Negative dielectric constant of water confined in nanosheets

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Electric double-layer capacitors are efficient energy storage devices that have the potential to account for uneven power demand in sustainable energy systems. Earlier attempts to improve an unsatisfactory capacitance of electric double-layer capacitors have focused on meso- or nanostructuring to increase the accessible surface area and minimize the distance between the adsorbed ions and the electrode. However, the dielectric constant of the electrolyte solvent embedded between adsorbed ions and the electrode surface, which also governs the capacitance, has not been previously exploited to manipulate the capacitance. Here we show that the capacitance of electric double-layer capacitor electrodes can be enlarged when the water molecules are strongly confined into the two-dimensional slits of titanium carbide MXene nanosheets. Using electrochemical methods and theoretical modeling, we find that dipolar polarization of strongly confined water resonantly overscreens an external electric field and enhances capacitance with a characteristically negative dielectric constant of a water molecule.

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A n electric double-layer capacitor (EDLC) is an important class of electrochemical capacitors, in which electrochemical double layers are formed on the electrode surface and polarized solvents between ions and the electrode act as a dielectric medium\(^1\). Due to the fact that the electrochemical double-layer formation is a fast and highly reversible surface process with minimal ion migration, EDLCs can operate intrinsically at high charge/discharge rates without degradation over millions of repeated cycles, which enables load-leveling of intermittent power from renewable energy sources. However, as capacitance of currently used EDLC electrodes is limited, energy density of EDLCs is not satisfactory to be widely distributed in power grids. Therefore, increasing the capacitance of EDLC electrodes has been an active area of research\(^3\)–\(^8\).

From a theoretical point of view, a conventional EDLC electrode can be considered as a parallel-plate capacitor that delivers a capacitance \((C)\) according to

\[
C = \frac{\varepsilon A}{d}
\]

where \(\varepsilon\) is the permittivity between the ions and the electrode, \(A\) is the electrode surface area, and \(d\) is the separation between the ions and the electrode (Supplementary Table 1)\(^1\). Consequently, increasing \(A\) of the EDLC electrodes using meso- or nanostructured materials is a classic approach toward realizing large specific capacitance and high energy density\(^3\)–\(^7\). Alternatively, in 2006, Chmiola et al.\(^5\) experimentally proved the confinement effect on \(d\) in microporous carbon EDLCs (pore size < 1 nm) that achieves an anomalous increase in the specific capacitance from 95 to 140 F g\(^{-1}\)\(^\text{–}^\text{18}–\text{10}\).

Two-dimensional materials, such as graphene sheets\(^11\), transition metal dichalcogenides\(^12\), and MXenes\(^5\), have recently been developed as electrode materials in EDLCs. Complete delamination of the two-dimensional materials increases the accessible surface area and the nanosheets with a large interlayer separation give a large specific capacitance greater than 240 F g\(^{-1}\)\(^\text{–}^\text{15}\). However, except for a few theoretical simulation results\(^13\), there has been very limited research carried out on the application of the confinement effect in two-dimensional materials as an additional strategy toward high-energy density capacitors.

Our aim was to quantify the contribution of the confinement effect to capacitance in EDLC electrodes consisting of two-dimensional materials, theoretically modeled as a slit capacitor (Fig. 1a)\(^9\),\(^13\). This conceptually straightforward but experimentally difficult study was performed using MXene EDLC electrodes. As pioneered by research groups led by Gogotsi and colleagues\(^5\),\(^14\),\(^15\), MXene is a class of two-dimensional materials with the following chemical formula: \(M_{n+1}X_nT_x\) (where \(M\) is a transition metal, \(X\) is carbon or nitrogen, \(T\) is surface termination group) and gives a large capacitance that is associated with ion intercalation\(^16\). Importantly, MXene maintains its stacked structure with a short interlayer distance during ion (de)intercalation, owing to strong interactions among the surface termination groups, intercalated ion species, and embedded solvents\(^17\). Such an anomalous interlayer interaction has led us to expect that MXene nanosheets strongly confine the intercalated ions and MXene is an ideal platform to study the guest confinement effect in two-dimensional materials.

Herein, using the MXene EDLC electrode as experimental and theoretical models for a slit capacitor, we demonstrate the negative dielectric constant of water confined between MXene nanosheets. This specific dipolar polarization of the confined

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**Fig. 1** Enlargement of the capacitance of a microslit capacitor. **a** Schematic illustration of a continuum model of a microslit capacitor consisting of MXene Ti\(_2\)CT\(_x\) nanosheets. Ti (dark cyan), C (brown), surface termination group T (gray) atoms are shown. **b** Schematic illustration of a bilayer-capacitor model. **c** Experimental specific capacitance of MXene Ti\(_2\)CT\(_x\) with aqueous Li\(^+\), Na\(^+\), K\(^+\), Rb\(^+\), TMA\(^+\) (tetramethylammonium), TEA\(^+\) (tetraethylammonium), and TBA\(^+\) (tetrabutylammonium) electrolytes. Each capacitance is calculated from the CV curve at the scan rate of 0.5 mV s\(^{-1}\). **d** Orders of bare-ion size, hydrated ion size, and observed capacitance. **e** Ion-MXene distance \((b−a_0)\) dependence of the experimental specific capacitance. The black dotted line shows a calculated capacitance based on the continuum model \((C = \frac{\varepsilon A}{d})\) with constant \(\varepsilon\varepsilon_0\), whereas the blue line shows a calculated capacitance based on the bilayer-capacitor model with variable \(\varepsilon\varepsilon_0\) from the 3D-RISM calculation.
water strongly overscreens an external electric field within the MXene EDLC electrode, leading to an anomalously enhanced capacitance.

**Results**

**Intercalation capacitance of MXene.** MXene Ti$_2$CT$_x$ was synthesized by removal of Al from Ti$_2$AlC (Supplementary Fig. 1) with LiF-HCl aqueous solution$^{17}$. The chemical composition of the resulting compound after complete dehydration at 200 °C (anhydrous MXene) was determined as Ti$_2$C(OH)$_{0.3}$O$_{0.7}$F$_{0.6}$Cl$_{0.4}$ using a standard microanalytical technique. As the water molecules can easily penetrate into the MXene interlayer, anhydrous MXene transforms to a hydrous form Ti$_2$CT$_x$·0.5H$_2$O (hydrous MXene) in ambient atmosphere. A transmission electron micrograph confirms a stacked structure of the MXene nanosheets (Supplementary Fig. 2), which enables a capacitance from ion intercalation (intercalation capacitance; Supplementary Note 1). The EDLC electrode consisting of the hydrous MXene was fabricated without delaminating the stacked structure of the Ti$_2$CT$_x$ layers. However, scanning electron micrographs (Supplementary Fig. 3) indicate an existence of partially exfoliated structures allowing a certain contribution to a capacitance from surface ion adsorption (surface capacitance)$^{18}$. To spotlight on the two-dimensional confinement effect on the intercalation capacitance of the MXene nanosheets, we carefully separated the two contributions using various aqueous electrolytes (Fig. 1a–e). First of all, to isolate the contribution from the surface capacitance, we measured capacitances with electrolytes consisting of small alkali cations (Li$^+$, Na$^+$, K$^+$, and Rb$^+$) at the scan rate of 0.5 mV s$^{-1}$. The MXene electrode gave a much larger specific capacitance (90–160 F g$^{-1}$) than the surface capacitance (Fig. 1c and Supplementary Fig. 4), and the ex situ XRD patterns indicate an increase in the interlayer distance upon charging (Supplementary Fig. 6). Furthermore, ex situ Ti K-edge spectroscopy suggests the reversible redox of Ti upon charge/discharge (Supplementary Fig. 7). All these experimental observations confirm the occurrence of intercalation capacitance. Cations are intercalated into nanoscale space between the MXene nanosheets, which gives a capacitance ($C$) of a slit capacitor with pore sizes < 2 nm expressed as follows$^{13}$:

$$C = \frac{\varepsilon_0 \varepsilon_a A}{b - a_0}$$

where $\varepsilon_0$ is the total dielectric constant between the electrode surface and the ion, $\varepsilon_a$ is the vacuum permittivity, $A$ is the total surface area of both walls, $a_0$ is the ionic radius$^{20,21}$, and $2b$ is the separation of the slit walls (Fig. 1a). It is important to note that, in contrast to a cylinder capacitor (Supplementary Table 1), $b$ for the slit capacitor depends on the alkali ion species intercalated in the slit. This equation predicts that the capacitance of the slit capacitor increases as the effective distance ($b - a_0$) between the electrode surface and the counterion decreases. However, contrary to the prediction of the above equation (black dotted line, Fig. 1e), the specific capacitance of the MXene electrode...
increased as $b - a_0$ increases ($\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$). The enlarged capacitance, e.g., for a Li$^+$ electrolyte is observed even at faster charge/discharge rates and during 300 charge/discharge cycles (Supplementary Fig. 8). The similar capacitance enlargement is generally observed for other MXenes (Ti$_3$C$_2$Tx and Mo$_2$CT$_x$) (Supplementary Figs. 9 and 10).

The anomalous increase of the MXene electrode capacitance in the order of Li$^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$ is further highlighted when considering that a conventional activated carbon EDLC electrode exhibits a roughly constant capacitance independent of the alkali ions species (Supplementary Figs. 11 and 12). XRD analysis shows that the intercalation of ions with larger “hydrated” ionic radii (Fig. 1d, Li$^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$) gave rise to a larger separation in the slit walls (Supplementary Fig. 6), whereas the $^1$H magic angle spinning (MAS) NMR indicates that the amount of confined water in MXene nanosheets increases after hydrated-ion intercalation (Supplementary Fig. 13). Therefore, water molecules are definitely co-intercalated (Fig. 1b) and we expect that the hydration shell has an important role in determining the structure inside the microslit and thus the anomalous capacitance.

**3D-RISM calculations of MXene.** To further understand and theoretically model the hydration structure in the MXene microslit capacitor for various alkali ions, we conducted a three-dimensional reference interaction site model (3D-RISM) calculation.\textsuperscript{22–23} The 3D-RISM calculation allows the simulation of a 3D distribution of solvent molecules, as well as calculations of solvation energy and optimal solvent density (Fig. 2a–f). Before cation intercalation (Fig. 2d), the atomic density profile along the $c$ axis (perpendicular to the MXene layers) suggests that both oxygen and hydrogen atoms primarily accumulate inside the microslit in the central plane of the microslit (away from the MXene interface). We presume that there is only a weak interaction between water and the MXene surface. Osti et al.\textsuperscript{26} also reported that water in pristine Ti$_3$C$_2$T$_x$ has bulk-like characteristics, which indicates the weak interaction between water and MXene.

3D-RISM calculations were then conducted for cation-intercalated Ti$_3$C$_2$T$_x$·$n$H$_2$O. The amount of H$_2$O between the MXene layers, $n$, was optimized energetically (Supplementary Fig. 14a) for each alkali ion with the fixed interlayer distance that was experimentally determined using the XRD patterns (Supplementary Fig. 6). The optimized hydration structures indicate the accommodation of larger amounts of water in MXene in the order of Li$^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$. This trend is explained by the increasing hydration energy of cations as their bare ionic radii decrease. The experimentally determined amount of water for each MXene using thermogravimetric (TG) analyses is in perfect agreement with the 3D-RISM calculation results (Supplementary Fig. 14b).

The oxygen distribution in the cation-intercalated MXenes (Fig. 2a) indicates that the oxygen atoms accumulate inside the hydration shells of the cations. Based on the radial distribution function of an ion–oxygen distance (Fig. 2c), the oxygen density immediately around Li$^+$ is much higher than that around Rb$^+$, suggesting the stronger hydration energy of Li$^+$ compared with Rb$^+$. Indeed, the oxygen density profile in the Li$^+$-intercalated MXene along the $c$ axis contains two peaks around Li$^+$ and these peaks are more intense than those around Rb$^+$ (Fig. 2e, f). Simultaneously, the hydrogen density profiles for the cation-intercalated MXene (Fig. 2b) indicate considerable hydrogen density close to the MXene surface. Considering a small hydrogen density near MXene before cation intercalation, the hydrogen...
atoms of water distributed along the surface of each MXene layer are predominantly due to the formation of the hydration shell around intercalated cations (Fig. 2e, f). The 3D-RISM calculations for a series of alkali ions show that the cations with smaller bare ionic radius tend to exhibit a larger hydrogen density near the MXene surface (Supplementary Fig. 15). The significant interference to water arrangement between Ti$_2$C$_2$Tx nanosheets by cation intercalation was also observed by Oستi et al. It is most likely to be that the hard hydration shell of strong Lewis acid cations such as Li$^+$ forces the hydrogen atoms to reside close to the surface of the MXene layer, whereas the soft hydration shell of weak Lewis acid cations such as Rb$^+$ deforms easily when confined within the microslit.

After confirming that the hydrogen and oxygen distributions in the microslit depend on the intercalated ionic species, we calculated the electrostatic potential profiles, relative to the MXene electrode (Fig. 3a, b and Supplementary Fig. 16). In the Rb$^+$-intercalated MXene (Fig. 3a), the electrostatic potential ($\Phi$) monotonically decreases from the MXene layer until very close to the ion location in the center of the microslit, as expected for a conventional capacitor sandwiching a dielectric layer. The charge density ($\rho$), electric field ($E$), and $\Phi$ are depicted schematically in Fig. 3c. For Li$^+$-intercalated MXene (Fig. 3b), in contrast, the profile change in $\Phi$ is not monotonic; $\Phi$ rises near the locus of Li$^+$, leading to a reduced total potential difference ($\Delta\Phi$). The 3D-RISM calculations for intercalation of a series of alkali ions show that the smaller cation-intercalated MXenes induces more reduced total $\Delta\Phi$ (Supplementary Fig. 16). Considering the capacitance ($C$) is expressed as,

$$ C = \frac{\Delta Q}{\Delta \Phi} \quad (3) $$

where $\Delta Q$ is the stored charge by applying $\Delta\Phi$ (Supplementary Note 1), the reduced $\Delta\Phi$ explains the larger capacitance of the MXene electrode in the order of Li$^+ >$ Na$^+ >$ K$^+ >$ Rb$^+$ (Fig. 1d). Indeed, the calculated $C$ based on the value of $\Delta\Phi$ from 3D-RISM well reproduces the experimental $C$ (blue line, Fig. 1e and Supplementary Fig. 17).

**Discussion**

Then, we consider the origin and implications of the reduced $\Delta\Phi$ specifically observed in Li$^+$-intercalated MXene. The electric-double layer formed in MXene system can be modeled as an equivalent circuit of a bilayer capacitor (Fig. 1b). The capacitance of a capacitor sandwiching two series of a contact layer and a water layer can be expressed as,

$$ C = \frac{A \varepsilon_0}{\lambda} \quad (4) $$

where

$$ \lambda = \frac{F}{\varepsilon_\ell} + \frac{\rho}{\varepsilon_\ell h} \quad (5) $$

with thicknesses ($F$, $\rho$) and dielectric constants ($\varepsilon_\ell$, $\varepsilon_\ell h$) for a contact layer and a water layer, respectively.

Based on density functional theory (DFT) calculations, in the first term $\frac{F}{\varepsilon_\ell}$ for the contact layer between the water and an electrode, $\varepsilon_\ell$ is small to be around 10$^9$ and $F$ is 2–3 Å. In the second term $\frac{\rho}{\varepsilon_\ell h}$ for the water layer confined in spaces ranging from macroslit (2b > 50 nm) to mesoslit (2 nm < 2b < 50 nm) (Supplementary Table 1), water molecules are weakly bounded to rotate freely and give a large positive $\varepsilon_\ell h$ of ~80, where the situation becomes as such $\frac{F}{\varepsilon_\ell} \gg \frac{\rho}{\varepsilon_\ell h}$, and hence $\lambda \sim \frac{F}{\varepsilon_\ell}$. Therefore, in macroslit and mesoslit capacitors, the dielectric contact layer (the first term) dominates the overall capacitance, where the water molecules do not have essential roles.

In striking contrast, in a microslit capacitor, the water layer (the second term) largely influences the overall capacitance. The increase in $\Phi$ near the locus of Li$^+$ indicates excess polarization (called, over-screening) and inversion of $E$ at the confined water layer (i.e., hydration shell) relative to the external electric field ($E_{ext}$, Fig. 3d). This inversion of $E$ (where $E = \frac{F}{\varepsilon_\ell}$) indicates that the dielectric constant of the hydration shell is negative. As theoretically shown by Bopp et al., a negative dielectric constant of water is possible under the condition of microscopic over-screening, which is realized by a resonant effect between dipolar polarization of water and an external electric field. Resonant conditions were suggested as follows: (i) an external electric field has several Å modulation and (ii) water is confined between a slit wall and an ion.

For a microslit (2b < 2 nm) capacitor, such as the MXene system described here, we presume that the resonant condition (i) on double-layer thickness is satisfied for all of Li$^+$, Na$^+$, K$^+$, and Rb$^+$ ions based on calculation results (Supplementary Fig. 16), whereas the resonant condition (ii) on firm water confinement is satisfied only by strong Lewis acid cations such as Li$^+$. The soft hydration shell of the weakly hydrated cations such as Rb$^+$ largely deforms even in the microslit as demonstrated in Fig. 2e, whereby water molecules are not confined effectively, and remain to have a positive dielectric constant. In contrast, the hard hydration shell of Li$^+$ is strongly confined between the MXene wall and Li$^+$ as evidenced in Fig. 2f, and water dipolar polarization resonantly overscreens the external electric field to induce an inverse $E$. It is this situation that can lead to a negative dielectric constant for the hydration layer and hence an increase in capacitance. Importantly, the overscreening of a hydration shell confined in a microslit capacitor is a general phenomenon: e.g., the 3D-RISM calculation for Li$^+$-intercalated Mo$_2$CT$_x$ also indicates the negative dielectric constant of confined water (Supplementary Fig. 18), explaining the capacitance enhancement experimentally observed for Mo$_2$CT$_x$ (Supplementary Fig. 10). As the simplest combination, the water confined in the microslit consisting of graphene is also predicted to exhibit the negative dielectric constant and the overscreening behavior (Supplementary Fig. 19). Furthermore, Geng et al. reported that the capacitance of metallic 1T MoS$_2$ with an aqueous Li$^+$ electrolyte is larger than that with an aqueous Na$^+$ electrolyte. These verifications strongly suggest that exploiting the water confinement effect is a versatile strategy to enhance the capacitance of microslit capacitors.

In general, the strategy of using larger surface area materials to increase the gravimetric capacitance severely suffers from smaller electrode density and smaller volumetric capacitance thereof. Our discovery of a negative dielectric constant of confined water and its contribution to larger capacitance of the microslit capacitor not only solve this long-standing dilemma but also offer an important prospect that stacked two-dimensional materials might be used to enhance capacitance and scalability of microslit capacitors by effecting interfacial desolvation, solid-electrolyte interphase formation, and co-intercalation. Moreover, existence of water molecules with a negative dielectric constant casts doubt on a conventional
capacitor model postulated by Stern with low-dielectric surface water layer and potentially leads to redefinition of how to construct theoretical models for EDLC electrodes. Further studies on similar confinement effects in other microporous materials are expected to stimulate a range of striking discoveries of EDLCs with higher gravimetric and volumetric energy densities.

**Methods**

**Synthesis of MXene.** Ti3AlC2 was prepared by high-frequency induction heating of a precursor mixture consisting of TiC, Ti, and Al at 1300 °C for 1 h under an Ar flow. Ti3CT, was synthesized by reacting 0.5 g of Ti3AlC2 powder with an aqueous mixture of LiF and HCl for 12 h at room temperature. The treated powder was dried under vacuum at 200 °C for 24 h (anhydrous MXene). The chemical composition of anhydrous MXene Ti3CT, was determined by the standard microanalytical method for C, H, F, and Cl, and by X-ray photoelectron spectroscopy for an O/ OH ratio. Calc. (Found) for Ti3C(OH)0.3O0.7F0.6Cl0.4: C: 8.03% (7.70%), H: 0.18% (0.25%), F: 6.28% (7.84%), Cl: 9.48% (9.22%).

**Characterization.** The powder XRD patterns were recorded on a Rigaku SMART-LAB powder diffractometer with Cu Kα radiation with a step of 0.02° over a 2θ range of 3°–80°. Samples for ex situ XRD patterns were prepared electrochemically and were used for the measurements without drying. The number of intercalated water molecules in MXene was estimated by TG analysis. The TG data were collected on a Seiko Exstar 6000 TG-DTA instrument over a 30–400 °C temperature range using an Ar gas atmosphere. The heating rate was fixed at 5 K min−1.

**Electrochemistry.** For the electrochemical measurements, the working electrode was fabricated by mixing Ti3CT, acetylene black, and polytetrafluoroethylene in 80:10:10 weight ratio. The resulting paste was pressed onto a nickel mesh. A three-electrode glass cell was assembled with a Pt mesh as the counter electrode and Ag/AgCl as the reference electrode. The 3D-RISM code is implemented using the Gaussian 09 program package (Gaussian Inc., Wallingford, CT). The 3D-RISM code combines plane-wave basis sets imposing cutoff energies of 30 and 300 Ry, Brillouin-zone summation was evaluated using a 3 × 3 × 1 k-point grid for structure optimization and total energy calculation. The convergence criteria for structure optimization included 10−4 eV per Bohr for forces and 10−4 Ry for the energy.

**Calculations.** The hydration energy and atomic distributions are calculated by using a 3D-RISM theory combined with DFT. The 3D-RISM code is implemented into a DFT simulation package named “Quantum Espresso.” The exchange–correlation functional was used within the generalized gradient approximation combined by Perdew et al.25,26. The ultrasoft pseudopotential scheme combined with plane-wave basis sets imposing cutoff energies of 30 and 300 Ry was used to describe the Kohn–Sham orbitals and electron density, respectively. The Brillouin-zone summation was evaluated using a 3 × 3 × 1 k-point grid for structure optimization and total energy calculation. The convergence criteria for structure optimization included 10−4 eV per Bohr for forces and 10−4 Ry for the energy.

The structural model of MXene Ti3CT, consisted of 2 × 2 × 3 rectangular supercell with four different surface functions (representing F, C, O, and OH). The chemical composition of hydrous MXene was assumed to be Ti3C (F24C18O9H6)0.5H2O. The lattice constants of the supercell were theoretically optimized as 12.326 × 21.349 Å2. The interlayer distance between the central Ti layer and the adjacent MXene sheets was set to experimentally determined values (i.e., 13.2, 13.1, 12.8, 12.7 Å for Li†, Na†, K†, and Rb†-intercalated models, respectively). Each intercalated model has two ions located at (1/4, 1/4, 1/2) and (3/4, 3/4, 1/2) in the fractional coordinates of each supercell. The validity of our structural models was confirmed by the perfect agreement between the experimentally determined and the theoretically optimized water contents (n) in various cation-intercalated MXenes (Supplementary Fig. 14). The calculated capacitance (C) for each cation-intercalated MXene (inset in Fig. 1b) was obtained by the equation as,

\[ C = \frac{\text{Surface Area}}{1 + \frac{\Delta V_{\text{intercalation}}}{\Delta V_{\text{calc}}}} \]  

where \( C_{\text{surface}} = 40 \ \text{F g}^{-1}, \Delta V_{\text{intercalation}} = 0.6 \ \text{eV g}^{-1} \) (0.125 cation intercalation per the formula unit), \( \Delta V(K)_{\text{calc}} = 1.17 \ \text{eV}, \Delta V(\text{Na})_{\text{calc}} = 1.0 \ \text{eV}, \) and \( \Delta V(\text{Li})_{\text{calc}} = 0.91 \ \text{eV}, \) respectively.

**Data availability**

The whole datasets are available from the corresponding author on request.

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Author contributions

M. Okubo and A.Y. conceived and directed the project. A.S. and S.K. synthesized and characterized MXenes. A.S. measured and analyzed the electrochemical properties. A.S., K.Y., and K.G. conducted and analyzed the $^1$H MAS NMR spectra. Y.A. and M. Otani conducted the 3D-RISM calculations. All authors wrote the manuscript.

Additional information

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