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Tuning the Electrochemical Performance of Titanium Carbide MXene by Controllable *in situ* Anodic Oxidation

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Abstract: MXenes are a class of two-dimensional (2D) transition metal carbides, nitrides and carbonitrides that have shown promise for high-rate pseudocapacitive energy storage. However, the effects that irreversible oxidation have on the surface chemistry and electrochemical properties of MXenes are still not understood. Here we report on a controlled anodic oxidation method which improves the rate performance of titanium carbide MXene ($Ti_3C_2T_x$, T_x refers to -F, =O, -Cl and -OH) electrodes in acidic electrolytes. The capacitance retention at 2000 mV/s (with respect to the lowest scan rate of 5 mV/s) increases gradually from 38% to 66% by tuning the degree of anodic oxidation. At the same time, a loss in the redox behavior of Ti_3C_2 is evident at high anodic potentials after oxidation. Several analysis methods were employed to reveal that preserving the structure and surface chemistry while simultaneously introducing defects, without compromising electrochemically active sites, are key factors for improving the rate performance of $Ti_3C_2T_x$. This study demonstrates improvement of the electrochemical performance of MXene electrodes by controlling the surface chemistry and transition metal stoichiometry.

Introduction

MXenes are a quickly growing class of two-dimensional (2D) nanomaterials comprised of transition metal carbides, nitrides, and carbonitrides, which exhibit a unique combination of hydrophilicity and metallic electrical conductivity.^[1–11] MXenes are typically synthesized by top-down wet chemical method through selective etching of A atoms from ternary layered MAX phases, where M stands for an early transition metal (Ti, Nb, Mo, V, Cr, Ta, etc), A is an element from group 13 or 14 (Al, Si, Ga, or In),

and X is carbon and/or nitrogen^[12]. The resulting MXenes can be described by the general formula $M_{n+1}X_nT_x$ ($n=1, 2, 3$), and T_x represents the surface functional groups such as -F, =O, -Cl and -OH. Their compositional versatility, variable transition metal redox chemistry, tunable interlayer spacing, and controllable surface chemistry, make MXenes suitable for a wide range of applications from electromagnet shielding to energy storage.^[13,14] MXenes exhibit intercalation pseudocapacitance where redox reactions take place with ultrafast ion kinetics, which is distinctly different from both, the sluggish ion diffusion in bulk battery electrodes and the formation of electrical double layers (EDL) at the surfaces of porous carbon electrodes.^[15,16] The ability of MXenes to rapidly intercalate a variety of cations is key for developing high rate electrodes for hybrid metal-ion capacitors and multi-valent ion batteries.^{[16–22]w}

Titanium carbide ($Ti_3C_2T_x$), the first reported and the best studied MXene, has the highest reported electronic conductivity among all MXenes (>10000 S/cm),^[23] good packing density (up to 4 g/cm³), and proton induced pseudocapacitance, which results in high volumetric capacitance, upwards of 1500 F/cm³ with high rate performance in relatively thin films.^[14] The 2D morphology, surface functionality, intercalated water layers, redox active transition metal oxide-like surfaces, and high electronic conductivity are the key factors for the high rate pseudocapacitive behavior of MXenes.^[24] It was reported that the origin of the pseudocapacitance of MXenes is mainly due to =O surface functional groups.^[25] However, the restacking of MXene sheets when they are reassembled into free-standing films impedes ion transport, limiting the overall rate performance.^[3,14] This restacking issue was circumvented through vertical alignment of liquid crystalline MXene electrodes, in which thickness independent capacitive behavior was demonstrated for industrial scale thicknesses (~ 200 μ m).^[3] Furthermore, methods using spacers such as carbon materials, polymers, and surfactants, or by the introduction of holes into the MXene sheets by chemical etching, were also used to improve electrochemical performance.^[22,26,27] However, these improvements were achieved at the expense of volumetric performance. There are no systematic studies on the influence of surface chemistry on the intrinsic electrochemical performance of titanium carbide electrodes. Previous work has shown that irreversible oxidation of Ti_3C_2 can increase the interlayer spacing, but this resulted in low capacitance due to the formation of titania and loss of electrochemically active titanium sites.^[28]

Herein, a new and simple approach of *in situ* anodic oxidation has been developed for improving the rate performance of restacked MXene electrodes. This controllable oxidation process slightly enlarges the interlayer spacing and introduces holes into the MXene structure, without damaging the electrochemical active sites, improving the rate performance of Ti_3C_2 . This finding may help in the design of advanced high-rate MXene based energy

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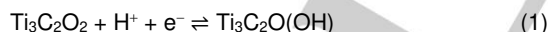
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storage devices, such as microsupercapacitors, energy storing textiles and electrochromic or energy-storing windows.

Results and Discussion

$\text{Ti}_3\text{C}_2\text{T}_x$ MXene operates at cathodic potentials and exhibits a pair of broad oxidation and reduction peaks in acidic electrolytes^[14]. The typical voltage window for cycling $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is negative (-1.2 V to -0.2 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$).^[13] The redox nature is attributed to the protonation/deprotonation of surface functional groups with concomitant changes of Ti redox state.^[29] However, at anodic potentials (> 0 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$), $\text{Ti}_3\text{C}_2\text{T}_x$ is prone to irreversible oxidation, as shown in Figure 1a. The reversible oxidation peak current (at a potential of -0.8 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) is only 14% of the magnitude of the current of the irreversible oxidation peak (at ~0.4 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$). Following irreversible anodic oxidation, $\text{Ti}_3\text{C}_2\text{T}_x$ becomes electrochemically inactive as evident from the reduction in the CV area (losing >50% of its initial capacitance) during cathodic potential window of operation (Figure 1b). This permanent change in the electrochemical behavior of $\text{Ti}_3\text{C}_2\text{T}_x$ is likely due to changes in the structure of $\text{Ti}_3\text{C}_2\text{T}_x$ beyond the modification of the surface composition.

To investigate the structural changes occurring due to irreversible oxidation, X-ray diffraction (XRD) patterns of $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes before and after oxidation are shown in Figure 1c. Interestingly, the (002) peak is downshifted, with a higher d -spacing of 1.5 nm, when compared to the (002) peak of pristine $\text{Ti}_3\text{C}_2\text{T}_x$, which has a typical d -spacing of 1.2 nm. Irreversible oxidation caused expansion of the titanium carbide lattice by changing the surface composition of $\text{Ti}_3\text{C}_2\text{T}_x$. By comparing the Raman spectra of pristine and anodically oxidized $\text{Ti}_3\text{C}_2\text{T}_x$, it is evident that the relative intensities of the MXene peaks at 205 and 723 cm^{-1} decrease and almost disappear (Figure 1d). The peaks at these two positions are assigned to out-of-plane vibrations of Ti, C, and O atoms in $\text{Ti}_3\text{C}_2\text{O}_2$, which is the origin of the pseudocapacitance of $\text{Ti}_3\text{C}_2\text{T}_x$, according to the following reversible redox reaction^[25]:



The decreased intensity of the peaks at 205 cm^{-1} and 723 cm^{-1} may be resulted from the directly removal of electrochemically active =O moieties on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$, resulting in diminished pseudocapacitance, or may be affected by the nearby defects and holes resulting that the out-of-plane vibrations became very weak. A broad peak is also observed in the range of 1100 to 1600 cm^{-1} following irreversible oxidation. This could be attributed to C-C bonds from amorphous carbon produced by the oxidation of $\text{Ti}_3\text{C}_2\text{T}_x$,^[30–32] which has been verified by the X-ray photoelectron spectroscopy (XPS) results showing a large amount of sp^3 bonding. This peak can also be due to the dissolution of oxidized titanium in the acidic electrolyte, which would expose carbon atoms on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$.

In order to study the effect of oxidation at low anodic potentials, cycling to 0.1 V vs $\text{Hg}/\text{Hg}_2\text{SO}_4$ was chosen as the potential for

partial oxidation (Figure 1a, dashed line). For controlling the extent of oxidation, multiple cyclic voltammetry (CV) sweeps were performed. The corresponding CV profiles at 100 mV/s are shown in Figure 2a and no significant changes can be observed. With an increase in the number of oxidation cycles, the reversible redox peaks gradually shift toward lower potentials and the peak current density increases slightly. The capacitive current density in the potential range of -0.4 to 0 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ also increases after the first sweep to 0.1 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ and remains almost constant during further cycles of partial oxidation. The current density in this potential range (-0.4 to 0 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) is mainly contributed by EDL capacitance, which is governed by the accessible surface area. Accordingly, the current density changes in this potential range imply that the interlayer space of $\text{Ti}_3\text{C}_2\text{T}_x$ is enlarged by a single CV sweep of partial oxidation and cannot be increased further with more cycles to the same potential. Similar results are obtained for the CVs in a negative potential window (-1.2 to -0.2 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) after partial oxidation, as displayed in Figure 2b. The increased current density for both the redox potential range (-1.2 V to -0.4 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) and EDL response region (-0.4 V to -0.2 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$), indicates improved charge storage. Even though the capacitance at low scan rates does not change much, the effect of partial oxidation is strongly pronounced at high scan rates. CVs for different scan rates are also shown in Figure S2 (Supporting Information) for comparison between the pristine and 9-cycles partially oxidized $\text{Ti}_3\text{C}_2\text{T}_x$ (0.1 V-9oxi). The advantage of 0.1 V-9oxi $\text{Ti}_3\text{C}_2\text{T}_x$ over pristine $\text{Ti}_3\text{C}_2\text{T}_x$ at higher scan rates indicates that partial oxidation increases the rate performance but not the intrinsic capacitance of $\text{Ti}_3\text{C}_2\text{T}_x$.

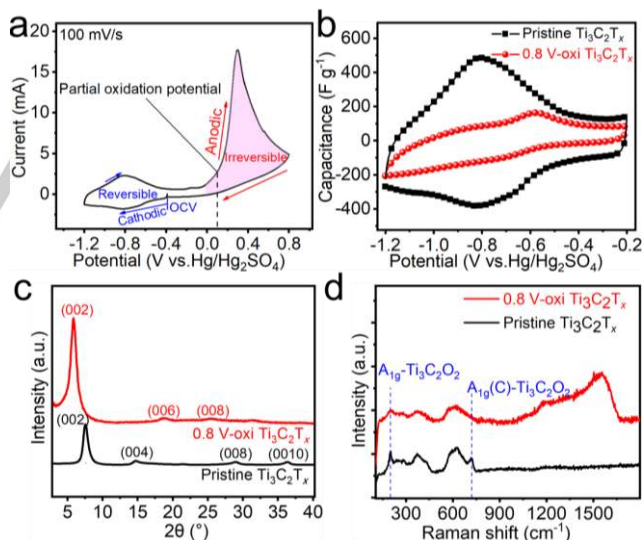


Figure 1. Reversible and irreversible electrochemical behavior of $\text{Ti}_3\text{C}_2\text{T}_x$. (a) Cyclic voltammogram (CV) of $\text{Ti}_3\text{C}_2\text{T}_x$ with a potential range beyond the stable operating potential of $\text{Ti}_3\text{C}_2\text{T}_x$ at a scan rate of 100 mV/s; (b) comparison of CVs of $\text{Ti}_3\text{C}_2\text{T}_x$ in the standard potential window for pristine MXene and after anodic oxidation at 0.8 V (0.8 V-oxi); *Ex situ* (c) XRD patterns and (d) Raman spectra of pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x$ anodically oxidized at 0.8 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$.

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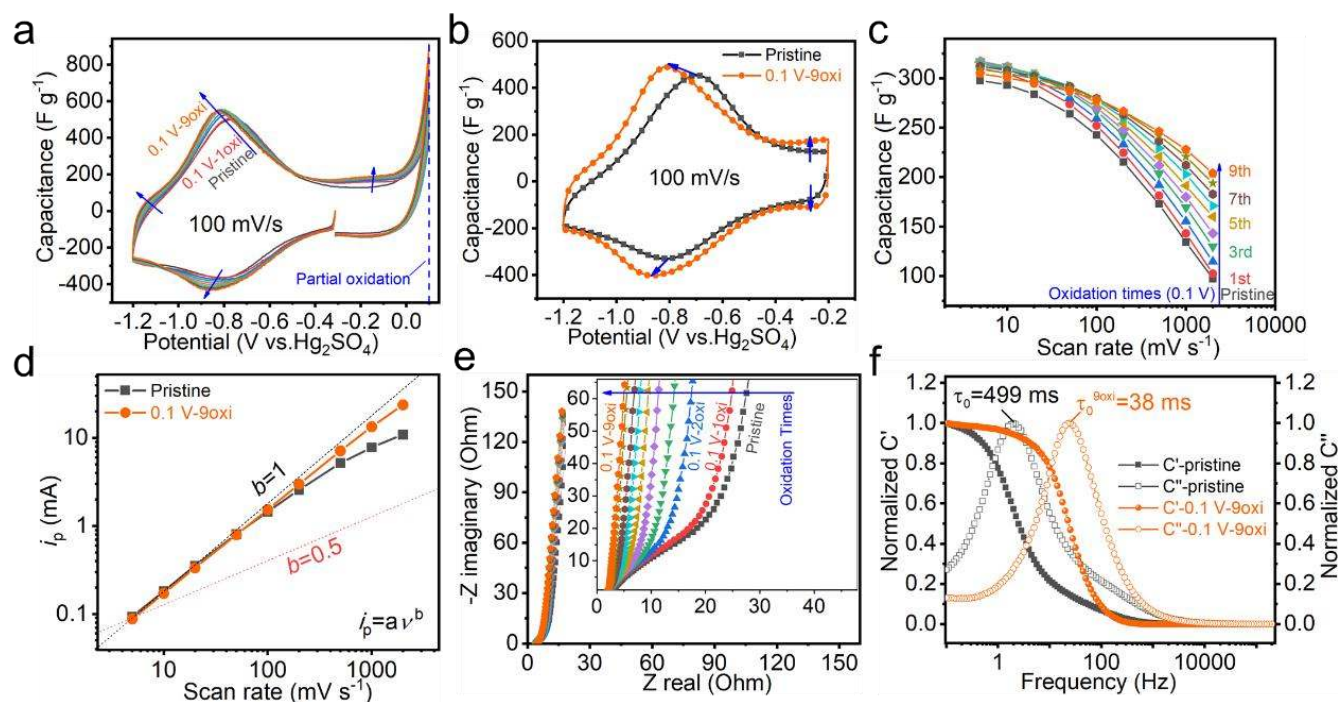


Figure 2. Controlling the rate performance of titanium carbide MXene through anodic oxidation. CV profiles of Ti₃C₂T_x (a) partially oxidized in 1M H₂SO₄ for nine cycles and (b) in the stable potential window before and after 9 cycles of partial oxidation (0.1 V-9oxi); (c) capacitance vs. scan rate; (d) plots of *b* values for pristine and 9-cycles oxidized Ti₃C₂T_x; (e) EIS spectra of Ti₃C₂T_x MXene after cycle of partial anodic oxidation; and (f) normalized real (C') and imaginary (C'') parts of capacitance versus frequency.

As a result, as shown in Figure 2c, the capacitance at 2000 mV/s increases significantly, as Ti₃C₂T_x is successively partially oxidized. The capacitance retention for 0.1 V-9oxi Ti₃C₂T_x at 2000 mV/s compared to that at 5 mV/s is 66%, which is almost two times higher than the capacitance retention of pristine Ti₃C₂T_x. It should be noted that the capacitance of Ti₃C₂T_x at lower scan rates (<20 mV/s) increases during the initial 5 cycles of partial oxidation but then decreases slightly when oxidized more than 5 cycles, as shown in Figure S3 (Supporting Information). The capacitance of 0.1 V-9oxi Ti₃C₂T_x at 5 mV/s decreases to nearly the same value as the pristine electrode, but then remains almost the same as the 0.1 V-8oxi Ti₃C₂T_x electrode as the scan rate increases to 2000 mV/s. In 3M H₂SO₄ electrolyte, the effect of anodic oxidation on the electrochemical performance of Ti₃C₂T_x has also been investigated and the same rate performance improvement was observed (Figure S4, Supporting Information). The oxidized Ti₃C₂T_x also showed excellent cycling performance with only a slight decrease in capacitance after 10000 cycles (Figure S13, Supporting Information). Anodic oxidation at different potentials can also be used to control the degree of oxidation (Figure S5, Supporting Information). Similar improvements in rate performance were observed for anodic oxidation performed below 0.3 V vs. Hg/Hg₂SO₄. When only one cycle of oxidation is performed, the best rate performance is obtained at 0.3 V, with 51% retention at 2000 mV/s of the initial capacitance at 5 mV/s. When the potential goes above 0.3 V, the capacitance decreases rapidly, likely due to complete oxidation of surface layer of Ti₃C₂T_x

and the formation of TiO₂. This result shows again that the rate performance can be tuned by controlling the degree of oxidation without decreasing the capacitance. To analyze the difference in charge storage kinetics between pristine and partially oxidized Ti₃C₂T_x, the relationship between the peak current and the scan rate are shown in Figure 2d. By using the equation

$$i_p = av^b, \quad (2)$$

where *v* is the scan rate and *i*_p is the peak current at different scan rates, and *a* and *b* are variables, the kinetic performance of the electrodes can be compared conveniently as the *b*-value is indicative of the charge storage kinetics. Surface controlled charge storage processes have a characteristic *b* value of 1, while diffusion-limited processes give *b* values of 0.5.^[33] For the pristine Ti₃C₂T_x film, the *b* value deviates from 1 when the scan rate is higher than 200 mV/s. However, after 9-cycles of partial oxidation, the *b* value is still near 1 up to scan rates of 2000 mV/s, further proving that partial oxidation improves the performance of Ti₃C₂T_x at high rates by improving accessibility to the MXene surface and minimizing diffusion limitations. Electrochemical impedance spectra (EIS) of partially oxidized Ti₃C₂T_x electrodes shown in Figure 2e are consistent with the rate performance data. The impedance of Ti₃C₂T_x in the medium frequency regime decreases gradually with partial oxidation cycle number, matching the gradually increasing rate performance. The decreased

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impedance in this frequency range corresponds to reduction in ion diffusion limitations, which contributes to the final rate performance. The improved electrochemical kinetics of the partially oxidized electrodes is further supported by their small relaxation time constants, τ_0 (the minimum time needed to discharge all energy stored with an efficiency greater than 50%).^[34] As shown in Figure 2f, τ_0 is around 500 ms for pristine

$\text{Ti}_3\text{C}_2\text{T}_x$ and $\tau_0^{90\text{xi}}$ is 38 ms, indicating that charge response of 0.1V-90xi $\text{Ti}_3\text{C}_2\text{T}_x$ is almost 13 times faster than pristine. The improvement in rate performance was also observed in KOH and Li_2SO_4 electrolytes, indicating that controlled anodic oxidation is universally applicable for improving the rate performance of $\text{Ti}_3\text{C}_2\text{T}_x$ in various electrolytes.

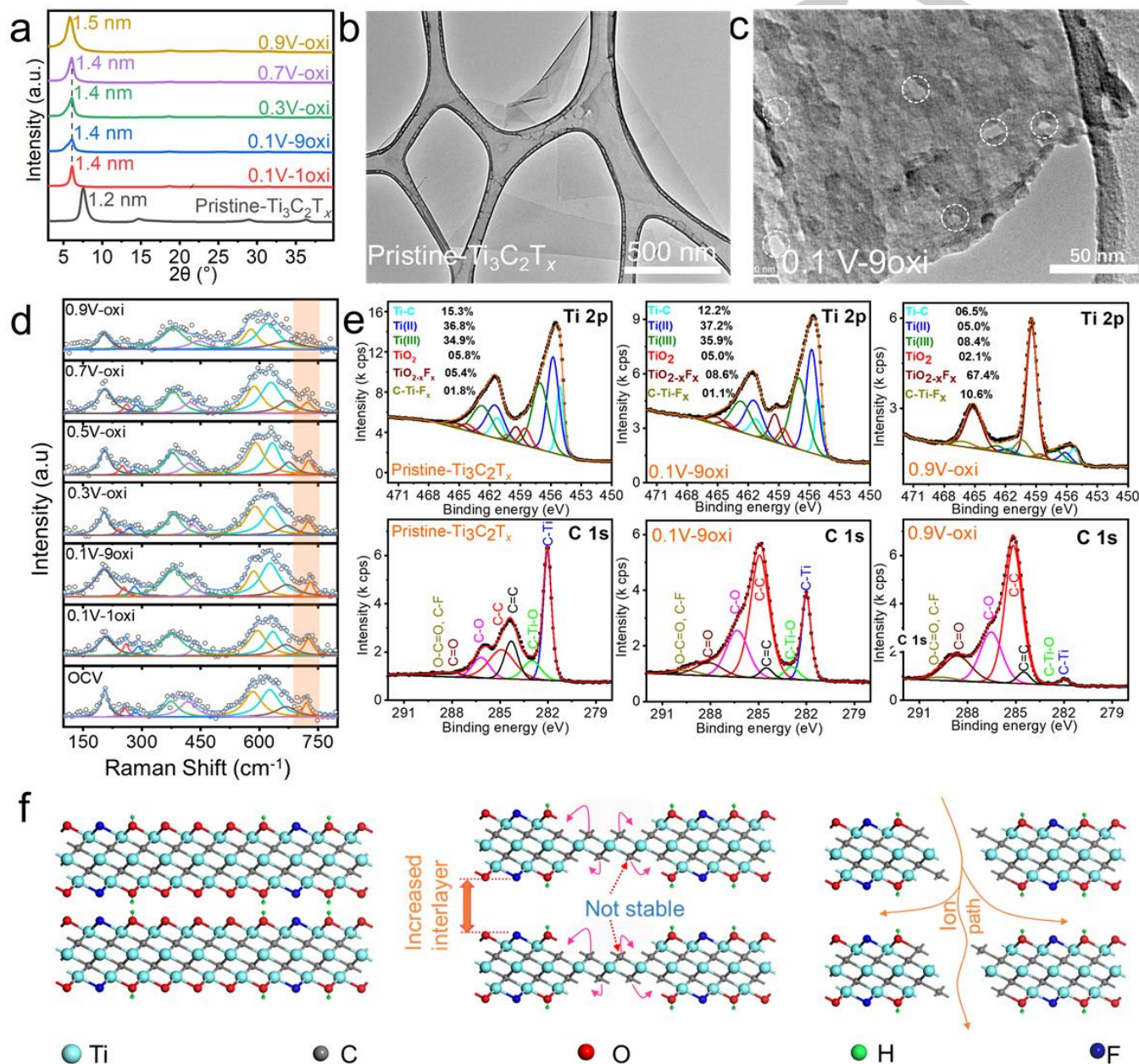


Figure 3. Understanding the mechanism of rate performance improvement of MXene electrodes. (a) XRD patterns of $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes oxidized at different potentials; TEM images of (b) pristine and (c) 0.1 V-90xi $\text{Ti}_3\text{C}_2\text{T}_x$ MXene; (d) *In situ* electrochemical Raman spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes at different anodic potentials; (e) Core level Ti(2p), C(1s) spectra for pristine, 0.1 V-90xi and 0.9V-oxi $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes; (f) schematic illustration of the anodic oxidation process.

RESEARCH ARTICLE

To understand the mechanism behind the rate performance improvements after partial oxidation, *ex situ* XRD experiments and *in situ* electrochemical Raman experiments were performed on the pristine $\text{Ti}_3\text{C}_2\text{T}_x$ and the oxidized $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes (Figure 3a and Figure 3d). The interlayer space can be increased at relatively low potential (0.1 V) and does not change noticeably until the potential increased to a higher value of 0.9 V (Figure 3b). The (002) peak of oxidized $\text{Ti}_3\text{C}_2\text{T}_x$ shifts toward smaller degrees, indicating increased interlayer space. For pristine $\text{Ti}_3\text{C}_2\text{T}_x$, the interlayer distance is 1.2 nm, which then increases to 1.4 nm by partial oxidation at 0.1 V. Oxidation at 0.9 V only increases the interlayer space by another 0.1 nm. Such kind of changes in the interlayer space is highly consistent with the current density changes in the double-layer capacitance region, as discussed in Figure 2a. High-potential oxidation results in dramatic changes to the surface chemistry as shown in Figure 3d. The peaks assigned to $\text{Ti}_3\text{C}_2\text{O}_2$ functional groups (205 cm^{-1} and 723 cm^{-1}) decrease significantly when the potential goes past 0.5 V and the G band of carbon appears (1580 cm^{-1} , Figure S7, Supporting Information). The removal of the $\text{Ti}_3\text{C}_2\text{O}_2$ group results in the dramatic capacitance fading for higher potential oxidation as shown in Figure 1b and Figure S5 (Supporting Information). In conclusion, oxidation at a safe potential of 0.1 V increases the interlayer spacing of $\text{Ti}_3\text{C}_2\text{T}_x$ while avoiding irreversible damage to the electrochemically active surface of 2D $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. As a result, improved high rate electrochemical performance is obtained without noticeable capacitance losses or even some improvement at low rates. Moreover, as shown in the TEM images in Figure 3b and 3c, the 2D $\text{Ti}_3\text{C}_2\text{T}_x$ sheets became porous following oxidation at 0.1 V for 9 cycles. Even more pores are visible when the electrode is oxidized at 0.9 V (Figure S1, Supporting Information). From a photograph from the *in situ* Raman microscope set up, we also observed a clear morphology change of the $\text{Ti}_3\text{C}_2\text{T}_x$ film from a smooth to a rough surface at 0.9 V (Figure S6, Supporting Information). This porous structure further facilitates permeation of the electrolyte through the stacked $\text{Ti}_3\text{C}_2\text{T}_x$ sheets leading to shortened ion diffusion pathways.

XPS investigations were performed to characterize the surface composition of the electrodes before and after oxidation and to determine if there were changes in the oxidation state of titanium. High resolution XPS spectra of Ti 2p and C 1s core levels from ($\text{Ti}_3\text{C}_2\text{T}_x$) samples (pristine, 0.1 V-9oxi, and 0.9 V-oxi) are shown in Figure 3e. We can clearly observe an increase of the contribution of components related to TiO_2 and $\text{TiO}_{2-x}\text{F}_x$ to the Ti 2p core level spectrum following anodic oxidation. Furthermore, we have observed a decrease of the contribution of Ti-C bonds relative to the contribution of C-C, C-O, and C=O bonds to the C 1s core level spectrum following electrochemical oxidation. In summary, during the oxidation process, C-Ti bonds are gradually broken and C-C and $\text{TiO}_{2-x}\text{F}_x$ species are formed.

Based on the *in situ* Raman, TEM, *ex situ* XRD, and XPS results, a possible mechanism of the micro-structure changes occurring during oxidation is schematically illustrated in Figure 3f. First, part

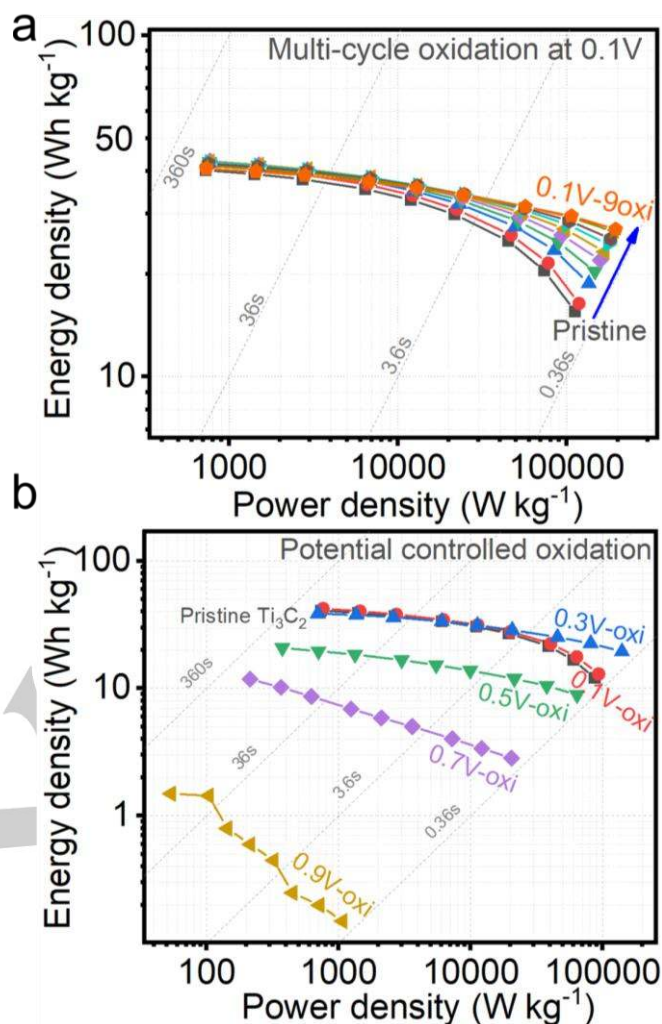


Fig. 4. Specific energy vs. power density plots of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes with varying degrees of anodic oxidation. Ragone plots of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes after (a) repeated oxidation cycles at 0.1 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) and (b) after a single oxidation cycle at different potentials (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$).

of the surface Ti atoms connected to =O moieties are removed during the anodic de-functionalization process forming $\text{TiO}_{2-x}\text{F}_x$, according to the XPS results. Several C atoms are then exposed at the surface so that the original Ti-C-Ti structure at the surface produces C atoms which likely bond with adjacent exposed C atoms with free electrons, forming a C-C bond (most likely in the form of amorphous carbon according to the XPS and Raman results). Continued oxidation and formation of TiO_2 will result in disruption of the MXene sheets and significant capacitance losses. The pin holes observed in the SEM and TEM micrographs are also likely being formed during this process (Figure S1, Supporting Information).

In summary, controlled anodic oxidation increases the interlayer space of $\text{Ti}_3\text{C}_2\text{T}_x$ and gradually creates pores in the 2D

RESEARCH ARTICLE

nanosheets without significantly depleting the electrochemically active oxygen functional groups on the surface of $Ti_3C_2T_x$, resulting in porous $Ti_3C_2T_x$ electrodes with improved ion transport. The improved high-rate charge storage capability of partially oxidized $Ti_3C_2T_x$ electrodes enables simultaneous high-power and high energy performance across a wider range of power densities, as shown in Figure 4. Though it is not advisable to calculate energy and power densities for 3-electrode cells, comparison of these performance metrics here is useful and fair since we are only comparing the energy and power densities of the electrodes from this study. All the electrodes exhibit a maximum specific energy density of $\sim 40 \text{ Wh kg}^{-1}$ at a power density of $\sim 750 \text{ W kg}^{-1}$. The energy density delivered by pristine $Ti_3C_2T_x$ is only 15 Wh kg^{-1} at a power density of 130 kW kg^{-1} , while the $0.1\text{V-9oxi } Ti_3C_2T_x$ delivers a much higher energy density of 27 Wh kg^{-1} at a higher power density of 193 W kg^{-1} . As shown in Figure 4b, there is an improvement in the high power performance of $Ti_3C_2T_x$ partially oxidized at relatively low potentials (0.1 V and 0.3 V vs. Hg/Hg_2SO_4). However, when the oxidation potential is extended beyond 0.3 V, both the energy and power densities decrease rapidly, indicating excessive oxidation. Based on the improvements in the electrochemical performance of the partially oxidized $Ti_3C_2T_x$ at high rates, this simple anodic oxidation can be used as pre-treatment (conditioning) to improve MXene-based supercapacitors.

Conclusion

The electrochemical performance of $Ti_3C_2T_x$ MXene was improved through a controlled electrochemical oxidation process. Repeated cycling of $Ti_3C_2T_x$ electrodes to anodic potentials slightly beyond their typical operational window increases the interlayer spacing between the 2D nanosheets and introduces pores into the MXene layers without damaging the electrochemically active sites. This optimized partial oxidation process can double the capacitance retention of $Ti_3C_2T_x$ in acidic electrolytes at high-rates. Partially oxidized $Ti_3C_2T_x$ electrodes exhibited $\sim 30\%$ improved kinetics and hence improved rate performance over pristine MXene electrodes.

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Keywords: MXenes, high-rate energy storage, pseudocapacitance, anodic oxidation, surface chemistry

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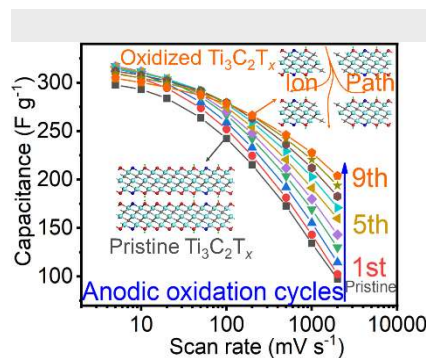
RESEARCH ARTICLE

Entry for the Table of Contents

Layout 1:

RESEARCH ARTICLE

Controllable anodic oxidation of 2D $\text{Ti}_3\text{C}_2\text{T}_x$ improves the rate performance of supercapacitor electrodes.



Jun Tang, Tyler S. Mathis, Narendra Kurra, Asia Sarycheva, Xu Xiao, Mohamed N. Hedhili, Qiu Jiang, Husam N. Alshareef, Baomin Xu, Feng Pan, and Yury Gogotsi*

Page No. – Page No.

Title