

Supporting Information:

**Towards Electrochemical Synthesis of Cement — An Electrolyzer-Based Process
for Decarbonating CaCO₃ While Producing Useful Gas Streams**

Leah D. Ellis,^a Andres F. Badel,^a Miki L. Chiang, Richard J.-Y. Park,^a Yet-Ming Chiang^{a*}

^aDepartment of Material Science and Engineering, Massachusetts Institute of Technology,
Cambridge, MA, 02139

* Corresponding author: ychiang@mit.edu

Key Words

Cement, deep decarbonization, green hydrogen, electrolysis, calcination, lime

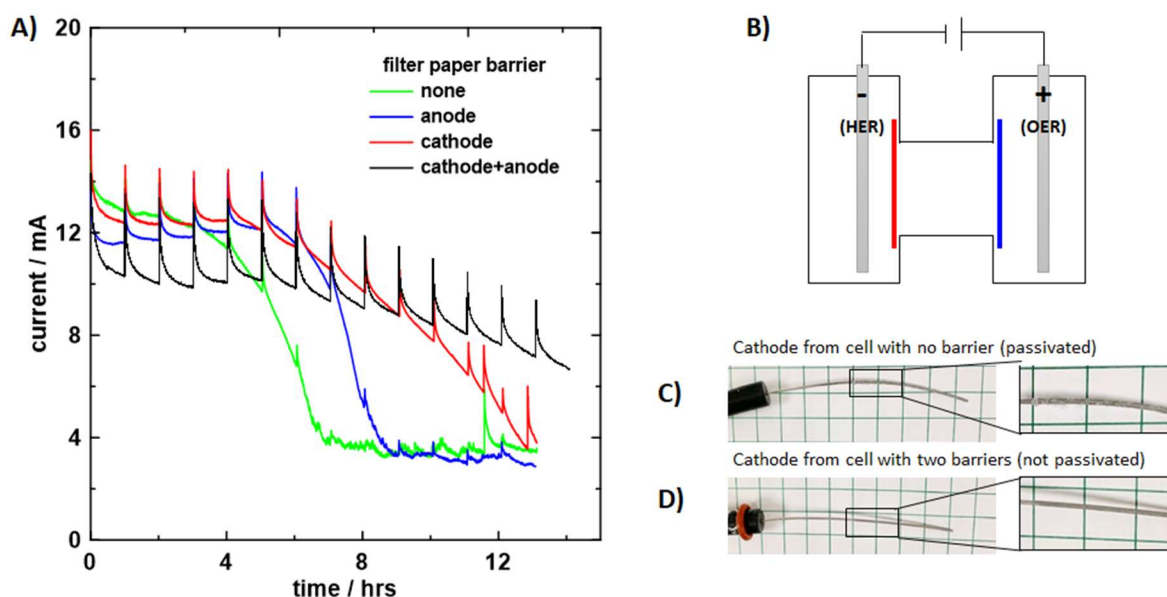
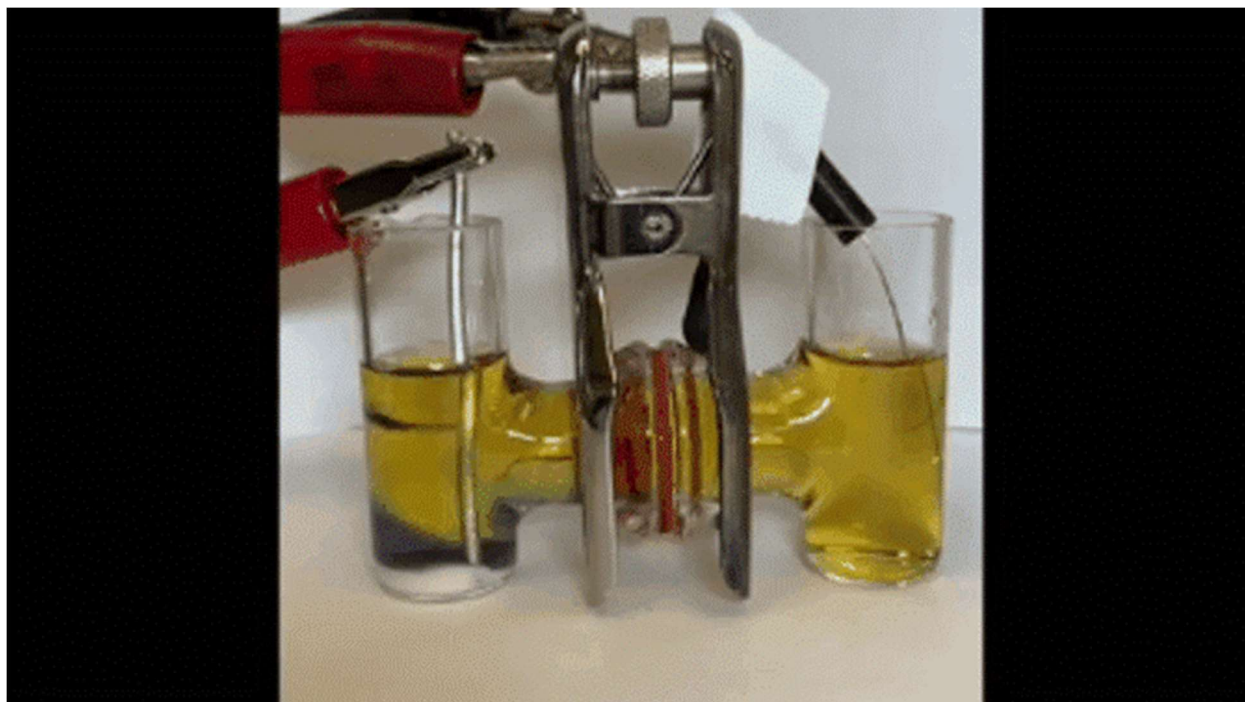


Fig. S1. Convective mixing of acidic and basic streams in the decarbonation reactor (illustrated in Figure 3D, E and Video S1) leading to passivation of the cathode by precipitated $\text{Ca}(\text{OH})_2$ is suppressed by use of porous separators in the H-cell. A) Shows current vs. time for decarbonation cells held at 3.5 V, with a short open-circuit hold every 1h. The cells used porous paper separators in front of either, or both of the electrodes, as shown in B). Without any separator, green curve, the current quickly falls as the platinum wire cathode becomes coated with $\text{Ca}(\text{OH})_2$, as shown in C). Protecting only the OER anode, blue curve, is less effective than protecting only the HER cathode, red curve. When separators are used in front of both electrodes, the cell operates stably over the 14h experiment, and the cathode is visibly less passivated, as shown in D). As shown in Fig. 3J, $\text{Ca}(\text{OH})_2$ then precipitates in the neck of the H-cell between the separators and is easily collected.



Video V1. [See separate video file] Time-lapse video of the decarbonation cell containing pH indicator dye, shown in Figure 3A-E. This decarbonation cell starts at pH 6, as indicated by the yellow color, and has no separators. Calcium carbonate powder has been placed at the bottom of the left chamber.



Video V2. [See separate video file] Time-lapse video of the decarbonation cell containing pH indicator dye, shown in Figure 3F-H. Porous paper separators have been placed in front of each electrode as shown schematically in Figure S1B, and CaCO₃ powder in a cup surrounding the OER electrode on the left.

Estimate of Energy Consumption for Electrochemical and Conventional Cement Processes

Referring to SI Appendix Fig. S2, the thermal energy requirement for the average cement plant in the US is 4.6 kJ/kg cement (1), shown as the dark horizontal line. The thermal energy requirement for a cement plant that uses $\text{Ca}(\text{OH})_2$ instead of CaCO_3 is lower at 2.8 MJ/kg, light horizontal line. This is calculated as the sum of the energy required to decompose $\text{Ca}(\text{OH})_2$ to CaO and H_2O at 900°C (1.6 MJ/kg, based on the standard free energy, which is 139 kJ/mol CaO , and assuming cement contains 65%wt. CaO) and the energy for sintering (~45% of the energy used by a kiln with a preheater and precalciner (2), which is 2.6 kJ/kg cement (3)). By comparison, the standard free energy for decomposition of CaCO_3 to CaO and CO_2 is 25% higher at 176 kJ/mole CaO . The net energy required for the electrochemical process is a function of the H_2/O_2 combustion efficiency, the abscissa in Fig. S2. The orange dotted line shows the thermal energy from H_2/O_2 combustion as a function of combustion efficiency. At 70% combustion efficiency, H_2/O_2 combustion supplies all of the thermal energy needed for sintering. Above this efficiency, excess energy is available (e.g., for other plant operations), while below this efficiency, supplemental energy is required (which may come from an excess of electrolyzer capacity or from supplemental fuels).

The net input electrical energy for the electrochemical cement process further depends on the operating voltage of the decarbonation cell, and the coulombic efficiency of decarbonation, which we assume to be 85% (see Fig. 4). For a lower bound we assume that the decarbonation cell operates at 2.0 V, and the combustion efficiency of H_2/O_2 is 80%. For an upper bound we assume that the decarbonation cell operates at 2.5 V and the combustion of H_2/O_2 is 60% efficient. These bounds correspond to an energy consumption of 5.2 and 7.1 MJ/kg cement for the electrochemical process, higher than the 4.6 MJ/kg average for conventional cement. The energy for CO_2 remediation is not included in this estimate. The respective energy costs of the electrochemical process is a function of the cost of electricity, as discussed in the main text.

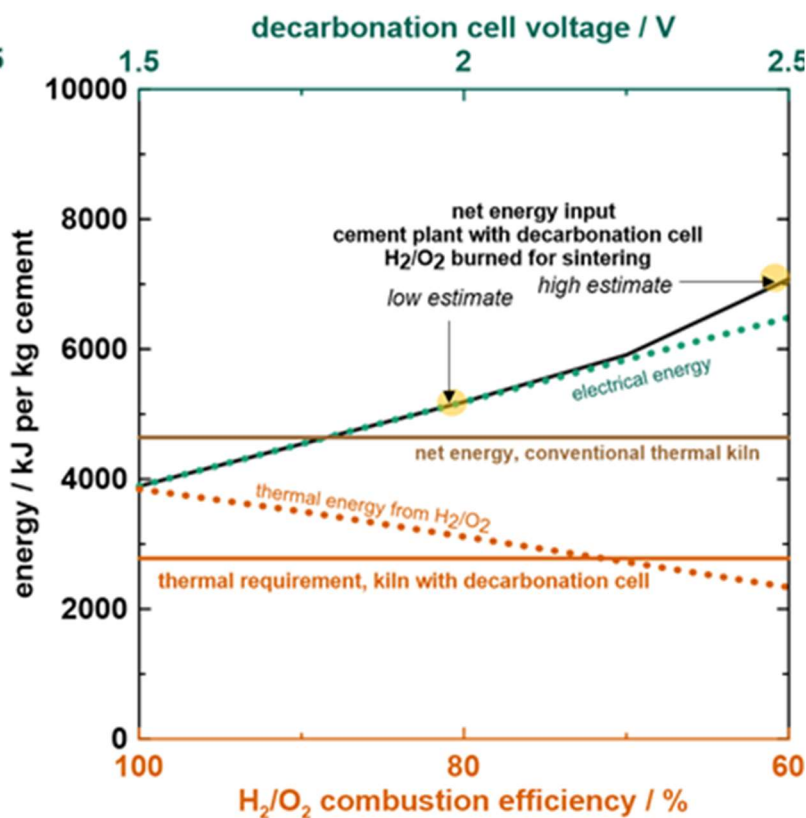


Fig. S2. Comparison of energy consumption per kilogram of cement produced, for a conventional cement plant and one using the present decarbonation cell with combustion of output H₂ and O₂ gasses to heat the sintering kiln.

References

1. Portland Cement Association Labor-Energy Input Survey. Available at: <https://www.cement.org/docs/default-source/market-economics-pdfs/more-reports/labor-energy-sample-2.pdf?sfvrsn=6&sfvrsn=6> [Accessed February 28, 2019].
2. Taylor HFW (1997) Cement Chemistry (Thomas Telford Publishing, London). 2nd Ed.
3. Galitsky C, Worrell E, Galitsky C (2008) Energy Efficiency Improvement and Cost Saving Opportunities for Cement Making. An ENERGY STAR Guide for Energy and Plant Managers doi:10.2172/927882.