Probing the mechanism of high capacitance in two-dimensional titanium carbide using in-situ X-Ray absorption spectroscopy

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The field of supercapacitors (electrochemical capacitors) is constantly evolving. The global motivation is to create devices that possess a significant energy density without compromising the power density^[1]. To achieve this goal, new materials must be discovered and complex electrode architectures developed^[2].

Several decades ago, impressive electrochemical properties of the hydrated ruthenium oxide were discovered.^[3] Important features of RuO₂ are: i) good conductivity, which is not typical of transition metal oxides, and, ii) surfaces that participate in reversible redox reactions during charge/discharge, enabling capacitance of 1000 to 1800 F/cm³ for thick (>20 μm) electrodes^[4] and up to 2800 F/cm³ for thin films (50-100 nm).^[5] However, the high cost of this material, along with a significant decline in charge storage capacitances with increased electrode thicknesses outweighs its outstanding volumetric capacitance, rendering this material unsuitable for applications beyond microscale energy storage.^[4a]

In search for alternatives, MXenes - a new but quickly expanding family of two-dimensional transition metal carbides (Nb₂C, Ti₃C₂, Ta₄C₃, etc.), captured the attention of researchers recently.^{[6],[7]} MXenes possess excellent conductivity, and offer a broad variety of chemistries.^[7a] MXenes are produced by the selective removal of the atomically thin aluminum layers from the MAX phase^[8] structure, e.g., Ti₃AlC₂, via wet chemistry routes,

such as etching in HF,^[9] NH₄HF₂^[10] or acidic solutions of fluoride salts, i.e. LiF in HCl.^[11] The described treatments result in mixed fluorine- and oxygen-containing terminations of transition metal atoms on the MXene surfaces. Thus, the general formula describing MXene composition is M_{n+1}X_nT_x, where M is an early transition metal, X is carbon and/or nitrogen, n = 1, 2 or 3, T is surface termination (-F, -OH, =O) and x is number of surface groups per formula unit^[7a].

This combination of terminated transition metal on the surface with a metallically conductive carbide core is believed to be key to the MXenes' promising performance as electrode materials for energy storage applications, such as Li-ion batteries,^[12] Li-S batteries^[13] and supercapacitors.^[6] In particular, impressively high volumetric capacitance reaching 900 F/cm³ (comparable only with hydrated RuO₂) was measured for Ti₃C₂T_x in aqueous electrolytes.^[11, 14] Our previous studies revealed that spontaneous intercalation of some cations takes place when MXene samples are exposed to aqueous electrolytes.^[6] In-situ XRD showed that variations of the distance between the Ti₃C₂T_x layers (which is proportional to the *c* lattice parameter, *c*-LP) during cycling is small (< 5%) and no phase changes were detected.^[6] Electrochemical quartz crystal admittance (EQCA) studies of Ti₃C₂T_x multilayer particles in several aqueous electrolytes with different cations revealed that cation insertion is accompanied by electrode deformations (expansion/contraction), facilitated by the presence of water molecules. These deformations occur so quickly, however, that they closely resemble 2D ion adsorption at solid-liquid interfaces.^[15] Moreover, it was found that surface chemistry has a significant effect on the capacitive response in acids: decreased amount of F-terminations, relative to those of O and OH, resulted in a significant increase in specific capacitance, i.e. almost doubling it.^[14]

These results notwithstanding, the understanding of what fundamental processes are responsible for the MXenes promising performance has been lacking. While double layer ion adsorption can be ruled out as the main mechanism, due to the relatively low specific surface

area of multi-stacked MXenes,^[6] possible pseudocapacitive storage mechanisms can be hydrogen storage or redox coupled capacitance of MXene (**Figure 1a**). In this communication, we report on a set of electrochemical experiments coupled with in-situ X-ray absorption spectroscopy (XAS) that shed light on the mechanism of capacitance in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene.

Typical electrochemical performance of the MXenes can be characterized by the nearly rectangular cyclic voltammetry loops as shown in **Figure 1b** for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (produced by etching of Ti_3AlC_2 MAX phase in the LiF- HCl solution)^[11] in 1 M H_2SO_4 . To ensure that the observed electrochemical behavior is not due to parasitic reactions and also to evaluate possible contributions from hydrogen evolution, a series of constant potential experiments - during which the current change with time was monitored (**Figure 1c**) – were performed. It is well established that di-hydrogen (H_2) evolution is a faradic process and its intensity (i.e., current) is dependent on the over-potential value. By collecting chronoamperometry (CA) data, at various fixed potentials, a better understanding of the underlying processes can be obtained - as compared to the cyclic voltammetry (CV), which is unlike CA is dynamic: the sample is subjected to a certain potential for no more than several seconds per cycle.

Based on the observed current density values (Figure 1c), we categorized the potentials at which the CA was performed into three regimes: i) a “safe” region where the current density does not exceed ~ 0.1 A/g (marked in green in Figure 1c), and no H_2 evolution is observed, ii) a H_2 -“storage” region, where the current density is in the 0.1-0.3 A/g range, (marked in yellow in Figure 1c), and where no noticeable bubble formation is observed. In this region, the CA profiles are smooth and it can be used when the electrode is cycled at scan rates of $> \sim 20$ mV/s, and, iii) a H_2 -evolution region (marked pink in Figure 1c), where the current density > 0.3 A/g and active H_2 evolution is observed. The onset of hydrogen evolution (beginning of Regime 3) limits the cathodic potential for the use of MXene electrode. It is worth noting, that this approach of selecting a voltage window and the estimating contributions of various parasitic reactions is applicable to other supercapacitor

materials/devices as well. In this case, it allowed us to evaluate the extent of H₂ evolution by simply measuring the current transients, where H₂ bubble formation is mirrored by an uneven current profile. It follows, that the lowest negative, and “safe”, voltage limit for Ti₃C₂T_x in 1 M H₂SO₄ is -0.35 V vs. Ag/AgCl.

As noted above, one of the potential mechanisms for high capacitance is electrochemical hydrogen storage, as has been shown for some carbon materials.^[16] However, it is unlikely to have a significant contribution due to i) acidity of the electrolyte used: it was reported that hydrogen storage has significant contribution to energy storage only in basic electrolytes, and ii) low specific surface area of MXenes.^[16]

We now turn our attention to intercalation pseudocapacitance, i.e. redox processes in the Ti₃C₂T_x during cycling. If that is the case, then Ti atoms would be changing their oxidation state during electrochemical cycling.

In order to investigate it, we performed electrochemical *in-situ* X-ray absorption near edge structure spectroscopy (XANES) for the Ti K-edge. It is well known that XANES is a powerful technique to probe oxidation states of elements, it was successfully applied in the past to shed light on the storage mechanism of MnO₂^[17] and RuO₂^[18] by tracking changes in metal edge position during electrochemical cycling. Herein, we monitored the shifts in the Ti edge energy at different points of the charge and discharge. *In situ* Ti K-edge XAS spectra were collected - for a sequence of applied potentials - starting from 0.275 and ending at -0.35 V, and then from -0.2 to 0.345 V on reverse scan, as shown on the CV curve in **Figure 2a**. The Ti K-edge XANES spectra presented in **Figure 2b** and **c** feature a relatively weak pre-edge peak ‘A’ at 4971 eV, and a strong main absorption peak ‘B’ at around 4985 eV. The weak pre-edge absorption involves the hybridization of the metal *3d* and carbon *2p* orbitals.^[19] That peak ‘A’ can be assigned to the transition of a *1s* electron to the hybridized t_{2g} (Ti *3d*+C *2p*) and e_g (Ti *3d*+C *2p*) orbitals. The main absorption peak ‘B’, however, is due to the dipole allowed transition of *1s* electrons to unoccupied Ti *4p* states.

Although the spectra did not show significant difference in the shape, the edge shifts are clearly recognized in both charge and discharge potential sweeps (insets in Figure 2b and c). A plot of the Ti K-edge energies, at half height of normalized XANES spectra, *versus* applied potential (**Figure 2d**) clearly shows the changes at each potential. Sweeping from 0.275 to -0.35 V, shifts the Ti edge to lower energies. Such a shift is consistent with a decrease in the average oxidation state of the Ti atoms. During the reverse scan to 0.345 V, the XANES spectrum shifts back to the higher energy (and higher Ti oxidation state).

This moderate edge shift in the XANES energy - corresponding to a reduction/oxidation of the Ti - is consistent with our previous study of $\text{Ti}_3\text{C}_2\text{T}_x$ in Li-ion batteries.^[20] In that case, an edge shift of ≈ 0.6 eV was observed over a potential window of ≈ 3.0 V (vs. Li^+/Li) during lithiation (i.e., reduction of Ti).^[20]

There is clear change in Ti oxidation state during cycling. To quantify the change, we plotted the Ti K-edge XANES spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ at applied potentials (i.e., -0.4 V and 0.1 V) together with the reference Ti oxides (i.e., TiO and anatase TiO_2) in **Figure 3a**. Based on the linear dependence between edge energy and Ti average oxidation state^[21], the latter can be estimated in the MXene sample during cycling (**Figure 3b**). From the inset shown in Figure 3b, we see that the average oxidation state of Ti changes from 2.33 to 2.43 (i.e. by $\approx 0.1 \bar{e}$ per Ti atom) over a 0.7 V window.

To explore the viability of this value we estimated capacitance using the following formula: $C_g = F \cdot \delta / (MW \cdot V)$, where C_g [F/g] stands for gravimetric capacitance, F [96485 C/mol] is a Faraday constant, δ is number of electrons participating in electrochemical reaction (equal to $0.1 \cdot 3 = 0.3$ in our case since there are 3 Ti atoms in $\text{Ti}_3\text{C}_2\text{T}_x$), MW [g/mol] is molar weight, V [V] is voltage window (0.7 V in this case) and assumed electrochemical reaction is:

Since the molar weights for O (16), OH (17) and F (19) are close, the overall formula weight can be assumed to be 202 g/mol. Thus we get specific capacitance values of 205 F/g. These values are in a good agreement with the experimental specific capacitances measured herein for $\text{Ti}_3\text{C}_2\text{T}_x$, which are ~ 230 F/g (when measured in Swagelok cell). Please note that in *in situ* XAS cell we measured specific capacitance of ~ 150 F/g (for *in situ* experiments, a hole was drilled in the center of the cell and it was impossible to create a good contact between the electrode and the current collector).

In conclusion, we performed a thorough analysis of the electrochemical behavior of the $\text{Ti}_3\text{C}_2\text{T}_x$ and analyzed factors contributing to MXene' capacitance. We demonstrated a procedure for the safe voltage window selection, which can be applied to other electrochemical systems and that provides an important insight into electrolyte decomposition processes. Electrochemical *in situ* XAS measurements detected changes in Ti oxidation state during cycling. Even though this method is semi-empirical and provides rough estimation, the estimated value is comparable with the value that we back-calculated from the sample's gravimetric capacitance assuming redox-only capacitance. Therefore, we can conclude that electrochemical behavior of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in sulfuric acid is predominantly pseudocapacitive. This makes $\text{Ti}_3\text{C}_2\text{T}_x$ MXene one of very few examples of materials that exhibit “true” pseudocapacitive behavior: it presents a continuous change in titanium oxidation state during charge/discharge, producing rectangular-shaped CVs. This behavior can be attributed to 2D nature of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene: spontaneous ion intercalation naturally provides access to electrochemically active transition metal oxide surfaces, while the conductive carbide layer ensures rapid charge transfer. Those properties are not available in titanium oxide or cubic TiC. The results obtained herein are important for another reason: namely, they indicate, as a first approximation, that the average Ti oxidation state in $\text{Ti}_3\text{C}_2\text{T}_x$ is much closer to +2 than +4.

Experimental Section

Electrochemical measurements: Preliminary electrochemical measurements were performed in a 3-electrode Swagelok cell, with Ag/AgCl as reference electrode, 6 mg $\text{Ti}_3\text{C}_2\text{T}_x$ electrode (containing 5 wt. % of PTFE binder and 5 wt. % of carbon black) as working electrode and 33 mg AC (containing 5 wt. % of PTFE binder) as counter electrode. During all measurements, the overall cell potential was monitored in order to controllably translate into the 2-electrode cell geometry used in the *in situ* XAS measurements.

In-situ X-ray Absorption Spectroscopy (XAS): In-situ Ti K-edge XAS measurement were performed at beamline X18A at the National Synchrotron Light Source (NSLS) of the Brookhaven National Laboratory (BNL) using a Si(111) double-crystal monochromator, detuned to 40% of its original maximum intensity to eliminate high-order harmonics.

The spectroscopic data was collected in fluorescence mode with a passivated implanted planar silicon (PIPS) detector in grazing incident geometry. The PIPS detector was placed normal to the incident beam and at a 45° angle to the sample. The Ti K-edge energy, 4966 eV, was calibrated using the first inflection point of the edge region of a metallic Ti foil recorded before and after measurement.

For the in-situ XAS measurements, during electrochemical testing, we used a two-electrode 2032 coin-type cells, with a hole (diameter: 3 mm) drilled on the working electrode side. The MXene served as the working electrode, and the activated carbon as the counter electrode. A glass fiber separator (Whatman) was soaked in a 1M H_2SO_4 aqueous electrolyte. The hole was sealed with a Mylar film.

Detailed information on sample and electrode preparation, electrochemical measurements can be found in Supporting Information file.

Supporting Information

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

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Figure 1. Electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. a) Schematic of $\text{Ti}_3\text{C}_2(\text{OH})_2$ structure - where atoms of Ti are yellow, C are gray and OH are red - and possible contributions of charge transfer to the capacitance, b) Cyclic voltammetry of $\text{Ti}_3\text{C}_2\text{T}_x$ in 1 M H_2SO_4 at 1 and 20 mV/s, c) Chronoamperometry data collected at different potentials.

Figure 2. Electrochemical *in situ* XAS data. a) Cyclic voltammogram collected in *in situ* XAS electrochemical cell at 1 mV/s in 1M H₂SO₄ electrolyte. Ti K-edge XANES spectra were collected, b) between 0.3 and -0.35 V and, c) between -0.2 to 0.35 V (vs. Ag/AgCl), d) Variation of Ti edge energy (at half height of normalized XANES spectra) vs. potential during full potential sweep between -0.35 to 0.35 V.

Figure 3. a) Ti K-edge XANES spectra of Ti₃C₂T_x at -0.4 V (blue line) and 0.1 V (green line), together with those of TiO (red line) and TiO₂ (black line). b) Average Ti oxidation state determination in Ti₃C₂T_x at various applied potentials (see inset), using the Ti K-edge energy shift of the reference TiO and TiO₂ compounds.

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Electrochemical *in situ* X-ray absorption spectroscopy of 2D titanium carbide MXene was used to probe mechanism of high capacitance of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. Changes in the Ti oxidation state were detected during cycling. This finding confirms that most of the electrochemical behavior of $\text{Ti}_3\text{C}_2\text{T}_x$ is due to changes in the oxidation states of the Ti, i.e. pseudocapacitance.

Keywords: capacitance, two-dimensional, MXene, in situ XAS, pseudocapacitance

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Title: Probing the mechanism of high capacitance in two-dimensional titanium carbide using in-situ X-Ray absorption spectroscopy

ToC figure

Supporting Information

Probing the mechanism of high capacitance in two-dimensional titanium carbide using in-situ X-Ray absorption spectroscopy

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Ti₃C₂T_x MXene synthesis: 30 mL of 6 M solution of hydrochloric acid (Fisher, technical grade) in distilled water was added to 1.98 g of LiF (Alfa Aesar, 98+%). The mixture was stirred for 5 minutes to dissolve the salt.

Three grams of Ti₃AlC₂ (synthesis description can be found elsewhere^[S1]) powders were then carefully added, over the course of 10 min., into the LiF containing solution in order to avoid its overheating as a result of the exothermic nature of the reactions. The reaction mixture was then held at 35 °C for 45 h under constant stirring, after which the mixture was washed ~ 5 times by the addition of distilled water, centrifugation (3500 rpm x 5 minutes for each cycle), and decantation of the supernatant, until the supernatant reached a pH of approximately 6. The final powder, with a small amount of water, was filtered through a cellulose nitrate filter (0.22 µm pore size).

Ti₃C₂T_x electrode preparation: Electrodes were prepared by mechanical processing of the pre-mixed slurry, containing ethanol (190 proof, Decon Laboratories, Inc.), Ti₃C₂T_x powder, polytetrafluoroethylene (PTFE) binder (60 wt.% in H₂O, Aldrich) and carbon black. The resulting electrodes used for all experiments contained 90 wt. % of Ti₃C₂T_x, 5 wt. % of carbon black, 5 wt. % of PTFE and were 50-100 µm thick with a mass density per unit area of 6-9 mg/cm².

Activated carbon (AC) counter electrodes: Activated carbon (AC) film electrodes were prepared following the same procedure as for the Ti₃C₂T_x electrodes, but without any

conductive additive. Resulting AC electrodes composition was 95 wt. % of YP-50 activated carbon (Kuraray, Japan) and 5 wt. % of the PTFE. They were 100-150 μm thick with mass density per unit area of 10-25 mg/cm^2 .

Cyclic voltammetry was performed using scan rates from 1 mV/s to 100 mV/s using a VMP3 potentiostat (Biologic, France). Chronoamperometry data was collected at -0.35, -0.3, -0.25, -0.2, -0.15, -0.1, -0.05, 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 V vs. Ag/AgCl.

In-situ X-ray Absorption Spectroscopy (XAS), additional information: Before collecting XAS data, the cell was subjected to ten CV cycles, with scan rate of 10 mV s^{-1} after which CV at scan rate of 1 mV s^{-1} was collected (Fig. 2a). The applied potentials during cyclic voltammetry were held constant for at least 25 min (until a steady-state current was attained) before the *in situ* XAS measurement and during the XAS signal acquisitions (about 30 min) as well. X-ray absorption near edge structure (XANES) spectra were processed using the ATHENA software package.^[S2] The photoelectron energy origin, E_0 , was chosen at the half-height of the normalized absorption edge jump.

Reference materials TiO (99.5% purity, metals basis) and TiO₂ (99.9%, metal basis) were purchased from Alfa Aesar.

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