Supplemental Information

Efficient CO₂ Utilization via a Hybrid Na-CO₂ System Based on CO₂ Dissolution

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Figure S1. The components of hybrid Na-CO$_2$ cell. Related to Figure 1. (A) The digital photograph of hybrid Na-CO$_2$ cell. (B) The anode and cathode assembly of Na-CO$_2$ cell. (C) The components of anode coin cell. Details are available in Transparent Methods. Related to Figure 1.
Figure S2. Mole fractions of the three different carbonate forms, *i.e.*, carbonic acid ion, bicarbonate ion, and carbonate ion, as a function of pH of dissolved solution (Note: carbonic acid ion here includes ionic carbon dioxide). Related to Figure 1.
Figure S3. Cathodic full-cell CV profiles measured by Pt/C+IrO₂ catalyst at 0.1 mV s⁻¹ in the hybrid Na-CO₂ system conducted in three-electrode configuration using Ag/AgCl. 

Related to Figure 3. CV profiles measured in O₂, N₂, or CO₂ saturated (A) 0.1 M NaOH (B) seawater. These profiles reveal the CO₂ dissolution could render a favorable electrochemical environment to HER.
Figure S4. The pH of the CO$_2$-saturated 0.1 M NaOH solution. Related to Figure 2. (A) before test and (B) after 1000 hours test.
Figure S5. Gas chromatography (GC) profiles of generated gas during discharge process, Related to Figure 3. The gas obtained during cathodic reaction proceeded in (A) CO₂ saturated 0.1 M NaOH (B) CO₂ saturated seawater.
Figure S6. XRD profile of the solidified aqueous solution via freeze-drying. Related to Figure 3. The inset shows the obtained white powder.
Figure S7. XRD profiles of the soluble product after discharge reaction obtained by various drying conditions. Related to Figure 3. (A) Dried at room temperature. Because non-marine evaporites precipitate in different proportions of chemical elements from those found in the aqueous environments, three different minerals (nahcolite: NaHCO₃, thermonatrite: Na₂CO₃·H₂O, and trona: Na₂CO₃·NaHCO₃·2H₂O) are naturally obtained. (B) Dried at 70 °C oven. Only Na₂CO₃ is formed when dried at high temperature.
Figure S8. The experimental CO$_2$ conversion efficiency. Related to Figure 3. (A) Theoretical CO$_2$ conversion rate at current of 100 mA. (B) The quantitative GC profiles of outlet CO$_2$ gas during practical measurement condition for different inlet CO$_2$ flow rate of 23.0 mL min$^{-1}$.

We have determined the efficiency of CO$_2$ conversion during the reaction time. First, theoretical CO$_2$ conversion rate is determined by calculating H$^+$ removal rate during discharge reaction. Because one CO$_2$ molecule can make one H$^+$ molecule from the dissolution process (i.e., $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$) and two H$^+$ molecules can make one H$_2$ molecule (i.e., $2H^+ + 2e^- \rightarrow H_2$), we can assume two CO$_2$ molecules can contribute to produce one H$_2$ molecule (100 % conversion efficiency). As shown in Figure S8A, the theoretical CO$_2$ conversion rate is determined at the current of 100 mA, i.e., 1.39 mL min$^{-1}$. Then, the quantitative GC profiles of outlet CO$_2$ gas during discharge reaction have been examined. As shown in Figure S8B, the measurement proceeds at the inlet CO$_2$ flow rate of 23.0 mL min$^{-1}$ and the outlet CO$_2$ flow rate was 22.34 mL min$^{-1}$. Accordingly, the practically converted CO$_2$ rate is determined, i.e., 0.66 mL min$^{-1}$. Thus, the practical efficiencies of CO$_2$ conversion were calculated to be 47.7 %. Although this value is lower than the theoretical conversion rate, it is meaningful in that proves the additional CO$_2$ dissolution during the discharge process. It is also expected that the time that CO$_2$ contacts the solution (i.e., it related to the depth of the solution.) will also affect the conversion rate.
Figure S9. The GC profile of generated gas during the oxidation process. Related to Figure 4 and Figure S10. The data indicates a generation of O$_2$ gas (In detailed GC profiles are available in Figure S10).
Figure S10. Raw data of gas chromatography profiles of evolved gas during charging process. Related to Figure S9 and Figure 4. As shown in Figure S9, the GC profile reveals the gas contains O₂, CO₂, N₂. This raw data of GC intensity profiles is obtained and total gas, and each gas component profiles are indicated. The total gas is obtained in order of GCounts \((1.25 \times 10^9)\). For O₂, it obtained in almost same intensity \((1.25 \times 10^9)\). For CO₂, however, the intensity is obtained in \(7.0 \times 10^7\), revealing the intensity is significantly smaller than that of O₂ (~ 2 order difference). Because the measuring is conducted in CO₂ purged aqueous electrolytes, the dissolved CO₂ could be generated. In the case of N₂, a bit more intensity is obtained in 3.0
$\times 10^8$. Since $N_2$ cannot be produced in any electrochemical oxidation reactions, it is arisen from the inflow of air during measuring process. Therefore, the evolved gas during charging process is confirmed to be $O_2$. 
Table S1. Concentration of various ions when CO₂ dissolves in water at normal atmospheric pressure. Related to Figure 1.

<table>
<thead>
<tr>
<th>pCO₂ (atm)</th>
<th>[CO₂(aq)] (mol L⁻¹)</th>
<th>[H₂CO₃(aq)] (mol L⁻¹)</th>
<th>[HCO₃⁻(aq)] (mol L⁻¹)</th>
<th>[CO₃²⁻(aq)] (mol L⁻¹)</th>
<th>[H⁺(aq)] (mol L⁻¹)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5 × 10⁻⁴</td>
<td>1.18 × 10⁻⁸</td>
<td>1.41 × 10⁻⁸</td>
<td>2.29 × 10⁻⁸</td>
<td>4.69 × 10⁻¹¹</td>
<td>2.29 × 10⁻⁸</td>
<td>5.64</td>
</tr>
</tbody>
</table>

Table S2. Comparison of various batteries capacity. Related to Figure 3.

<table>
<thead>
<tr>
<th>This work</th>
<th>Current density (mA g⁻¹)</th>
<th>Catalyst loading (mg cm⁻²)</th>
<th>Gravimetric capacity (mAh g⁻¹)</th>
<th>Area specific capacity (mAh cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-CO₂ battery (Zhang et al., 2015)</td>
<td>200</td>
<td>2</td>
<td>210,000</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.27-0.45</td>
<td>14,723</td>
<td>6.5</td>
</tr>
<tr>
<td>Li-CO₂ battery (Qie et al., 2017)</td>
<td>300</td>
<td>0.3</td>
<td>16,006</td>
<td>4.8</td>
</tr>
<tr>
<td>Na-CO₂ battery (Hu et al., 2016)</td>
<td>1,000</td>
<td>0.071</td>
<td>60,359</td>
<td>42.9</td>
</tr>
<tr>
<td>Na-CO₂ battery (Das et al., 2013)</td>
<td>70</td>
<td>0.76-1.28</td>
<td>3,478</td>
<td>4.5</td>
</tr>
<tr>
<td>Mg-CO₂ battery (Al Sadat and Archer, 2016)</td>
<td>70</td>
<td>0.76-1.28</td>
<td>2,540</td>
<td>3.3</td>
</tr>
<tr>
<td>Al-CO₂ battery (Al Sadat and Archer, 2016)</td>
<td>70</td>
<td>0.5-1.0</td>
<td>13,322</td>
<td>13.3</td>
</tr>
<tr>
<td>Li-O₂ battery (Kang et al., 2006)</td>
<td>280</td>
<td>0.72</td>
<td>11,060</td>
<td>8.0</td>
</tr>
<tr>
<td>Li-ion battery (Wang et al., 2012)</td>
<td>280</td>
<td>6.66</td>
<td>225</td>
<td>1.5</td>
</tr>
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</table>
Transparent Methods

Half-cell configured electrochemical analysis.

In three-electrode half-cell measurements, a platinum wire was used as both of working electrode and counter electrode with Ag/AgCl (saturated KCl filled) reference electrode in 0.1 M sodium hydroxide (NaOH, Sigma-Aldrich Co.) in pure water and seawater (taken from sea of Ulsan and filtered to remove visible impurities). To estimate pH and hydrogen evolution potential in the solution, a reversible hydrogen electrode (RHE) calibration was conducted in H₂-saturated solutions where platinum wires were used as the working, counter electrodes and Ag/AgCl as a reference electrode at a scan rate of 1 mV s⁻¹. For all half-cell configured experiments, iR correction was applied by measuring the resistance of solution (0.1 M NaOH, CO₂-saturated 0.1 M NaOH, seawater, CO₂-saturated seawater). The ohmic resistances of before CO₂-saturated 0.1 M NaOH, after CO₂-saturated 0.1 M NaOH, before CO₂-saturated seawater, and after CO₂-saturated seawater have been confirmed as 12.5, 35.8, 4.2 and 4.0 Ω, respectively. A rotating disk electrode testing was conducted by using a mixture of 20wt.% Pt/C and IrO₂ catalyst (Sigma-Aldrich Co., mixed in 1 : 1 gravimetric ratio) on RRDE-3A (ALS Co.). The mixture of catalyst was prepared into a catalyst ink by dispersing 10 mg of the catalyst in 1 mL of a binder solution (45 : 45 : 10 = ethanol : isopropyl alcohol : 5 wt.% Nafion solution (Sigma-Aldrich Co.), volumetric ratio) followed by a bath sonication process. The oxidation RDE profiles were measured by 5 μL of the catalyst ink drop-coated glassy carbon disk electrode, where area is 0.1256 cm², at a scan rate of 10 mV s⁻¹. All electrochemical tests were carried out using Biologic VMP3.

Characterization techniques.

The soluble solid products after discharge process in CO₂-saturated 0.1 M NaOH were obtained through various drying process such as freeze-drying, natural drying at room-temperature, high temperature drying at 70°C oven. The phase identification of the obtained products was
confirmed by X-ray powder diffraction (XRD) (Bruker diffractometer, Cu Kα radiation) at a scan rate of 1° min⁻¹. The power patterns were analyzed using JADE 6.5 software. The generated gas from discharge process was collected using three-electrode configuration in CO₂-saturated seawater and 0.1 M NaOH by water substitution method using U tube. Then the gas was analyzed by gas chromatograph (Agilent 7820A GC instrument) with a thermal conductivity detector (TCD) and a packed column (Agilent carboxen 1000). The gas used for GC measurement were controlled using a mass flow controller (MFC) (Atovac GMC1200) and the exact volume value of gas was calibrated through a bubble flow meter. The gas evolved from the charging process were also collected by three-electrode configuration (Pt wires as a counter electrode, Pt/C+IrO₂ catalyst loaded carbon felt as a working electrode, and Ag/AgCl as a reference electrode) in 0.1 M NaOH. The gas was analyzed by 450-GC chromatograph and 320-MS (Bruker Co.). The morphological analysis of the working electrode before and after discharge process in hybrid Na-CO₂ system was examined by scanning electron microscopy (Nova FE-SEM, FEI Co.).

**Full-cell measurements.**

For testing the hybrid Na-CO₂ system, the commercial Na-air battery (seawater battery) system was purchased at 4TOONE Co. and we modified the system into hybrid Na-CO₂ system. The hybrid Na-CO₂ system is composed of Na metal / organic electrolyte / solid electrolyte / aqueous electrolyte / cathode. For the organic electrolyte, 1 M Sodium trifluoromethanesulfonate (NaCF₃SO₃, Sigma-Aldrich Co.) in tetraethylene glycol dimethyl ether (TEGDME, Sigma-Aldrich Co.) was used. And NASICON-type (NASICON: Na super ionic conductor) Na₃Zr₂Si₂PO₁₂ with a thickness of 1 mm and a diameter of 16 mm was used as the solid electrolyte. The anode coin cell was assembled in Ar-filled glove box where the water and oxygen concentrations were kept less than 1 ppm. The sodium metal (Sigma-Aldrich Co.) with a diameter of 16 mm and a thickness of 0.5 mm was loaded on the stainless-steel
metal support and the prepared organic electrolyte was filled between sodium metal and NASICON. After assembling the anode coin cell with proper sealing, the assemblage was moved out from the glove box. The assembled coin cell is 24 mm in diameter and 6.5 mm in thickness (2465 size). For the aqueous electrolyte, 150 mL of 0.1 M NaOH and seawater were used. The cathode was prepared by drop-coating the catalyst ink (Pt/C+IrO$_2$ ink) in a carbon felt electrode (Fuel Cell Store Co.) with a loading density of 2 mg cm$^{-2}$. The current density was normalized with the loading density of the catalysts. A titanium wire was used as a current collector of the cathode and the aqueous electrolytes were saturated by CO$_2$ at a rate of 50 mL min$^{-1}$ at the ambient air condition for electrochemical measurements in hybrid Na-CO$_2$ system. All electrochemical tests were conducted using Biologic VMP3.
References


