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Electrolytic control of hydrogen peroxide release from calcium peroxide in aqueous solution

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Abstract

The in situ generation of hydrogen peroxide (H_2O_2) for water treatment is more practical than the use of liquid H_2O_2 , which is costly to store and transport. Calcium peroxide (CaO_2), a solid carrier of H_2O_2 , can release H_2O_2 on dissolution in water. However, the constant H_2O_2 release rate of CaO_2 has been a bottleneck constraining its wider application. In this study, a practical electrochemical method using a divided cell is developed to control the rate of release of H_2O_2 from CaO_2 . The results show that the rate of H_2O_2 release from CaO_2 is enhanced in the anolyte. The increase in H_2O_2 release is positively correlated with the current. Under a current of 100 mA, the H_2O_2 concentration was 2.5 times higher after 30 min of electrolysis than in the control experiment in which no current was applied. Water electrolysis in the anodic compartment generates protons that not only: (i) enhance dissolution of CaO_2 and release of H_2O_2 , but also (ii) neutralize the alkaline pH resulting from CaO_2 dissolution, thus providing new advantages for the use of CaO_2 . This effective technique may be suitable for the sophisticated control of H_2O_2 release in environmental applications.

Keywords

Calcium peroxide; Electrochemistry; H_2O_2 releasing manipulation

1. Introduction

Calcium peroxide (CaO_2) is a solid metal-peroxy chemical that can produce H_2O_2 over a wide pH range (Eq. (1)) [1, 2]. Recent studies indicate that CaO_2 is an efficient solid “ H_2O_2 ”, but is more stable than liquid H_2O_2 , and can work as a promising oxidant in Fenton-based *in situ* chemical oxidation (ISCO) [3–10]. Due to the poor solubility of CaO_2 , the H_2O_2 release rate is controlled by the dissolution rate, which can minimize the H_2O_2 loss during the transport and injection steps in ISCO remediation [3, 10]. However, the slow H_2O_2 release rate of CaO_2 is a disadvantage in remediation processes, which relies on

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efficient pollutants to less harmful substances [11, 12]. In addition, the increase in solution pH due to CaO_2 dissolution and the formation of Ca(OH)_2 are disadvantages in ISCO remediation (Eq. (1)), as this alkaline pH can cause release of O_2 instead of H_2O_2 (Eq. (2)) [3, 11–14].

Several studies have reported that synthesizing nano-scale CaO_2 can increase the H_2O_2 release rate [9–11], but the nano CaO_2 also exacerbates H_2O_2 loss in the injection and transport steps, the H_2O_2 release rate is still regulated by the synthesized CaO_2 , and an alkaline pH is still produced. Although adjusting the solution pH can change the rate of release of H_2O_2 from CaO_2 , the implementation can be challenging [11].

Electrochemical processes are powerful techniques for water treatment. While the anode or cathode have the ability to oxidize or reduce pollutants [15–18], typical electrochemical processes employ two- and three-electrode systems with different materials in divided and undivided reactors to enhance redox conditions based on water hydrolysis (Eqs. (3) and (4)) [18–22]. Combining water electrolysis and other technologies will enhance water treatment technologies [23]. Electrochemical processes can also easily be used to regulate pH [20, 24–26]. The migration of H^+ and OH^- can control the chemistry during electrokinetic remediation, which allows for control of pH-sensitive processes. Since CaO_2 decomposition is pH-dependent, electrochemical processes have the potential to control the decomposition of CaO_2 and subsequent release of H_2O_2 .

Here, we evaluate the electrochemical manipulation of the rate of H_2O_2 release from CaO_2 . We measure the effect of electric current on enhancing the rate of H_2O_2 release, and present an empirical formula to describe the relationship between the current and the H_2O_2 release rate. We further propose possible mechanisms of increasing H_2O_2 release by the electrochemical methods.

2. Methods

2.1. Material and experimental design

Calcium peroxide (CaO_2) was purchased from Sigma-Aldrich, sodium sulfate (Na_2SO_4) was obtained from Fisher Chemical. The water used in all experiments was 18.0 M Ω cm obtained from a Millipore Milli-Q system.

A divided electrolytic cell was used as the reactor, and the anode compartment was separated from the cathode compartment with a Nafion membrane (Fuel Cell Store). The anode and cathode were made of Ti/mixed metal oxide (MMO, 3N International, 1.0 cm $\times$ 4 cm $\times$ 1.8 mm), which have IrO_2 and Ta_2O_5 coating on titanium. Both anode and cathode were vertically mounted. An Agilent E3612A supplied the constant direct current.

In each experiment, 200 mL sodium sulfate (50 mM) was transferred into the anode and cathode compartments, and 5 mM CaO_2 was introduced to the test compartment. The reaction started when the constant current was applied. The magnetic stirrer was used to keep the solution homogeneous. Samples were taken at pre-determined times for H_2O_2 , pH, turbidity, and particle size analyses. All experiments were conducted at least in duplicate, and average results are presented.

2.2. Analytical method

For the analysis of H_2O_2 , a 0.5 mL filtered sample was analyzed at 405 nm by a Shimadzu UV–Vis spectrometer after the color reaction with TiSO_4 [27]. A pH meter (Thermo Scientific Orion 3 star) equipped with an electrode (Thermo Scientific Orion pH/ATC electrode) was used to record the pH. For the turbidity analysis, 25 mL samples were withdrawn at the pre-determined times and measured by a turbidity meter (HACH 2100N). A particle size analyzer (Brookhaven Instrument 90 plus) was used to determine the particle sizes: samples were collected in a 3 mL cuvette, and then measured by dynamic light scattering at 90° for 10 runs. X-ray diffraction (XRD) patterns of the CaO_2 particles were collected on a Rigaku Rapid II curved detector system, and the diffraction patterns were analyzed using Jade MDI Jade software.

3. Results and discussion

3.1. The influence of current on H_2O_2 generation

Fig. 1 shows the influence of current on H_2O_2 generation from CaO_2 . Preliminary experiments indicated that the electrode-generated H_2O_2 could be neglected under these experimental conditions.

3.1.1. Anode compartment—In the anode compartment, H_2O_2 concentration increases as the current increases from 0 to 100 mA. With no current, 1.3 mM of H_2O_2 is generated after 30 min compared to 3.3 mM under 100 mA (Fig. 1a–1). The increase in H_2O_2 release is attributed to electrochemically accelerated H_2O_2 generation from CaO_2 while the effect of direct electrogeneration of H_2O_2 is limited since only the reduction of O_2 at the cathode surface would sufficiently contribute to the H_2O_2 concentration.

As the anode can consume H_2O_2 , the detected H_2O_2 is the concentration of H_2O_2 *in situ* rather than the overall H_2O_2 production [15, 28]. In order to evaluate the H_2O_2 consumption, 1 mM H_2O_2 and 5 mM $\text{Ca}(\text{OH})_2$ were transferred into 200 mL anolyte to simulate the loss of H_2O_2 under experimental conditions. The results are shown in Fig. 1a–2, where it can be seen that the maximum H_2O_2 loss is less than 0.5 mM during the 60 min period. Based on the estimated H_2O_2 loss, the calculated generation of H_2O_2 under experimental conditions is shown in Fig. 1a–3, and this reconfirms the increased H_2O_2 generation from CaO_2 by electrolysis. The H_2O_2 release curves fit pseudo-zero-order kinetics, and the reaction rate constants are 6.5, 15.78, 31.08, and $34.56 \times 10^{-4} \text{ M h}^{-1}$ for current values of 10, 50, 80 and 100 mA, respectively. Since the increased H_2O_2 generation under 10 mA was less than that consumed by the anode (Fig. 1a–2–3), the H_2O_2 concentration detected was lower than that without current. The relationship between the H_2O_2 release rates and the applied current is given by Eq. (5):

$$k_1 = 5 \times 10^{-5} \times I - 0.001 \quad (I: 10 \sim 100 \text{ mA}), R^2 = 0.9776 \quad (5)$$

where k_1 (M h^{-1}) and I (mA) represent the pseudo-zero-order reaction rate constant and the current, respectively (Fig. 1c–1). Based on Eq. (5), the predicated amounts of H_2O_2 generated at 40 mA and 60 mA are presented in Fig. 1c–2 and c–3, and the actual H_2O_2 concentrations lay within the predicted concentration ranges.

Since CaO_2 is almost insoluble in water and H_2O_2 is generated from decomposition of CaO_2 in water (Eq. (2)), the turbidity of the CaO_2 solution is then used to reflect CaO_2 decomposition. As shown in Fig. 2a, the increasing current enables the decomposition of CaO_2 in the anode compartment, and the turbidity trend is quite consistent with the H_2O_2 yield in the anode compartment. The current can be used to accelerate CaO_2 decomposition, and a higher H_2O_2 yield follows with a lower CaO_2 turbidity. In contrast, the turbidity decline of the CaO_2 solution is depressed in the catholyte (Fig. 2b).

3.1.2. Cathode compartment—Fig. 1b–1 shows that the cathode can restrain H_2O_2 yield from CaO_2 . Since the cathodic consumption (Eqs. (6) and (7)) can lead to the observed H_2O_2 declines, the H_2O_2 concentration decreases as the catholyte current increases from 0 to 100 mA, but the results show no clear correlation between the currents and the H_2O_2 yields. The calculated H_2O_2 yield (Fig. 1b–3) further proves that the current inhibits the re-release of H_2O_2 from CaO_2 and the inhibition increases with increasing current. Therefore, the catholyte current cannot be used to stall the generation of H_2O_2 from CaO_2 without causing H_2O_2 loss.

With the current, the slow turbidity decline indicates that the cathodic condition is not in favor of CaO_2 dissolution. The CaO_2 particle size analysis confirms the hypothesis: the CaO_2 particle size shrinks faster in the anolyte as the current increases, while the CaO_2 particle size shrinks more slowly in the catholyte as the current increases (Fig. 2, inset graphs). These results show the influence of current on the behavior of CaO_2 during the dissolution process and therefore on the generation of H_2O_2 .

3.2. Mechanism of electrochemical control of H_2O_2 yield from CaO_2

The CaO_2 powder quickly spreads in water and the CaO_2 particles produce calcium (Ca^{2+}) and peroxide (O_2^{2-}) ions on the particle surface, and the O_2^{2-} can combine with H^+ to generate H_2O_2 [1, 30]. Hence, CaO_2 is sensitive to the solution pH, which can induce different reactions during CaO_2 decomposition [1, 3, 14, 30, 31]. Clearly, acidic conditions are better for producing H_2O_2 from CaO_2 , and the rate of H_2O_2 release increases with decreasing pH [3, 30]. Fig. 3a shows the mechanisms of electrolytic control of H_2O_2 release from CaO_2 . Electrolysis induces acidic conditions at the anode and alkaline conditions at the cathode [20, 26, 29]. Without electricity, a specific CaO_2 concentration can produce a known amount of O_2^{2-} , leading to a specific rate of H_2O_2 release in solution. With the application of electricity, the generation of O_2^{2-} is still determined by the CaO_2 concentration, but the H^+ yield is influenced by the current [15, 25]. H^+ is continuously produced at the anode which enhances production of H_2O_2 , and the higher H^+ yield under higher currents enables faster CaO_2 decomposition and H_2O_2 generation. OH^- formation at the cathode limits the reaction between O_2^{2-} and H^+ , which also limits H_2O_2 generation. This H_2O_2 regulation hypothesis has been further confirmed by the XRD results. Fig. 3b shows the XRD patterns of CaO_2 from the anode/cathode compartments with and without current. These XRD patterns are very similar, which suggests that current only changes the speed of the CaO_2 dissolution process rather than leading to new dissolution pathways. Electrolytic manipulation to enhance H^+ yield by varying the current is a straightforward and practical process, the migration of H^+ can control the chemistry during electrokinetic remediation, and H_2O_2 generation from CaO_2 is then successfully manipulated through an electrochemical method.

4. Conclusion

The release of H_2O_2 from CaO_2 is successfully controlled by electrolysis, which has been shown to be a simple and practical method of regulating H_2O_2 release in CaO_2 -based ISCO remediation. *In situ* or *ex situ* implementation for water treatment will require a practical system to be engineered, however, the divided compartments are essential to study the mechanism. Based on the results, more research is needed to design systems for pH control for implementation and manipulation. The use of CaO_2 can minimize the loss of H_2O_2 during the injection and transport process, and the H_2O_2 release process can then be manipulated according to the actual requirements when CaO_2 is transferred to the zone of *in situ*

treatment. Compared with synthesizing nano CaO_2 and adjusting the solution pH, the electrochemical procedure has the advantage of flexible manipulation of H_2O_2 release and pH optimization. In addition, the actual groundwater varies depending on the geological conditions, and the electrochemical method will require more investigation in order to optimize the release of H_2O_2 .

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Fig. 1.

The H_2O_2 yields from CaO_2 in (a) anode compartment and (b) cathode compartment: (1) Detected H_2O_2 , (2) Electrode consumed H_2O_2 , (3) Total H_2O_2 ; (c): (1) the relationship between the current and H_2O_2 generation in the anode compartment, and the comparison of predicted and actual H_2O_2 generation at (2) 40 mA and (3) 60 mA in anode compartment. (The conditions for (a-1), (b-1), (c-2), (c-3): $[\text{CaO}_2]_0 = 5 \text{ mM}$, $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$. for (a-2) and (b-2): $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$, $[\text{Ca}(\text{OH})_2]_0 = 5 \text{ mM}$, $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$; (a-3) and (b-3): Total $\text{H}_2\text{O}_2 = \text{detected } \text{H}_2\text{O}_2 + \text{consumed } \text{H}_2\text{O}_2$; the predictive boundaries were based on Eq. (5)).

Fig. 2. The turbidity of CaO_2 solution in (a) anode compartment and (b) cathode compartment. (The conditions for (a) and (b): $[\text{CaO}_2]_0 = 5 \text{ mM}$, $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$). Inset graph: the particle size of CaO_2 in (a) anode and (b) cathode compartment.

Fig. 3. (a) The mechanism of manipulation of H_2O_2 via electrode; (b) the XRD patterns of the CaO_2 particles ($[\text{CaO}_2]_0 = 5 \text{ mM}$, $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$, $I = 50 \text{ mA}$, $t = 30 \text{ min}$).