Direct Assessment of Nanoconfined Water in 2D Ti$_3$C$_2$ Electrode Interspaces by a Surface Acoustic Technique

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Supporting Information

ABSTRACT: Although significant progress has been achieved in understanding of ion-exchange mechanisms in the new family of 2D transition metal carbides and nitrides known as MXenes, direct gravimetric assessment of water insertion into the MXene interlayer spaces and mesopores has not been reported so far. Concurrently, the latest research on MXene and Birnessite electrodes shows that nanoconfined water dramatically improves their gravimetric capacity and rate capability. Hence, quantification of the amount of confined water in solvated electrodes is becoming an important goal of energy-related research. Using the recently developed and highly sensitive method of in situ hydrodynamic spectroscopy (based on surface-acoustic probing of solvated interfaces), we provide clear evidence that typical cosmotropic cations (Li$^+$, Mg$^{2+}$, and Al$^{3+}$) are inserted into the MXene interspaces in their partially hydrated form, in contrast to the insertion of chaotropic cations (Cs$^+$ and TEA$^+$), which effectively dehydrate the MXene. These new findings provide important information about the charge-storage mechanisms in layered materials by direct quantification and efficient control (management) over the amount of confined water in a variety of solvated battery/supercapacitor electrodes. We believe that the proposed monitoring of water content as a function of the nature of ions can be equally applied to solvated biointerfaces, such as the ion channels of membrane proteins.

INTRODUCTION

Two-dimensional (2D) solids containing nanoconfined fluids (water, organic molecules, and partially solvated ions) have been recently recognized as promising electrode materials for improved electrochemical energy storage. 1−3 2D transition metal carbides and nitrides (MXenes) are especially attractive in this respect: MXenes possess high electronic conductivity, which enables fast, reversible insertion of different cations in organic, aqueous, and acidic environments. 4−6 Previous investigations into aqueous-based electrolytes revealed that insertion of hydrophilic and hydrophobic cations is accompanied by simultaneous insertion of water molecules, 7,8 however, the charge-storage mechanism of these materials is still under investigation. Hu et al. examined the MXene Ti$_3$C$_2$ in acidic and neutral electrolytes by in situ electrochemical Raman spectroscopy. 9 Their findings demonstrated a pseudo-capacitive mechanism in the acidic electrolyte and pure adsorption response in neutral electrolyte solutions. The existence of a Faradaic response in acidic medium was also proven by in situ electrochemical X-ray absorption spectroscopy of Ti$_3$C$_2$. 10 Further studies have revealed that electrochemical or spontaneous intercalation of various cations into Ti$_3$C$_2$ layers in aqueous electrolyte solutions results in the insertion of additional water molecules in accordance with the solvation ability of the respective cation. X-ray diffraction (XRD) 11 and neutron scattering 12 investigations of the spontaneous intercalation of ions resulted in further understanding of the effects that ion intercalation has on Ti$_3$C$_2$, namely, the extent of Ti$_3$C$_2$ expansion was correlated to the amount of coinserted water. A recently reported calorimetric study on the spontaneous intercalation of alkali metal ions (Li$^+$, Na$^+$, and K$^+$) into free-standing Ti$_3$C$_2$ electrodes suggests there is preferential intercalation of K$^+$ cations due to their smaller hydration radius (compared to those of Li$^+$ and Na$^+$). 13 Yet, these studies addressed only the nonelectrochemical insertion of ions, and hence, future mechanistic studies of Ti$_3$C$_2$ should be extended to include studying the charging mechanisms of this energy-storage material.

Recognizing the fact that kinetics of ion transport in 2D layered materials (possessing hierarchical porous structure) strongly depend on the incorporation of nanoconfined...
solvent, which, in turn, is affected by the interlayer ion solvation/desolvation, quantification and efficient control (management) over the amount of confined solvent in 2D layered electrodes become challenging for increasing their energy, power, and cycling performance. Indeed, the latest research shows that such solvated electrodes as MXene and Birnessite significantly improve their gravimetric capacity and rate capability with the amount of nanoconfined water contained in their structures.

The benefits of electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) for in situ monitoring of intercalation-induced changes in Ti$_3$C$_2$ electrodes have been recently demonstrated using acoustically thick film electrodes. The assessment and continuous monitoring of the amount of nanoconfined solvent in 2D layered electrodes require application of an alternative EQCM-D approach to a simultaneous monitoring of gravimetric and hydrodynamic responses in acoustically thin electrode coatings (thickness is much less than the wavelength of sound; hence, any viscoelastic effect is negligible). In the case of absence of both hydrodynamic and viscoelastic effects linked to the character of the electrode structure, the use of conventional EQCM or (alternating current) AC-electrogravimetry on single (fundamental) frequency can be sufficient to evaluate the amount of solvent molecules coadsorbed or cointercalated into the electrodes together with the related ions.

Herein, using a recently developed method of in situ hydrodynamic spectroscopy, we first quantify the amount of water confined between the Ti$_3$C$_2$ sheets (interspace), distinguishing it from the water located in the mesoporous space of the hierarchically porous electrode assembly. This approach was further extended to quantification of the amount of nanoconfined water coinserted/coextracted during intercalation of multiple-charged cations having different hydrophilicities and hydrophobicities, respectively. Whereas hydrophilic (cosmotropic) cations are inserted with a part of their solvation shell, the hydrophobic (chaotropic) cations remain essentially unsolvated, showing a clear tendency to push water molecules out of the confined interspaces of the Ti$_3$C$_2$ electrode. Our gravimetric/hydrodynamic study of the electrochemical insertion of different cations into the Ti$_3$C$_2$ electrode coupled with water insertion/extraction contributes to a better understanding of the mechanisms of insertion of multiply charged cations into 2D layered electrodes.

■ RESULTS

Gravimetric and Hydrodynamic Modes of EQCM-D. When a quartz crystal (QC) is loaded with a rigid and uniformly spread coating, the width of the resonance peak ($\Delta W/n$) does not change; thus, the entire rigidly attached coating moves synchronously with the surface of the oscillating QC. In this case, the resonance frequency ($\Delta f/n$) decreases proportionally with any added mass ($\Delta m_{\text{mass}}$) following the Sauerbrey equation:

$$\Delta f/n = -C_m \times \Delta m_{\text{mass}}$$

(1)

where $C_m$ is the mass sensitivity constant and $n$ is the overtone order. Equation 1 shows that mass measurements on different overtone orders are equivalent to measurements at the fundamental frequency (i.e., $n = 1$) if the related frequency change is normalized by the overtone order.

Even though the Sauerbrey equation gives a straightforward and convenient way for tracking gravimetric changes, the demands for a rigid and uniform coating are not always practically implemented. Viscoelastic films, for instance, tend to move in a way that is not synchronized with the QC oscillations, which is expressed by additional contributions to the recorded frequency change, resulting in errors in the gravimetric calculations. With this in mind, we have focused in the present Article on the frequency response of acoustically thin Ti$_3$C$_2$ electrodes (60 nm thick) with a loading mass around 15.9 $\mu$g/cm$^2$: very small dissipation factors of this coating in air were measured at different overtone orders, and the negligibly small changes of the dissipation factors during the process of ions insertion in contact with electrolyte solutions prove the rigid character of the electrode, suitable for both hydrodynamic analysis of the electrode under OCV (open-circuit voltage) conditions and gravimetric analysis of ions and solvent insertions in the electrolyte solutions.

Building on this result, we applied the principle of in situ hydrodynamic spectroscopy to quantify the amount of water confined in the porous Ti$_3$C$_2$ electrodes. This method makes use of two structural characteristics of porous hydrated electrodes, namely, the permeability length, $\xi$ (linked to porosity via the Kozeny–Carman equation), and the thickness of the interfacial porous layer, $h$. The hydrodynamic solid–liquid interactions occurring in a porous electrode are reflected by the resonance frequency ($\Delta f/n$) and resonance width ($\Delta W/n$) changes, which, in turn, depend on both parameters of porous solid, $\xi$ and $h$, and on the characteristic acoustic characteristic of liquid, called the penetration depth, $\delta$. Penetration depth is a natural variable independent parameter of the hydrodynamic problem of solid–liquid interactions characterizing damping (decay) of the shear wave amplitude from the oscillating crystal toward the liquid’s interior as a function of the liquid’s viscosity/density ratio ($\eta_L/\rho_L$) and shear wave overtone order, $n$ (see Supporting Information, eq S1). When $\xi \ll \delta$ (i.e., either the electrode’s porosity is small or the liquid used is too viscous, or, finally, lower overtone orders are used—see Supporting Information, eq S1), the liquid moves synchronously with the crystal and rigid porous electrode host. Hence, the liquid is completely trapped in the narrow pores of the electrode matrix. In contrast, when $\xi \gg \delta$ (wide pores), most of the liquid in the pore interior is not trapped and, hence, is moveable with respect to the oscillating crystal. In the first case, the trapped liquid contributes to the frequency change only (the resonance width remains unchanged). In contrast, moveable liquid in the wide pores contributes to both frequency change and resonance width changes. To avoid any confusion, we would like to specifically emphasize that both the moveable and nonmoveable states of liquid are defined with respect to the oscillating crystal.

For the selected thin-layer porous Ti$_3$C$_2$ electrode, the condition $\xi \leq \delta$ is an intermediate one between the above-mentioned two limiting cases, implying that, due to the features of the porous structure of this electrode, a significant amount of liquid is trapped in the interspaces of the electrode particles. At the same time, the true mass of the trapped liquid can be assessed only after making a correction of the total experimental frequency change, $\Delta f/n$, accounting for the hydrodynamic effect of the moveable liquid in the vertical interparticle pores and horizontal interstack gaps of the Ti$_3$C$_2$ electrode. A full discussion of the porous Ti$_3$C$_2$ electrode structure and its acoustic probing, proof of rigidity of the Ti$_3$C$_2$.
coatings in air, and details of hydrodynamic modeling are presented in Figures S1 and S2, respectively.

Tracking distribution of water in Ti3C2 electrode in a quasi-stationary state (no external polarization) is shown in Figure 1.

Figure 1. Hydrodynamic spectroscopy of a thin Ti3C2 electrode after impregnation with pure water (a). Dashed lines correspond to normalized Δf/n and ΔΓ/n changes of an ideally flat surface. The normalized quantities are expressed as (Δf/n) × 109/ρf0ΔΓ/n = 109/μf0ΔΓ/n, for frequency and resonance half-width, respectively, where f0 is fundamental frequency and ρ is the liquid’s density. The same quantities for the Ti3C2 electrode after consecutive replacement of water with 1 M solutions of LiCl and CsCl are shown by solid and open symbols, respectively, as indicated. Red solid lines denote the response obtained by fitting the model of uniform porous layer to the experimental EQCM-D data. The frequency response due to water trapped in the Ti3C2 interspaces is indicated by the two oppositely directed arrows. The high-resolution (HR) SEM images of the Ti3C2 electrode of lower and higher resolutions are shown in (b) and (c), respectively. Scale bars are 2 μm and 500 nm, respectively.

The normalized changes of frequency (Δf/n) and resonance half-bandwidth (ΔΓ/n) for the Ti3C2 electrode fully impregnated with water are shown by closed and open red circles, respectively, in Figure 1a. For comparison, the hydrodynamic response of the ideally flat surface of the neat crystal (serving as a reference state) is shown by dotted black straight lines.25 The downward and upward deviations of the experimental Δf/n and ΔΓ/n changes, respectively, for the Ti3C2 electrode from the straight lines describing the response of the neat crystal imply that the Ti3C2 electrode has a porous structure containing both moveable and trapped water. As mentioned previously, moveable water contributes to both Δf/n and ΔΓ/n changes, whereas trapped water results in only negative Δf/n changes. To distinguish between the moveable and trapped water, a suitable hydrodynamic model for fitting the experimental values of Δf/n and ΔΓ/n changes should be used. As mentioned in the Supporting Information and explained in detail in ref 21, the particular EQCM-D signatures of different types of rough/porous electrode structures can be analyzed by using appropriate hydrodynamic models that are selected on the basis of other surface-structure-sensitive techniques, e.g., scanning electron microscopy (SEM) or atomic force microscopy (AFM) images. SEM images of the Ti3C2 electrodes used in this study are shown in Figure 1b and c. The lower-resolution image shows that there is an absence of gross features of the external roughness on the scale of the penetration depths of water, and the latter ranges from 68 to 140 nm for the 13th and 3rd overtones, respectively. The higher-resolution image shows that the maximal lateral size of the platelet-like flakes does not exceed 500 nm. According to the Ti3C2 synthetic procedure used, the individual flakes are expected to be a single layer or a few layers thick.7

We distinguish between two types of nanoconfined space in Ti3C2 electrodes that were impregnated with water (after removal of air from the pores of the electrode structure by vacuum in a hermetically closed bottle): (I) 2–3 nm size interspaces between the closely packed single/few layer thick sheets in the lamelas and (II) mesoscopic-size vertical interparticle pores and horizontal interstack gaps (see Figure S1). Assuming that mesoscopic pores and gaps make up a system of interconnected pores through which water moves during shear oscillation of the coated crystal, we apply the model for uniform porous layers for analyzing the obtained EQCM-D responses.

To distinguish between the location of water molecules in the interspaces and the mesoporous volume, we first fitted the model to the experimental ΔΓ/n changes (red open circles in Figure 1a; the red solid line represents the best fit), finding two optimal model structural parameters (discussed earlier): ξ = 28 nm and h = 45 nm (Supporting Information, eqs S2a and S2b). In the next step, the evaluated parameters were inserted into eq S2a to calculate the hydrodynamic contribution of the moveable water to the Δf/n changes (red solid line in Figure 1a). It is clearly seen in the same figure that there is an approximate n-independent downward (negative) shift of Δf/n for the experimental values (red solid symbols and the related thin straight line) from the model curve (red solid line). Such a shift corresponds to inertial loading of the crystal due to the water in the Ti3C2 coating being in an unmoveable (confined) state, i.e., completely trapped in the Ti3C2 interspaces. From the dimensionless frequency change denoted by two arrows (corresponding to the frequency change of 65 Hz), we can easily calculate the ratio between the amount of confined water and the Ti3C2 entities. Here we are assuming the chemical composition of the Ti3C2 is Ti3C2(OH)F based on previous studies31 (molecular mass 204 g/mol). The coating on the quartz crystal had an areal mass density of 0.078 μmol/cm². Using the Sauerbrey equation for the earlier-mentioned frequency shift of 65 Hz, the amount of water molecules trapped in the Ti3C2 interspaces was calculated to be 0.0638 μmol/cm². Thus, after impregnation of water under vacuum, the composition of the Ti3C2 coating was found to be Ti3C2(OH)F(H2O)0.82.

It is seen that the molar ratio of the surface functionality −OH to that of the confined water is close to 1, suggesting weak hydrogen bonding of water molecules to the −OH surface groups. The ratio of the amount of water trapped in
Ti$_3$C$_2$ interspaces and located in the interparticle pores and interlayer gaps (moveable water) can be roughly estimated as 1:3. This follows from application of the Sauerbrey equation to the $\Delta f/n$ shift assigned to the moveable water (i.e., located between the straight line for the plane surface and the red solid line for the model in Figure 1a), taking into account that the shift of $\Delta \Gamma/n$ is smaller than the related shift of $\Delta f/n$. As a result, the estimated amount of water, 0.186 $\mu$mol/cm$^2$, attributed to the mesoporous voids of the electrode is about triple more than the amount of water confined in the electrode interspaces. Figure 1a relates to quasi-stationary EQCM-D measurements of Ti$_3$C$_3$ electrode at OCV when the pure water in the cell is replaced first by a 1 M solution of LiCl. After 10 full fast cycles, the solution is replaced by a 1 M CsCl solution, and the EQCM-D measurements are conducted again at OCV. The normalized bandwidth and frequency change for all three fluids remain practically unchanged. Therefore, the amount of water trapped in the interspaces of the electrode also remains essentially constant.

Dynamic EQCM-D Measurements during Insertion Cations Intercalation into Ti$_3$C$_2$ Electrodes. In this section we report on the number of water molecules that the electrochemically inserted cations can coinsert/coextract into/from the Ti$_3$C$_2$ interspace, thereby changing the total water content of the electrodes. Because the insertion of all the studied cations results in negligibly small changes of $\Delta \Gamma/n$ (see Figures 2 and 3 for a series of hydrophilic and hydrophobic cations, respectively) the Sauerbrey equation (eq 1) is used to translate the related frequency changes into the effective masses of inserted cations. This is further transformed into the molar ratios of the desolvated cations (calculated from the related masses of the inserted cations), whereas the rest of the frequency change (either positive or negative) is assigned to the number of moles of water accompanying the insertion of the cations (this simple calculation routine was reported previously for nanoporous carbons in full detail$^{26}$).

Figure 2. Time-dependent changes of $\Delta f/n$ and $\Delta \Gamma/n$ during insertion/extraction of Li$^+$ (a), Mg$^{2+}$ (b), and Al$^{3+}$ (c) cations into/from the Ti$_3$C$_2$ electrode (scan rate 50 mV/s) collected at 3rd, 7th, and 11th overtones. The frequency change calculated from the charge was obtained by integration of the related CVs (d, e, and f, respectively) and is shown by the dashed lines ($\Delta f/n_{Faraday}$) in panels a, b, and c, respectively.

Figure 3. Time-dependent changes of $\Delta f/n$ and $\Delta \Gamma/n$ during insertion/extraction of Ba$^{2+}$ (a), Cs$^+$ (b), and TEA$^+$ (c) cations into/from the Ti$_3$C$_2$ electrode (scan rate 50 mV/s) collected at 3rd, 7th, and 11th overtones. The frequency change calculated from the charge obtained by integration of the related CVs (d, e, and f, respectively) is shown by the dashed lines ($\Delta f/n_{Faraday}$) in panels a, b, and c, respectively.
electrode charge density (mC/cm²), \( a_{\text{exper}} \) and \( a_{\text{Faraday}} \) respectively:\textsuperscript{26}

\[
m_w = \left( \frac{a_{\text{exper}} - a_{\text{Faraday}}}{a_{\text{Faraday}}} \right) \times \frac{M_{\text{ion}}}{M_{H_2O}}
\]

\( M_{\text{ion}} \) and \( M_{H_2O} \) denote the molecular masses of unsolvated ion and water, respectively. The Faradaic population change of inserted cations is linked to the Faradaic frequency change, \( \Delta f/\ n_{\text{Faraday}} \) via Sauerbrey’s equation.

A closer inspection of Figure 2 shows that, for the series of hydrophilic cations, Li\(^+\), Mg\(^{2+}\), and Al\(^3+\), the absolute value of the experimental frequency change, \( \Delta f/\ n_{\text{exper}} \), with respect to that of \( \Delta f/\ n_{\text{Faraday}} \), increases in the same order, signifying an increase in the number of water molecules accompanying cation insertion. In contrast, for large cations (Ba\(^{2+}\), Cs\(^+\), and TEA\(^+\)), in this order, \( \Delta f/\ n_{\text{Faraday}} \) appears to be larger by its absolute value than that for \( \Delta f/\ n_{\text{exper}} \), implying that the large cations remove water molecules during their insertion into the Ti\(_3\)C\(_2\) interspace (Figure 3). Moreover, we were able to observe the transfer from the behavior typical for the cosmotropic and chaotropic cations within the entire alkaline-metal cations series: the behavior of the first and last members of this series (i.e., Li\(^+\) and Cs\(^+\) cations) are shown in Figure 2a and d and Figure 3b and e, respectively, whereas the data for Na\(^+\) and K\(^+\) cations are shown in Figure S3a and c and Figure S3b and d, respectively.

Note that the described approach is valid only for the so-called permselective character of intercalation/adsorption process, implying insertion of major counterions (e.g., cations during a negative polarization of the electrode).\textsuperscript{18,27} At a small polarization, e.g., in the vicinity of potential of zero charge of carbon electrodes, or in case of the presence of fixed (localized) charged groups in the electrode structure, the cations participate in the charge-compensation process in the electrode in addition to that of the counterions, and in this case, the use of electrogravimetric method becomes especially attractive because of the high selectivity of this technique to the nature of inserted ions and solvent molecules.\textsuperscript{28}

The results from quantifying the number of moles of water accompanying the insertion of different cations into the Ti\(_3\)C\(_2\) interspace (i.e., \( m_w \), see eq 2) are presented in Figure 4. The comparison of the slopes of \( a_{\text{exper}} \) and \( a_{\text{Faraday}} \) which visualizes the method of calculation of \( m_w \) is shown in Figure 5, using the intercalation of Ba\(^{2+}\) and Mg\(^{2+}\) cations as an example.

In the case of Al\(^{3+}\) cation (which is subjected to hydrolysis in aqueous solution, resulting in appearance of H\(^+\) ions), the charge obtained from the related CV (Figure 2f) is significantly larger than that for the insertion of Li\(^+\) and Mg\(^{2+}\) cations due to the insertion of H\(^+\) cations into the Ti\(_3\)C\(_2\) interspaces. We have assumed that the charge due to the insertion of Al\(^{3+}\) ions is approximately equal to that for the insertion of Li\(^+\) and Mg\(^{2+}\) cations and, in addition, that this charge is linked to the \( \Delta f/\ n \) quantity obtained from \( \Delta f/\ n_{\text{exper}} \) by subtraction of the contribution of H\(^+\) cations (for clarity, a very detailed calculation of \( m_w \) for Al\(^{3+}\) cation is included in the Supporting Information).

As follows from Figure 5 for two double-valent cations with different unsolvated radii (Mg\(^{2+}\) and Ba\(^{2+}\)), the insertion of the larger Ba\(^{2+}\) cations is characterized by \( a_{\text{exper}} \) being practically equal to \( a_{\text{Faraday}} \) (hence, the Ba\(^{2+}\) cation is inserted into the Ti\(_3\)C\(_2\) electrode in its effectively nonsolvated form), whereas for insertion of the smaller Mg\(^{2+}\) cation, a significantly larger experimental slope, \( a_{\text{exper}} \), is observed as compared to that of \( a_{\text{Faraday}} \). According to eq 2, this implies a positive value of \( m_w \), meaning that insertion of this cation into the Ti\(_3\)C\(_2\) is accompanied by coinsertion of water molecules.

Figure 4. Number of water molecules coinserted per intercalated hydrophilic cation (positive values) or extracted from the electrode during intercalation of hydrophobic cations (negative values). The quantity \( m_w \) was obtained from raw experimental frequency changes as compared to the Faradaic frequency change due to insertion of unsolvated cations using eq 2. The standard errors were calculated from the measurements of four independent electrode coatings of similar mass.

Figure 5. Changes of the effective amount of Mg\(^{2+}\) and Ba\(^{2+}\) cations as a function of the electrode charge density (circles and squares, respectively). The solid red line (called the Faraday line) was obtained by conversion of the experimental intercalation charge for both cations into the related mass change using the Faraday equation (this slope is designated as \( a_{\text{Faraday}} \)). The experimentally measured frequency changes for the intercalated Ba\(^{2+}\) and Mg\(^{2+}\) cations were converted into the mass changes using the Sauerbrey equation, and then, assuming insertion of unsolvated cations, the mass changes were transformed into the related molar changes (see dashed black lines with different slopes, \( a_{\text{exper}} \)). The population changes expressed by these lines were averaged over the entire range of overtone orders, \( n \). The differences in the slopes of the experimental lines and the Faraday line, which reflects the coinsertion of water molecules during cation intercalation, were introduced into eq 2 to quantify the number of water molecules per each cation coinserted into the electrode (see Figure 4). Intercalation starts at a charge density equal to zero and results in a change of \( \Delta f/\ n_{\text{exper}} \), which appears to be larger by its absolute value than that of \( \Delta f/\ n_{\text{Faraday}} \) (see Figure 3a). When \( \Delta f/\ n_{\text{exper}} = \Delta f/\ n_{\text{Faraday}} \) (see Figure 3a), the cation intercalates in its effectively desolvated form, meaning no water is gained or lost by the electrode. When the absolute value of the \( \Delta f/\ n_{\text{exper}} \) is smaller than \( \Delta f/\ n_{\text{Faraday}} \) (this case is not shown in Figure 5), the intercalation of the hydrophobic cation is accompanied by dehydration of the electrode (see Figure 3b and e).
Similar calculations have been performed for gravimetric analysis of intercalation of hydrophilic and hydrophobic cations of alkaline and alkaline-earth series, $\text{Al}^{3+}$ and $\text{TEA}^+$ cations. As shown in Figure 5, insertion of the hydrophilic cations increases the content of water molecules in the $\text{Ti}_3\text{C}_2$ interspaces, whereas insertion of the hydrophobic cations decreases the water content. The “dehydration” effect of large cations significantly increases when coming from $\text{K}^+$ to $\text{Cs}^+$ and, more gradually, when coming further to $\text{TEA}^+$. This tendency is in good agreement with an earlier prediction that intercalation of large ions results in removal of water molecules from the interspaces implied from the studies of the actuation and nanoscale viscoelastic properties of MXene electrodes. 29,30

As an example, we have estimated that the insertion of $\text{Li}^+$ cations increases the initial water content in the $\text{Ti}_3\text{C}_2$ interspace by 20% whereas a similar insertion of $\text{Cs}^+$ cations dehydrates the electrode by 41%.

## DISCUSSION

The number of water molecules either coinserted or, alternatively, extracted by ions inserted during the electrochemical cycling of $\text{Ti}_3\text{C}_2$ electrodes depends strongly on the ion–water interactions, which is a function of the different ions’ charge-per-size ratio. The existence of such a relationship obtained experimentally by EQCM-D technique can be perfectly explained by a combination of two concepts implying that (I) the cosmotropic or chaotropic nature of small and large cations, respectively, determines their behavior in bulk aqueous solutions,31 and (II) the essentially confined space in the $\text{Ti}_3\text{C}_2$ electrode (van der Waals interspaces), containing water molecules prior to when the cations are electrochemically inserted into the electrode, modifies the former bulk effect.

Table 1 collects the data listing the unhydrated and hydrated radii of cations and the hydration numbers for several different cations used in our study. The last column indicates the viscosity $B$-coefficient used in the Jones–Dole equation,32

$$\eta/\eta_0 = 1 + A\eta^1/2 + B\eta + C\eta^2 + \ldots$$

(3)

where $\eta$ and $\eta_0$ are viscosities of solution and pure solvent, respectively, $c$ is the electrolyte solution concentration, and $A$, $B$, and $C$ are the related coefficients.

The Jones–Dole coefficient $B$ characterizes the strength of ion–water interaction, with positive values representing structure-making cations (cosmotropes) and negative values representing the structure-breaking cations (chaotropes). It is implied that small-size multivalent cations modify the hydrogen bonds existing in the water in close vicinity to the cosmotropic cations by the formation of hydration shells; these cations are said to possess hydrophilic properties. The enthalpic gain from the water–cation interactions exceeds the entropic loss due to the rearrangement of the water molecules.32

Because of the decrease of the strength of the cation–water interaction in the sequence $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Ba}^{2+} > \text{Li}^+$, the viscosity coefficient $B$ decreases. For the large monovalent $\text{Cs}^+$ cation with only weak hydrophobic ability, $B$ is small and negative, implying that this cation perturbs the water structure slightly so that the reorganization of hydrogen bonds easily occurs. In contrast, larger-size monovalent structure-breaking cations such as tetraalkyl ammonium cations (with increasing hydrophobicity for the cations with longer chains) profoundly disturb the bulk water structure in close proximity to the ions. Strengthening and reorganization of the hydrogen bonds between the water molecules in the form of the iceberg-like structure take place in the bulk of the electrolyte solution, which results in the increase of $B$. Surely this process is accompanied by a large entropy decrease.31 Moreover, large hydrophobic cations, when located at a short enough distance, knock out the water molecules, significantly decreasing the water density (and, hence, content) down to that of water vapor.32

The above scenario seems to describe the behavior of the six selected cations when electrochemically inserted into the $\text{Ti}_3\text{C}_2$ electrode, taking into account the effect of the confined space. In fact, as follows from our EQCM-D study, three typically cosmotropic cations ($\text{Al}^{3+}, \text{Mg}^{2+},$ and $\text{Li}^+$) are characterized by a smaller number of water molecules linked to the cations when coinserted into the $\text{Ti}_3\text{C}_2$ electrode (see Figure 4) compared to the bulk hydration number for the same cations (see Table 1). Thus, the partial dehydration of the cosmotropic cations (enhancing with the increase of the charge-to-size ratio) is a direct consequence of the confined effect of $\text{Ti}_3\text{C}_2$ interspaces. The effect of the larger size of $\text{Ba}^{2+}$ cation is counterbalanced by the effect of its higher charge so that its insertion only slightly perturbs the water structure in the $\text{Ti}_3\text{C}_2$ electrodes.

A gradual transition from the cosmotropic to the chaotropic behavior was observed along the entire series of alkaline-metal cations (see Figure 4). For both hydrophobic $\text{Cs}^+$ and $\text{TEA}^+$ cations, an excluded-volume region is formed in close proximity to the cations in which the water density is smaller than that in the bulk water.32 Our EQCM-D studies clearly confirm this conclusion by calculation of the average number of water molecules replaced by the inserted $\text{K}^+$, $\text{Cs}^+$, and $\text{TEA}^+$ cations. The excluded-volume effect exists already for the hydrophobic cations in bulk solution. However, the confined character of the hydrophobic cations inserted into the $\text{Ti}_3\text{C}_2$ electrode makes the excluded-volume effect the dominant one, whereas the iceberg-like water structure typical for the strongly hydrophobic cations in bulk solutions32 is not formed because of the confined space of the $\text{Ti}_3\text{C}_2$ electrode.

Although our study relates to heavily exfoliated single/few layer thick $\text{Ti}_3\text{C}_2$ particles, the main results are in agreement with that obtained in a recent calorimetric study of ions exchange in multilayered claylike $\text{Ti}_3\text{C}_2$.33 The conclusion about a weak interaction of water with the $\text{Ti}_3\text{C}_2$ interspace is in accord with our result of the existence of almost 1:1 ratio of the number of $\text{OH}$ functionalities and the number of inserted water molecules. The evidence obtained in the present EQCM-D study that hydrophilic cations bring water molecules into the $\text{Ti}_3\text{C}_2$ interspaces is in accord with the conclusion

<table>
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<th>Cation</th>
<th>$r_{\text{ch}}$(Å)</th>
<th>$r_{\text{hydr}}$(Å)</th>
<th>$n$</th>
<th>$B$</th>
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<td>0.216</td>
</tr>
<tr>
<td>$\text{Cs}^+$</td>
<td>1.70</td>
<td>2.19</td>
<td>2.1</td>
<td>$-0.047$</td>
</tr>
<tr>
<td>$\text{TEA}^+$</td>
<td>3.37</td>
<td>3.45</td>
<td>1.1</td>
<td>0.385</td>
</tr>
</tbody>
</table>
about the expansion of the interplanar Ti$_3$C$_2$ spacing caused by the coinserted water.\(^1\)

**CONCLUDING REMARKS**

Using multiharmonic EQCM-D, we have applied a new method of in situ hydrodynamic spectroscopy to quantify the amount of water in the Ti$_3$C$_2$ electrode after its impregnation with water. The hydrodynamic modeling of the frequency and resonance width changes allows us to distinguish between the water trapped in the Ti$_3$C$_2$ interspaces and the moveable water located in the vertical interparticle pores and horizontal interstack gaps of the Ti$_3$C$_2$ electrode. To understand the effect of the inserted cations on the amount of water in the Ti$_3$C$_2$ interspaces, eight hydrophilic and hydrophobic cations with different charge-to-size ratios have been selected. Four typically hydrophilic cations (Na$^+$, Li$^+$, Mg$^{2+}$, and Al$^{3+}$) coinsert water of the inserted cations on the amount of water in the Ti$_3$C$_2$ electrode. To locate the expanded interspaces of Ti$_3$C$_2$ electrode is equally applicable for the characterization of supercapacitive nanoporous carbons and solvated battery and redox-type supercapacitive electrodes.

**EXPERIMENTAL SECTION**

**Electrode Preparation.** Ti$_3$C$_2$ was synthesized using HCl + LiF as an etchant. The full synthesis method was reported elsewhere.\(^1\) The prepared Ti$_3$C$_2$ was mixed in double deionized water (4 mg in 20 mL) and sprayed on a quartz sensor placed on a hot plate at 40 °C, using an airbrush supplied with compressed nitrogen. The coated crystal (after removal of air from the pores of the electrode by vacuum) was impregnated with either double-distilled water or a 1 M electrolyte solutions of the chloride salts of the examined cations (all salts mentioned were purchased from Sigma-Aldrich).

**EQCM-D Characterization.** Multiharmonic quartz-crystal measurements were performed by QSense E1 module (QCM-D from BioLogic) using 5 MHz Au-coated QCM sensors (q-sense Scientific AB, Swedenising). Frequency and dissipation responses were simultaneously collected from 3rd to 13th overtones. The coated QCM (which served as a working electrode) was assembled in a home-designed 3-electrode cell using Pt as a counter electrode and Ag/AgCl/KCl (sat.) as a reference electrode. Electrochemical measurements were conducted by BioLogic VSP-300 with EC-Lab software.

**Complementary Morphological Characterizations.** HR SEM imaging was performed using Magellan XHR 400L FE-SEM (FEI Company). Ti$_3$C$_2$ electrode thickness was measured (relative to an arbitrary height AB, Swedenising) and basics of in situ hydrodynamic spectroscopy (PDF)

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b04862.

Discussion of gravimetric and nongravimetric EQCM and basics of in situ hydrodynamic spectroscopy (PDF)

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**Notes**

The authors declare no competing financial interest.

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