

Formation of CaO-TiO₂ composite film via electrodeposition for CO₂ adsorption

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With increasing awareness on global warming and climate change, the carbon dioxide (CO₂) capture has been studied extensively for the reduction of its emission to our atmosphere. In the present study, the calcium oxide (CaO) - titanium dioxide (TiO₂) has been developed via electrodeposition technique for better CO₂ adsorption purpose. Based on the FESEM micrographs, CaO-TiO₂ was appeared in micro-size composite film. The CO₂ adsorption capacity was obtained by thermogravimetric analysis (TGA). The results revealed that the highest Ca content (34.51%) of CaO-TiO₂ composite film exhibited CO₂ adsorption capacity of ≈ 2.80 mmol/g. In this case, CaO could reversibly bind with CO₂ gas and form calcium carbonate (CaCO₃) via carbonate looping process.

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1. Introduction

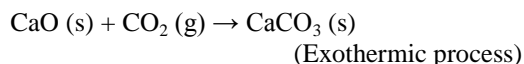
In recent years, CO₂ has become the focus of the attention as CO₂ is the primary greenhouse gas (GHG) in the atmosphere. The mean global atmospheric CO₂ concentration has increased from 280 ppm in the pre-industrial level in the 1970s to 384 ppm in 2007, and is expected to reach 550 ppm by 2050 even if the emission of CO₂ into the atmosphere is stable [1-2]. The major environmental impact of the accumulation of atmospheric CO₂ is global warming. The average temperature of Earth's atmosphere has been increased with the proportional to the atmospheric CO₂ concentrations. The CO₂ emissions are related to human activities mainly due to the burning of fossil fuels and various chemical processes [2-4].

New technologies and processes for CO₂ capture, storage (sequestration) and utilization (CSU) are developed to control the atmospheric CO₂ concentrations in the past few years [5]. The sorption-based technologies and processes are the majority of the research activities and often relate to solid-based adsorbents. The solid adsorbents can be used over a wider temperature range from ambient temperature to 700 °C as compare to the liquid adsorbents. In addition, the benefits of solid adsorbents is yielding the less waste during cycling process, and the spent solid adsorbents can be disposed without creating environmental problems [6].

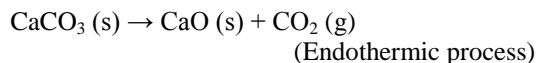
Although many materials could be potentially used for CO₂ adsorption, CaO has been identified as the most promising candidate because of its stoichiometric reactive sorption capacity, low cost, and the abundance of its natural precursors [7]. Calcium carbonates (CaCO₃) liberate CO₂ and form CaO when treated at high

temperatures. The operation of the materials can be defined by a carbonation–calcinations cycle as follow equations:

Carbonation:



Calcination (decomposition):



However, the major obstacles for the use of CaO are the requirement of high operating temperature ($\sim 700^\circ\text{C}$) and low efficiency [7]. Based on the literature reviews, cyclic stability of CaO-based sorbent can be improved by incorporating inert materials such as CaC₂O₄ and Ca(OH)₂, Al₂O₃, La(NO₃)₃·6H₂O, Al(NO₃)₃·9H₂O and CaTiO₃, Ca(NO₃)₂·4H₂O, and Ca(CH₃COO)₂·H₂O [2]. Thus, this study aims to form the CaO-TiO₂ composite foil for improving CO₂ adsorption using electrodeposition technique.

2. Experimental procedure

First of all, Ti foils were cut into a dimension of 10 mm x 50 mm. Prior to electrochemical deposition, the Ti foils were degreased by sonicating in acetone using ultrasonic cleaning. Then, several set of electrolyte solutions were prepared for electrodeposition studies as shown in the Table 1. The listed chemicals were mixed in deionized water and stirred for 60 minutes in order to

ensure the mixture was homogeneous prior to electrodeposition process. The electrodeposition experiments were carried out using conventional two-electrode systems with a graphite rod as anode and Ti foil as cathode. Anode was connected to positive of a dc power supply and cathode to negative terminal. All experimental works were conducted at 20 V for 1 hour because it favors the formation of well-distributed oxide layer on the Ti foil based on our preliminary studies. After the electrodeposition process, the sample was first soaked in acetone and subsequently cleaned in ultrasonic bath for 45 seconds. Then the sample was rinsed in distilled water for few times and dried under the flow of nitrogen. The morphologies of the resultant samples were characterized using Field Emission Scanning Electron Microscopy (FESEM), using Zeiss SUPRA 35VP (Oberkochen, Germany) at a working distance of around 5 mm. The elemental analysis that is atomic percentage of the CaO-

TiO₂ composite film can be determined with energy dispersion X-ray (EDX), which is equipped in the FESEM. The CO₂ adsorption on selected CaO-TiO₂ samples was carried out by using a Simultaneous Thermal analyser (STA 6000, Perkin Elmer/USA) to perform carbonation experiments. A small amount (1 g) of sample was placed in a sample crucible and heated from 30 °C to the carbonation temperature of 400 °C at a rate of 10 °C/min in the N₂ flow of 20 mL/min. Once the carbonation temperature was reached and stabilized, CO₂ flow of 20 mL/min was introduced into the TGA. The carbonation period was hold for 30 min, and then cooled down to 300 °C in N₂ flow at rate of 10 °C/min. The weight percentage changed, temperature and time was recorded using computer with the help of PerkinElmer Thermal Analysis software.

Table 1. Experimental parameters of the electrodeposition studies.

No.	Electrolyte	Time (min)	Temperature (°C)	Voltage (V)
1	0.01 M CaCl ₂ .2H ₂ O	60	Room temperature	20
2	0.01 M Ca(NO ₃) ₂ .4H ₂ O	60	Room temperature	20
3	0.01 M CaCl ₂ .2H ₂ O + 0.01 M KMnO ₄	60	Room temperature	20
4	0.01 M Ca(NO ₃) ₂ .4H ₂ O + 0.01 M KMnO ₄	60	Room temperature	20

3. Results and discussion

In recent years, TiO₂ has attracted considerable scientific interest due to its unique chemical and physical properties. Then, design and development of TiO₂-based composite material has gained significant interest among our scientist community. In the present study, a set of experiment was carried out to study the possible formation of high specific surface area of CaO-TiO₂ composite film using electrodeposition from various types of electrolyte as shown in Table 1. 0.01 M Ca²⁺ ions had been added into the electrolyte using two different calcium cations sources, such as calcium chloride dihydrate and calcium nitrate tetrahydrate. In addition, 0.01 M of oxidizing agent of KMnO₄ was incorporated into the electrolyte for oxidizing the calcium compound into the Ca²⁺ cations. Thus, the resultant Ca²⁺ cations could be attracted to cathode and then deposited on the surface of the Ti foil. The ultimate aim was to improve the stoichiometric reactive sorption capacity using the high specific surface area of CaO-TiO₂ composite foil. Fig. 1(a) to (d) showed the surface

morphological analysis for the resultant samples under different electrolytes at 20 V for 1 hour. Based on the FESEM observation, CaO was successfully deposited on the TiO₂ film through electrodeposition. All of the samples showed similar structure of spherical shape on Ti film. From Fig. 1(a), it could be seen that the CaO layer was sparingly deposited on the foil for CaCl₂ electrolyte with thickness of 3.8 μm. For the Ca(NO₃)₂ electrolyte, a CaO layer of oxide with irregular shape was formed as presented in Fig. 1(b). The thickness of the layer is approximately 4.5 μm. The nodule like CaO structure was produced might be attributed to the oxidizing reactions on the Ti film, which triggers by the oxidizing agent (KMnO₄). The resultant surface morphologies were showed in Fig. 1(c) and Fig. 1(d), which is having a thickness of 5.8 μm and 6.5 μm, respectively. In this manner, the strong oxidizing agent of KMnO₄ was oxidized the calcium sources to form calcium cations (Ca²⁺) and helped in increasing the deposition rate of CaO on Ti film.

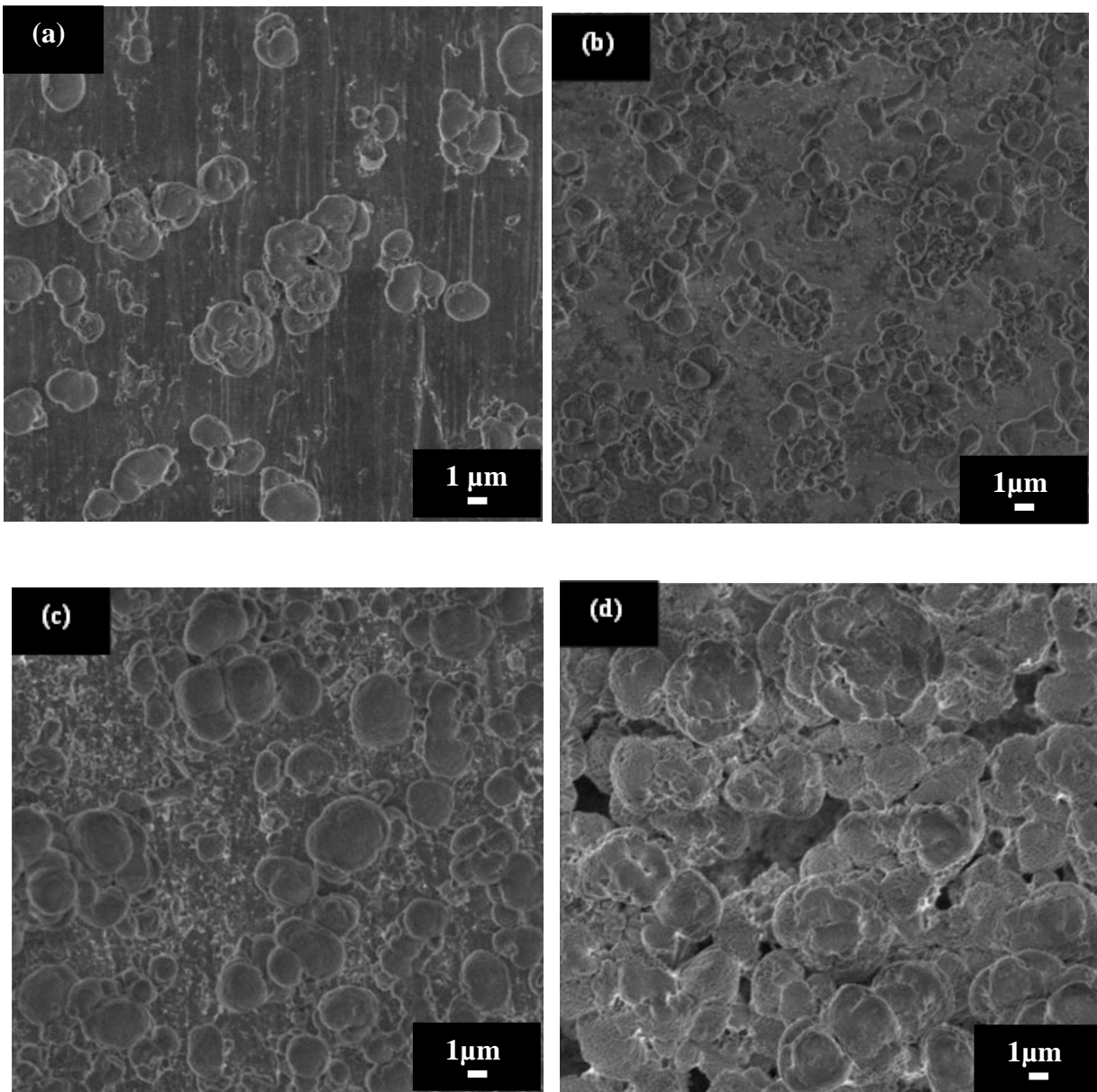


Fig. 1. FESEM image of electrodeposited CaO from (a) $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ electrolyte; (b) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ electrolyte; (c) $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and KMnO_4 electrolyte; and (d) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and KMnO_4 electrolyte.

Next, energy dispersive X-ray (EDX) analysis was carried out to determine the weight percentage of the elements presents in the samples. The EDX spectra are shown in Fig. 2 and Fig. 3 and the results are summarised in Table 2. The peaks in the spectra indicate the existence of Ti, O, Ca and C elements on the samples.

The intensity of the Ca recorded on the sample produced from $\text{Ca}(\text{NO}_3)_2$ electrolyte is higher than that from CaCl_2 electrolyte for with or without KMnO_4 added. This indicates that $\text{Ca}(\text{NO}_3)_2$ is most suitable electrolyte to be used for CaO deposition as compare to the CaCl_2 .

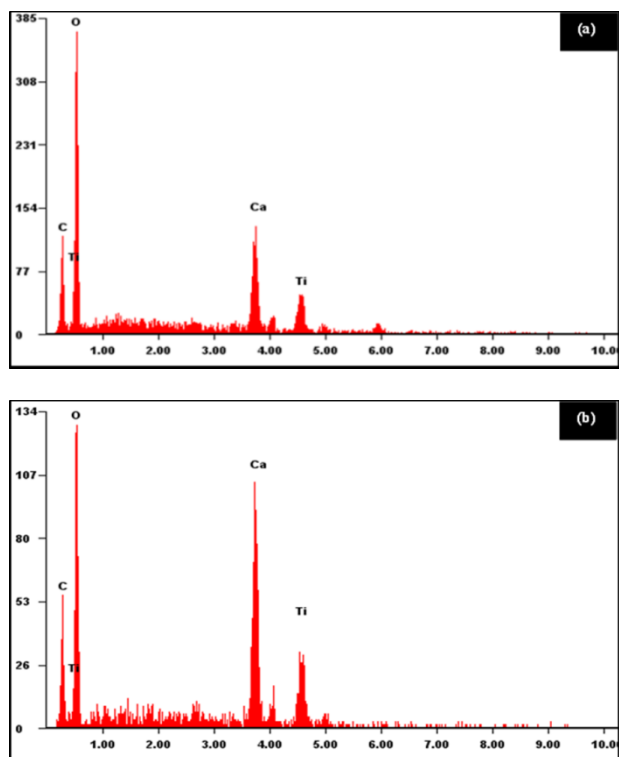


Fig. 2. EDX spectra of electrodeposited sample from electrolyte of 0.01 M (a) $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and (b) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

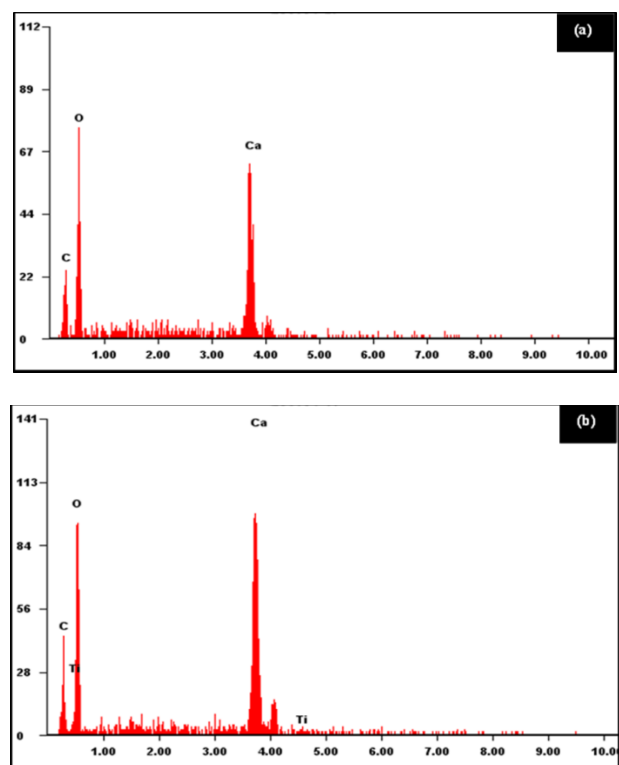
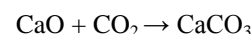


Fig. 3. EDX spectra of electrodeposited sample from electrolyte of 0.01 M (a) $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and (b) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, with 0.01 M KMnO_4 .

Table 2. EDX result of electrodeposition products with different electrolytes.

Element	Ti (at%)	O (at%)	Ca (at%)	C (at%)
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	09.31	55.55	14.66	20.48
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	12.03	48.30	23.27	16.40
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O} + \text{KMnO}_4$	-	51.41	30.38	17.75
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{KMnO}_4$	00.28	48.96	34.51	16.24

The use of TGA analysis to investigate the sorption CO₂ ability has been conducted. This selected sample was produced from electrolyte of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with KMnO_4 , which showed the highest Ca content on CaO-TiO₂ composite film. Fig. 4 showed the TGA curves of CO₂ adsorption by carbonation/regeneration reactions. The carbonation of CaO is through the following reaction:



The weight of the sample was increasing when starting the N₂ flow at a rate of 10 °C/min. The weight gain of the sample might be attributed to the residual oxygen in the furnace chamber had oxidize the Ti into TiO₂ [8]. Interestingly, the abrupt increase in the adsorbent weight could be observed when CO₂ was introduced at 400 °C. Based on the results obtained, an assumption has been concluded that all the weight gain in the present study was related to the CO₂ absorption. The carbonation temperature is hold for 30 min before cold down to 300 °C by N₂ gas. From the TGA analysis the CO₂ adsorption capacity of sample was 2.80 mmol/g. This result was confirmed that conversion of CaO into CaCO₃ could be achieved during the carbonate looping process [9]. The determination of CO₂ adsorption capacity was shown as below:-

$$\begin{aligned}
 &\text{CO}_2 \text{ adsorption capacity in 1 g of sample} \\
 &= \text{Weight changed when CO}_2 \text{ introduced} / \\
 &(\text{Mr of CO}_2 \times 1 \text{ g}) \\
 &= (101.603 - 101.480) \text{ g} / (44 \text{ gmol}^{-1} \times 1 \text{ g}) \\
 &= 0.123 \text{ g} / (44 \text{ gmol}^{-1} \times 1 \text{ g}) \\
 &= 2.80 \times 10^3 \text{ mol/g} \\
 &= \underline{2.80 \text{ mmol/g}}
 \end{aligned}$$

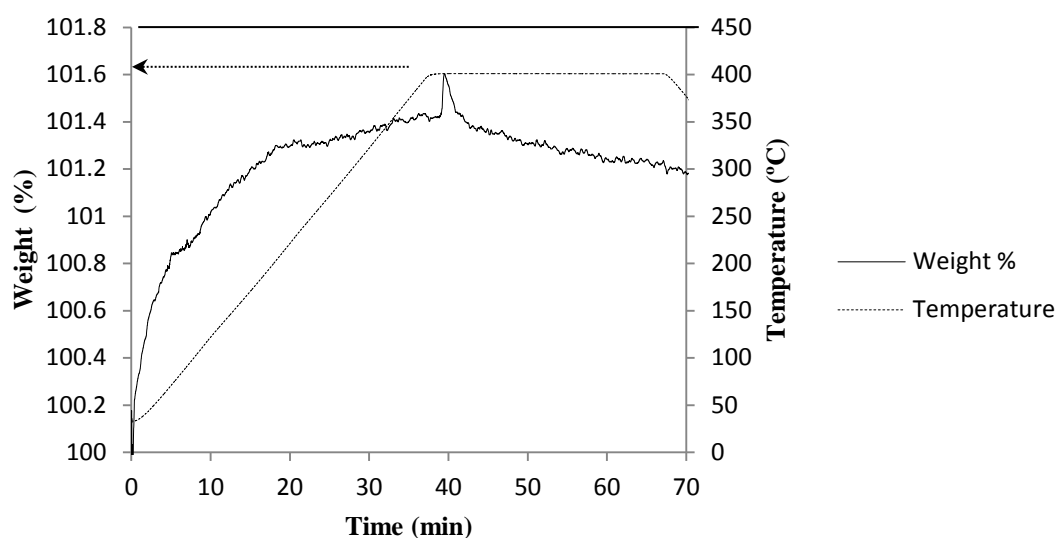


Fig. 4. TGA curve of CO_2 adsorption for the sample synthesized electrolyte of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with KMnO_4 with the highest Ca content (34.51 at%).

4. Conclusion

The CaO-TiO_2 has been developed via electrodeposition technique for CO_2 adsorption purpose. The highest Ca content (34.51 at%) was successfully formed using the electrolyte of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with KMnO_4 at 20 V for 60 minutes. The CO_2 adsorption capacity of sample was 2.80 mmol/g using TGA analysis. The adsorption CO_2 capacities are increased during the carbonate looping process from CaO into CaCO_3 .

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References

- [1] Q. Wang, J. Z. Luo, Z. Y. Zhong, A. Borgna, *Energy & Environmental Science*, **4**, 42 (2011).
- [2] S. Wang, S. Yan, X. Ma, J. Gong, *Energy & Environmental Science*, **4**, 3705 (2011).
- [3] R. Siriwardane, M. Shen, E. Fisher, J. Poston, D. H. Smith, *Energy & Fuels*, **15**, 279 (2001).
- [4] Z. Yong, V. G. Mata, A. E. Rodrigues, *Adsorption*, **7**, 41 (2001).
- [5] M. G. Plaza, C. Pevida, B. Arias, M. D. Casal, C. F. Martin, J. Feroso, F. Rubiera, J. J. Pis, *Journal of Environmental Engineering*, **135**, 426 (2009).
- [6] D. P. Harrison, *Greenhouse Gas Control Technologies* **7**(2), 1101 (2005).
- [7] S. Choi, J. H. Drese, C. W. Jones, *ChemSusChem*, **2**, 796 (2009).
- [8] L. H. Chiu, D. C. Nagle, L. A. Bonney, *Metallurgical and Materials Transactions A*, **30A**, 781 (1999).
- [9] C. W. Lai, *Journal of Nanomaterials*, 2014, Article ID: 876571 (2014).

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