

**PREPARATION AND CHARACTERIZATION OF
LITHIUM ORTHOSILICATE SORBENT FOR
CARBON DIOXIDE REMOVAL**

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**PREPARATION AND CHARACTERIZATION OF LITHIUM
ORTHOSILICATE SORBENT FOR CARBON DIOXIDE REMOVAL**

by

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**PENYEDIAAN DAN PENCIRIAN PENJERAP LITIMUM ORTOSILIKAT
UNTUK PENYINGKIRAN KARBON DIOKSIDA**

oleh

NURUL AZRIN BINTI ZUBBRI

**Tesis yang diserahkan untuk
memenuhi keperluan bagi
Ijazah Sarjana Sains**

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LIST OF ABBREVIATIONS

GHG	Greenhouse gas
EPA	Environmental Protection Agency
EDGAR	Emission Database for Global Atmospheric Research
PBL	Netherlands Environmental Assessment Agency
IPCC	Revised Intergovernmental Panel on Climate Change
ASEAN	Association of Southeast Asian Nation
EIA	Energy Information Administration
MEA	Monoethanolamine
DGA	Diglycolamine
DEA	Diaethanolamine
DIPA	Diisopropylamine
TEA	Triethanolamine
MDEA	Monodiethanolamine
SESMR	Steam methane reforming system
BET	Brunauer–Emmett–Teller
TEOS	Tetraethylorthosilicate
TGA	Thermogravimetric Analyzer
ppmv	Part per million by volume
SEM	Scanning electron microscopic
XRD	X-Ray Diffractometry
OFAT	One factor at a time

PENYEDIAAN DAN PENCIRIAN PENJERAP LITIUM ORTOSILIKAT UNTUK PENYINGKIRAN KARBON DIOKSIDA

ABSTRAK

Pada masa kini, dunia masih menghadapi cabaran pemanasan dan isu-isu perubahan iklim global. Setakat ini, banyak usaha telah diambil untuk mengurangkan pelepasan CO₂ termasuk penggunaan penjerap yang kukuh untuk menjerap CO₂. Pepejal litium ortosilikat (Li₄SiO₄) adalah satu daripada penjerap yang digunakan untuk menjerap CO₂ pada suhu tinggi. Dalam kajian ini, Li₄SiO₄ telah disediakan melalui kaedah sol-gel dengan menggunakan litium nitrat (LiNO₃) dan silikon etoksida (SiC₈H₂₀O₄) sebagai bahan asas. Pengaruh nisbah molar Li:Si (1-5), suhu pengkalsinan (600-800°C), tempoh masa pengkalsinan (1-8 jam) dan nisbah molar H₂O:Si (1-5) dikaji semasa proses sintesis penjerap. Kapasiti penjerapan oleh penjerap itu dinilai melalui beberapa ujian penjerapan CO₂ dengan menggunakan Penganalisis Termogravimetri (TGA). Suhu pengkalsinan (700-800°C) dan suhu pengkarbonan (500-700°C) diubah semasa ujian pengkarbonan. Penjerap terbaik yang mempunyai kapasiti penjerapan CO₂ tertinggi dianalisa menggunakan XRD untuk mengesahkan kehadiran spesies Li₄SiO₄. Penjerap dengan kapasiti penjerapan CO₂ tertinggi akhirnya diuji dengan beberapa ujian kitaran untuk mengkaji ketahanan penjerap melalui 10 ujian proses penjerapan-pembebasan CO₂. Ciri fizikal-kimia penjerap sebelum dan selepas ujian pengkarbonan dikaji melalui analisis SEM dan XRD. Hasil kajian menunjukkan bahawa penjerap yang disediakan dengan nisbah molar Li:Si 1:1, nisbah molar H₂O:Si 5:1, pengkalsinan pada suhu 700°C selama 5 jam mempunyai kapasiti penyerapan CO₂ tertinggi. Suhu

pengkalsinan 800°C dan suhu pengkarbonan 700°C dipilih sebagai suhu terbaik yang menyumbang kepada kapasiti penyerapan sebanyak 7.947 CO₂ mmol/g penjerap, yang juga bersamaan dengan 93% daripada hasil teori. Selepas sepuluh proses kitaran, kapasiti penyerapan CO₂ oleh penjerap jatuh 16.2% dari kitaran pertama hingga kesepuluh. Penjerap Li₄SiO₄ telah menunjukkan potensi untuk mempunyai keupayaan penyerapan CO₂ yang tinggi dan prestasi kitaran yang stabil.

PREPARATION AND CHARACTERIZATION OF LITHIUM ORTHOSILICATE SORBENT FOR CARBON DIOXIDE REMOVAL

ABSTRACT

Nowadays, the world is surviving the challenge of global warming and climate change issues. So far, many efforts have been undertaken to mitigate CO₂ emission among which is the use of solid sorbents for CO₂ capture. Solid lithium orthosilicate (Li₄SiO₄) is one of the sorbents used to capture CO₂ at high temperature. In this research, Li₄SiO₄ was synthesized by sol-gel method using lithium nitrate (LiNO₃) and silicon ethoxide (SiC₈H₂₀O₄) as precursors. The influences of Li:Si molar ratio (1-5), calcination temperature (600–800°C), calcination time (1–8h) and H₂O:Si molar ratio (1-5) were investigated during the sorbent synthesis. The sorption capacity of the developed sorbent was evaluated through CO₂ capture tests performed using a Thermogravimetric Analyzer (TGA). The calcination temperature (700-800°C) and carbonation temperature (500-700°C) were varied during the carbonation test. The best sorbent with the highest CO₂ sorption capacity was analyzed with XRD to confirm the appearance of Li₄SiO₄ species. The sorbent with highest CO₂ sorption capacity was finally introduced to some cyclic tests to study the durability of the sorbent through ten CO₂ sorption-desorption tests. The physicochemical properties of the developed sorbent before and after carbonation tests were investigated through SEM and XRD analyses. The results showed that the sorbent prepared with 1:1 molar ratio of Li:Si, 1:1 molar ratio of H₂O:Si and calcined at 700°C for 5h has the highest CO₂ sorption capacity. Calcination temperature of 800°C and carbonation temperature of 700°C were chosen

as the best values which resulted in the sorption capacity of 7.947 mmol CO₂/g sorbent which is 93% of the theoretical yield. Throughout ten cyclic process, CO₂ sorption capacity of the sorbent dropped about 16.2% from the first to tenth cycle which seems to be reasonable. Li₄SiO₄ was found to be a potential solid sorbent that has high CO₂ sorption capacity besides its stable cyclic performance.

CHAPTER 1

INTRODUCTION

1.1 Global Warming

It is widely known that the atmosphere has been warming over the past half century which is believed to be caused by the greenhouse gases. Global warming is a term used to describe a gradual increase of temperature thus changing the Earth's climate. The heat emitted from the Earth's surface is trapped by the greenhouse gases thus radiated back towards the Earth. Only little amount of the heat emitted from the surface passes through the atmosphere directly to the space. Therefore, increasing the concentration of greenhouse gases increases the warming of the Earth's surface and slowing down the loss of energy to the space (Hansen *et al.*, 2010).

In a positive way, without the greenhouse gases our Earth's temperature would be about 0°F (-18°C) instead of its present 57°F (14°C). So, the important thing is not to eliminate the greenhouse gases but whether the human activities are leading to an enhancement of the greenhouse effect by the emission of greenhouse gases through fossil fuel combustion and deforestation (Shindell, Faluvegi, Bell and Schmidt, 2005).

1.2 Greenhouse Gas

Greenhouse gases emitted by human activities are carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and fluorinated gases (F-gases). Figure 1.1 illustrates the portion contributed by greenhouse gases emissions in 2010 by main sectors and gas types. CO₂ emissions from fossil fuel use and cement production declined in 2009 due to the recession but increased sharply afterwards in 2010 and

2011. Besides that, global emissions of CH₄ and N₂O increased in 2010 by 0.5% while emissions of F-gases increased by 7% and now contributing 2% to global total greenhouse gas emissions. CO₂ is the major gas that has been emitted by human activities with 76% of total GHG emissions. CH₄ and N₂O emissions contributed 16% and 6% respectively to total CO₂ equivalent emissions in 2010.

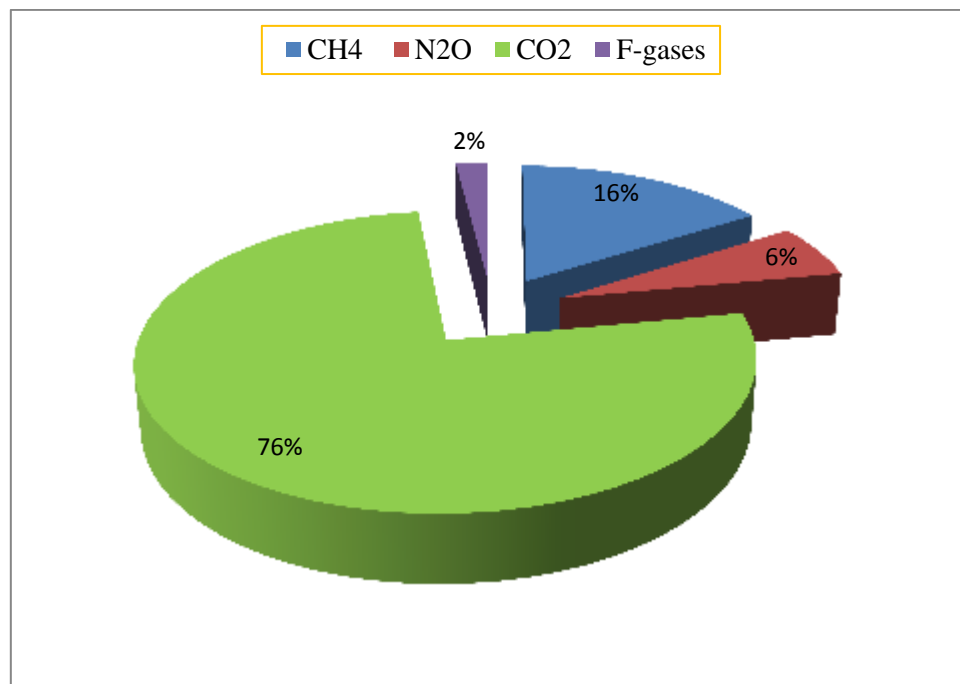


Figure 1.1. Sources of global greenhouse gas emissions in 2010 by gas type
(Oliver, 2013)

CO₂ emissions originated from many sources such as fossil fuel from energy plant, deforestation, transportation, improvement of soils and other activities. They naturally absorb and emit CO₂ as part of the carbon cycle which is through the animal and plant respiration, volcanic eruptions and ocean-atmosphere exchange. Throughout 800,000 years apart, the current CO₂ level is highly increased. In 2010,

the CO₂ concentration approached 390 part per million by volume (ppmv) from 280 ppmv in the 18th century (NRC, 2010).

1.3 Carbon Dioxide (CO₂)

Average annual concentration of CO₂ in atmosphere in 2013 was 396.48 ppm while 2012 average was 393.82 ppm (Ed Dlugokencky, 2014). Figure 1.2 illustrates the trend of CO₂ concentration in the atmosphere in the past decade (2003-2013). For the past decade (2004-2013), the average annual increase was 2.1 ppm per year. The average increase of prior decade (1994-2003) was 1.9 ppm per year. This shows that the atmospheric CO₂ is increasing at an accelerating rate. Research suggested that it is due to the fossil fuels that are being burned at an enhanced rate, the ending of the long term trend of increasing carbon efficiency of economies and the ocean's diminishing absorption of CO₂ (Canadell *et al.*, 2007).

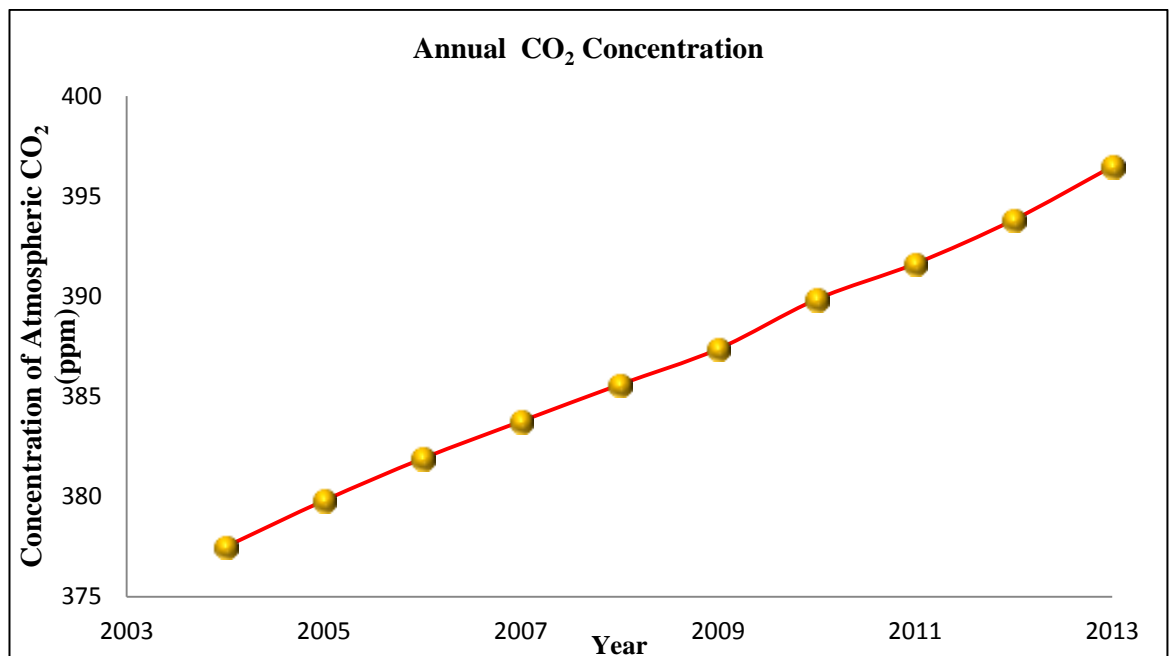


Figure 1.2. Annual atmospheric CO₂ concentration from 2003 until 2013

(Ed Dlugokencky, 2014)

Figure 1.3 shows the CO₂ emission per capita of several developing countries in Asia. Within the Association of Southeast Asian Nation (ASEAN), CO₂ emission intensity in Malaysia is the second lowest after Singapore. CO₂ emission recorded in Malaysia was 216.62, 213.57 and 216 Mt CO₂/year for 2010, 2011 and 2012 respectively. It can be concluded that the emission remain consistent over the past three years. China recorded the highest CO₂ emission among the other developing ASEAN countries with 8280.13, 9086.87 and 9620.67 Mt CO₂/year in 2010, 2011 and 2012 respectively.

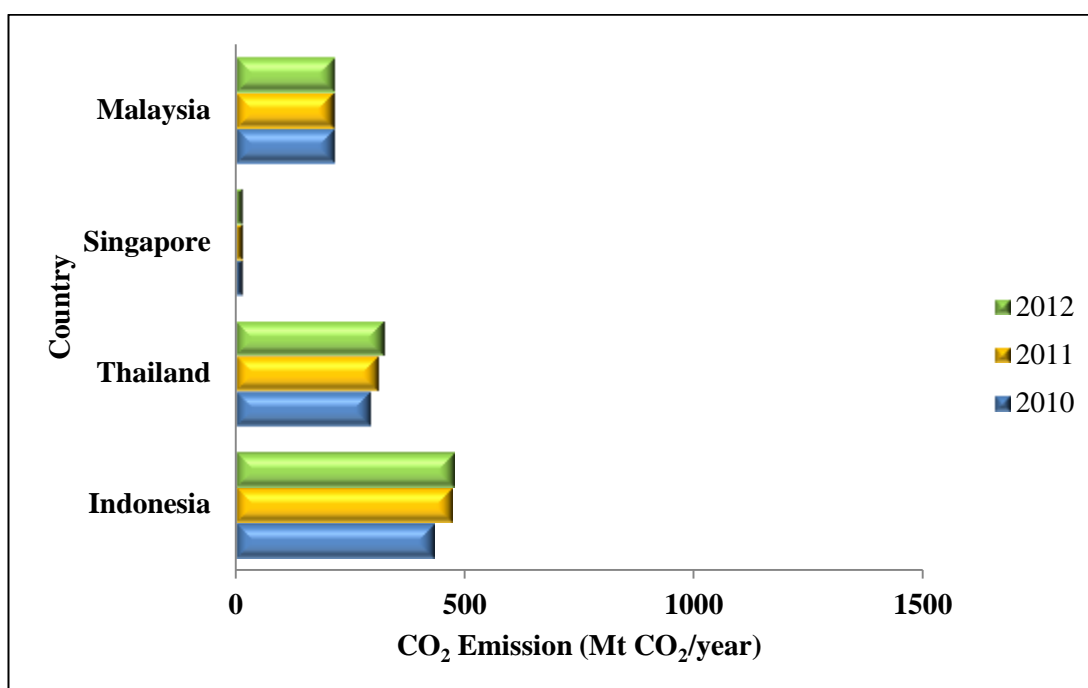


Figure 1.3. CO₂ emission for several developing ASEAN countries in from 2010 to 2012 (EDGAR, 2014)

According to the U.S Energy Information Administration (EIA) data, CO₂ emission in Malaysia was 6.196 Mt per capita as in 2007 and increased to 6.664 Mt per capita in 2011. In 1980, the CO₂ emission was high with 4.13964 Mt but

successfully minimized the problem by reducing them in 1983 to 3.88382 Mt (EIA, 2014). However, CO₂ emissions had been increased widely but it was fluctuated time by time throughout thirty years. Figure 1.4 illustrates the trend of CO₂ emissions in Malaysia from 2007 until 2011.

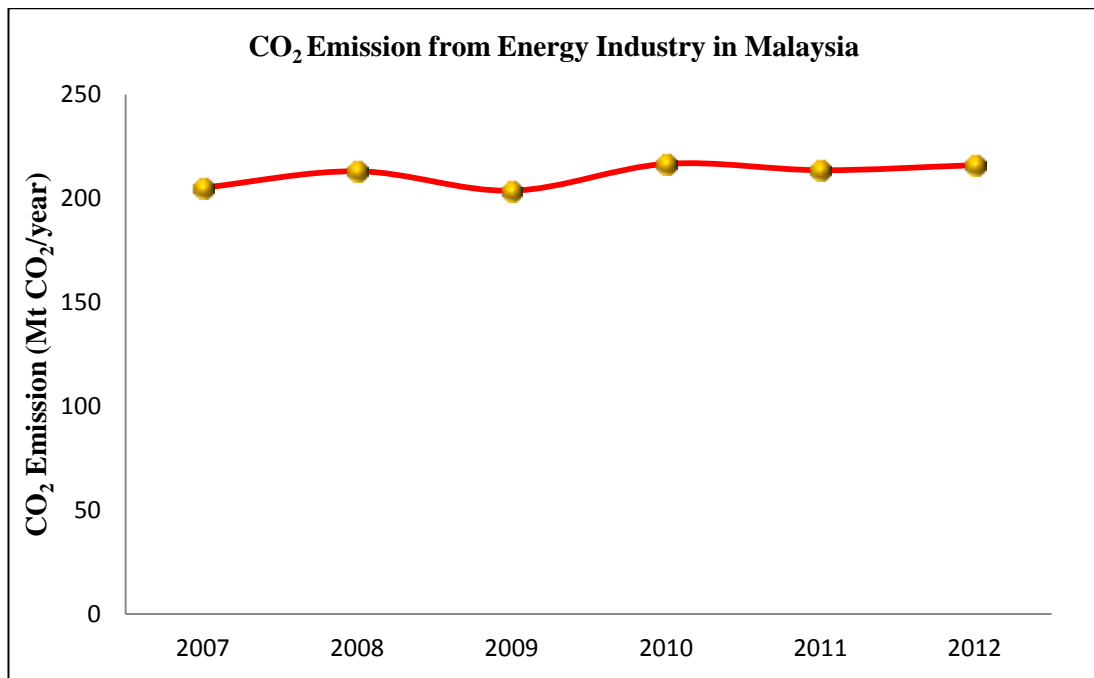


Figure 1.4. Carbon dioxide emission from energy industries in Malaysia from 2007 until 2011 (EIA, 2014)

There was a misconception in making the fact of the cause of global warming where CO₂ is believed to be responsible for the rise of the earth's temperature. It is true that human's activities produced more CO₂ than other GHGs but some of other GHGs trap the heat are more powerful than CO₂ did. It was suggested that different GHGs have different heat-trapping ability (Hansen *et al.*, 2010).

1.4 Cause of Global Warming / Major Source of GHG Emission

There are two major reasons of global warming which are anthropogenic causes (human-induced) and natural causes. The big contributor to the natural causes of global warming is deforestation caused by forest fire. Deforestation can be explained as the cutting down of the trees and plants for the purpose of development activity which enhances the concentration of carbon dioxide (CO₂) in the air. However, it will take time for the new planted trees to grow large enough for the purpose to absorb the high concentration of carbon dioxide in our atmosphere and produce sufficient oxygen. Deforestation comes along with new development projects, requirement of land for homes and factories, requirement for wood and also soil erosion (Howden, 2007).

The Earth's climate also can be affected by the volcanoes when there is a major explosive eruption that leads to the production of a large amount of volcanic gas, aerosol droplets and ashes. Researchers estimated the CO₂ emission rate for all sub aerial (on land) and submarine volcanoes to be in the range from 130 Mt to 440 Mt per year (Friedlingstein *et al.*, 2010). Furthermore, some of CO₂ emission comes from natural activity such as volcanic eruptions and people breathing, however the Earth can easily absorb them into regenerative process to keep the system stable.

Anthropogenic causes such as fossil fuel combustion by cars, factories and electricity production are also among the major contributors to CO₂ emission. Most of the power plants generate power by burning fossil fuels for the purpose of delivering the electricity to people. The world anthropogenic CO₂ emission for 2010 is projected to be 35000 Mt which is 135 times larger than that of 260 Mt per year of the highest global volcanic CO₂ emission (Gerlach *et al.*, 2002).