Supporting Information for

The Impact of Cation Intercalation on the Electronic Structure of Ti₃C₂T_x MXenes in Sulfuric Acid

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reference electrode

counter electrode

Figure S1. Schematic of the electrochemical flow cell used in this work for in situ XAS. A silicon nitride window (1.0 mm x 0.5 mm) transparent to soft X-rays is used to separate the electrolyte environment (10 mM H₂SO₄ in this work) from the vacuum chamber (~10⁻⁶ mbar). The zoom in on the right shows that the window consists of a 75 nm-thick silicon nitride layer coated with a 10 nm-thick gold layer (5 nm of chromium was used as an adhesive layer, these membranes were purchased from Silson). The cation-intercalated Ti₃C₂T_x MXenes were drop-cast on the membrane and dried in air before mounting in the cell. The 10 mM H₂SO₄ aqueous electrolyte was flown through using a syringe pump.

Table S1: The *c*- lattice parameter of pristine, Li-, Na-, K-, and Mg-intercalated Ti₃C₂T_x MXenes before and after exposure to 10 Mm H₂SO₄.

MXene sample	<i>c</i> -lattice parameter (Å)	<i>c</i> -lattice parameter (Å) After exposure to 10 mM H₂SO₄	Difference (Å)
Pristine Ti ₃ C ₂ T _x	24.76	27.01	+2.25
Li-Ti ₃ C ₂ T _x	23.81	24.60	+0.79
Na-Ti ₃ C ₂ T _x	23.69	25.17	+1.48
K-Ti₃C₂T _x	24.46	25.24	+0.78
Mg-Ti ₃ C ₂ T _x	28.58	29.54	+0.96



Figure S2. O K-edge XA spectra of dried pristine, Li-, Na-, K-, and Mg-intercalated $Ti_3C_2T_x$ MXene samples and TiO_2 nanoparticles dispersed initially in water measured in TEY mode. In Li- and Na- intercalated $Ti_3C_2T_x$ MXenes, a peak is found at about +0.6 eV compared to the t_{2g} contribution, which is tentatively attributed to Li-O or Na-O bonds.



Figure S3. XA spectra at the K L-edge measured in TEY mode of dried K-intercalated $Ti_3C_2T_x$ MXene samples (initially dispersed in H_2O and 10 mM H_2SO_4) under vacuum conditions. The XA spectra show the two distinctive peaks of the K L-edge after K⁺ intercalation (black) and then exposure to the 10 Mm H_2SO_4 (blue).



Figure S4. Normalized XRD patterns of pristine, Li-, Na-, K-, and Mg-intercalated $Ti_3C_2T_x$ MXenes. Before and after dispersion in H_2SO_4 then dried in (a) air and (b) dried in air followed by vacuum annealing at 110 °C for 4h. In (a) the XRD patterns showing the 002 diffraction order peak before (solid line) and after dispersion in 10 mM H_2SO_4 (dotted line). In (b) thinner lines are for H_2SO_4 dispersed samples after vacuum annealing while thick lines are for as prepared samples after vacuum annealing.



Figure S5. XA spectra measured in TEY mode of dried samples (initially dispersed in 10 mM H₂SO₄) under vacuum conditions at the Ti L-edge of pristine, Li-, Na-, K-, and Mg-intercalated Ti₃C₂T_xMXenes. There are three distinctive regions, the feature (1) shows no change in the Ti oxidation state as the pre-edge region of these different cation-intercalated MXenes does not shift relative to each other. The onset energy position of these cation-intercalated Ti₃C₂T_x MXenes significantly shifts to lower energies relative to the TiO₂ NPs. The feature (2) shows no intense L₃ t_{2g} peak, suggesting lower Ti oxidation state compared to the samples initially dispersed in water. The feature (3) reveals no clear L₂ e_g peak intensity, which agrees with the lower observed Ti oxidation state from the other two features. These XA spectra are compared to the Ti L-edge of TiO₂ NPs.



Figure S6. In situ chronoamperometry shows the current response in Na-, K-, and Mg-Ti₃C₂T_x MXene samples investigated in this study. These current responses demonstrate that the electrochemical oxidation is achieved within the first minutes. The XA spectra were recorded over several hours and no clear changes were observed over time, therefore irreversible oxidation of the MXene samples was already achieved by the first spectrum collected.



Figure S7. In situ Ti L-edge XA spectra of Na-Ti₃C₂T_x MXenes in 10 mM H_2SO_4 at open potential (brown) compared to +0.6 V (black) vs. Ag/AgCl reference electrode. The spectra indicate changes in their oxidation states as demonstrated by the relative shift in their pre-edge onset energy positions.



Figure S8. In situ Ti L-edge XA spectra of K-Ti₃C₂T_x MXenes in 10 mM H₂SO₄ at open potential (violet) compared to +0.6 V (black) vs. Ag/AgCl reference electrode. The spectra are almost identical, indicating very similar Ti oxidation states, as demonstrated by the same pre-edge onset energy positions. However, the t_{2g} peak at +0.6 V applied potential is enhanced relative to the e_g peak which could indicate a relatively higher Ti oxidation state.



Figure S9. In situ Ti L-edge XA spectra of Mg-Ti₃C₂T_x MXenes in 10 mM H₂SO₄ at open potential (cyan) compared to +0.6 V (black) vs. Ag/AgCl reference electrode. These spectra indicate changes in Ti oxidation state as demonstrated by a relative shift in the pre-edge onset energy position as well as the increase of the relative intensity of the L₃ t_{2q} peak.



Figure S10. In situ Ti L-edge XA spectra of different cation-intercalated $Ti_3C_2T_x$ MXenes in 10 mM H_2SO_4 and +0.6 V applied potentials vs. Ag/AgCl. (a) after introducing the sulfuric acid to different cation-intercalated $Ti_3C_2T_x$ MXenes at open circuit potential including the error bar. (b) Na- $Ti_3C_2T_x$. (c), K- $Ti_3C_2T_x$. (d), Mg- $Ti_3C_2T_x$. The spectrum in black in (b), (c), and (d) corresponds to +0.6 V applied potential. The error bar of each XA spectrum is shown in green.