



## Atmospheric CO<sub>2</sub> capture for the artificial photosynthetic system

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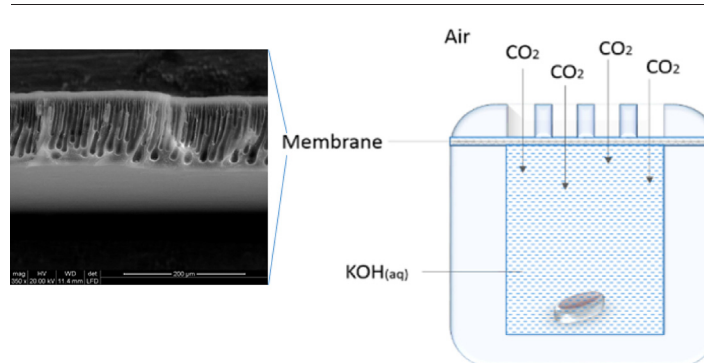
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### HIGHLIGHTS

- A membrane contactor was developed for ambient CO<sub>2</sub> capture studies.
- The influence of membrane characteristics on the absorption was evaluated.
- CO<sub>2</sub> assimilation ability of stomata mimicking unit is comparable to the natural one.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The aim of these studies is to evaluate the ambient CO<sub>2</sub> capture abilities of the membrane contactor system in the same conditions as leaves, such as ambient temperature, pressure and low CO<sub>2</sub> concentration, where the only driving force is the concentration gradient.

The polysulfone membrane employed was made by a phase inversion process and characterized by ESEM micrographs which were used to determine the thickness, asymmetry and pore size. Besides, the porosity of the membrane was measured from the membrane and polysulfone density correlation and the hydrophobicity was analyzed by contact angle measurements. Moreover, the compatibility of membrane and absorbent was evaluated, in order to exclude wetting issues by means of swelling, dynamic contact angle and AFM analysis. The prepared membranes were introduced into a cross flow module and used as contactors between CO<sub>2</sub> and the absorbing media, a potassium hydroxide solution. The influence of the membrane thickness, absorbent stirring rate, solution pH and absorption time on CO<sub>2</sub> capture were evaluated. Absorbent solution stirring rate showed no statistically significant influence on absorption. We observed a non-linear correlation between the capture rate and the increase of absorbent solution pH as well as absorption time. The results showed that the efficiency of our CO<sub>2</sub> capture system is similar to stomatal carbon dioxide assimilation rate, achieving stable value of 20 μmol/m<sup>2</sup>·s after 1 h of experiment.

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### 1. Introduction

Growth in carbon dioxide concentration of Earth's atmosphere is one of the main issues troubling the modern world. Since the Industrial Revolution started, global average level of CO<sub>2</sub> concentration rose from 280 ppm to 404 ppm (as of May 2016) and it is the highest recorded in

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last 650,000 years. Another important issue is its growth rate (Canadell et al., 2007).

At present almost half of CO<sub>2</sub> emission is absorbed by lands and oceans (Ballantyne et al., 2012). Studies show that global increase in total carbon dioxide concentration will enhance the storage, but simultaneously climate change will tend to release land's and ocean's carbon to atmosphere (Friedlingstein et al., 2006). Fossil fuel combustion emission, which is the main cause of the carbon dioxide atmospheric growth, is increasing year by year. In the past 50 years the fraction of CO<sub>2</sub> that remains in atmosphere grew from 40 to 45% (2009) (Le Quééré MRR et al., 2009). These factors require the invention of new technologies as well as development of the ones already existing to reduce global warming effects. The best inspiration for scientists has always been nature. Our planet had been taking care of the balance of CO<sub>2</sub> for billions of years through, among others, photosynthesis.

The approach of the present work is to capture CO<sub>2</sub> from atmosphere, such as photosynthetic organisms do. The system works as a leaf, where CO<sub>2</sub> is captured directly from air through the membrane pores and passes to the next compartments to be finally converted to methanol or other hydrocarbons to be used as fuel in fuel cells (Olah and Surya Prakash, 2009; Wang et al., 2011). The electrochemical device converts the chemical energy of a fuel directly into electrical energy, through a chemical reaction.

The first step, which is the CO<sub>2</sub> fixation, is the process rate determining step. CO<sub>2</sub> assimilation rate in stomata reaches between 15 and 40 μmol/m<sup>2</sup>·s (Martínez-Lüscher et al., 2015; Peter Teszlaka et al., 2013; Radglou, 1996; Tezara et al., 1999). Stomata are small adjustable pores located on the leaf surface. The main role of stomata is regulating gas exchange between the inside of the leaf and the external environment, e.g. during photosynthesis it allows CO<sub>2</sub> to diffuse into the leaf. The system designed for carbon dioxide capture process mimics stomata function. It consists of a porous polysulfone membrane contactor which uses a basic solution to absorb carbon dioxide. The membrane contactor is permeable for the gas and provides high contact surface area. Recently they started to be used for carbon dioxide capture as a hybrid of membrane separator and chemical absorption.

In the membrane contactor, the porous membrane separates the gas and liquid phases and the absorption process is driven by pressure or concentration gradient. The mass transfer process includes following steps: convective-diffusive transport of the solute from the bulk gas to the membrane surface, transfer through the membrane pores to the liquid membrane surface and a convective-diffusive transfer of a solute to the bulk liquid followed by physical or chemical absorption. The overall mass transfer coefficient takes in account every individual resistances. The resistances are: the gaseous phase boundary layer (1/k<sub>G</sub>), the membrane (1/k<sub>m</sub>) and the liquid phase boundary layer (1/k<sub>L</sub>). The overall process is well-known as a “resistance in series” model and overall mass transfer resistance (1/K<sub>0</sub>) can be obtained by adding the individual resistances (Dindore et al., 2004).

$$\frac{1}{K_0} = \frac{1}{k_G} + \frac{1}{k_m} + \frac{1}{k_L} \quad (1)$$

A precise knowledge of mass transfer coefficient is essential for simulation, industrial design and use of membrane contactors. Simplified equation for its theoretical value is:

$$k_m = \frac{D * \varepsilon}{\tau * z} \quad (2)$$

In this equation *D* stands for effective diffusion coefficient of CO<sub>2</sub>, *ε* is the membrane porosity, *z* is membrane thickness and *τ* is a tortuosity coefficient. It is essential to know that this is simplified equation and deviations from reality are highly possible to appear (E. Favre, 2012).

A great number of polymers have been studied as materials for membranes in CO<sub>2</sub> capture studies including polyacetylenes (Stern,

**Table 1**  
Membrane preparation process details.

Process	Immersion precipitation
Polymeric solution	20% polysulfone in NMP
Coagulation bath	Distilled water
Casting knife [μm]	250, 200, 100
Support	Glass

1994), polyaniline (Illing et al., 2001), poly(ethylene oxide) (H. Lin, 2004), polyolefin (Feron, 2002), polypropylene (Witek-Krowiak et al., 2012) and others (Yang et al., 2008). Polysulfone, chosen in the study, is a thermally and chemically stable polymer, easy to handle. Besides, control of polysulfone membrane morphology is easily achieved by changing preparation conditions, a useful feature for membranes (Torrás, 2005).

Previous studies on polysulfone membrane contactors for ambient CO<sub>2</sub> capture were performed in the system equipped with a peristaltic pump in order to decrease the absorbent mass transfer resistance by increase of the liquid flow rate (Nogalska et al., 2018). In the current study, experiments are carry out in static conditions in which the liquid flow is zero to evaluate the impact of the pump. Membranes of the same morphology with different thickness, macrovoids size and the hydrophobicity were used in the research. The influence of the membrane characteristics, absorbent liquid resistance and absorption time were analyzed.

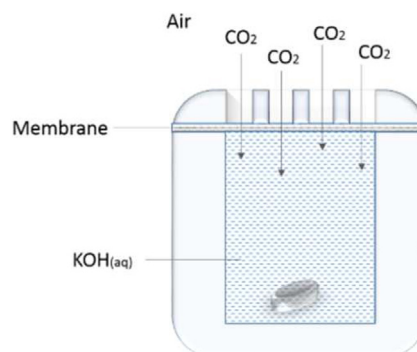
## 2. Materials and methods

### 2.1. Materials

Polysulfone (SIGMA-ALDRICH) in form of pellets was used for membrane preparation with *N*-Methyl-2-pyrrolidone (NMP) ≥ 99,0% (SIGMA-ALDRICH). Potassium Hydroxide (85%, pellets) (SIGMA-ALDRICH) were used as absorption liquid for CO<sub>2</sub>.

### 2.2. Flat sheet membranes preparation

Polysulfone membranes were made via phase inversion method. The preparation conditions are summarized in Table 1. Polymeric solution used for the fabrication consisted of 20% wt. polysulfone dissolved in 1-Methyl-2-pyrrolidone after 48 h stirring. The resulting solution was cast on a glass support by using a casting knife of particular thickness and immediately immersed into water, where the membrane precipitates as a result of exchanging solvent (NMP) with non-solvent (water). Prepared flat sheet membranes were dried at ambient conditions. As the only changed factor in the process is thickness, further



**Fig. 1.** Module scheme.

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