



Low Voltage Electrochemical Process for Direct Carbon Dioxide Sequestration

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Today, alkalinity, in the form of sodium hydroxide (NaOH), is primarily produced from the chlor-alkali process. Alkalinity produced by the chlor-alkali industry is used in a multitude of different processes: pulp and paper products, food and beverage industry, aluminum production, and as a key component in many chemical processes. Additionally, the use of alkalinity to sequester carbon dioxide (CO₂) from carbon-intensive power and industrial plants has become an important new topic in recent years. However, there are two severe penalties that come with the chlor-alkali process, namely, high energy consumption and the coproduction of toxic chlorine gas. Here we show two patented novel low-energy electrochemical processes that produce alkalinity and directly sequester carbon dioxide while generating pure streams of sodium bicarbonate (NaHCO₃) and hydrochloric acid (HCl) at +0.82 and -0.42 V, theoretically. As a result, the theoretical energy demand for producing alkalinity is reduced by 81% (Process 1) and 137% (Process 2) compared to the chlor-alkali process, chlorine gas production is avoided, carbon dioxide is sequestered, and valuable acid is produced.

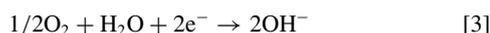
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Table I shows the thermodynamic advantages of the two proposed novel electrochemical processes for the production of alkalinity. In practice, cells in chlor-alkali plants typically operate at 3.0 to 3.6 V at current densities of 3.0–5.0 kA/m² to account for the inherent voltage drops from membrane and solution resistances as well as electrode overpotentials.¹ As a result of the high energy consumption, the market price of alkalinity is high and sequestering carbon dioxide from power plants using alkalinity from the chlor-alkali process is not feasible due to the inherent energy consumption and carbon dioxide footprint.

As shown in an aqueous carbon dioxide speciation diagram (Figure 1), sequestering carbon dioxide in a carbonate form in an aqueous process requires a source of alkalinity. In Calera Corporation's Mineralization via Aqueous Precipitation (MAP) process,^{2,3} calcium or magnesium chloride is added to the alkaline-dependent carbonate solution to produce cement and thus provides a mechanism for permanent carbon dioxide sequestration while also supplanting CO₂ emissions from conventional manufacturing.

Figure 2 (top) is a schematic representation of the improved electrochemical cell for Process 1.^{4–11} Similar to the chlor-alkali process, brine is the feedstock, and the sodium cation passes through a cation exchange membrane to combine with the hydroxide produced at the cathode (Equation 1) resulting in the formation of sodium hydroxide.



The cathode is the same catalyst-coated mixed-metal oxide electrode used in the chlor-alkali industry and also produces hydrogen. There are two significant differences between the proposed electrochemical process and chlor-alkali. First, the introduction of carbon dioxide to the re-circulated catholyte stream forms sodium carbonate or sodium bicarbonate (depending on catholyte pH), which in turn can equilibrate with the produced sodium hydroxide. Second,

chlorine gas evolution is replaced by a gas diffusion electrode where hydrogen generated from the cathode is oxidized (Equation 2) to form protons. These protons are generated at the anode and combine with the chloride ion to form a pure stream of hydrochloric acid. While in the figures NaCl is shown as the salt, and HCl is the acid, sodium sulphate or sodium nitrate can be used and would allow the flexibility to produce different acids such as sulphuric acid and nitric acid, respectively.

Process 2 shown in Figure 2 (bottom) is a modification of Process 1. The alkaline water reduction reaction at the cathode in Process 1 is replaced with the oxygen reduction reaction (Equation 3) using an oxygen depolarized cathode (ODC). Using the same hydrogen oxidation reaction (Equation 2) as Process 1 results in a cell voltage reduced by 1.23 V making it theoretically galvanic at +0.82 V at a pH of 7. Table I shows that Process 2 produces alkalinity at no cost from electricity because the cell is operated at a current density such that the cell voltage is 0.0 V. Since the cathode no longer produces hydrogen to be oxidized at the anode, an external source of hydrogen is required. Combining Process 2 with the waste hydrogen generated from chlor-alkali plants essentially yields an energy-free process for alkalinity production. The oxygen source for the cathode is air. However, if hydrogen from steam methane reformation is used for Process 2, minimal energy of 165 kJ/mol¹² is required (stoichiometric equivalence to 275 kWh/tonne NaOH). In addition, the carbon dioxide produced from methane reforming can be directly fed to the catholyte.

These two processes are novel due to the direct carbonation of the catholyte from power or industrial plant carbon dioxide emissions. The acid gas lowers the pH thus proportionally reducing the cathodic half-cell potential by as much as 50% in theory for Process 1 and increases the galvanic capability of Process 2 by 100%. Overall, the theoretical cell emf for Process 1 is -0.83 V without CO₂ injection and as low as -0.415 V with CO₂ addition to a pH of 7.0. Likewise for Process 2, the theoretical cell emf is +0.40 V without injecting carbon dioxide to the catholyte and +0.82 V for carbon-injected catholyte at a pH of 7.

Figure 3 shows experimental results for Process 1 that demonstrate the pH effect of the catholyte (controlled by CO₂ injection) on the voltage of the cell. The starting anolyte and catholyte were 1 M HCl and 1 M NaOH while the brine was maintained at 5 M NaCl. Ultra-pure carbon dioxide was sparged into the catholyte recirculation

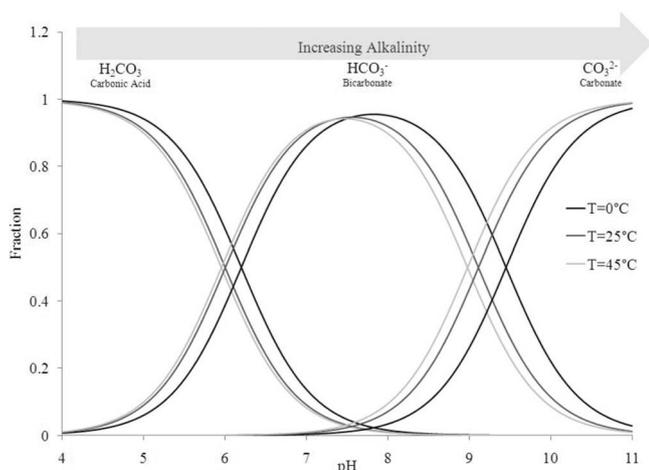
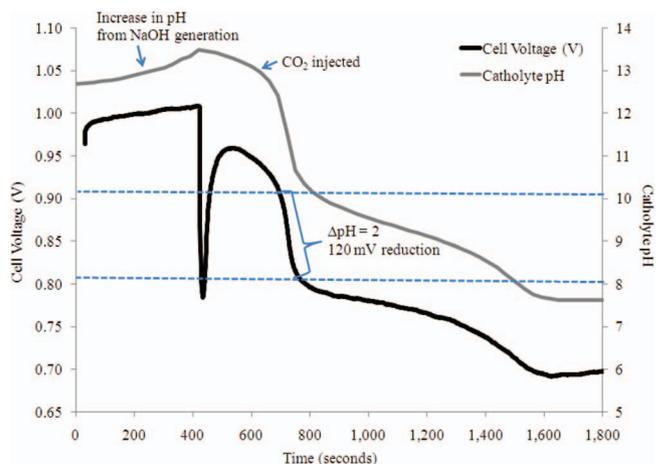
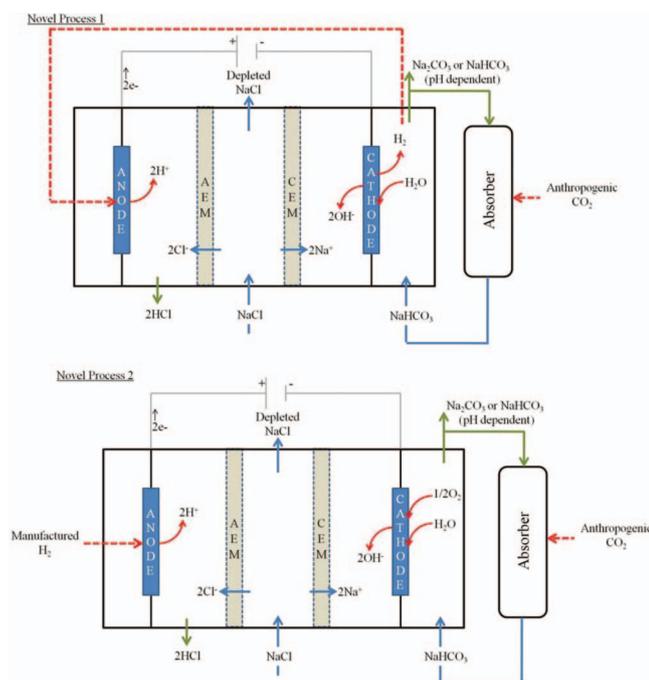
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Table I. Theoretical advantages of proposed electrochemical processes versus the chlor-alkali process.

Process	Theoretical Cell Voltage (V)	Energy (kW/tonne NaOH)	Cost (\$/tonne NaOH) ^a
Chlor-Alkali	2.19 (electrolytic)	1,468	73
Process 1 ^b	0.42 (electrolytic)	278	14
Process 2	0.82 (galvanic)	275 ^c	14

^a Energy cost of \$50/MWh.^b Operated at a pH of 7.0.^c Assuming hydrogen generated from steam methane reforming. If flared hydrogen from the chlor-alkali process or another industrial process is used, this would be -594 and the cost would be ~ 0 .**Figure 1.** Temperature and pH effect on aqueous carbon dioxide speciation.**Figure 3.** Experimental results of Process 1 showing the effect of adding CO_2 on the pH and operating cell voltage for the, low energy, direct carbon capturing electrochemical process.**Figure 2.** Schematic representations of the two novel electrochemical processes that generate alkalinity with low energy consumption: (top) Process 1; (b) Process 2. AEM and CEM are abbreviations for anion exchange membrane and cation exchange membrane, respectively.

stream after 400 seconds. A Solartron 1287 potentiostat was used for electrochemical measurements in conjunction with a Symphony SB70P pH meter.

The increase in pH during the first 400 seconds is due to the production of NaOH at the cathode (Equation 1). The horizontal dashed lines in Figure 3 show that a pH decrease from 10.1 to 8.1 reduced the cell voltage by 120 mV, which is theoretically predicted from the pH-Nernstian dependent cathode reaction of $\Delta E^0 = -0.059 \times \text{pH}$. Figure 3 also proves that alkalinity can be produced below 0.7 V in practice compared to the 3.0–3.5 V required for the chlor-alkali process.

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