Feasibility of CO$_2$ desorption and electrolytic regeneration of potassium carbonate solution in an anion exchange membrane cell

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Abstract

In this work, an electrolytic process was introduced for coupled regeneration of potassium carbonate (K$_2$CO$_3$) solution and water electrolysis by using an anion exchange membrane cell. The process made the CO$_2$ separation from O$_2$ much easier with respect to the existing cationic exchange membrane process. The solution of K$_2$CO$_3$ was used in the cathode chamber to simulate the solution after absorbing CO$_2$. The solution of sulfuric acid (0.1 mol/L H$_2$SO$_4$) was charged in the anode chamber. The feasibility of the process was discussed. The effects of various operation parameters, including temperature, current density, and electrolysis time, were studied. The results indicate that both the yield rate of CO$_2$ and the current efficiency increase initially and decrease afterward with temperature. The yield rate of CO$_2$ increases while the current efficiency decreases with the current density. A low current density can reduce the energy consumption for producing the same amount of CO$_2$. The processes using anion exchange membrane electrolysis can regenerate the absorbent solution to achieve 89% current efficiency, and the simultaneous production of three pure gases, CO$_2$, H$_2$, and O$_2$, makes this method promising.

Keywords: Membrane electrolysis, Benfield, regeneration, carbon dioxide
INTRODUCTION

In the past 40 years, the global climate and environment have been deteriorating, and the temperature has been rising. The use of fossil energy produces a large amount of carbon dioxide (CO$_2$), which makes the total amount of CO$_2$ in the atmosphere continue to rise, resulting in the greenhouse effect, rising sea levels, and frequent extreme weather. In order to improve its status, China has proposed a policy to achieve a carbon peak by 2030 and carbon neutrality by 2060. In 2020, carbon emissions in China reached 9.9 billion tons, of which CO$_2$ emissions from industrial flue gas accounted for the main part.

Pure CO$_2$ is an important chemical raw material, and its separation and purification in flue gas is the premise of its resource utilization. Some processes have been investigated and developed for separation and purification of CO$_2$, such as physical and chemical absorption\cite{1-6}, membrane separation\cite{7-10}, chemical looping\cite{11-13}, and cryogenic separation\cite{14}.

Chemical absorption is one of the most widely used methods in comparison with other post-combustion CO$_2$ absorption processes\cite{15}. Among those non-organic-based chemical solvents, including potassium carbonate (K$_2$CO$_3$), sodium carbonate, and aqueous ammonia, K$_2$CO$_3$ is the most effective, economical, and traditional solvent\cite{16}. The hot aqueous solution of K$_2$CO$_3$ has been widely used in the process of removing CO$_2$ such as natural gas sweetening or the production of pure hydrogen for ammonia synthesis\cite{17}. CO$_2$ is separated from the flue gas by chemical reactions between CO$_2$ and K$_2$CO$_3$ solution to produce potassium bicarbonate (KHCO$_3$). The absorbent is regenerated in subsequent steps, and CO$_2$ is desorbed by low pressure or high temperature.

The hot K$_2$CO$_3$ process (Benfield process) requires a considerable amount of heat for regeneration\cite{18}. Martin and Kubic\cite{19} developed an innovative process called Green Freedom for the capture and recovery of atmospheric CO$_2$ through ion-exchange-membrane electrolysis. In the new process, the recovery of captured CO$_2$ is realized by electrolytic stripping. The process was developed to recover CO$_2$ from rich K$_2$CO$_3$ solutions, and it drastically reduced the energy needed for CO$_2$ stripping and regeneration of the absorbent solution. In addition, Zhao et al. investigated the mechanism and energy consumption for this process\cite{20}. The electrolysis process is conducted in which CO$_2$ is released in three steps as the following: (1) No CO$_2$ release step- Reaction 1 takes place; (2) Enhanced CO$_2$ release step- Reaction 2 occurs to produce CO$_2$; (3) Steady CO$_2$ release step- CO$_2$ is released from this step through Reaction 3.

\begin{equation}
4\text{K}_2\text{CO}_3 + 6\text{H}_2\text{O} \rightarrow 4\text{KHCO}_3 + 4\text{KOH} + 2\text{H}_2 + \text{O}_2 \tag{1}
\end{equation}

\begin{equation}
2\text{KHCO}_3 + \text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 2\text{KOH} + \text{H}_2 + 0.5\text{O}_2 \tag{2}
\end{equation}

\begin{equation}
(2-y)\text{K}_2\text{CO}_3 + (3-y)\text{H}_2\text{O} \rightarrow 2(1-y)\text{KHCO}_3 + y\text{CO}_2 + 2\text{KOH} + \text{H}_2 + 0.5\text{O}_2 \tag{3}
\end{equation}

They concluded that energy requirements can decrease by around 16.6% for electrolytic regeneration processes and 25.8% for the total CO$_2$ capture and compression process using electrolytic regeneration.

However, the present electrolysis process can only obtain a mixture of CO$_2$ (~70%) and O$_2$ in the anode chamber\cite{16,19,20}. It is necessary to separate them by additional processes. In this paper, the authors introduced a modified electrolytic regeneration process by which three pure gases, CO$_2$, O$_2$, and H$_2$, are produced. Our process uses an anionic exchange membrane as compared to a cationic exchange membrane, as reported by other researchers\cite{19,20}. Because of the modification, CO$_2$ and O$_2$ are produced in the anode compartment, yet at two separate positions (membrane and electrode surfaces, respectively), thus making the CO$_2$ separation
from O₂ much easier with respect to the cationic exchange membrane process. Figure 1 shows a chemical absorption system with the modified electrolytic regeneration process. The CO₂-rich solution is pumped into the electrolytic regenerator, in which desorption of CO₂ occurs with regeneration of the absorbent solution. The hydrogen as a by-product produced in the process and CO₂ can be done via catalytic reactions to form methanol. The electricity used in this process comes from clean energy.

In the paper, the regeneration mechanism of K₂CO₃ solution after absorption of CO₂ using the modified ion-exchange membrane electrolysis process and the effects of various operation parameters, including temperature, current density, and electrolysis time, have been studied.

METHODS

The solution of K₂CO₃ purchased with a purity of 99% (K₂CO₃) was used in the cathode chamber to simulate the solution after absorbing CO₂. The solution of sulfuric acid (0.1 mol/L H₂SO₄) was charged in the anode chamber. The solution of 200 mL was used in the experiments. The cells were separated by the anion exchange membrane (Huamotech AEM8040). Titanium plate and Titanium plate with IrO₂ coating were used as the cathode and the anode, respectively. The electrolysis reactions were carried out at constant current density with an electrode area of 20 cm². The whole cell was placed in a water bath to change the experimental temperature. The conductivity of the electrolytic solution was monitored by using a conductivity meter. The concentrations of K₂CO₃ and KOH in the electrolytic solution were determined by acid-base titration methods. The concentration changes in the electrolyte solutions were monitored by drawing samples at regular intervals and analyzing them by titration, and they were used to calculate the yield of CO₂. The yield rate of CO₂ and the current efficiency were calculated by Eqs. (4) and (5), respectively.

\[ w = \frac{(C_1 - C_{i+1}) \times F \times 22.4 \times 1000}{j \times S \times 22.4 \times 1000 \times 3600} \]  \hspace{1cm} (4)

\[ \eta = \frac{w \times e \times F}{j \times S \times 22.4 \times 1000 \times 3600} \]  \hspace{1cm} (5)
Where \( w \) (mL/h) is the yield rate of CO\(_2\), \( C_i - C_{i+1} \) (mol/L) the concentration changes of CO\(_2^\cdot\) at the interval of 1 h, \( V \) (L) the solution volume, \( 22.4 \) (L/mol) the molar volume of the gas, \( \eta \) the current efficiency, \( j \) (A/cm\(^2\)) the current density, \( S \) (cm\(^2\)) electrode area, \( z \) the number of electrons transferred and \( z = 2 \) in this work, and \( F \) the Faraday constant.

The energy requirement in the bench scale for producing CO\(_2\) per unit volume was calculated as Eq. (6).

\[
W = \frac{IU}{w} \times 1000
\]

Where \( W \) (kW·h/m\(^3\)) is the energy requirement in the bench scale for producing CO\(_2\) per unit volume, \( I \) (A) represents the electrolytic current, and \( U \) (V) signifies the average cell voltage after the electrolytic process is stabilized.

RESULTS AND DISCUSSION

Regeneration mechanism

Figure 2 shows an anion exchange membrane cell proposed in this work for electrolytic regeneration of KOH. The sulfuric acid (H\(_2\)SO\(_4\)) solution was charged in the anode chamber instead of the absorbent solution. Carbonate ions were transferred into the anode chamber by the AEM and reacted with H\(^+\) according to Eq. (7). CO\(_2\) was, thus, produced on the surface of the AEM in the anode chamber. The consumed H\(^+\) was replenished by water electrolysis, and the simultaneous production of O\(_2\), according to Eq. (8), was on the surface of the anode. A partition could be added between the anode and the AEM to avoid the mixture of CO\(_2\) and O\(_2\). In the cathode chamber, H\(_2\) was produced from the water reduction reaction, and the absorbent KOH solvent was regenerated simultaneously according to Eqs. (9)-(11). The overall reaction of the cell can be summarized as Eq. (12).

\[
\begin{align*}
2H^+ + CO_3^{2-} & \rightarrow H_2O + CO_2↑ \\
H_2O - 2e & \rightarrow 2H^+ + 1/2O_2↑ \\
H_2O & \rightarrow H^+ + OH^- \\
2H^+ + 2e & \rightarrow H_2↑ \\
K^+ + OH^- & \rightarrow KOH \\
K_2CO_3 + 2H_2O & \rightarrow 2KOH + H_2↑ + 1/2O_2↑ + CO_2↑
\end{align*}
\]

It is worth noting that OH\(^-\) in the cathode chamber was also able to transfer into the anode chamber by the AEM and reacted with H\(^+\) to produce H\(_2\)O, which is the main reason for the decrease of the current efficiency.

Stability of the electrolytic regeneration process

The changes of cell voltage, yield rate of CO\(_2\), and current efficiency with electrolysis time were investigated. Figure 3 shows the effect of electrolysis time on the cell voltage. The cell voltage increases with the current density, but the increase is disproportionate. The almost constant cell voltage throughout the electrolysis process indicated that the process was stable.
Figure 2. AEM cell for electrolytic regeneration of KOH with simultaneous H₂, O₂, and CO₂ generation.

Figure 3. Effect of electrolysis time on the cell voltage.

Figure 4 shows the effect of electrolysis time on the yield rate of CO₂. The production rate of CO₂ dramatically decreases in the initial 2 h of electrolysis and tends to be stable in the following 3 h. The change of current efficiency with electrolysis time is shown in Figure 5. The current efficiencies are larger than 100% in the initial 2 h and tend to be stable in the following 3 h. In the initial stage, a large number of CO₃²⁻ exchange with AEM surface groups. The concentration of CO₃²⁻ in solution is thus reduced, but the exchange process is not the effect of the current.

Effect of temperature
It requires 2 h for the system to be stabilized, as mentioned above. The average values of yield rates of CO₂ and current efficiency were calculated by the data obtained from the 3rd to 5th h. Figure 6 shows the effect of temperature on yield rates of CO₂ and current efficiency. Both the yield rate of CO₂ and the current efficiency increase initially and decrease afterward with temperature. The initial upward stage is due to the increasing conductivity of the solution with temperature [Figure 7]. However, OH⁻ is easier than CO₃²⁻ to
Figure 4. Effect of electrolysis time on the yield rate of CO$_2$.

Figure 5. Effect of electrolysis time on current efficiency.

Figure 6. Effect of temperature on yield rates of CO$_2$ and current efficiency.
cross the AEM, resulting in a decreased trend with a further increase in temperature. The values of the yield rate of CO$_2$ and the current efficiency reached 129.7 mL/h and 77.6% at the conditions of 30 °C and 0.02 A/cm$^2$, respectively.

**Effect of current density and CO$_3^{2-}$ initial concentration**

Figure 8 shows the synergistic influence of current density and CO$_3^{2-}$ initial concentration on yield rates of CO$_2$ and current efficiency. The larger yield rate of CO$_2$ was obtained in a higher current density in Figure 8A, while the current efficiency has an opposite trend [Figure 8B]. The current efficiency is larger in a lower current density. The reason is that a larger number of OH$^-$ ions are produced in a higher current density or a higher CO$_3^{2-}$ initial concentration, resulting in a decrease of the current efficiency. The current efficiency reached 89% at the current density of 0.01 A/cm$^2$ and the CO$_3^{2-}$ initial concentration of 0.7 mol/L.

**Energy consumption**

Figure 9 shows the effects of current density and CO$_3^{2-}$ initial concentration on energy consumption. The energy consumption increases with current density. A low current density can reduce the energy consumption.

In conclusion, (1) the processes using membrane electrolysis can regenerate the absorbent solution to achieve 89% current efficiency, and the simultaneous production of H$_2$ makes this method promising; (2) CO$_2$ was produced on the surface of the AEM in the anode chamber, while O$_2$ was produced on the surface of the anode. The mixture of CO$_2$ and O$_2$ can be avoided by adding a partition between the anode and the AEM; (3) The effects of various operation parameters, including the temperature, the current density, and CO$_3^{2-}$ initial concentration, have been studied. Both the yield rate of CO$_2$ and the current efficiency increase initially and decrease afterward with temperature. The yield rate of CO$_2$ increases while the current efficiency decreases with the current density. A low current density can reduce the energy consumption for producing the same amount of CO$_2$. 

![Figure 7. Effect of temperature on the conductivity of the solutions.](image)
Figure 8. Effects of current density and CO$_3^{2-}$ initial concentration on (A) yield rates of CO$_2$ and (B) current efficiency.

Figure 9. Effects of current density and CO$_3^{2-}$ initial concentration on energy consumption.

DECLARATIONS
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Availability of data and materials
The corresponding author will provide the datasets used or analyzed during the current work upon reasonable request.
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Conflicts of interest
All authors declared that there are no conflicts of interest.

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