Supporting information

Supplementary figures

**Figure 1** The composition of inlet and outlet gases in cathode chamber measured by GC. (a) Inlet gas; (b) outlet gas. In this study, N₂ flows in cathode chamber at the rate of 20 mL/min. According to the flow rate of N₂ and peak area of N₂ and H₂, H₂ was calculated to be generated at a rate of 0.578 mL/min.

**Figure 2** The composition of inlet and outlet gases in anode gas chamber measured by GC. (a) Inlet gas; (b) outlet gas. In this study, N₂ mixed with certain ratio of H₂ was flowed into anode gas chamber and the flow rate of N₂ was controlled to be 20 mL/min. According to the flow rate of N₂ and change of peak area of N₂ and H₂, the consumption rate of H₂ in anode gas chamber was calculated to be 0.580 mL/min.

**Figure 3** Dependence of electricity generation on the presence of H₂ in anode gas chamber. The data was collected by flowing 10 mL/min H₂ in gas chamber. 100 mg Ca(OH)₂ was added in anode chamber, sodium chloride (1 mol/L) was in salt chamber and sodium chloride (1 mol/L) in cathode chamber with CO₂ bubbled in. The current density was set to be 22.5 A/m². After generating electricity for a few minutes, 10 mL/min H₂ was displaced by 10 mL/min N₂. When the output power decreased to 0 W/m², H₂ was re-injected and then changed to N₂ again.
Illustration of refined process for obtaining solid NaHCO₃.

The first step: Saturated NaHCO₃ solution was used as starting electrolyte at the cathode side, but CO₂ was not injected immediately at the beginning of the reaction. Without CO₂ in the cathode side, part of the existing H₂CO₃ in solution provided the H⁺ to promote the electricity generation and transformed into CO₂⁻, forming aqueous Na₂CO₃ and NaHCO₃.

The second step: The stream of the cathode side was pumped out to react with CO₂ in a separated vessel, in which the CO₂⁻ in solution reacted with CO₂. The solid NaHCO₃ can be produced at the bottom of the this vessel because the formed NaHCO₃ exceeded its maximum solubility and then precipitated.

The third step: Solid NaHCO₃ was collected by filtration, the remaining saturated NaHCO₃ solution was re-fed into the CUPC system to start the electricity generation again.

Figure 4 The Change of power output during obtaining solid NaHCO₃.

Figure 5 The XRD pattern of the obtained solid, which was characterized as nahcolite (syn.) using Jade 9 software.
Figure 7  The thermal decomposition measurement of the obtained solid.

Figure 8  The change of pH value at the cathode side during testing the performance of electricity generation when different concentration of CO₂ was injected.