Microscopic Insights into the Efficiency of Capacitive Mixing Process

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Significance

With a theoretical study on the maximum energies that Capacitive mixing can output under different realistic conditions, we confirm that both hydrophilic electrode surfaces and electrolytes containing monovalent ions with smaller size are in favor of energy extractions. In addition, the temperature difference between salt and fresh water makes significant contribution. The theoretical predictions, matching experimental observations well, allow us to reveal the mechanisms through which the extracted energy can be much improved.

Keywords: Capacitive mixing, Energy extraction; Salinity difference; Efficiency

Spontaneous transport of ions in nature has nowadays been elaborately exploited to produce clean energy\textsuperscript{1-3}, and several novel technologies\textsuperscript{4} have been developed among which the Capacitive mixing (Capmix) techniques\textsuperscript{5,6} have attracted much attention as they are designated to harvest clean energy directly at the occasions where two types of solution with different ion concentrations are mixed. Indeed, besides the estuaries of rivers where river water mixing with seawater, in large petrochemical plants massive salinity water is mixed massively with fresh water. In fact, due to the substantial utilization of metal catalyst, the recycling water in chemical
plants consequentially contains salt ions. The high-salinity water flow not only causes serious corrosion of expensive equipment but also significantly depresses the degradation efficiency of organic contaminants. Whereas many purification technologies have been proposed in environmental science for the removal of salt ions from waste water, the conventional strategy in petrochemical plants is still to dilute the recycling water by blending fresh water. For the purpose of energy-saving, a novel process may be designed to extract the energy by using, e.g., one Capmix technique. Capacitive energy extraction, relying on cyclic double layer expansions (CDLE), is one of the Capmix techniques, and it depends on the repeated process in which the electrodes charge in fresh water and discharge in salt water. Because of the spontaneous ion transport, the decrease in free energy when salt water mixing with fresh water continuously gives rise to a net output of electrical energy.

There have been a number of experimental efforts to measure the energy output of CDLE processes. Most experimental works focus on the exploration of appropriate electrode materials. For example, it has recently been found that porous electrodes with hydrophilic surface could bring larger energy output than those with hydrophobic surface. Ahualli et al. investigated the electrode coated with ion-exchange membrane, and illustrated that the presence of divalent counterions in solution produced a fall in the cell potential, and this was attributed to the “uphill” transport of these ions against their concentration gradients inside the membranes. Marino et al. investigated various types of activated carbon electrodes modified in prior by means of the adsorption of charged molecules, and they reported that these electrodes gave a very high cell voltage rise of about 90 mV within the Capmix process. Different electrolyte solutions other than pure sodium chloride solution at different temperatures were also examined experimentally, and it has been found that the energy extraction could be depressed when
introducing multivalent ions\textsuperscript{12}, and improved by up to 5 folds if the temperature of the river water is raised to 50 °C above that of the seawater\textsuperscript{11,13}. The temperature gradient may be found in the power plants where the hot fresh water is collected from a refrigeration process or in the circumstance where the fresh water meeting with seawater comes from hot springs.

A few mathematical models have also been proposed to estimate the output energy. For instance, a modified Poisson-Boltzmann theory based on a lattice gas model was applied for investigating temperature effects\textsuperscript{13}, while ionic correlations and variable dielectric permittivity, as considered to be essential in the current model, were totally neglected. Basing on primitive model for electrolyte, the electrode hydrophilicity was analyzed by density functional theory with modeling the dielectric profile as piecewise constants\textsuperscript{20}. The maximum net output of the energy is associated with a thermodynamic cycle schematically displayed in Fig. 1. As shown, the thermodynamic cycle for the CDLE process consists of four stages, and two of them in open circuit and two in closed circuit. In stage 1, the electrodes are charged with an electrical potential difference $V_0$ applied and in equilibrium with salt water. During the first step of the thermodynamic cycle from stage 1 to stage 2, the circuit is switched off, and the salt water inside the electrical cell is gradually replaced by fresh water. In this step the surface charge density at the electrode remains unchanged due to the open circuit, while the decrease in bulk ion concentration raises the open-cell voltage from $V_0$ to $V_0 + \Delta V_{\text{fresh}}$. In the next step from stage 2 to stage 3, the circuit is switched on, and electrochemical cell outputs energy by discharging. After the voltage falls, e.g., back to $V_0$, the electrical cell is switched off again, and the fresh water in the cell is gradually replaced with the salt water during the step from 3 to 4. The rise in ion concentration further decreases the open-cell potential from $V_0$ to $V_0 - \Delta V_{\text{salt}}$. Finally, the thermodynamic cycle is closed by charging the electrodes in salt water again (from 4 to 1).
Because the electrical work is related to the product of the surface charge and the electrical potential difference, the grey area surrounded by this cycle in Fig. 1 represents the net energy that can be extracted from the thermodynamic cycle\textsuperscript{21}. Clearly, the key point of boosting the output energy is to raise the voltage range $V_{\text{fresh}} + V_{\text{salt}}$ showed in the figure, or the surface charge difference $\sigma_{12} - \sigma_{34}$, or both. In this letter, we employ a realistic model of electric double layers (EDLs) to analyze the output energy under various conditions. The theoretical analysis is based on our recent developments on the modified Poisson-Boltzmann theory\textsuperscript{22-24}. Specifically, we explore the mechanisms how the electrode surface hydrophobicity and solution composition affect the output energy and the capacitance of EDL capacitors pertinent to the thermodynamic cycle.

Most electrodes are made of activated carbon\textsuperscript{25,26}. The pore structure of carbon electrolyte might be characterized by micropore of 1-2 nanometer (nm), mesopore of 5-50 nm and macrospore of 60-100 nm\textsuperscript{26}, depending on the activation time and temperature\textsuperscript{27}. It has been argued that a pore size distribution in the range 2-5 nm represents a way to improve the energy density and the power capability\textsuperscript{26}. However, anomalously high capacitance was observed when the fine-tuned carbon electrode contains a large numbers of small micropores\textsuperscript{28-30}. Inside these micropores, where the average pore size is less than or comparable with one Debye length in electrolyte solution, the overlapping of the EDL should be taken into account\textsuperscript{31}. Toward this issue, several models\textsuperscript{32,33} have been developed including the MPB employed in this work\textsuperscript{34}. Nevertheless, we note that for the carbon electrode used in Capmix the most abundant pores are typically less than 10 nm in diameter\textsuperscript{11,12,35}, and thus the fully developed EDLs were attempted\textsuperscript{11-13,21}. These models can be expected to properly capture the essentials of the CDLE mechanism although in reality the pores will be neither parallel nor equally sized.
In the current theoretical investigation, a series of capacitors with two planar and parallel electrodes is considered. The separation between two electrodes is sufficiently large so that the bulk state of electrolyte solution exists in the middle of EDLs. Between the electrodes, the solvent is modelled as continuum with position-dependent dielectric coefficient reflecting the surface hydrophobicity of the electrodes as discussed below. Cations and anions are treated as spheres with different radii \((a_i)\) and charge valences \((z_i)\) (see the \textit{supporting information}, SI). The ion bulk concentrations are 0.02 mol/L (M) for fresh water and 0.4 M for salt water for simulating the river water and saltwater\(^{12}\). Another ion concentration for salt water (i.e., 0.6 M) is also tested when examining the temperature effect. Following the thermodynamic cycle presented in \textbf{Fig. 1}, the maximum output work \((W)\) can be calculated by integrating the surface charge density \((\sigma)\) with respect to electrodes potential difference \((V)\), namely,

\[
W = \int_{V_0}^{V_0 + \Delta V_{\text{fresh}}} \sigma dV - \int_{V_0 - \Delta V_{\text{salt}}}^{V_0} \sigma dV + \sigma_{12} \Delta V_{\text{fresh}} - \sigma_{34} \Delta V_{\text{salt}}. \tag{1}
\]

Here \(\sigma_{12}\) and \(\sigma_{34}\) are the surface charge densities on the electrodes at stage 1 (or 2) and 3 (or 4), respectively. In order to carry the calculation for the output work, one only needs to identify the relation between the surface charge density and electrode surface voltage.

The electrode surface hydrophobicity can be macroscopically measured with contact angle and microscopically described by using the ratio of the solvent-solvent interaction energy to that of the substrate-solvent interaction energy\(^{36,37}\). Here we adopt a phenomenological approach to address the contribution of the surface hydrophobicity to the capacitance. On the guidance of Bonthuis \textit{et al.}\(^{38}\), the hydrophobicity of the electrode surface affects the local water distribution in the vicinity of the electrodes. We can thus represent it effectively by the following spatial distribution of dielectric permittivity\(^{39}\),
Here, $x$ is the distance from the electrode, $\varepsilon_n$ is the dielectric constant of bulk water and its value depending on the solvent temperature is collected in Table S2, and $\varepsilon_s$ is the dielectric constant at the electrode surface, and in this work we set it as $\varepsilon_s = 10$ representing carbon\textsuperscript{40} or silicon\textsuperscript{41} electrode surface. $\lambda$ is the control parameter and it takes different values for describing the hydrophobicity of the electrode surface\textsuperscript{39}. Typically, $\lambda = 0.3$ nm accounts for a hydrophilic surface, and $\lambda = 1.5$ nm for a hydrophobic surface. In the intermediate region of this parameter, namely $\lambda = 0.9$ nm, the electrode surface is designated as moderate. In the vicinity of hydrophilic (case I), moderate (case II) and hydrophobic (case III) electrode substrate surface, the dielectric coefficient profiles as well as the resultant ion local concentration profiles at two representative bulk ion concentrations are presented and justified in the Fig. S3.

The relation between the surface voltage and charge density is investigated by adopting the modified Poisson-Boltzmann theory developed in our previous work\textsuperscript{22,24}. In this molecular theory, a treatment decomposing the EDL into an ion-free Stern layer with thickness of the smallest ion’s radius and a diffuse layer is proposed with the inclusion of significant effects of ionic correlations and size. In the present approach, the electric potential in space, designated as $\Phi(x)$, satisfies the classical Laplace equation in the Stern layer, while in the diffusion layer $\Phi(x)$ is described by a modified Poisson-Boltzmann (MPB) equation in which the ion size effect is accounted for by considering the Born energy due to the varying dielectric coefficient, and ion-ion correlations are all included by involving a potential of mean force (PMF) for each ion. As detailed in the SI, the MPB theory incorporating with the dielectric coefficient distribution in Eq. (2) is solved by means of a finite-difference numerical method with two-level
iterations, and this theory gives satisfactory ion concentration distributions compared with particle simulations\textsuperscript{22}. Once the system is solved iteratively, the charge distribution is obtained for a given surface potential, and the dependence of the surface change density on the surface potential difference between electrodes is then determined upon the neutrality condition. By performing MPB calculations, the effects of electrode materials, ionic valences, ionic sizes and electrolyte temperatures are analyzed.

Firstly, by translating the effects of electrode hydrophobicity into dielectric coefficient profile near the electrode surface (Fig. S3a), we investigate three different cases (case I, II and III) from hydrophilic to hydrophobic surfaces. The local density profiles of ion nearby the electrodes with different wettability are depicted in Fig. S3b for ion bulk concentration $c_b = 0.02 \text{ M}$ and in Fig. S3c for $c_b = 0.4 \text{ M}$. As shown, the local density of counterion is much higher near a hydrophilic surface than that near a hydrophobic surface. This gives rise to a decrease of the potential range as increasing the surface hydrophobicity (Fig. 2a) and suppresses the extracted energy per unit area (Fig. 2b). This prediction agrees qualitatively with the experimental observation\textsuperscript{17}. Iglesias et al. examined two carbon electrode samples with almost identical pore size distribution but quite different surface wettability, and they found\textsuperscript{17} that the hydrophobic sample with contact angle 125 degree presented a voltage rise of 9.5 mV and a output energy 6.7 $\mu \text{J}$, while the hydrophilic sample with contact angle 29 degree presented a voltage rise of 33.4 mV and a much larger output energy 680 $\mu \text{J}$. It is noteworthy that in an inhomogeneous dielectric environment the PMF plays an important role for the EDL structure, and precisely, the hydrophilic electrode leads to a more attractive PMF to ion (Fig. S4), hence a larger surface charge density at the same applied voltage, which promotes the energy output.
Secondly, electrolytes with asymmetric sized ions are examined and the numerical results
of extracted energies are plotted in Fig. 2c for three kinds of electrolyte solutions with \( a_+ = 0.4 \)
\( \text{nm} \) and \( a_- = 0.2, 0.3 \) or \( 0.4 \) \( \text{nm} \). The charge valence remains \( z_+: z_- = 1:\text{--}1 \) and the electrode
surface is hydrophobic (i.e., case III discussed above) in three systems. We observe that smaller
size of ion gives rise to larger extracted energy, but this effect is not significant when the applied
potential is less than \( 0.2\text{V} \). This is because the ion size effect is noticeable only in the region with
high ion crowding density. To explain this more clearly, we plot the density profiles of
counterions with different ion sizes at a fixed surface potential \( V_s = 0.2 \text{ V} \) in Fig. 2d. Although
the thickness of the Stern layer in the first layer decreases as the ion size becomes small, which is
favorable for energy extraction, the density peak decreases as well, and the completion between
both effects finally leads to a slightly enhanced extracted energy.

Thirdly, when three electrolytes with different valence compositions are studied, we
demonstrate that the presence of multi-valence ions lowers down the voltage range (Fig. 3a) and
thus the energy extraction (Fig. 3c). In addition to the obvious effect of valence in the so-called
steric PB model\(^1\) which has been applied as a theoretical explanation, we argue that the local
density of ion with multivalence is less sensitive to the increase of applied potential when it is
relatively large. To demonstrate, we calculate the rise of surface charge density from fresh water
to salt water at given applied electrode surface potential for three kinds of salt water with
\( z_+: z_- = 1:\text{--}1, 2:\text{--}1 \) and \( 2:\text{--}2 \). In each circumstance, the salt concentration satisfies \(|z_+|c_b = 0.4 \text{ M} \) for salt water and \( 0.02 \text{ M} \) for the \( 1:\text{--}1 \) fresh water. To reduce the ion size effect, the ion
size is set uniformly as \( 0.3 \text{ nm} \). The rise of surface charge density in function of applied potential
is depicted in Fig. 3b, and three curves clearly show that the rise of surface charge density
overall increases with the increase of applied potential. While for the case of \( z_+: z_- = 2:\text{--}2 \), the
curve reaches a plateau quickly, indicating that the local density rise remains almost unchanged when the applied potential is greater than 0.2V. In practice, different ions can be found in natural river water and seawater, and these ion components generally have different charge valences and sizes. Fernandez et al.\textsuperscript{42} studied the multi-ionic effect by comparing the energy extraction from the salinity exchange of the following electrolyte solution with its diluent: sodium chloride solution (NaCl), simulated seawater (SSW) and real seawater (RSW). The solution composition and ion concentrations in these electrolyte solutions were different, which are copied in Table S1. Neglecting the ion size effect first, we calculate the extracted energy by taking into account the charge valence effect together with a linear combination of the contribution from ion concentrations. The calculation result is displayed in Fig. 3d, showing a satisfactory comparison with the experimental measurement from Fernandez\textsuperscript{42}.

Finally, we show that the potential rise $\Delta V_{\text{fresh}}$ (Fig. 4a) and energy extractions (Fig. 4b) are almost in linear dependence on the temperature of fresh water when the temperature of the salt water remains at 25°C. Our numerical results tend to match well with the experimental results\textsuperscript{11} qualitatively (Fig. 4c), although the deviation turns to be more obvious for a larger $V_0$ (0.4 V). The experimental value of the extracted energy per unit apparent surface area was measured with porous carbon electrodes. Whereas the most abundant pores in these electrodes were typically less than 5 nm, micropores with pore size as low as 1 nm exist. The contribution for energy extraction from micropores, which is not addressed here, can be largely enriched at high charging potential since in this case large energy is supplied for ions going in micropores after dehydration. To provide a better theoretical description, both fully developed and overlapping EDLs should be considered. It has to be mentioned that the increment of temperature leads to the decrement of the inverse of thermal energy $\beta = 1/(k_B T)$ with $k_B$ the
Boltzmann constant, and meanwhile reduces the bulk dielectric constant (Table S2 in SI), which causes stronger ion-ion correlations. Both effects are favorable for promoting the energy extraction.

In brief, we present a comprehensive theoretical study on the effects of electrode hydrophobicity, solution composition and temperature on the performance of the Capmix techniques for energy extraction by using the MPB theory. In agreement with experiments, the theoretical study predicts that: (1) a hydrophilic electrode yields a larger capacitance and boosts higher energy extraction amount in comparison to a hydrophobic electrode, owing to that a hydrophilic electrode brings a more attractive PMF to ions; (2) the ion size presents non-negligible effect to the energy extraction, and under the same condition if the anion size is smaller the output work is larger, and this effect becomes nonnegligible when the applied voltage is large; (3) the presence of divalent ions suppresses the output energy, and this is because multivalence increases the surface charge for a given surface potential but decreases the potential difference for a fixed surface charge between fresh and salt water; (4) increasing the temperature of fresh water can almost linearly raise the voltage range and thus boost output energy. This theoretical study gives clues for the efficient application of these energy extraction methods.

SUPPORTING INFORMATION
The modified Poisson-Boltzmann theory and the calculation details are presented. This material is available free of charge via the Internet at http://onlinelibrary.wiley.com.

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Notes
The authors declare no competing financial interest.

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References:


Figure captions

**Figure 1.** Representation of the thermodynamic cycle in the capacitive mixing technique.

**Figure 2.** a) the potential range versus the surface wettability; b) the extracted work per unit surface area versus the potential difference for three electrodes with different hydrophobicity. In both a) and b) the symmetry electrolyte with $a_\pm = 0.3$ nm is applied; c) the extracted work per unit area versus the potential difference with cations’ size $a_+ = 0.4$ nm while anions’ sizes $a_- = 0.4$, 0.3 and 0.2 nm for a hydrophobic electrode (case III); d) the counterions’ density profiles near the surface for difference sizes of anions with surface potential $V_s = 0.2$ V. In all cases, the ion charge ratio is $1: -1$, and the bulk concentration is $c_b = 0.4$ M for salt water and 0.02 M for fresh water.

**Figure 3.** a) the voltage ranges between electrodes for three electrolytes with ion charge valence $1: -1$, $2: -1$ and $2: -2$ ($a_\pm = 0.3$ nm); b) the rise of surface charge density versus the applied electrode surface potential; c) the extracted work per unit area versus the applied surface potential; d) comparison of predicted extracted work with experimental results for three different electrolyte solutions subject to applied surface potential 0.4 V: NaCl, Simulation Sea Water (SSW), and Real Sea Water (RSW). In all cases, the bulk concentration satisfies $|z_+|c_b = 0.4$ M for salt water and 0.02 M for the $1: -1$ fresh water.

**Figure 4.** The effect of the temperature of fresh water. $1: -1$ symmetry electrolytes ($a_\pm = 0.3$ nm) with different temperatures are studied: a) the potential rise $\Delta V_{\text{fresh}}$ versus the temperature of fresh water; b) the extracted work per unit area versus the electrodes potential difference for
fresh water in different temperatures; c) comparison of predicted extracted work with experimental results. In all cases, salt water is in 25°C and fresh water is in 25°C ~ 65°C. The bulk concentration is $c_b = 0.6$ M for salt water and 0.02 M for fresh water.
Figure 2
Figure 3

(a) Potential range (Voltage) vs. Charge valence ($z_+ : z_-$)

(b) Change in conductivity ($\Delta \sigma$) vs. Voltage ($V$)

(c) Work ($W$) vs. Voltage ($V$)

(d) Energy ($E$) vs. Type of Solution (NaCl, SSW, RSW)
Figure 4
Supporting Information

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1. Model and Method

The capacitor with two electrodes as two electric double layer (EDL) capacitors connected in series is shown in Fig. S1. Both electrodes are assumed as smooth and flat plates, and are connected with an external power for maintaining a potential difference $V$ between electrodes when closing the circuit. The distance between two electrodes are thought as much larger than the Debye length of the bulk such that two EDLs are well separated by the middle region where the bulk state of electrolyte solution is expected to exist. Under normal physical intuition, we assume balanced electrode charges $\sigma$ and $-\sigma$ on positive and negative electrodes at the equilibrium state, which was also mentioned in the asymmetric electrodes model\textsuperscript{1}. However, potential differences across EDLs near positive and negative electrodes are in general not expected to be $V/2$ and $-V/2$ respectively for asymmetric electrolytes. We need to study each EDL individually by varying the surface potential $V_s$ in order to obtain the corresponding surface charge density and afterwards the capacitance. The final measured capacitance should be the integrated one via series calculation of two connected EDLs.
It’s to be noted that there are numerous research works focusing on supercapacitors wherein the porous materials are utilized for preparing the electrodes. The theoretical models of these supercapacitors are usually quite different from the simple EDL model employed here, and in their cases different geometrical pores within the porous material of one electrode, in which electrolyte solution was adsorbed subject to the charged walls carrying same kind of charge, were analyzed. These models are, however, physically identical to the simple EDL model except that the surface area therein is dramatically large and that there may exist interesting ion size effects if the pore size of the target pore reduces to nano-scale.

The electrolyte solution considered here is composed of water and ions. The water solvent is treated as continuum which contributes a position-dependent dielectric coefficient $\varepsilon(x)$ with $x$ being the direction perpendicular to the electrode surface. The cations and anions are modeled by charged spheres with individual ion size. The radius of each cation is denoted as $a_+$, the charge valence is $z_+$ and the bulk concentration is $c_+^b$. Accordingly, the radius, charge valence and bulk concentration for anions are $a_-$, $z_-$ and $c_-^b$, respectively.
**Figure S1:** Schematic representation of a capacitor with positive and negative electrodes under a given potential difference $V$ between two electrodes. The red circles denote for cations and purple for anions. Both EDLs are decomposed into an ion-free Stern layer with width $H$ and a diffuse layer from $x = H$ to $L$ with $L$ much larger than the Debye length.

For one EDL, the theoretical calculation of the surface charge density ($\sigma_s$) with a given surface potential ($V_s$) is based on a recent developed self-consistent field (SCF) model\(^5\) for investigating supercapacitance\(^6\). In this model, the one-dimensional electric potential $\Phi(x)$ is satisfied by the following Laplace equation in the Stern layer ($0 < x < H$) with $H$ being the smallest ion’s radius in this work and the modified Poisson-Boltzmann (MPB) equation in the diffuse layer ($H < x < L$),

$$
\left\{ \begin{array}{l}
-\varepsilon_0 \frac{\partial}{\partial x} \left[ \varepsilon(x) \frac{\partial \Phi(x)}{\partial x} \right] = 0 & \quad 0 < x < H, \\
-\varepsilon_0 \frac{\partial}{\partial x} \left[ \varepsilon(x) \frac{\partial \Phi(x)}{\partial x} \right] = e \sum_{i=x} z_i e^{b_i \varepsilon} \exp[-\beta U_i(x)] & \quad H < x < L.
\end{array} \right. \hspace{1cm} (S1)
$$

Here $\varepsilon_0$ is the permittivity in vacuum and $\varepsilon(x)$ is the relative position-dependent dielectric permittivity. $\beta = 1/(k_B T)$ is the inverse thermal energy. $U_i$ is the potential of mean force (PMF) accounting for correlation effects:

$$
U_i(x) = z_i e \Phi(x) + \frac{1}{2} z_i^2 e^2 u_i(x). \hspace{1cm} (S2)
$$

Worth noting is that the MPB Eq. (S3) can be simplified into a canonical Poisson-Boltzmann (PB) equation by the treatment of neglecting the second term and hence correlations in Eq. (S4), which originates from the self-energy, and $u_i(x)$ is defined as following:
\[ u_i(x) = \lim_{r' \to r} \left[ G_i(r, r') - G_0(r, r') \right], \]  
(S5)

where \( G_0 \) is the free-space Green’s function described by \( -\varepsilon_0 \nabla^2 G_0(r, r') = \delta(r - r') \) with \( r = (x, y, z) \), while the function \( G_i \) is described by a generalized Debye-Hückel (DH) equation,

\[-\varepsilon_0 \nabla \cdot \varepsilon_i(r, r') \nabla G_i(r, r') + 2 I_i(r, r') G_i(r, r') = \delta(r - r'). \]  
(S6)

Here the dielectric constant \( \varepsilon_i \) and the local ionic strength \( I_i \) are defined as

\[
\varepsilon_i(r, r') = \begin{cases} 
1 & |r - r'| < a_i \\
\varepsilon(x) & \text{otherwise,}
\end{cases}
\]  
(S7)

and

\[
I_i(r, r') = \begin{cases} 
0 & |r - r'| < a_i \text{ or } x < H, \\
I(x) = \frac{1}{2} \beta e^2 \sum_i z_i^2 c_i(x) & \text{otherwise.}
\end{cases}
\]  
(S8)

In the above equation, \( c_i(x) \) is the local concentration of component \( i \).

After the potential field \( \Phi(x) \) of the above equation system with Dirichlet boundary conditions \( \Phi(0) = V_s \) and \( \Phi(L) = 0 \) is solved efficiently, the surface charge density is then obtained by the Neumann boundary condition

\[
\sigma_s = -\varepsilon(x) \left. \frac{\partial \Phi(x)}{\partial x} \right|_{x=0}. \]  
(S9)

The differential capacitance can be then calculated through equation \( C_{\text{diff}} = d\sigma_s / dV_s \). Eq. (S9) describes the surface charge density \( \sigma_s \) as function of the surface voltage \( V_s \). We use trapezoidal rule to integrate the formula in Eq. (1) and thus the extracted energy can be obtained.

2. Calculation method and details
In order to solve the self-consistent equation system consisting of Eqs. (S1-S4) efficiently, we have involved both asymptotic methods and finite difference numerical algorithms. First, we approximate the solution of Eq. (S10) as

\[ u_i(x) \approx \frac{\tilde{u}}{1 - 4\pi\varepsilon_v\varepsilon a_i \tilde{u}} + \frac{1}{4\pi\varepsilon_v a_i} \left( \frac{1}{\varepsilon} - 1 \right), \]  

(S11)

with similar treatments in Ref. 6, here \( \tilde{u} = \lim_{r \to r'} (\tilde{G} - \tilde{G}') \) and

\[
\begin{align*}
-\varepsilon_0 \nabla \cdot \varepsilon \nabla \tilde{G} + 2I(r)\tilde{G} &= \delta(r - r'), \\
-\varepsilon_0 \varepsilon (r') \nabla^2 \tilde{G}' &= \delta(r - r').
\end{align*}
\]

(S12)

Above equations are solved by sparse inversion techniques after the Fourier transform with respect to \( y - y' \) and \( z - z' \). Once \( u_i(x) \) is obtained in each iteration, we use a two-level self-consistent iterative algorithm to solve Eqs. (S1-S4) with given boundary conditions. The first iteration consists of two alternating steps: for given density profiles and potential \( \Phi(x) \), solve \( u_i(x) \); and with solved \( u_i(x) \), solve Eq. (S13) to obtain updated density profiles and potential \( \Phi(x) \). The iterative steps are performed until some convergence criteria is arrived. The second sub-level iterative scheme is embedded in the solution of the nonlinear MPB (S14) with more details referred to Ref. 6.

We have compared the solutions of the MPB [Eqn. (S15)] with results obtained from particle-based Monte Carlo (MC) simulations and the canonical PB model for electrolytes around a dielectric sphere. Two examples for comparison are given in Fig. S2 while more general cases are referred to Ref. 5.
**Figure S2:** Comparison of the predicted local density profiles from Monte Carlo (MC) simulations, modified Poisson-Boltzmann (MPB) method and Poisson-Boltzmann (PB) method for cation and for anion around a sphere with radius 2 nm. The electrolyte solution is composed of cation and anion with 1:−1 charge valence and the cation bulk density is: (a) 50 mM and (b) 100 mM.

In this case study, the surface charge density on the sphere is \(-0.2 \, e/\text{nm}^2\), and the relative dielectric constant for the solute sphere is 10 while that for electrolyte bulk solution is fixed as 80. The dielectric profile near the electrode surface is determined by Eq. (2) with \(\lambda = 0.2 \, \text{nm}\). The radial distribution functions of cation and anion are shown versus the distance to the sphere surface. The good agreement between MPB and MC in two bulk concentrations validates the application of MPB method in the present study.

**3. Description of the electrode surface hydrophobicity**

The electrode surface hydrophobicity has a profound effect on the charge distribution in space. Here we adopted a phenomenological method to describe the surface hydrophobicity by
mimicking the spatial distribution of dielectric coefficient. As detailed in Eq. (2), the surface hydrophobicity can be characterized by assigning different values to the control parameter $\lambda$. Typically we take $\lambda = 0.3$ nm for representing a hydrophilic electrode surface (designated as case I), and 0.9 nm for a moderate electrode surface (case II), and 1.5 nm for a hydrophobic electrode surface (case III). The dielectric profiles determined by Eq. (2) for three different cases are plotted in Fig. S3a, displaying that the dielectric profile gradually increases starting from $\varepsilon_{a}$ (the dielectric constant of the electrode) to $\varepsilon_{b}$ (the dielectric constant of bulk electrolyte solution). In addition, Fig. S3a shows that the interfacial zone with suppressed dielectric constant is larger if the electrode surface is more hydrophobic, and this trend mainly owns to the fact that hydrophobic surface suppresses the water density in the vicinity, and thus decreases the dielectric constant.

**Figure S3b** plots the density profiles of anion near the electrode surface calculated with MPB method. The surface potential is fixed as $V_{s} = 0.2$ V, and three curves correspond to three different hydrophobicity of the electrode as depicted in Fig. S3a, and the ion bulk concentration is $c_{b} = 0.02$ M accounting for fresh water. Similar curves are plotted in Fig. S3c for salt water with ion bulk concentration $c_{b} = 0.4$ M. Both figures show that when the electrode surface is more hydrophilic, the anion density at the first layer is higher, and seemingly hydrophilic surface is more attractive to ion than hydrophobic one.
Figure S3: (a) Dielectric profiles for different cases I, II and III; (b) the density profiles of anion near the electrode surface with a fixed surface potential $V_s = 0.2 \text{ V}$ at three different hydrophobicity cases described in (a), and the ion bulk concentration is $c_b = 0.02 \text{ M}$ accounting for fresh water; (c) same as (b) but for salt water with ion bulk concentration $c_b = 0.4 \text{ M}$.

The potential of mean force (PMF) reflects the strength of such an attraction between the electrode surface and the ion. Figure S4 plots the PMF distribution between an ion and electrodes with different hydrophobicity in fresh water and in salt water. As shown, the PMF is stronger when the surface is more hydrophilic disregarding the ion bulk concentration, verifying that a more hydrophilic electrode surface is more attractive to ions.
Figure S4: PMF distributions between an ion and electrodes in the fresh water and salt water. Three cases describe the surface wettability of the electrodes as in Fig. S3.

4. Calculation details for charge valence effect

The solution composition and ion concentrations for the experiments from Fernandez et al.\textsuperscript{7} are copied in Table S1.

Table S1: The solution composition and ion concentrations for sodium chloride (NaCl), simulated seawater (SSW) and real seawater (RSW) for the experiments of Fernandez et al.\textsuperscript{7}.

<table>
<thead>
<tr>
<th>ion component</th>
<th>NaCl (mM)</th>
<th>SSW (mM)</th>
<th>RSW (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>600</td>
<td>500</td>
<td>400</td>
</tr>
<tr>
<td>MgSO\textsubscript{4}</td>
<td>/</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>CaCl\textsubscript{2}</td>
<td>/</td>
<td>/</td>
<td>10</td>
</tr>
<tr>
<td>MgCl\textsubscript{2}</td>
<td>/</td>
<td>35</td>
<td>20</td>
</tr>
<tr>
<td>KCl</td>
<td>/</td>
<td>/</td>
<td>10</td>
</tr>
</tbody>
</table>
We use our theoretical model to consider the charge valence effect by studying three different electrolytes for seawater: 1:−1, 2:−1 and 2:−2 electrolytes with the same value of $|z_+|c_b$, which is fixed as the saltwater ion bulk concentration 0.4 M here. Those three cases with all monovalent ions, half multivalent ions and all multivalent ions are thought to approximately correspond to the pure NaCl solution, SSW and RSW, respectively.

5. Description of the temperature-dependent dielectric constant

Table S2: Temperature considered in this work and the corresponding dielectric constant in bulk solvent on the guidance of Ref. 8.

<table>
<thead>
<tr>
<th>$T\ (\degree C)$</th>
<th>$\varepsilon_b$</th>
</tr>
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<tbody>
<tr>
<td>25</td>
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<td>35</td>
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<td>65.2</td>
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</table>

References:
