Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Materials for

Tracking ion intercalation into layered Ti_3C_2 MXene films across length scales

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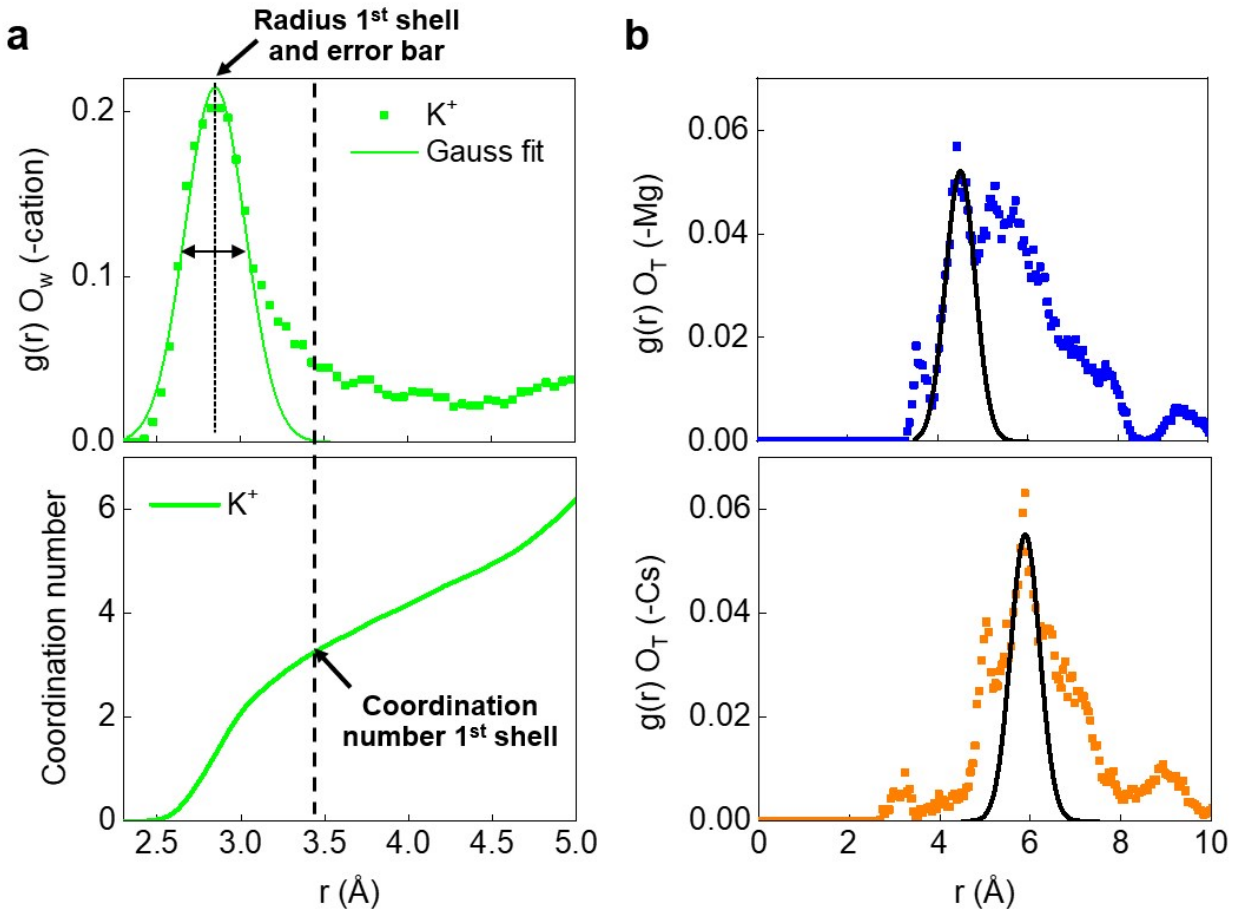


Figure S1. First peak analysis in g(r). (a) First peaks are fitted by gaussian curves to extract position, width, and area under the peaks (upper panel). The standard deviations of the gaussian peaks are equal to the corresponding error bars in the plots vs. distance in Figure 1c of the main text. The integral of g(r) allows to determine the number of neighbors around cations (bottom panel), and the integral to the first minimum (dash line) gives the coordination number. (b) First peak fit for Cs^{+} and Mg^{2+} to extract the number of neighbors around them from terminational oxygen. In cases where the first peak in g(r) was significant smaller than the second, the position of the second peak was used to determine the cation distance.

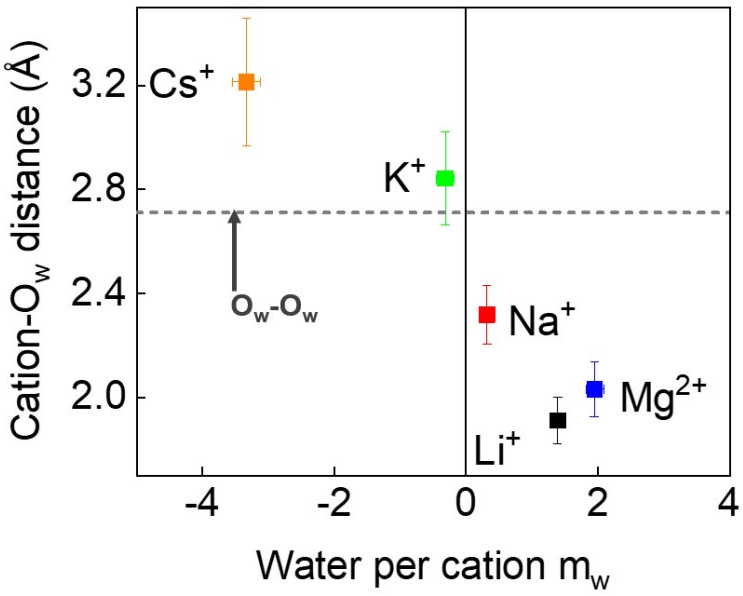


Figure S2. Cation/water exchange reactions. Relation between cation-O_w distance and reported values for water exchange in Ti_3C_2 MXene per cation measured by EQCM.[1] Water per cation m_w defines the number of water molecules co-intercalated with cations or extracted from the MXene layers during intercalation of cations.

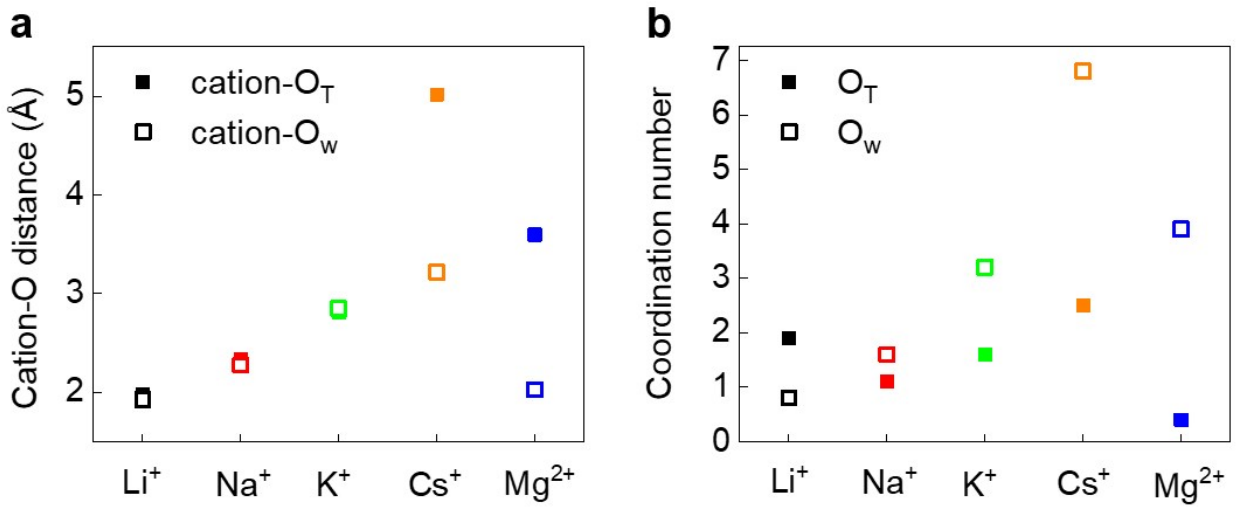


Figure S3. First peak analysis in g(r) summary. (a) The distance obtained from g(r) between cation and terminational oxygen as well as oxygen in water. (b) Coordination numbers counting the coordination with water and MXene surface terminations.

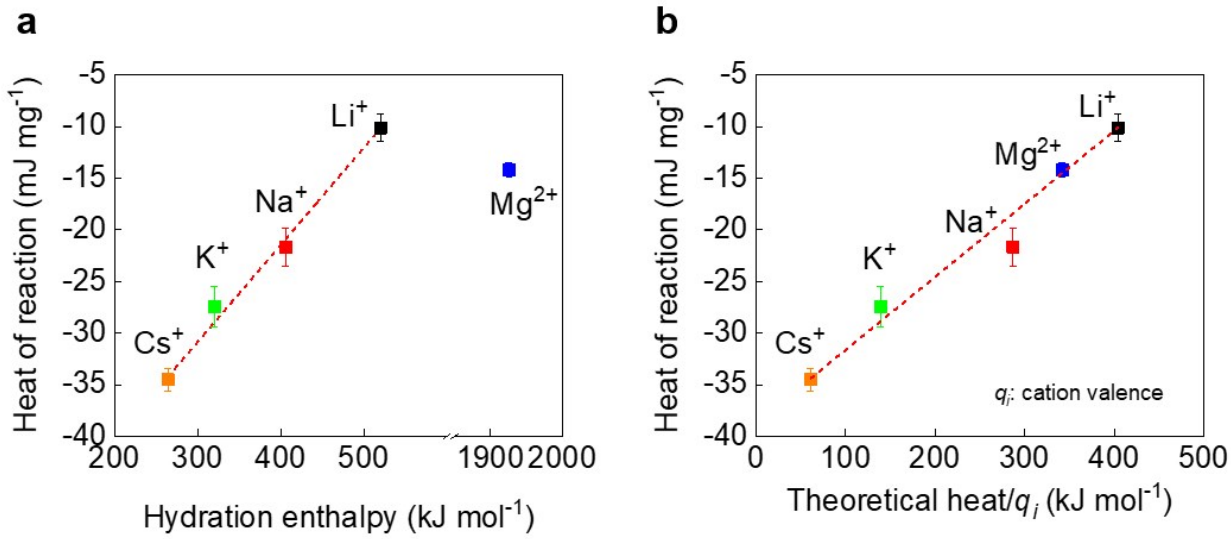


Figure S4. Correlation between Heat of reaction and bulk hydration enthalpy[2] (a) and theoretical heat of reaction (b) due to cation dehydration divided by cation valence, *i.e.*, alkali cation by 1 and Mg^{2+} by 2. It does not show any well correlation by simply divided by 2 with hydration enthalpy in Fig. S4a.

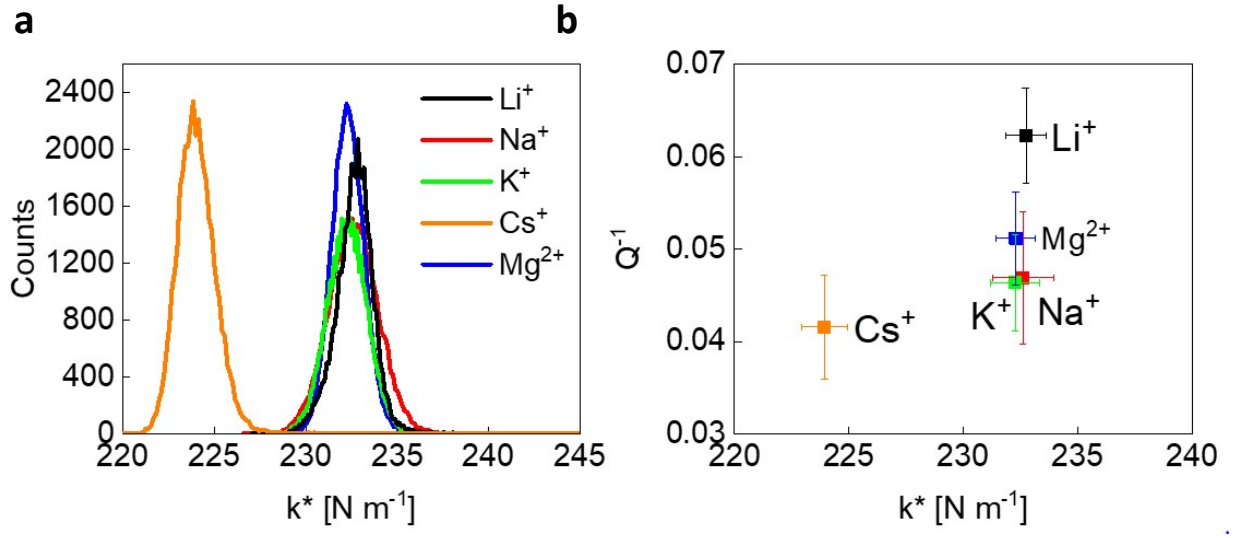
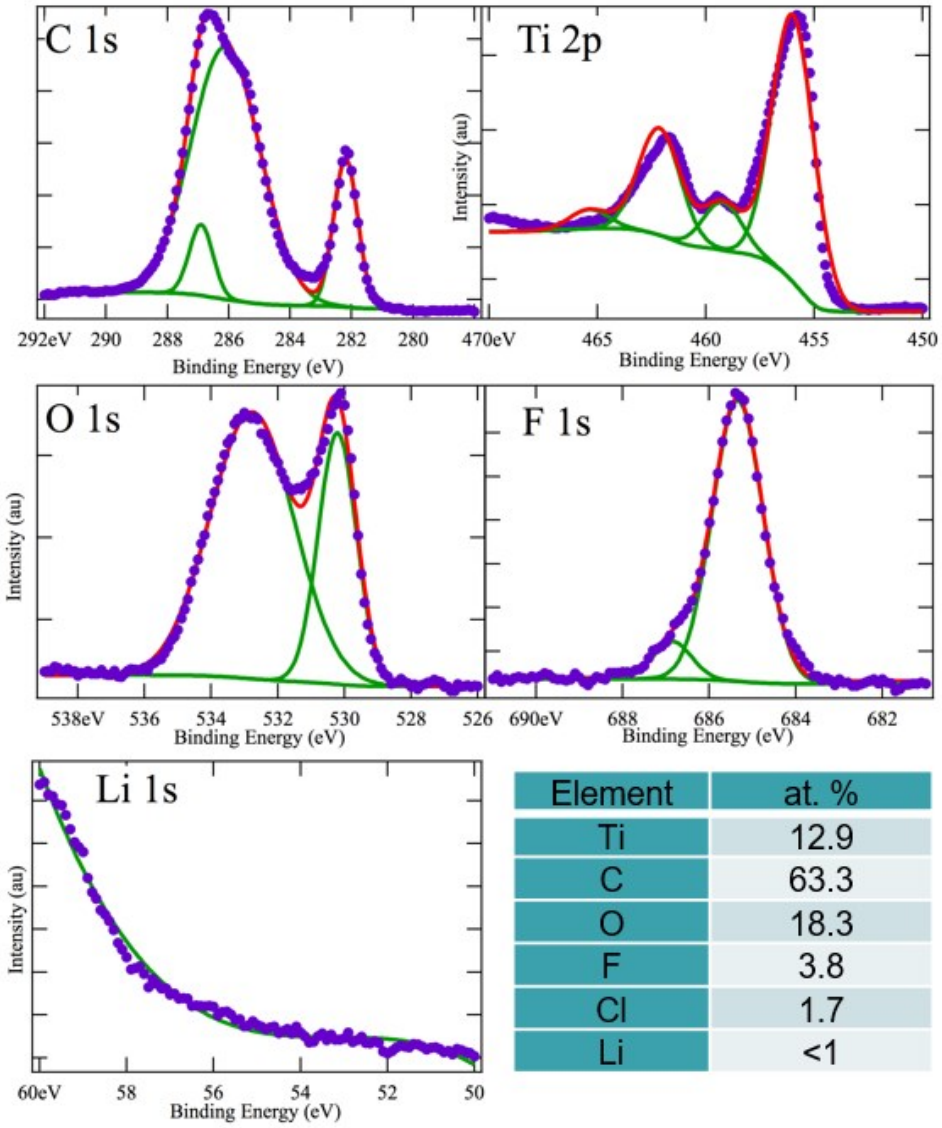
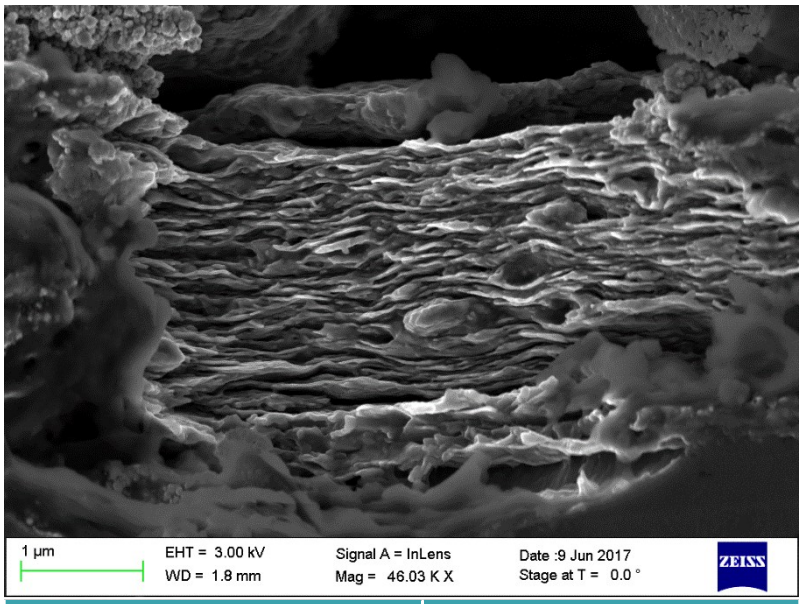


Figure S5. (a) Histograms of tip-sample contact stiffness K* variations with aqueous ions present no clear changes by varying cations types. K* is determined through the measured resonance frequency as described in Ref.[3] (b) There is no well-defined correlations between Q energy loss and K*, indicating the energy loss is independent on K*.



Element	at. %
Ti	12.9
C	63.3
O	18.3
F	3.8
Cl	1.7
Li	<1

Figure S6. X-ray photoelectron spectroscopy (XPS): the component peak-fitting spectra for $Ti_3C_2T_x$ MXene as received. It clearly shows no detectable Lithium signals below 1 at.% of residual Li^+ from etching processes. The identical analysis for lithium intercalated MXene sample, the estimated values for the lithium content as listed in Fig. S7. XPS measurements were performed at room temperature in ultrahigh vacuum using a SPECS Focus 500 monochromated Al Kα x-ray source and PHOIBOS-150 hemispherical analyzer operated in the medium area mode. Analysis corrected for transmission and elemental sensitivities.



Cation	Concentration at. %
Li^+ (XPS)	3.50
Na^+	3.48
K^+	1.53
Cs^+	2.16
Mg^{2+}	0.95

Figure S7. Cross-sectional scanning electron microscopy (SEM) images of the studied $Ti_3C_2T_x$ MXene and relevant quantification of intercalated cations determined by energy-dispersive X-ray (EDX). SEM images and EDX were performed in Carl Zeiss Merlin SEM Microscope operating at 3 kV. Due to technical limitations of EDX, it cannot detect lithium amount, and therefore, we determined the amount of Lithium from XPS.

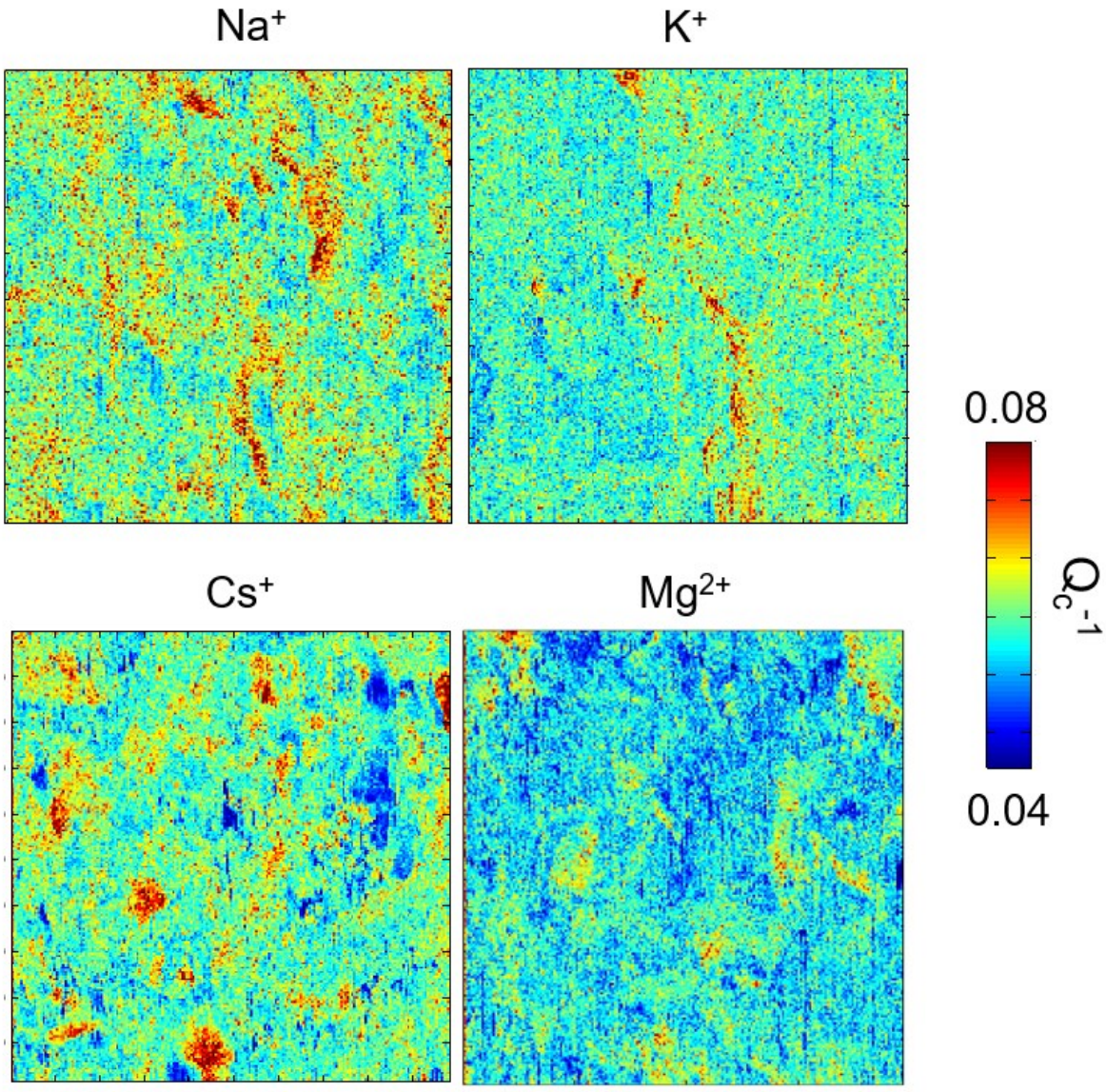


Figure S8. Spatial map (10×10 um) of local energy losses for MXene samples measured in Na_2SO_4, K_2SO_4, Cs_2SO_4, or $MgSO_4$ at a concentration of 0.5 M recorded at the immersed time point of two hours.

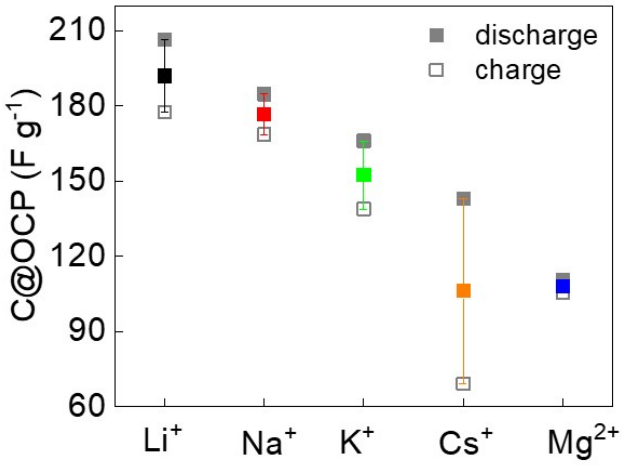


Figure S9. Open circuit potential (OCP) during charge and discharge for each cation.

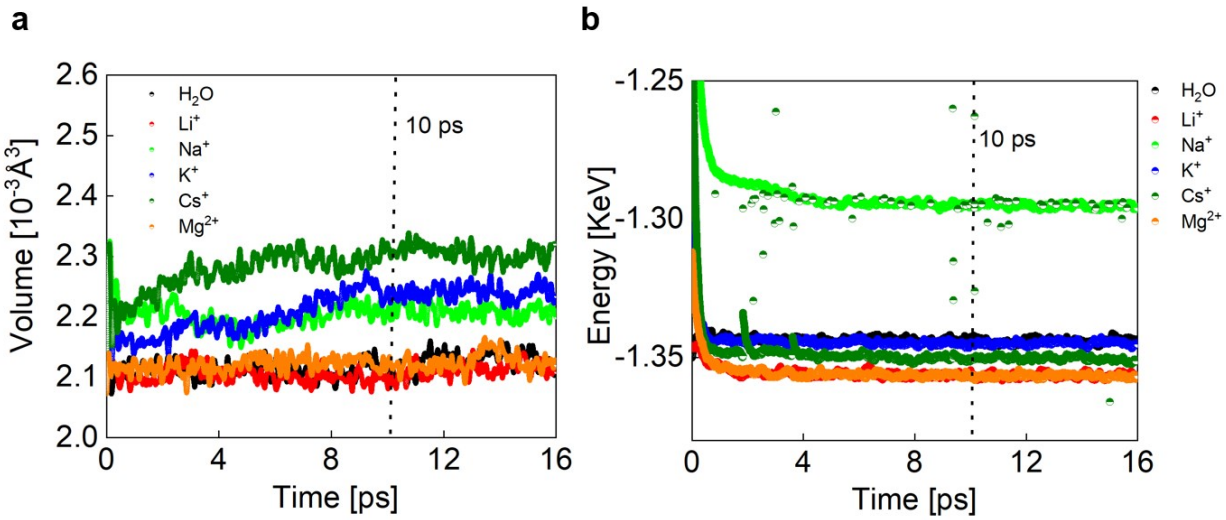


Figure S10. (a) Time dependence of simulation cell volume. (b) Time dependence of total energy during AIMD for each intercalated cation and for intercalated water only. Both quantities are well equilibrated after an initial ~10ps, indicated by the vertical dashed line.

References

1 Shpigel, N. *et al.* Direct assessment of nano-confined water in 2D Ti3C2 (MXene) electrode interspaces by a surface acoustic technique. *Journal of the American Chemical Society* **140**, 8910-8917, doi:10.1021/jacs.8b04862 (2018).

2 Smith, D. W. Ionic hydration enthalpies. *Journal of Chemical Education* **54**, 540, doi:10.1021/ed054p540 (1977).

3 Nina, B. *et al.* Quantification of surface displacements and electromechanical phenomena via dynamic atomic force microscopy. *Nanotechnology* **27**, 425707 (2016).