Thermal Dependence of Nanofluidic Osmotic Energy Conversion by Reverse Electrodialysis

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The theoretical model of surface charge density

The curve of the surface charge density $\sigma_s$ versus pH with respect to temperature is analytically deduced using the site-binding model for a silica surface in contact with a 1 M KCl aqueous solution.\textsuperscript{S1–S4} The two main reactions on the silica surface are given by

\begin{align*}
\text{SiOH} & \rightleftharpoons_{K_{i0}} \text{SiO}^- + H^+ \quad \text{..................................................................................................................(S1)} \\
\text{SiOH} + H^+ & \rightleftharpoons_{K_{(+)}} \text{SiOH}_2^+ \quad \text{..................................................................................................................(S2)}
\end{align*}

where $K_{(-)}$ and $K_{(+)}$ are the intrinsic equilibrium constants of each reaction and can be defined by the following relationships:

\begin{align*}
K_{(-)} &= \frac{N_{\text{SiOH}^+}}{N_{\text{SiOH}}} c_{H^+}^S \quad \text{..................................................................................................................(S3)} \\
K_{(+)} &= \frac{N_{\text{SiOH}_2^+}}{N_{\text{SiOH}}} c_{H^+}^S \quad \text{..................................................................................................................(S4)}
\end{align*}

Here, $N_i$ is the ionic surface density of available sites, and $c_{H^+}^S$ is the concentration of protons in the Stern layer, which can be described by the Boltzmann distribution as follows:

\begin{equation}
\begin{split}
c_{H^+}^S &= c_h^B \exp\left(-\frac{e \varphi_d}{k_B T}\right) \quad \text{..................................................................................................................(S5)}
\end{split}
\end{equation}

where $c_h^B$, $e$, $\varphi_d$, $k_B$, and $T$ are the bulk concentration of the solution, the electron charge, the electric potential at the outer Helmholtz plane (OHP) in the electrical double layer (EDL) in the Gouy–Chapman–Stern model, the Boltzmann constant, and the absolute temperature, respectively.

Assuming that adsorption of ions ($K^+$ and $Cl^-$) to the surface can be neglected, the surface charge density at the OHP is calculated by the site-binding model:

\begin{equation}
\begin{split}
\sigma_s &= eN_s \frac{K_{(+)} c_{H^+}^S - K_{(-)} / c_{H^+}^S}{1 + K_{(+)} c_{H^+}^S + K_{(-)} / c_{H^+}^S} \quad \text{..................................................................................................................(S6)}
\end{split}
\end{equation}
where \( N_s \) is the total surface site density and is defined as \( N_s = N_{SiO^-} + N_{SiOH} + N_{SiOH^2} \). For an aqueous 1:1 electrolyte solution, the modified Grahame equation can be used to estimate the surface charge density at the OHP (\( \sigma_d = \sigma_a \)) as follows:

\[
\sigma_a = \sqrt{8\varepsilon_0\varepsilon_r k_B T} 10^3 N_A (c+10^{\text{pH}}+10^{\text{pH}-pK_w}) \sinh\left(\frac{-e\sigma_d}{2k_B T}\right)
\]

where \( \varepsilon_0, \varepsilon_r, N_A, c, \) and \( pK_w \) are the permittivity of vacuum, the dielectric constant of the electrolyte solution, the Avogadro number, the bulk concentration, and the dissociation constant of water, respectively. From the requirement of electroneutrality, the following relationship should be satisfied:

\[
\sigma_s + \sigma_d = 0
\]

In addition, the equilibrium constant of the surface reaction, the dielectric constant of the electrolyte solution, and the dissociation constant of water are given as functions of temperature.\(^{55-57}\)

\[
K_s(T) = K_s(T_0) \exp \left\{ -\frac{\Delta H^o}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right\}
\]

\[
\varepsilon_r = 87.740 - 0.40008T_c + (9.398 \times 10^{-4})T_c^2 - (1.410 \times 10^{-6})T_c^3
\]

\[
K_w = 8.754 \times 10^{-10} \times \exp \left( -1.01 \times 10^6 \times \frac{1}{T^2} \right)
\]

Equation S9 is the van’t Hoff equation, where \( \Delta H^o, R, \) and \( T_0 \) are the enthalpy change of the reaction, the gas constant, and the initial temperature, respectively. In eq S10, \( T_c \) is the temperature in degrees Celsius. Here, \( \Delta H^o = 30 \text{ kJ mol}^{-1}, N_s = 1.3 \text{ sites} \text{ nm}^{-2}, \) and \( pK_w(-) = 7.5 \) are employed as the best-fitting model parameters for the experimental results for SBA-15 mesoporous silica at 298 K reported by Salis et al.\(^8\) The \( pK_w(+) \) can be calculated from \( \text{pH(PZC)} = -0.5 \times \log (pK_w(-)/pK_w(+)) \), where \( \text{pH(PZC)} \) is the pH.
value at which the surface charge density becomes zero and is assumed to be pH(PZC) = 3 for silica. It is reported that the enthalpy change of the reaction, $\Delta H^\circ$, for silica (SiO$_2$) is between 15 and 90 kJ mol$^{-1}$ and the pK$_{(-)}$ varies from 5.7 to 9.8.\textsuperscript{33} Figure S1 shows the $\sigma_s$ versus pH curves calculated from eqs S1–S11 for a 1 M KCl aqueous solution. The value of $\sigma_s$ is positive at pH < 3, whereas it is negative at pH > 3; it becomes increasingly negative with increasing pH and then approaches a constant value at approximately pH = 12. At a given pH, $\sigma_s$ decreases gradually with increasing temperature. When the EDLs are overlapped (in the surface-charge-governed regime), higher ionic conductance can be obtained at higher $\sigma_s$; therefore, higher ionic conductance can be obtained at higher pH and higher temperature.

![Figure S1](image-url)

Figure S1. Analytically deduced $\sigma_s$ vs. pH curves for a 1 M KCl aqueous solution at various temperatures.
S2. Activity coefficient with respect to temperature

If the concentration of an aqueous solution is less than 2 mM, the Debye–Hückel limiting law can generally be employed to calculate the activity coefficient of the solution as\(^{59}\)

\[
\log \gamma_i = -Az_i \sqrt{I} \quad \text{..........................................................(S12)}
\]

Here, \(\gamma_i\) and \(z_i\) are the activity coefficient and valency of ion species \(i\), respectively, and \(I\) is the ionic strength of the electrolytes, which is defined as 

\[
I = \left(\frac{1}{2}\right) \sum_i m_i z_i^2
\]

where \(m_i\) is the molar concentration of ion species \(i\). \(A\) is a temperature-dependent constant; its experimental value for water is 0.509 mol\(^{-1/2}\) kg\(^{1/2}\) at 298 K.

In this work, highly concentrated (up to 1 M) aqueous solutions at various temperatures are used to clarify the energy conversion characteristics; thus, the Debye–Hückel limiting law cannot be used to calculate the activity coefficient of the solution. Here, we use the Pitzer model considering the temperature effects. In this model, \(\gamma(T)\) can be expressed as follows: \(^{50-52}\)

\[
\ln \gamma_M(T) = z_M^2 f^{\gamma}(T) + 2 \sum_X m_X G_{MX}(T) + \sum_M \sum_X m_M m_X G_{M}(T) \quad \text{..............................(S13)}
\]

\[
\ln \gamma_X(T) = z_X^2 f^{\gamma}(T) + 2 \sum_M m_M G_{MX}(T) + \sum_M \sum_X m_M m_X G_{X}(T) \quad \text{..............................(S14)}
\]

where the subscripts \(M\) and \(X\) refer to the cation and anion, respectively. In eqs S13 and S14, the electrostatic term, \(f^{\gamma}(T)\), is given by

\[
f^{\gamma}(T) = -A^g(T) \left\{ \frac{\sqrt{I}}{(1+b\sqrt{I})} + \frac{2}{b} \ln \left(1+b\sqrt{I}\right) \right\} \quad \text{..............................(S15)}
\]

where \(b\) is a constant and is assumed to be 1.2 at all temperatures, and \(A^g(T)\) is the Debye–Hückel coefficient for the osmotic function, which is given by
\[ A^\alpha(T) = \frac{1}{3} \left( \frac{2\pi N_A \rho_w(T)}{10^3} \right)^{1/2} \left( \frac{e^2}{4\pi \varepsilon_r(T)\varepsilon_0 k_B T} \right)^{3/2} \]  

(S16)

where \( \rho_w(T) \) and \( \varepsilon_r(T) \) are the temperature-dependent density and the dielectric constant of water, respectively. \( \rho_w(T) \) is given by

\[
\rho_w(T) = 10^3 \left( 1 - \frac{(T + 288.9414)(T - 3.9863)^2}{508929.2(T + 68.12963)} \right)
\]  

(S17)

\[ G_{Mx}(T), G'_m(T), \text{ and } G'_x(T) \] are given by

\[
G_{Mx}(T) = B_{Mx}(T) + \frac{1}{2} \left( \sum_i m_i |z_i| \right) C_{Mx}(T)
\]  

(S18)

\[
G'_m(T) = z_m^2 B'_{Mx}(T) + z_m C_{Mx}(T)
\]  

(S19)

\[
G'_x(T) = z_X^2 B'_{Mx}(T) + |z_X| C_{Mx}(T)
\]  

(S20)

where \( C_{Mx}(T) \) is given by

\[
C_{Mx}(T) = \frac{C_{Mx}^d(T)}{2\sqrt{|z_m z_X|}}
\]  

(S21)

For 1:1 electrolytes, \( B_{Mx}(T) \) and \( B'_{Mx}(T) \) are given by

\[
B_{Mx}(T) = \beta_{Mx}^{(0)}(T) + \frac{2 \beta_{Mx}^{(1)}(T)}{\alpha^2 I} \left\{ -\left( 1 + \alpha \sqrt{I} \right) \exp \left( -\alpha \sqrt{I} \right) \right\}
\]  

(S22)

\[
B'_{Mx}(T) = \frac{2 \beta_{Mx}^{(1)}(T)}{\alpha^2 I^2} \left\{ -1 + \left( 1 + \alpha \sqrt{I} + \frac{1}{2} \alpha^2 I \right) \exp \left( -\alpha \sqrt{I} \right) \right\}
\]  

(S23)

where \( \alpha \) is a constant and is assumed to be 2.0. The derivatives of the interaction parameters \( C_{Mx}^d(T), \beta_{Mx}^{(0)}(T), \text{ and } \beta_{Mx}^{(1)}(T) \) with respect to temperature are summarized in Table S1.
Table S1. Temperature Derivatives of Interaction Parameters $C_{MX}^{(0)}$, $\beta_{MX}^{(0)}$, and $\beta_{MX}^{(1)}$ for KCl\textsuperscript{S13}

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$\frac{\partial C_{MX}^{(0)}}{\partial T}$</th>
<th>$\frac{\partial \beta_{MX}^{(0)}}{\partial T}$</th>
<th>$\frac{\partial \beta_{MX}^{(1)}}{\partial T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>$-5.095\times 10^{-4}$</td>
<td>$5.794\times 10^{-4}$</td>
<td>$10.71\times 10^{-4}$</td>
</tr>
</tbody>
</table>

Figure S2 shows the activity coefficient of the solution versus the concentration [$\gamma(T) - c$] calculated by the Pitzer model for KCl aqueous solutions at various temperatures.

![Figure S2. Activity coefficient of the solution vs. concentration [$\gamma(T) - c$] for KCl aqueous solutions. Temperature varies from 293 to 323 K.](image-url)
S3. Redox potential with respect to temperature

To calibrate the Ag/AgCl electrodes, the redox potential \( V_{\text{redox}}(T) \) between KCl aqueous solutions with different concentrations is measured in an electrochemical cell system at different temperatures. In the measurement of \( V_{\text{redox}} \), qualitative filter papers (ADVANTEC No. 1 type, Toyo Roshi Kaisha, Ltd., Japan) are used as a salt bridge. The filter papers are 200 µm thick and retain coarse and gelatinous precipitates. The temperature of the solutions in the electrochemical cell is controlled by a thermostat (Proline RP 845, Lauda, Germany), and the temperature is measured by type-K thermocouples. In this study, \( V_{\text{redox}}(T) \) is measured at four temperatures: 283, 293, 303, and 313 K. Furthermore, \( V_{\text{redox}}(T) \) is calculated by the Nernst equation:

\[
V_{\text{redox}}(T) = \frac{RT}{zF} \ln \frac{\gamma_{c_H}(T)c_H}{\gamma_{c_L}(T)c_L}
\]

where \( R, F, z, \) and \( \gamma \) are the gas constant, Faraday constant, charge valency, and activity coefficient, respectively. The \( \gamma(T) \) in eq S24 is calculated by the Pitzer model considering temperature variation. Figure S3 shows the measured and calculated \( V_{\text{redox}} \) values as a function of temperature.

Figure S3. Measured and calculated \( V_{\text{redox}} \) as a function of temperature for different concentration gradients. Dashed lines are the fitted lines.
The measured $V_{\text{redox}}$ is smaller than the calculated one, and the difference increases with increasing $\log(c_H/c_L)$. The measured $V_{\text{redox}}$ versus temperature curves are fitted by a linear function:

$$V_{\text{redox}}(T) = a + bT \quad \text{(S25)}$$

where $a$ and $b$ are fitting parameters. The fitted parameters are summarized in Table S2.

Table S2. Fitted Parameters $a$ and $b$ for $V_{\text{redox}}$ Prediction

<table>
<thead>
<tr>
<th>log $(c_H/c_L)$</th>
<th>1</th>
<th>1.477</th>
<th>2</th>
<th>2.477</th>
<th>3</th>
<th>3.477</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ / mV</td>
<td>−0.0036</td>
<td>0.00152</td>
<td>0.00868</td>
<td>−0.00408</td>
<td>0.00008</td>
<td>0.0082</td>
<td>−0.01152</td>
</tr>
<tr>
<td>$b$ / mV K$^{-1}$</td>
<td>0.002</td>
<td>0.00026</td>
<td>0.00034</td>
<td>0.00046</td>
<td>0.00054</td>
<td>0.0006</td>
<td>0.00074</td>
</tr>
</tbody>
</table>

In the nanofluidic device shown in Figure 2b, electrical power can be created by applying an ion concentration gradient, that is, by filling two reservoirs with aqueous solutions at different concentrations. To evaluate the thermal effect on the energy conversion of this device, experiments are performed at several different temperatures in a temperature range of 293–333 K. Although the temperature measured by a type-K thermocouple attached to the top surface of the device is equal to the temperature to which the thermoelectric device is set, the temperature of the solutions measured by type-K thermocouples inserted in the reservoirs is slightly lower than the set temperature. Figure S4 illustrates the locations of the Ag/AgCl electrodes and type-K thermocouples. The Ag/AgCl electrodes and type-K thermocouples inserted in the reservoirs are located in the second poly(dimethylsiloxane) chip layer approximately 6 mm above the thermoelectric device. Because the ambient temperature is approximately 293 K and the heat release from the solution surface is not negligible, the measured temperature of the solutions in the reservoirs is slightly lower than the set temperature. The
measured temperatures of the solutions in the reservoirs and the set temperature of the thermoelectric device are summarized in Table S3.

![Diagram of experimental setup](image)

Figure S4. Locations of Ag/AgCl electrodes and type-K thermocouples.

<table>
<thead>
<tr>
<th>Set $T$ [K]</th>
<th>293</th>
<th>303</th>
<th>313</th>
<th>323</th>
<th>333</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir $T$ [K]</td>
<td>292.3</td>
<td>298.8</td>
<td>305</td>
<td>311.3</td>
<td>314.4</td>
</tr>
</tbody>
</table>

$V_{\text{redox}}(T)$ is attributed only to the asymmetric redox reaction at each interface between the Ag/AgCl electrode and electrolyte. Therefore, $V_{\text{redox}}(T)$ is calculated from eq S25 using the measured temperature of the solution in the reservoirs.
S4. Nonconductive state above threshold temperature

Figure 5a,b show that the measured $V_{oc}$ and $I_{sc}$ increase with increasing temperature until a certain temperature level. But as the temperature increases further they decrease and finally become zero. To confirm the process to reach a nonconductive state, the time history of the measured ionic current was recorded in the temperature range of 283–353 K. Figure S5 shows the measured ionic current with respect to time at different temperatures from 283 to 353 K. $V_{out}$ is kept constant at 0.1 V. The reservoirs are filled with $c_L = 10^{-4}$ M and $c_H = 3 \times 10^{-3}$ M KCl aqueous solution, respectively. As the temperature is increased from 283 to 343 K, the ionic current shows a stable conductive state. However, when the temperature is increased up to 353 K, the ionic current gradually decreases for about 15 s and eventually becomes almost zero, i.e. a nonconductive state, owing to extraction of gases from the solution and blockage of the ionic current. This suggests that there is a threshold temperature where the MPS film changes from conductive to nonconductive states.

![Figure S5](image)

Figure S5. Measured ionic current with respect to time at different temperatures from 283 to 353 K. $V_{out}$ is kept constant at 0.1 V. The reservoirs are filled with $c_L = 10^{-4}$ M and $c_H = 3 \times 10^{-3}$ M KCl aqueous solution, respectively.
References


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