Electrolyte pH modulation for efficient and durable electrochemical cement clinker precursor production

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Current efficiency calculation:

The electrochemical reactions during the cement clinker precursor production process are shown as follows:

Anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

$2CaCO_3 + 4H^+ \rightarrow 2Ca^{2+} + 2CO_2 + 2H_2O$

Cathode: $4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$

$2Ca^{2+} + 4OH^- \rightarrow 2Ca(OH)_2$

Overall reaction: $2CaCO_3 + 4H_2O \rightarrow 2Ca(OH)_2 + 2CO_2 + O_2 + 2H_2$

Theoretically, one mole of $CaCO_3$ and one mole of $Ca(OH)_2$ will be dissolved and produced, respectively, for every two moles of electrons transferred, which represents a current efficiency of 100%. Based on this correlation, the current efficiency of the anode and cathode can be expressed by Eq. (S1) and Eq. (S2), respectively. However, the previous studies also use Eq. (S1) to evaluate the cathode current efficiency because it is difficult to recover all of the products. This is unreasonable because the production rate of $Ca(OH)_2$ may be different from the rate of $CaCO_3$ consumption in practice. In this work, the electrolyzer design and the large current density make it possible to collect all of the products and calculate the production rate and cathode current efficiency by Eq. (S2). The result is a measured value with high enough accuracy, which is different from the previous studies.

$$\text{Anode current efficiency (\%)} = \frac{\text{mole of CaCO}_3\text{ dissolved during electrolysis}}{It/2F} \qquad \text{(S1)}$$

$$\text{Cathode current efficiency (\%)} = \frac{\text{mole of Ca(OH)}_2\text{ produced during electrolysis}}{It/2F} \qquad \text{(S2)}$$

where *I* and *t* are the current and time, respectively, for electrolysis, and *F* represents Faraday's constant (96500 C/mol)

Ca^{2+} transference number calculation:

In theory, one mole of Ca^{2+} will migrate into the cathode chamber for every two moles of electrons produced or consumed. The Ca^{2+} transference number is calculated by comparing the practical and theoretical moles of Ca^{2+} transferred into the cathode chamber [Eq. (S3)].

$$t_{\mathrm{Ca}^{2+}} = \frac{\text{mole of Ca}^{2+}\text{ in initial anolyte+mole of Ca}^{2+}\text{ dissolved from CaCO}_3\text{-mole of Ca}^{2+}\text{ in final anolyte}}{It/2F} \tag{S3}$$

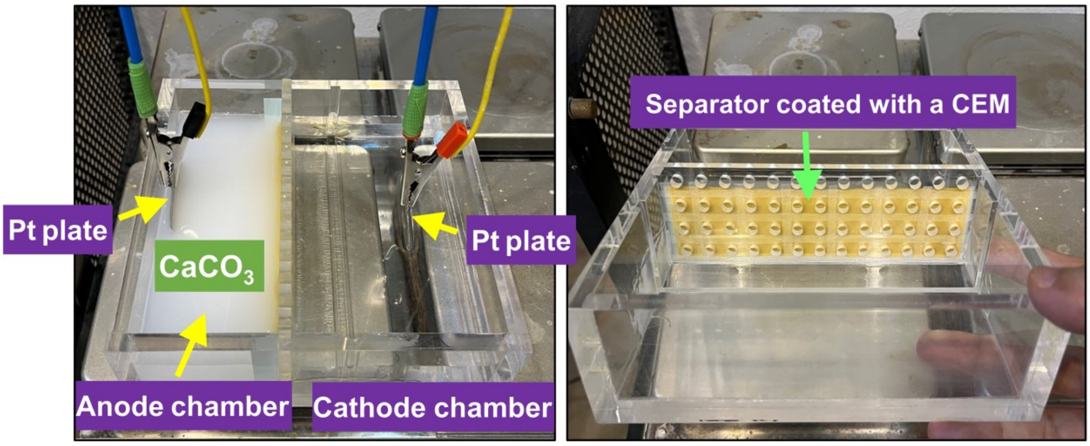

Fig. S1 Photograph of the electrochemical experiment setup for cement clinker precursor production (H-type cell: 14 cm × 14 cm × 4 cm).

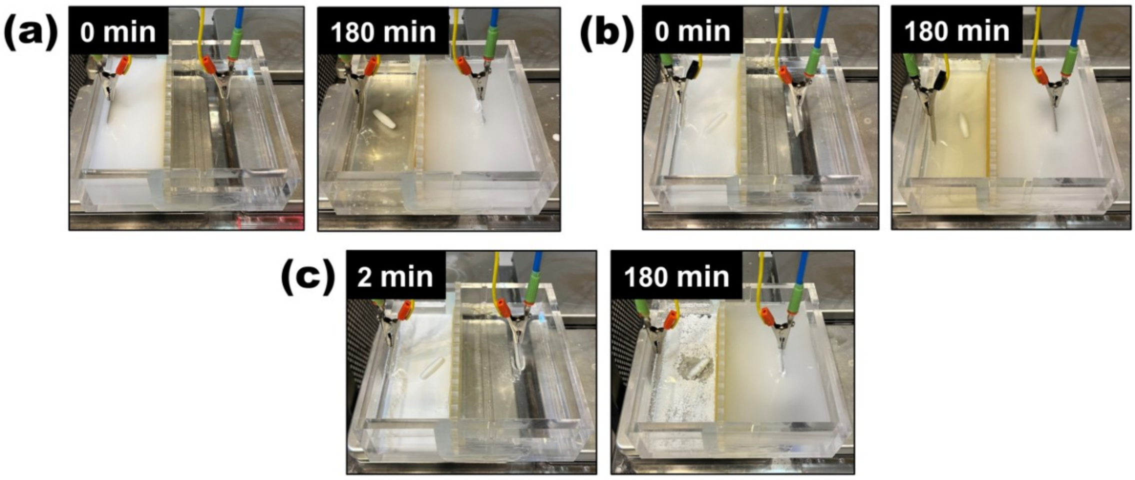

Fig. S2 Photographs showing the changes of the feedstock in the anode chamber before and after electrolysis at various stirring frequencies (the mole of $CaCO_3$ added into the electrolyzer is equivalent to that of H_2 theoretically produced at the cathode in 3 h). (a) under continuous stirring; (b) under intermittent stirring; (c) without stirring. The almost complete consumption of $CaCO_3$ after electrolysis under continuous or intermittent stirring suggests an excellent anode current efficiency, while the high residue level in the anode chamber under no stirring demonstrates a significant decrease in this efficiency.

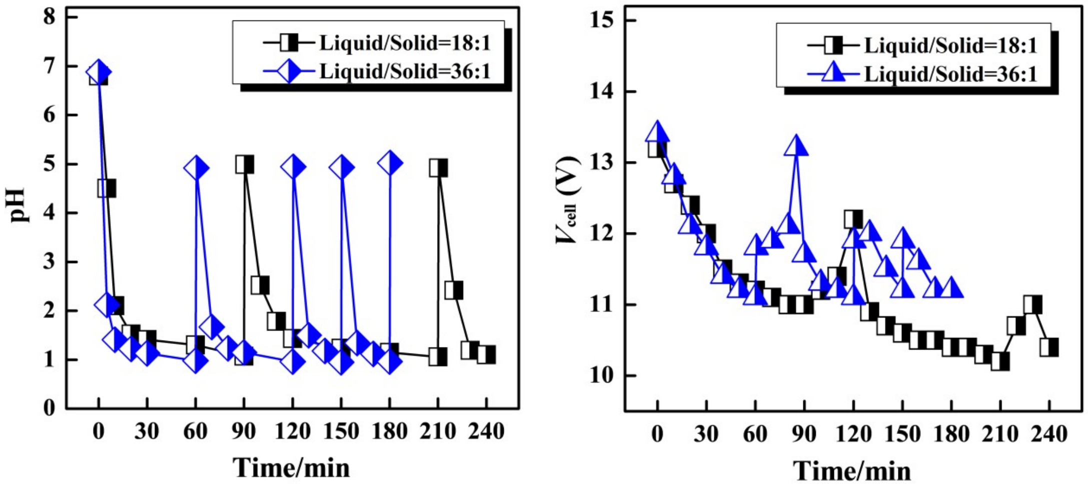

Fig. S3 pH and voltage evolution with time under different liquid-solid ratios. The pH declines more slowly at lower liquid/solid ratios under no stirring, suggesting faster reaction kinetics. This change ensures a high anode current efficiency (>93%) under a lower stirring frequency (every 90~120 min) and leads to a lower voltage level.

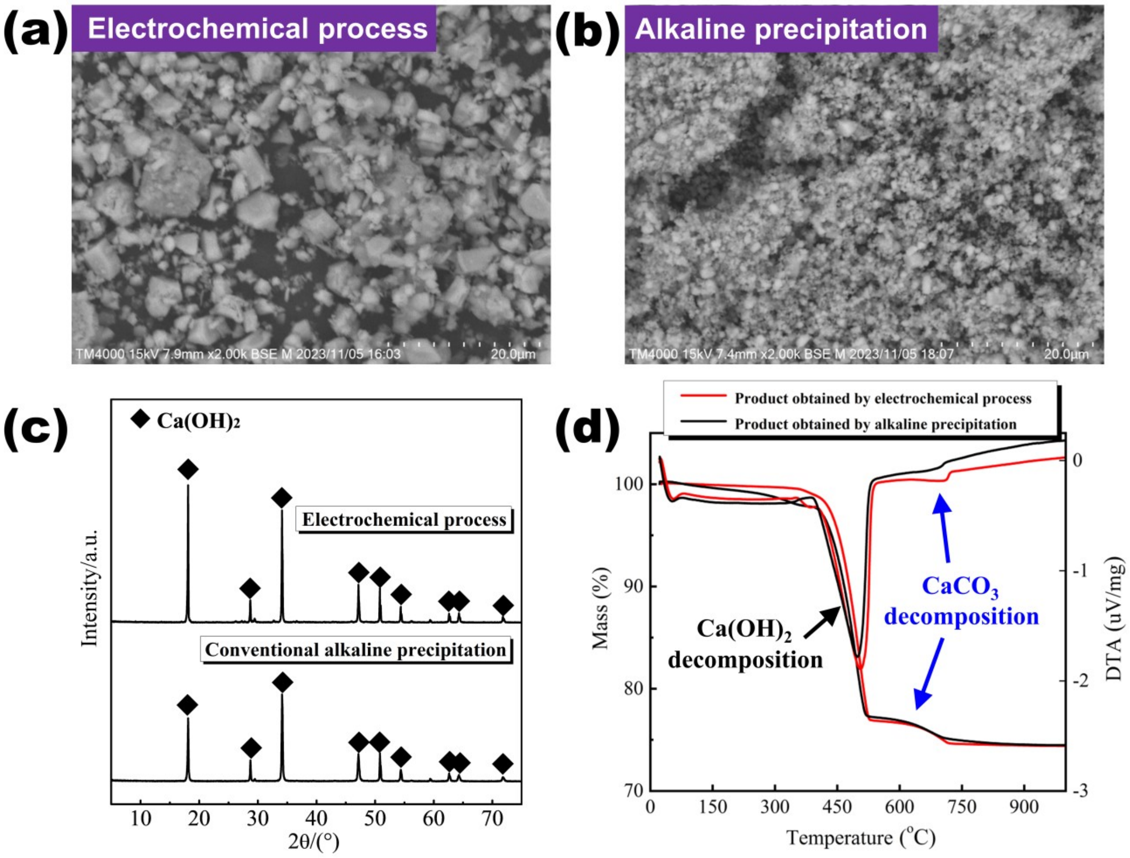

Fig. S4 Comparison of the SEM images [(a) and (b)], XRD patterns (c), and TG–DTA curves (d) of $Ca(OH)_2$ products obtained by electrolysis for 3 h (with 0.5 M $Ca(NO_3)_2$ solution as the anolyte and 1.0 M $NaNO_3$ + 0.2 M $Ca(NO_3)_2$ solution as the catholyte) and conventional alkaline precipitation (reaction for 3 h at pH of 12.6 with stirring of 500 rpm). Stronger diffraction peaks and larger particle sizes suggest significant grain growth of $Ca(OH)_2$ during electrolysis. The TG-DTA analysis reveals the presence of some $CaCO_3$ impurity (~7%) in the product in both conditions, suggesting that carbonation reactions may occur during the drying process.

Videos

Time-lapse videos of the cathode chamber showing the precipitation process of $Ca(OH)_2$ after electrolysis for 30 min. Movie S1: without Ca^{2+} in the initial catholyte; Movie S2: with 0.2 M Ca^{2+} in the initial catholyte. The $Ca(OH)_2$ precipitation is much stronger under Ca^{2+}-containing catholyte, accelerating the consumption of OH^- produced at the cathode and leading to a lower pH.