ELECTROCHEMICAL CARBON DIOXIDE CAPTURE
TO CLOSE THE CARBON CYCLE

Supporting Information

Authors: R. Sharifian¹², R.M. Wagterveld², I. A. Digdaya³, C. Xiang³, D. A. Vermaas¹

¹ Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, The Netherlands.
² Wetsus, European Centre of Excellence for Sustainable Water Technology, Leeuwarden, The Netherlands.
³ Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, USA.

This supporting information provides additional data, calculations, and correlations to the main
text in three sections as described separately below.

1 Solubility of CO₂(g) and carbonate minerals

The underlying correlations for obtaining Figure 4.a and b of the main paper are given here. Subsequently, the values of the solubility product (i.e., K_{sp}) of the three main forms of calcium carbonate minerals and the effect of temperature and pH on K_{sp} are provided.

1.1 Solubility of CO₂(g): Effect of the temperature, salinity, and pressure

The temperature (T, in K) dependent CO₂ solubility coefficient (K₀, in mol L atm⁻¹) and carbonic acid dissociation constants (K₁ and K₂) in water at 1 atm are given by:[1]

\[
\log K_0 = 108.3865 + 0.01985076T - 6919.53/T - 40.45154 \log T + 669365/T^2
\]

\[
\log K_1 = -356.3094 - 0.06091964T + 21834.37/T + 126.8339 \log T - 1684915/T^2
\]

\[
\log K_2 = -107.8871 - 0.03252849T + 5151.79/T + 38.92561 \log T - 1684915/T^2
\]

In seawater, K₀ depends on the salinity (S, in ‰) and temperature (T, in K), as expressed by:[2]

\[
\ln K_0 = -58.0931 + 90.5069(100/T) + 22.2940 \ln(T/100) + S[0.027766 -0.025888(T/100) + 0.0050578(T/100)^2]
\]

The carbonic dissociation constants (K₁ and K₂) in seawater at 1 atm are represented by the following equations:[3]

\[
\log K_1 = 43.6977 + 0.0129037S - 1.364 \times 10^{-4}S^2 - 2885.378/T - 7.045159 \ln T
\]

\[
\log K_2 = 452.0940 - 13.142162S + 8.101 \times 10^{-4}S^2 - 21263.61/T - 68.483143 \ln T - (581.4428S + 0.259601S^2)/T - 1.967035S \ln T
\]

where S is the salinity (in ‰). At an average seawater S = 34.8‰, the pressure dependent K₁
and $K_2$ of carbonic acid is given by:[4]

$$\log \left( \frac{K_1^P}{K_1^1} \right) = 0.013 + 1.319 \times 10^{-3} P - 3.061 \times 10^{-6} P T - 0.161 \times 10^{-6} T^2 - 0.02 \times 10^{-6} P^2$$

$$\log \left( \frac{K_2^P}{K_2^1} \right) = -0.015 + 0.839 \times 10^{-3} P - 1.908 \times 10^{-6} P T + 0.182 \times 10^{-6} T^2$$

where $K_1^1$ and $K_2^1$ are $K_1$ and $K_2$ at 1 atm, and $K_1^P$ and $K_2^P$ at $P$ atm. These equations are valid for temperature range between 2 °C and 22 °C and pressures up to 1000 atm.

### 1.2 Solubility of carbonate minerals: Effect of the temperature and pH

Uptake and release of carbon at alkaline pH usually involve precipitation of carbonate mineral through the reaction of $\text{CO}_3^{2-}$ with divalent cation such as $\text{Ca}^{2+}$ (i.e., $\text{CaCO}_3$). The solubility of $\text{CaCO}_3$ depends on the pH due to the hydrolysis of $\text{CO}_3^{2-}$. At 25 °C and 1 atm the Solubility product ($K_{sp}$) is $3.31 \times 10^{-9}$ for calcite, $4.61 \times 10^{-9}$ for aragonite, and $1.22 \times 10^{-8}$ for vaterite. Figure S.1a and b below show the $K_{sp}$ of various $\text{CaCO}_3$ crystal forms at temperature range between 0 and 90°C and the calcite solubility as a function of pH and temperature, respectively.

![Fig. S.1](image)

**Fig. S.1** | (a) Solubility product ($K_{sp}$) of three different crystal forms of $\text{CaCO}_3$ as a function of temperature. (b) Logarithmic calcite solubility in water as a function of the water pH and temperature.

The solubility products of calcite ($K_{sp, \text{calcite}}$), aragonite ($K_{sp, \text{aragonite}}$), and vaterite ($K_{sp, \text{vaterite}}$) at temperature range between 0 and 90 °C are given by:[1]

$$\log K_{sp, \text{calcite}} = -171.9065 - 0.0077993 T + 2839.319 / T + 71.595 \log T$$

$$\log K_{sp, \text{aragonite}} = -171.9773 - 0.0077993 T + 2903.293 / T + 71.595 \log T$$

$$\log K_{sp, \text{calcite}} = -172.1295 - 0.0077993 T + 3074.688 / T + 71.595 \log T$$

In seawater, at salinity range between 27 and 43‰ and temperature range between 2 and 25 °C, $K_{sp, \text{calcite}}$ is given by:[5]

$$K_{sp} = [-34.452 - 39.866S^{1/3} + 110.21 \log S - 7.5752 \times 10^{-6} T^2] \times 10^{-7}$$
The values of $K_{sp, \text{calcite}}$ as a function of pressure ($P$, in atm) in seawater is expressed by:[6]

$$
\ln \left( \frac{K_{sp, \text{calcite}}}{P} / K_{sp, \text{calcite}}^1 \right) = 0.071320 + 0.0080412P - 2.2544 \times 10^{-5} PT
$$

where $K_{sp, \text{calcite}}^1$ is the solubility product of calcite at 1 atm and $K_{sp, \text{calcite}}^P$ is the solubility product of calcite at elevated pressure.

## 2 Electrical energy consumption for CO$_2$(g) capture: Electrolysis vs. BPMED

In this section, the underlying assumptions and calculations for obtaining Figure 14 of the main article body are provided. The aim here is to compare the electrical energy required for the CO$_2$(g) capture and recovery using a pH-swing generated via (membrane) electrolysis and BPMED. As an example, the magnitude of pH swing here is considered to be $\Delta\text{pH} = 14$. The required voltage (hence the energy consumption) of both methods depends strongly on the magnitude of the applied $\Delta\text{pH}$. Note that a milder $\Delta\text{pH}$ can enable lower energy consumptions.

Using both electrolysis and BPMED, 1 mole of OH$^-$ and 1 mole of H$^+$ per mole of electron can be produced. Assuming the following reactions, each produced OH$^-$ (or H$^+$) ion, contributes to 1 mole of CO$_2$(g) being captured (or recovered):

\[
\begin{align*}
\text{CO}_2(\text{g}) + \text{OH}^- & \leftrightarrow \text{HCO}_3^- \quad \text{at pH} > 8.5 \text{ for the capture step} \\
\text{HCO}_3^- + \text{H}^+ & \leftrightarrow \text{CO}_2(\text{g}) \quad \text{at lower pH for the recovery step}
\end{align*}
\]

According to the Faraday's law, the electric quantity (Q) to produce 1 mole CO$_2$(g) is 1 Faraday constant (F = 96485 C/mol). The energy involved in the pH swing can be calculate from eq. 11 from the main paper:

$$
E = \frac{i \cdot A \cdot V}{r_{\text{CO}_2(\text{g})}}
$$

Assuming the Coulombic efficiency for the acid-base production is 100%, the energy consumption per mole of capture CO$_2$(g) can then be calculated via $E = F \cdot V$

The required voltage for (membrane) electrolysis can be written as [7]:

$$
V_{\text{electrolysis}} = E_{\text{anode}}^0 - E_{\text{cathode}}^0 + i \sum R = E_{\text{cell}}^0 + \eta_{\text{H}_2/\text{O}_2} + i \sum R_{\text{tot}}
$$

Where $E_{\text{anode}}^0$ is the standard anode potential for oxygen evolution reaction (OER), $E_{\text{cathode}}^0$ is the standard cathode potential for hydrogen evolution reaction (HER), $i$ is the applied current density, $R_{\text{tot}}$ is the total ohmic resistivity and $\eta_{\text{H}_2/\text{O}_2}$ is the over potential at the anode and
cathode for OER and HER (i.e., the Tafel plot). The estimated value for each term is given in Table 1.S below.

Similarly, the required voltage for BPMED can be written as [8]–[10]:

\[ V_{BPMED} = 0.059 \Delta pH + \eta_{WDR} + i \sum R_{tot} \]

Where \( \Delta pH \) is the difference of the pH over the BPM and \( \eta_{WDR} \) is the over potential associated with the water dissociation reaction in the junction layer of the BPM. The estimated value for each term is given in Table 2.S below.

For the calculations, electrochemical cells as shown in Figure S.2 are assumed. For BPMED, the effect of the end electrodes is neglected as multiple cell pair (CEM-AEM-BPM) can be stacked up in one unit, overruling the electrodes overpotential. In electrolysis stacking is not possible and the process is strongly dependent on the electrode reactions.

![Figure S.2 | Schematic of the (membrane) electrolysis cell (a) and the BPMED cell (b) used for calculation of the electrical energy consumption of the electrochemical CO2(g) capture & recovery.](image)

**a) (Membrane) electrolysis: \( E_{cell}^0 + \eta_{H2/O2} + i \sum R_{tot} \)**

1. The standard cell potential, \( E_{cell}^0 \) according for the water redox is as follow:
   - Cathode: \( 2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \) \( E_{cathode}^0 = -0.829 \text{ V vs. SHE at pH=14} \)
   - Anode: \( 2H_2O \rightarrow 4e^- + O_2(g) + 4H^+ \) \( E_{anode}^0 = 1.23 \text{ V vs. SHE at pH=0} \)

\[ E_{cell}^0 = E_{anode}^0 - E_{cathode}^0 = 1.23 - (-0.829) = 2.059 \text{ V for creating a } \Delta pH =14. \]

2. \( \eta_{H2/O2} \) is approximately \( 2 \times 0.1 = 0.2 \text{ V at current density } i = 20 \text{ mA/cm}^2 \) (based on the Tafel plot for HER and OER).

3. The ohmic voltage drop is \( i \sum R_{tot} \), where \( R_{tot} = R_e + R_m + R_b + R_c \) as shown in Table 1.S:
Table 1.S Summary of the ohmic resistances and the subsequent voltage losses in (membrane) electrolysis.

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_e ) (electrolyte resistance) for 0.5 M NaCl</td>
<td>20 ( \Omega ). cm(^2) (^a)</td>
</tr>
<tr>
<td>( R_m ) (membrane resistance)</td>
<td>4 ( \Omega ). cm(^2) (^b)</td>
</tr>
<tr>
<td>( R_c ) (circuit resistance)</td>
<td>neglected</td>
</tr>
<tr>
<td>( i \times R_b ) (H(_2)(g) and O(_2)(g) bubble ohmic losses)</td>
<td>0.2 V</td>
</tr>
</tbody>
</table>

Assuming \( i = 20 \text{ mA/cm}^2 \):
\[
i \left( R_e + R_m + R_b \right) = 0.68 \text{ V}
\]

\(^a\) Assuming a 0.5M NaCl electrolyte: a conductivity of 47 mS/cm and a cell total thickness of 0.5×2 =1 cm so that \( R_e = 20 \Omega \). cm\(^2\). \(^b\) Assuming an ion exchange membrane from Fumasep B.V. (FAB).

b) Ex-situ BPMED: \( 0.059 \Delta pH + \eta_{WDR} + i \sum R_{tot} \)

Ex-situ here means that a neutral salt stream (e.g., NaCl) is used to produce high purity NaOH and HCl in BPMED. The produced acid and base are then used for CO\(_2\)(g) capture and recovery in external gas absorption and desorption steps.

1. The reversible Nernstian voltage based on the free enthalpy for creating a \( \Delta pH =14 \) over the BPM is \( 0.059 \times 14 = 0.826 \text{ V} \) [10].
2. \( \eta_{WDR} \): reaction overpotential is estimated at 0.15 V [9].
3. \( i \sum R \): The ohmic voltage losses can be estimated as shown in Table 2.S.

Table 2.S Summary of the ohmic resistence and voltage losses in Bipolar membrane electrodialysis (BPMED).

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_e ) (electrolyte resistance) for 0.5 M NaCl</td>
<td>20 ( \Omega ). cm(^2) (^a)</td>
</tr>
<tr>
<td>( R_m ): ( R_{CEM} + R_{BPM} + R_{AEM} )</td>
<td>4+10+4 =18 ( \Omega ). cm(^2) (^b)</td>
</tr>
<tr>
<td>( R_c ) (circuit resistance)</td>
<td>neglected</td>
</tr>
</tbody>
</table>

Assuming \( i = 20 \text{ mA/cm}^2 \):
\[
i \left( R_e + R_m \right) = 0.76 \text{ V}
\]

\(^a\) Assuming a 0.5M NaCl electrolyte: a conductivity of 47 mS/cm and a cell total thickness of 0.5×2 =1 cm so that \( R_e = 20 \Omega \). cm\(^2\). \(^b\) assuming an IEM & BPM from Fumasep B.V.

3 The market size and price of CO\(_2\) utilization products

Table S.3 below gives the values associated with Figure 17 of the main article body, showing the market size and price of CO\(_2\) utilization products in various regions between 2018 and first quarter of 2020 (unless otherwise noted). CO\(_2\) and H\(_2\) market size and price are included for reference.
<table>
<thead>
<tr>
<th>CO₂ utilization products</th>
<th>Market size (megatonne year⁻¹)</th>
<th>Price ($ tonne⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>120.27</td>
<td>139 – 180</td>
<td>[14]–[17]</td>
</tr>
<tr>
<td>Propane</td>
<td>195b</td>
<td>317 – 374</td>
<td>[18]–[22]</td>
</tr>
<tr>
<td>Ethylene</td>
<td>184</td>
<td>474 – 609</td>
<td>[23]–[25]</td>
</tr>
<tr>
<td>Propylene</td>
<td>100</td>
<td>551 – 800</td>
<td>[26]–[29]</td>
</tr>
<tr>
<td>Methanol</td>
<td>98.9</td>
<td>174 – 235</td>
<td>[30]–[32]</td>
</tr>
<tr>
<td>Ethanol</td>
<td>86.8</td>
<td>45 – 1026</td>
<td>[33]–[36]</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>2.15</td>
<td>750 – 3670</td>
<td>[37]–[39]</td>
</tr>
<tr>
<td>Acetone</td>
<td>6.1</td>
<td>906 – 1770c</td>
<td>[40], [41]</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>17.28</td>
<td>330c</td>
<td>[42], [43]</td>
</tr>
<tr>
<td>Formic acid</td>
<td>1.02</td>
<td>225 – 332c</td>
<td>[44], [45]</td>
</tr>
<tr>
<td>Urea</td>
<td>187.8</td>
<td>214 – 860</td>
<td>[46]–[49]</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>150</td>
<td>236d</td>
<td>[50]</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>230</td>
<td>15 – 120</td>
<td>[51]</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>102</td>
<td>1640 – 2500</td>
<td>[52]–[54]</td>
</tr>
</tbody>
</table>


**References**


2020


