.54\text{ }^\circ\text{C}$,[43] but likely lowered due to immersion in the sulfuric acid electrolyte). If we consider b values above 0.8 from $1\text{--}100\text{ mV s}^{-1}$ (~ 10 secs to 20 mins charge/discharge times, respectively), pseudocapacitance in this electrochemical energy storage system is maintained from $-40\text{ }^\circ\text{C}$ to $100\text{ }^\circ\text{C}$. Notably, because low-temperature performance in our system is likely limited by freezing of the reference electrode, pseudocapacitance can be achieved at even lower temperatures in actual two-electrode devices.[44]

In summary, micron-thick $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes are pseudocapacitive from at least $-40\text{ }^\circ\text{C}$ to $100\text{ }^\circ\text{C}$ and can deliver a capacitance above 700 F cm^{-3} (200 F g^{-1}) and a capacity above 80 mAh g^{-1} in the seconds-to-minutes time regime.

Floating test of $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes in sulfuric acid

To assess the electrochemical stability of $\text{Ti}_3\text{C}_2\text{T}_x$, we performed a high-temperature floating test to accelerate aging and compared it with the open-circuit potential (OCP) condition.[45, 46] Floating at -0.9 V vs. YP-50F ($-0.83\text{ V vs. Hg/Hg}_2\text{SO}_4$, calibration method in Supplementary Note 1) simulates real-world use of $\text{Ti}_3\text{C}_2\text{T}_x$ as an anode, and the OCP condition simulates $\text{Ti}_3\text{C}_2\text{T}_x$ storage in an uncharged electrochemical cell. The experiments were performed at $70\text{ }^\circ\text{C}$ for 30 days in a two-electrode configuration against an over-capacitive YP-50F counter electrode. During aging, cyclic voltammetry was performed every 24 hrs at a sweep rate of 20 mV s^{-1} to evaluate $\text{Ti}_3\text{C}_2\text{T}_x$'s electrochemical performance. Under the floating condition, $\text{Ti}_3\text{C}_2\text{T}_x$ retained 95% of its initial capacitance through day 28 and, after 30 days, maintained 1216 F cm^{-3} (249 F g^{-1}), corresponding to 91% of the initial capacitance and showed close to 100% Coulombic efficiency throughout the measurement (**Fig. 2a** and Supplementary Fig. 10). In contrast, under OCP conditions, $\text{Ti}_3\text{C}_2\text{T}_x$ retained over 95% of the initial capacitance and Coulombic efficiency until day 23 but then degradation accelerated, showing lower Coulombic efficiency and 53% capacitance retention at day 30, which corresponds to 761 F cm^{-3} (146 F g^{-1}) (**Fig. 2b** and Supplementary Fig. 11). Under floating and OCP conditions, electrode degradation followed a similar pattern: they showed minimal degradation early on, with more than 95% capacitance retention for more than 20 days, after which electrode degradation accelerated, albeit at a much faster rate at OCP.

Compared to literature results, $\text{Ti}_3\text{C}_2\text{T}_x$ shows considerably better retention than carbon-based aqueous supercapacitors and outperforms a large fraction of carbon-based non-aqueous supercapacitors tested under floating conditions (**Fig. 2c**). The mechanism of different capacitance loss behavior is highly material-, electrolyte-, and voltage-window-specific.[47] Carbon-based supercapacitors in aqueous electrolytes frequently degrade due to corrosion of electrode materials and current collectors, electrolyte decomposition, and gas evolution. In organic electrolytes, degradation can be attributed to gas evolution and passivation-layer formation arising from electrolyte decomposition. Although studies on the aging of pseudocapacitive materials under floating conditions are limited, the degradation of birnessite MnO_2 and $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ due to transition-metal dissolution and structural changes has been well studied.[48–50] These studies

motivate us to investigate the degradation mechanism of $\text{Ti}_3\text{C}_2\text{T}_x$ in 5 M H_2SO_4 under floating and OCP conditions, thereby informing us on how to further prolong their service life.

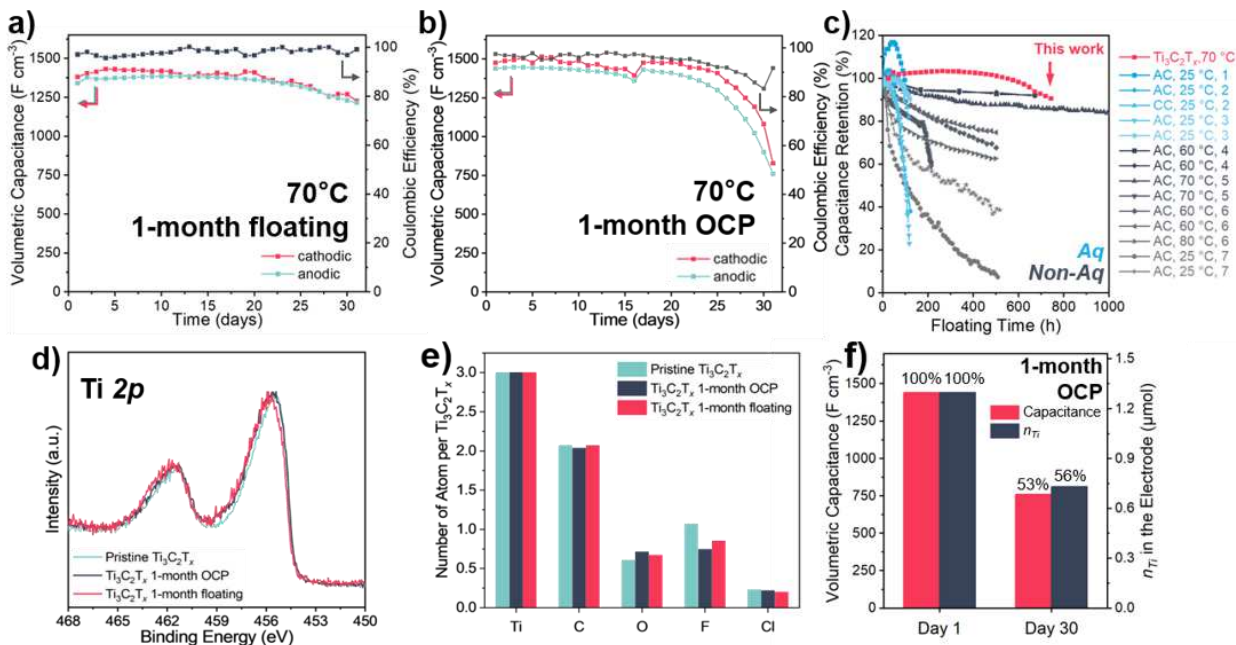


Fig. 2 | Electrochemical stability of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes in 5 M H_2SO_4 . (a-b) Month-long electrochemical characterization performed at 70 °C in a two-electrode configuration against an over-capacitive activated carbon counter electrode, with $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes (a) floating at a constant potential of -0.9 V vs. YP-50F (-0.83 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) and (b) at open-circuit potential (OCP). (c) Capacitance retention of $\text{Ti}_3\text{C}_2\text{T}_x$ -based supercapacitor compared to carbon-based aqueous (Aq) and non-aqueous (Non-Aq) full supercapacitor cells under floating tests reported in the literature (Supplementary Table 1). (d) High-resolution X-ray photoelectron spectroscopy (XPS) spectra of pristine and aged MXene electrodes in the Ti 2p region. (e) Elemental quantification of the XPS spectra. (f) Comparison of capacitance retention and the remaining number of moles of soluble Ti species (n_{Ti}) in the $\text{Ti}_3\text{C}_2\text{T}_x$ electrode quantified from inductively coupled plasma optical emission spectroscopy (ICP-OES) on day 1 and day 30.

As oxidation and hydrolysis are the most prominent degradation mechanisms of $\text{Ti}_3\text{C}_2\text{T}_x$ in aqueous solution at high temperatures,[22, 51] we performed post-mortem XPS analyses of the electrodes under floating and OCP conditions for 30 days. XPS spectra suggest that the chemistry of $\text{Ti}_3\text{C}_2\text{T}_x$ after aging under both floating and OCP conditions is similar. The Ti 2p spectra in **Fig. 2d** show no change in the oxidation state of the transition metals, while the O 1s spectra in **Supplementary Fig. 12** show a slight increase in the oxygen content from adventitious carbon and oxygen surface terminations and/or hydroxyl surface terminations. Elemental quantification in **Fig. 2e** suggests the increase in oxygen surface terminations (O:Ti increase from ~0.6 to ~0.75) is due to the removal of some fluorine and chlorine surface terminations (F:Ti from ~1 to ~0.75 and Cl:Ti from ~0.3 to ~0.2). The drop in F and the increase in O content are slightly higher under the OCP condition. XPS analysis suggests that some MXene may be dissolved, with amorphous carbon deposits remaining on the surface, and the remaining MXene is left in relatively pristine condition. Similar chemistry of the post-mortem electrodes compared to the pristine one suggests

that the capacitance loss was likely caused by degradation pathways that did not involve the formation of oxides.

The degradation of $\text{Ti}_3\text{C}_2\text{T}_x$ by dissolution was investigated with inductively coupled plasma optical emission spectroscopy (ICP-OES). Since the degradation of the floating cell was less than 10%, ICP-OES was only performed on the post-mortem electrolyte of the 30-day OCP cell (**Supplementary Table 2**). The concentration of soluble Ti species in the electrolyte was converted to the number of moles of soluble Ti species, and the number of moles (n_{Ti}) of soluble Ti species in the electrode was calculated (**Supplementary Table 3** and details in **Supplementary Note 2**). We then compared n_{Ti} and the remaining percentage of $\text{Ti}_3\text{C}_2\text{T}_x$ with the capacitance retention in Fig. 2f, which shows good agreement (56% $\text{Ti}_3\text{C}_2\text{T}_x$ remained after the experiment based on ICP-OES and 53% capacitance retention). Knowing that the chemistry of the remaining $\text{Ti}_3\text{C}_2\text{T}_x$ is close to pristine, the agreement between capacitance retention and the remaining percentage of $\text{Ti}_3\text{C}_2\text{T}_x$ in the electrode suggests that chemical dissolution is the main degradation mechanism of $\text{Ti}_3\text{C}_2\text{T}_x$ in H_2SO_4 electrolyte under the OCP condition.

The acceleration of degradation towards the end of the 30 days suggests a long incubation period and an activation barrier to the degradation of $\text{Ti}_3\text{C}_2\text{T}_x$ in 5 M H_2SO_4 . The delayed onset of degradation under negative-potential floating conditions suggests that applying negative potential to $\text{Ti}_3\text{C}_2\text{T}_x$ increases the activation barrier for degradation. This observation is consistent with molecular dynamics simulations, which predicted that a negative potential mitigates the initiation of water-mediated attack on Ti sites in $\text{Ti}_3\text{C}_2\text{T}_x$. [23, 52–54] Applying a negative potential shifts the Fermi level of $\text{Ti}_3\text{C}_2\text{T}_x$ upward and makes the surface more protonated. The negatively charged surface may reorient the O atoms in water away from the surface, resulting in a higher concentration of –OH groups of water molecules pointing away from the surface. This may lead to a higher Fermi level (lower work function) and a lower concentration of –O surface terminations, improving the surface stability of $\text{Ti}_3\text{C}_2\text{T}_x$. As a result, chemical dissolution is suppressed, and higher capacitance is retained by the end of 30 days.

In summary, $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits >90% capacitance retention in 5 M H_2SO_4 after 30 days at 70 °C under a floating condition of -0.83 V vs. Hg/Hg₂SO₄, which is better than the OCP condition (53%). It outperforms carbon-based aqueous supercapacitors (Supplementary Table 1). Degradation in this system occurs primarily through chemical dissolution of $\text{Ti}_3\text{C}_2\text{T}_x$, and this degradation appears to be suppressed by applying a negative potential.

Degradation mechanisms of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene suspensions in 5 M H_2SO_4 vs. deionized water

The electrochemical stability tests provided new insights into the degradation of $\text{Ti}_3\text{C}_2\text{T}_x$. However, electrochemical measurements are inherently influenced by potential-driven processes, electrolyte composition, interfacial reactions, and mass transport, making it difficult to decouple intrinsic chemical degradation pathways. The dissolution-mediated degradation mechanism of $\text{Ti}_3\text{C}_2\text{T}_x$ is less well studied than oxidation and hydrolysis. Thus, 0.5 g L⁻¹ $\text{Ti}_3\text{C}_2\text{T}_x$ suspensions in 5 M H_2SO_4 and deionized water were sealed and stored at 70 °C for 49 days to investigate the

effect of air exposure and monitor degradation periodically using Raman spectroscopy (**Fig. 3a**; experimental details and digital photographs in **Supplementary Fig. 13**).

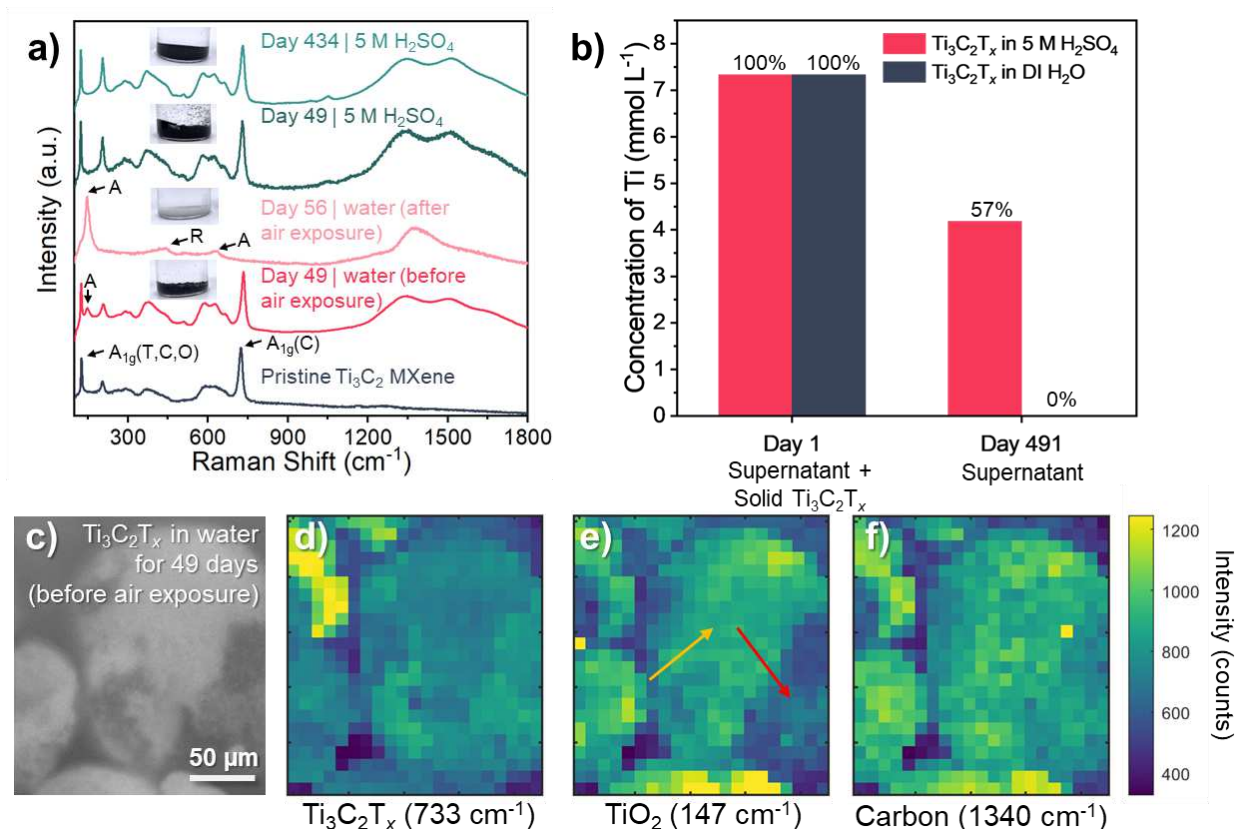


Fig. 3 | Chemical stability of Ti₃C₂T_x MXene in 5 M H₂SO₄ and deionized water. (a) Raman spectra of 0.5 g L⁻¹ Ti₃C₂T_x suspensions in 5 M H₂SO₄ and deionized water over time, collected through the glass vials shown in the inset, in comparison to a pristine Ti₃C₂T_x free-standing film. The letter ‘A’ indicates the E_g modes of anatase TiO₂ at 147 and 632 cm⁻¹, and the letter ‘R’ indicates the E_g mode of rutile TiO₂ at 441 cm⁻¹. (b) Comparison of the concentration of titanium in 0.5 g L⁻¹ (7.33 mmol L⁻¹) Ti₃C₂T_x suspensions in 5 M H₂SO₄ and deionized water on day 1 to the concentration of titanium in the supernatant (dissolved titanium) of the suspensive solutions on day 491. (c) Optical micrograph of the suspension in deionized water after 49 days at 70 °C and (d-f) corresponding Raman maps of the intensity at (d) 733 cm⁻¹ for Ti₃C₂T_x MXene (out-of-plane carbon vibrations), (e) 147 cm⁻¹ for anatase TiO₂, and (f) 1340 cm⁻¹ for disordered carbon. In (e), the yellow arrow points to the TiO₂-rich area and the red arrow points to the TiO₂-deficient area.

Within minutes of adding Ti₃C₂T_x to sulfuric acid, hydronium ions cause the MXene sheets to flocculate and rapidly sediment because of electrostatic self-assembly between the negatively charged sheet surfaces and the positively charged ions (**Supplementary Fig. 13**). Over several weeks, MXene sheets also slowly flocculate and settle in DI water. In H₂SO₄, there was no visible degradation, while in water, a small amount of white solid was visible (**Fig. 3c**). Raman spectra collected through the vial without opening the cap provide further insight into the chemical changes. In H₂SO₄, Ti₃C₂T_x remained pristine, with disordered carbon observed as a degradation product, consistent with previous reports.[55] The intensity ratio of the out-of-plane vibrations of

$A_{1g}(T,C,O):A_{1g}(C)$ at ~ 200 and 733 cm^{-1} , respectively, increased, which suggests better layer-to-layer stacking, consistent with the observed electrostatic self-assembly. In water, $Ti_3C_2T_x$ is more spatially heterogeneous (Fig. 3c-f), with the averaged spectrum showing a combination of $Ti_3C_2T_x$, anatase TiO_2 (E_g), and disordered carbon (Fig. 3a). The bright white areas are correlated with the TiO_2 -rich areas (yellow arrow), $Ti_3C_2T_x$ -poor areas, and carbon-rich areas. This spatial correlation suggests that carbon and TiO_2 form on the surface of $Ti_3C_2T_x$ as it degrades in water. The intensity ratio between the carbon D-band at 1340 cm^{-1} and the $A_{1g}(C)$ peak is 0.60 in water, lower than the ratio of 0.87 in H_2SO_4 . It suggests that disordered carbon is a common degradation product in both solutions, and that its generation is slightly less in water. Given the surface sensitivity of Raman, the relatively low intensity of the E_g peak of anatase TiO_2 in comparison to the $A_{1g}(C)$ peak of $Ti_3C_2T_x$ indicates that the amount of TiO_2 is limited. Since degradation in water involves oxidation and hydrolysis, we hypothesize that the initial slow degradation is due to a combination of oxygen exhaustion in a sealed environment and slow kinetics of hydrolysis.

To test the oxygen exhaustion hypothesis, we uncapped the vials after 49 days to let air in for 30 mins, then resealed them. Within hours, $Ti_3C_2T_x$ in water turned completely white. ICP-OES of the supernatant shows 0% Ti dissolution, suggesting that all $Ti_3C_2T_x$ was converted to TiO_2 . Raman spectrum of the white solid product shows complete degradation of $Ti_3C_2T_x$ into anatase and rutile TiO_2 as well as disordered carbon (Fig. 3a). The sequence of rutile TiO_2 formation after anatase TiO_2 agrees with the literature.[56, 57] The intensity ratio of the anatase E_g peak to the carbon D-band increased from 0.67 to 1.84 post-air-exposure storage. These observations support the significant contribution of oxygen to the accelerated degradation of $Ti_3C_2T_x$ in water.

In H_2SO_4 , air exposure did not degrade $Ti_3C_2T_x$, despite similar oxygen solubilities in sulfuric acid and in water.[58] It remained visually unchanged even after storage at room temperature for > 1 year (**Supplementary Fig. 13**). Raman spectra collected on day 49 and 434 are similar, with D-band-to- $A_{1g}(C)$ -peak-intensity ratio of 0.87 and 0.77, respectively, within measurement error (Fig. 3a). ICP-OES of the supernatant after 491 days (Fig. 3b) shows dissolution of 57% of Ti (43% remaining as MXene), $\sim 30\%$ more than in the electrochemical cell at OCP and 70°C for 30 days. Because in this experiment $Ti_3C_2T_x$ was kept at 70°C for 49 days (63% longer than 30 days), $Ti_3C_2T_x$ here dissolved slightly more slowly. In agreement with the previous report, in which at room temperature $Ti_3C_2T_x$ retained 90% of its capacitance over 400 days of cycling in 3 M H_2SO_4 ,[18] our results further support our hypothesis that degradation of $Ti_3C_2T_x$ occurs predominantly via Ti dissolution at elevated temperatures, such as 70°C , and is significantly slower at room temperature.

The experimental observations above suggest new strategies to protect MXenes. In water, removing dissolved oxygen can be an effective strategy to protect stoichiometric MXenes. In strong acids, the dissolution mechanism implies that we may take advantage of the common ion effect to suppress MXene degradation by adding the corresponding dissolved transition metal ions to the solution. Moreover, our work suggests simplifying experiments by considering that oxygen does not affect degradation in acidic solutions and that purging the electrolyte with nitrogen/argon may not be necessary for electrochemical experiments.

The thermodynamic origin of $\text{Ti}_3\text{C}_2\text{T}_x$ chemical stability in sulfuric acid

The pH- and potential-dependent degradation of $\text{Ti}_3\text{C}_2\text{T}_x$ suggests that Pourbaix diagrams could be useful to understand its degradation behavior.[59] Because protons and hydronium ions can intercalate into $\text{Ti}_3\text{C}_2\text{T}_x$ at lower potentials, we calculated Pourbaix diagrams for $\text{Ti}_3\text{C}_2(\text{O},\text{F})_2$ and $\text{Ti}_3\text{C}_2(\text{OH},\text{F})_2$ at room temperature (**Fig. 4**), with the former representative of pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and the latter of electrochemically protonated $\text{Ti}_3\text{C}_2\text{T}_x$ at lower potentials.

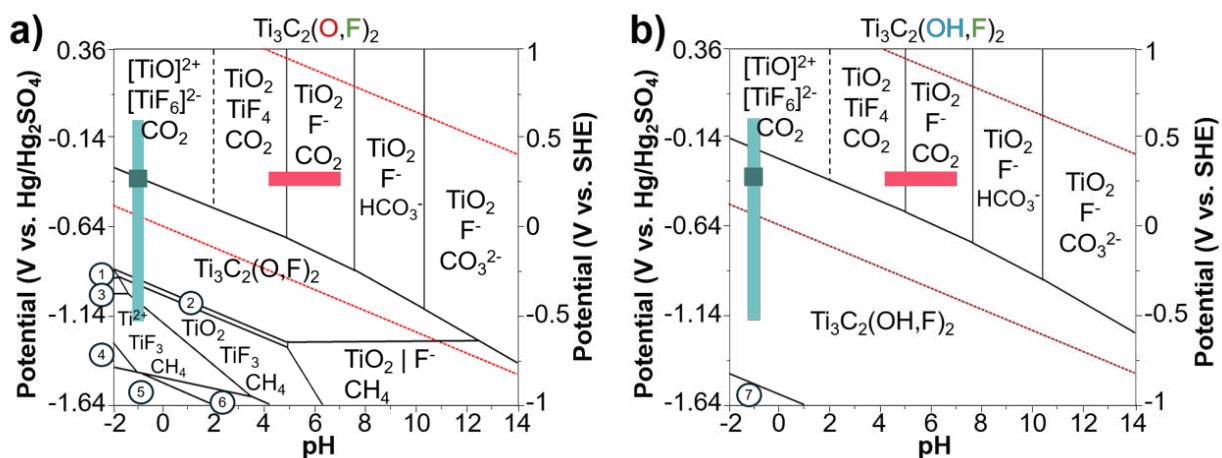


Fig. 4 | Pourbaix diagram of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene with different surface terminations. (a) $\text{Ti}_3\text{C}_2(\text{O},\text{F})_2$ and (b) $\text{Ti}_3\text{C}_2(\text{OH},\text{F})_2$ in aqueous solutions from pH of -2 to 14 and potential of -1.64 V to 0.36 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ in saturated K_2SO_4 , which is equivalent to -1 V to 1 V vs. standard hydrogen electrode (SHE). The lower and upper red dashed lines represent the conditions for hydrogen and oxygen evolution reactions, respectively. The black vertical dashed lines represent a literature-informed boundary, on the left side of which titanyl ($[\text{TiO}]^{2+}$)[60, 61] and hexafluorotitanate complex ($[\text{TiF}_6]^{2-}$)[62–64] are soluble species unavailable in the database used to construct the Pourbaix diagrams. The three colored blocks represent the conditions of the aging experiments, with the light-teal-colored block for electrochemical cycling in 5 M H_2SO_4 , the dark-teal-colored block for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene suspended in 5 M H_2SO_4 , and the magenta-colored block for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene suspended in DI H_2O . The numbered circles represent regions where the following combinations are stable: ① $\text{Ti}^{3+} + \text{TiF}_4 + \text{CH}_4$, ② $\text{TiF}_4 + \text{TiO}_2 + \text{CH}_4$, ③ $\text{Ti}^{3+} + \text{CH}_4 + \text{TiF}_3$, ④ $\text{Ti}^{2+} + \text{CH}_4 + \text{HF}$, ⑤ $\text{TiH}_2 + \text{CH}_4 + \text{HF}$, ⑥ $\text{TiF}_3 + \text{TiH}_2 + \text{CH}_4$, and ⑦ $\text{F}^- + \text{TiH}_2 + \text{CH}_4$.

$\text{Ti}_3\text{C}_2\text{T}_x$ in water was represented by the magenta-colored block. $\text{Ti}_3\text{C}_2\text{T}_x$ typically has an open-circuit potential around -300 mV vs $\text{Hg}/\text{Hg}_2\text{SO}_4$. It spans the pH range from 4.2 to 7 because a pH of 4.2 was measured in the supernatant after complete degradation of $\text{Ti}_3\text{C}_2\text{T}_x$ to TiO_2 and disordered carbon in water. In both diagrams, TiO_2 , F^- , and CO_2 were predicted to be stable products at this potential and pH range, which agrees with the literature.[22] We did not characterize gaseous products but hypothesized that disordered carbon could be a metastable phase that competed with CO_2 formation.

The experimental condition of $\text{Ti}_3\text{C}_2\text{T}_x$ in 5 M H_2SO_4 is presented by the dark-teal-colored block, assuming a pH of -1 for 5 M H_2SO_4 . At OCP, the MXene phase appears to be thermodynamically stable in the $\text{Ti}_3\text{C}_2(\text{OH},\text{F})_2$ Pourbaix diagram. In contrast, in the $\text{Ti}_3\text{C}_2(\text{O},\text{F})_2$ diagram, it lies on the phase boundary separating the single-phase region of MXene and the region with a combination of $[\text{TiO}]^{2+}$, $[\text{TiF}_6]^{2-}$, and CO_2 in which MXene is unstable. The formation of soluble colorless titanium species is consistent with the experimentally observed dissolution of $\text{Ti}_3\text{C}_2\text{T}_x$ in 5 M H_2SO_4 . On the other hand, because the experimental conditions lie close to the

predicted phase boundary, the thermodynamic driving force for decomposition of MXene into $[\text{TiO}]^{2+}$, $[\text{TiF}_6]^{2-}$, and CO_2 is expected to be relatively small. This is consistent with the limited degradation of $\text{Ti}_3\text{C}_2\text{T}_x$ observed at room temperature in 5 M H_2SO_4 . At higher temperatures, the phase boundary is expected to shift downward toward lower potentials, thereby reducing the stability of the MXene phase. This shift is attributable to the greater entropy contributions of the soluble and gaseous products compared with those of the solid MXene phase. Accordingly, nearly 50% dissolution of $\text{Ti}_3\text{C}_2\text{T}_x$ in 5 M H_2SO_4 was experimentally observed after a month at 70 °C.

Lastly, the potential window of cyclic voltammetry was represented by the light teal-colored block. When cycled towards more negative potential, $\text{Ti}_3\text{C}_2(\text{O},\text{F})_2$ gradually transitions to $\text{Ti}_3\text{C}_2(\text{OH},\text{F})_2$. The comparison between Figs. 4a and 4b shows that the $\text{Ti}_3\text{C}_2(\text{OH},\text{F})_2$ phase is more stable at negative potentials, which agrees with our experimental observations. In the positive direction, both Pourbaix diagrams predicted $[\text{TiO}]^{2+}$, $[\text{TiF}_6]^{2-}$, and CO_2 as stable phases, which may explain the degradation of $\text{Ti}_3\text{C}_2\text{T}_x$ under the floating condition, since we cycled the electrode daily to positive potentials during capacitance measurements. The wide thermodynamically stable window of $\text{Ti}_3\text{C}_2\text{T}_x$ at reducing potentials is consistent with the long cycle life reported in the literature.[18]

Pourbaix diagrams successfully predicted the TiO_2 formation at OCP in water, the dissolution of $\text{Ti}_3\text{C}_2\text{T}_x$ at OCP and higher potentials in 5 M H_2SO_4 , and the improved stability of protonated $\text{Ti}_3\text{C}_2\text{T}_x$ at reducing potentials in 5 M H_2SO_4 . Some disagreement may arise from the presence of metastable competing phases and temperature differences. Our results show that Pourbaix diagrams can guide the selection of an appropriate pH and potential window to achieve chemical stability in aqueous electrochemical energy storage systems.

Conclusion

We performed high-rate cycling of $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes in 5 M H_2SO_4 and investigated their degradation mechanisms across temperatures ranging from extremely low (-70 °C) to very high (100 °C). By adjusting the charge/discharge protocol to maximize energy storage and minimize parasitic reactions, 1–2.5 μm -thick $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes can deliver a capacitance above 700 F cm^{-3} (200 F g^{-1}) and a capacity $\sim 80 \text{ mAh g}^{-1}$ at a rate of 300C (12-sec charge/discharge time) between -40 and 100 °C. After 30 days at 70 °C, $\text{Ti}_3\text{C}_2\text{T}_x$ retained 91% of its initial capacitance under the floating condition of -0.83 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ and 53% of its initial capacitance at open-circuit potential, suggesting that a reducing potential suppresses $\text{Ti}_3\text{C}_2\text{T}_x$ degradation. Degradation of $\text{Ti}_3\text{C}_2\text{T}_x$ in 5 M H_2SO_4 occurs through the dissolution of Ti and the formation of disordered carbon at elevated temperatures and is not evident at room temperature. Reducing the electrolyte volume in the cell should minimize or even eliminate this degradation pathway. Its degradation in water involves a different mechanism by forming TiO_2 and disordered carbon. The dissolution mechanism underscores the importance of ICP analysis for MXene degradation studies. The significant pH-, potential-, and temperature-dependence of the degradation can be explained by Pourbaix diagrams, whose accuracy improves if we consider the ion-intercalated material as a new material. Together, we demonstrate the capabilities and limitations of $\text{Ti}_3\text{C}_2\text{T}_x$ as a promising

electrode material for aqueous high-rate electrochemical energy storage applications at extreme temperatures and suggest that Pourbaix diagrams are a valuable computational tool for evaluating durable aqueous electrode materials. The demonstrated pathways to improve MXene stability will help expand their applications in energy storage and beyond.

Methods

MXene synthesis

Briefly, Ti_3AlC_2 MAX phase powders were prepared via high-temperature solid-state synthesis, and two-dimensional $\text{Ti}_3\text{C}_2\text{T}_x$ MXene suspensions were prepared by chemical etching of Al from the MAX phase and subsequent delamination. See published protocols for detailed information.[25, 28]

MAX phase: TiC (Alfa Aesar, 99.5%, 2 μm powder), Ti (Alfa Aesar, 99.5%, 325 mesh), and Al (Alfa Aesar, 99.5%, 325 mesh) powders were mixed in a 2:1.25:2.2 molar ratio by ball milling at 70 rpm for 18 hrs. The resulting powder was sintered at 1380 $^\circ\text{C}$ for 2 hrs under an inert atmosphere with 100 sccm of Ar flow. The temperature ramp rate was 3 $^\circ\text{C}/\text{min}$ for heating and cooling. The sintered block was ground into powder using an end mill and washed with 9 M HCl (Certified ACS Plus, Fisher Scientific, U.S.), followed by a water wash, to remove impurities and intermetallic byproducts. The Ti_3AlC_2 MAX powders were collected by vacuum filtration, dried, and sieved through a 450-mesh (32 μm) screen.

MXene: 1 g of MAX phase powder was etched using 20 mL of etchant. The etchant was a 6:3:1 volume mixture of 12 M HCl, DI water, and 50 wt.% HF (Acros Organics, Fair Lawn, NJ). Powders were added slowly to the etchant and stirred at 350 rpm for 38 hrs. The resulting multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene powder was washed with DI water until pH > 6 via multiple cycles of centrifugation and decantation, and then added to 50 mL of 0.5 M LiCl solution. The suspension was shaken in a Habril 5-gallon heavy-duty shaker (Fluid Management, U.S.) for 30 min at room temperature to complete Li-ion intercalation. The excess LiCl in the suspension was washed by repeated centrifugation at 2550 rcf for 10 mins. After the sediment swelled, the suspension was centrifuged at 7230 rcf for 3 mins. The resulting supernatant contained two-dimensional $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. Free-standing MXene films were obtained by vacuum-assisted filtration through a polypropylene membrane (3501, Celgard). The films were used for electrochemical and physical characterization.

Electrochemical characterizations

All electrochemical characterizations were performed in two-electrode or three-electrode configurations. A $\frac{1}{4}$ inches Tee-shaped PFA tube fitting (Swagelok, U.S.) was used to house the electrodes. The working electrode was the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film (vide supra, $\varnothing = 3$ mm), the counter electrode was a piece of activated carbon film (YP-50F with 5% PTFE binder, $\varnothing = 5$ mm), and the reference electrode was Hg/Hg₂SO₄ in saturated K₂SO₄ (CH Instruments). The electrolyte was a 5 M H₂SO₄ solution, which was bubbled with Ar gas for at least 15 mins before use. Two layers of polypropylene membrane (3501, Celgard, $\varnothing = 7$ mm) were used as a separator between the

working and counter electrodes. Glassy carbon electrodes (CH Instruments) were used as the current collectors for the working and counter electrodes. New PTFE ferrule sets (Swagelok) and PTFE thread tape were used for each experiment to ensure a tight seal. The procedure for three-electrode cell assembly is publicly available on the EChem Channel on YouTube. In the two-electrode setup, a 1/4-inch PFA plug (Swagelok) was used to seal the opening for the reference electrode. The electrochemical stability test was performed without a reference electrode, because the electrolyte dried quickly at 70 °C.

All electrochemical characterizations were performed with a potentiostat (VMP3, Bio-Logic, France). The potential windows used in cyclic voltammetry and the potential windows and current density used in galvanostatic charge/discharge tests at all temperatures are listed in **Supplementary Table 4**. Consistent temperature control was achieved by testing the cells in a climate chamber (MCB-1.2 Benchtop, Cincinnati Sub Zero, U.S.).

The kinetics of proton intercalation were quantified using the relationship between the peak current in the anodic scan ($i_{p,a}$) and sweep rate (ν):

$$i_{p,a} = a\nu^b \quad (1)$$

where a and b are constants. The b value was used to assess kinetics in the manuscript.

Electrochemical impedance spectroscopy measurements were performed using a three-electrode Swagelok cell configuration. A constant potential of -0.9 V vs. Hg/Hg₂SO₄ was applied during EIS measurements with a sinusoidal perturbation amplitude of ± 10 mV. The frequency range was scanned from 100 kHz to 10 mHz. Temperature-dependent EIS measurements were conducted over the range -70 °C to 100 °C in 10 °C increments. At each temperature, the cell was held at -0.9 V vs. Hg/Hg₂SO₄ for 30 min prior to measurement to ensure thermal and electrochemical stabilization. The Warburg coefficient (σ) was obtained from the slope of the linear fit of the real impedance (Z_{real}) versus $\omega^{-1/2}$ in the low-frequency region (20 mHz). The diffusion coefficient was calculated using equation (2)

$$D_{H^+} = \frac{0.5R^2T^2}{A^2n^4F^4C^2\sigma^2} \quad (2)$$

where D_{H^+} is the diffusion coefficient of protons, R is the universal gas constant, T is the absolute temperature, A is the geometric area of the electrode, n is the number of electrons transferred, F is the Faraday constant, C is the bulk concentration of the diffusing species, and σ is the Warburg coefficient at 20 mHz.

Physical characterization

SEM images and EDS spectra were acquired using a field-emission scanning electron microscope (Zeiss Supra 50 VP) equipped with a 40-mm energy-dispersive spectrometer (UltiMax, Oxford, UK). XRD analyses were performed using a diffractometer with a Cu K α X-ray source (40 kV, 44 mA) and height alignment functions (SmartLab, Rigaku, Japan). Raman spectra were collected using an inverted confocal Raman microscope (Invia, Renishaw, UK) with a 785 nm diode laser, 20 $\times$ (NA = 0.4) and 63 $\times$ (NA = 0.7) objectives, a 1200 line/mm diffraction grating,

and a diffraction-based room-temperature CCD spectrometer. The power of the lasers was kept below 1 mW.

XPS spectra were collected using a spectrometer (VersaProbe 5000, Physical Electronics, U.S.) with a 100 μm and 25 W monochromatic Al-K α (1486.6 eV) X-ray source. Survey scans were collected using pass energy and energy resolutions of 50 and 0.5 eV, respectively. The high-resolution scans' pass energy and energy resolution were 23.5 and 0.05 eV. The C1s peak at 282.0 eV of Ti₃C₂T_x was used to correct the binding energy scale. CasaXPS was used for quantification and peak fitting.

ICP-OES was performed using an Agilent 5900 inductively coupled plasma–optical emission spectrometer (ICP–OES). Calibration curves were constructed using Ti and Li standard solutions at concentrations of 0, 0.01, 0.1, and 1 ppm, prepared by serial dilution of certified reference standards (Agilent Technologies) in Milli-Q water. Sample solutions were collected, diluted as necessary, and filtered through a 0.22 μm mixed cellulose esters syringe filter (Millex-GS, Millipore) prior to analysis. Measurements were conducted at an RF power of 1.2 kW, with plasma, auxiliary, and nebulizer gas flow rates of 12, 1, and 0.7 L min⁻¹, respectively. Ti was quantified at 334.941 nm, and Li at 670.783 nm. Y (371.029 nm) and Sc (361.383 nm) were used as internal standards for signal correction and instrumental drift compensation.

pH measurements were performed using a pH titrator (808 Titrando, Metrohm).

Density Functional Theory Calculations and Pourbaix Diagram Construction

First-principles calculations for the structural relaxation and formation energy of the MXene phases were performed using the Vienna ab initio simulation package (VASP).[65] The projector augmented-wave (PAW) method[66, 67] was employed to describe electron wavefunctions. The generalized gradient approximation (GGA) functional developed by Perdew-Burke-Ernzerhof (PBE)[68] was adopted to describe the exchange-correlation interactions. The special quasi-random structure (SQS) method was employed to model the effects of mixed terminations, $-(\text{F}, \text{O})$ and $-(\text{F}, \text{OH})$. [69] In the present work, the SQSs were constructed using the Alloy Theoretic Automated Toolkit (ATAT).[70] The energy convergence criterion of the self-consistency was set to a value of 10^{-8} eV. The Gaussian-smearing method was used for Brillouin-zone integration of the electronic structure with a smearing width of 0.05 eV. The plane-wave cutoff energy was set to 600 eV. Structural relaxation was terminated when the atomic forces were smaller than 0.002 eV/Å. A $15 \times 15 \times 1$ Γ -centered k-point mesh was employed for Brillouin-zone sampling. The DFT-D3 method with zero damping was employed to model the dispersion interactions between individual MXene layers. To calculate the formation energy of MXenes, a reaction method referenced to the most stable bulk phases was employed.[71] As a result, the calculated formation energies shared the same reference state of enthalpy with the Materials Project database.[72]

Using the calculated formation energies of MXenes, the Python Materials Genomics (pymatgen)[73] package was used to construct the Pourbaix diagrams following the method developed by Persson et al.[74] The free-energy data for other relevant solid phases, aqueous ions, and molecules were obtained from the database implemented in the pymatgen package.

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Author contributions

R.W. and Y.G. conceived the idea and designed the experiments. R.W. and Y.Z. performed electrochemical characterization and data analysis. M.A. conducted XPS measurements and data analysis. Y.Z. performed the ICP-OES measurements. M.N.N. and Y.-J.H. performed computational research. T.Z. synthesized the MXene used in this study. R.W. and M.S. performed MXene degradation studies. R.W., K.S., and M.A. performed Raman measurements and data analysis. R.W., M.A., Y.Z., M.N.N., Y.-J.H., and Y.G. helped with the draft of the manuscript. All the authors discussed the results and approved the final version of the manuscript.

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Data availability

Data utilized in this work are available from the corresponding author upon reasonable request.

Declarations

Competing interests

All authors declare that there are no competing interests.

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