Current research project was devoted to the development of the double layer composite membrane for efficient separation of carbon dioxide. Polydimethylsiloxane was used as a support layer and phthalic acid incorporated titanium dioxide as a selective layer. Developed membranes demonstrated unique gas separation performance with high selectivity separation of carbon dioxide and nitrogen.

The mechanism of gases separation was attributed to the abundance of the carboxylic groups originated from the incorporated acids. The mechanism of material selectivity was verified using theoretical calculations (density functional theory). According to the calculations we have succeeded to create CO2-philic sites in the composite phthalic acid/titanium dioxide layer. These sites exhibit much higher attractive force for carbon dioxide gas compared to nitrogen. As a result we have in fact achieved the translation of the molecular level property (chemical affinity) to the material (high selectivity).
1. 研究開始当初の背景

Prevention of the carbon dioxide emission into atmosphere requires proper carbon capture and storage solutions introduced in the points of massive CO₂ emissions such as coal-burning power plants or certain type of chemical plants. Development of reliable and economically reasonable CO₂ capture technology are crucial for the global environment in order to decrease the total concentration of the greenhouse gases in atmosphere. CO₂ gas separation with the usage of membranes is a promising, yet not used widely, method for industrial carbon capture that has potential to reduce capture costs to the economically feasible values.

Organic polymers represent the most investigated class of materials for the membrane preparation, however despite the good results achieved in the separation of CO₂ from other gases, polymers are lacking other necessary features for the membrane utilization. The most important of such features is the high gas permeability of the materials which is needed to maintain high gas fluxes leading to ability to capture (separate) huge amounts of CO₂ from the flue gas of the conventional power plants. Moreover, the trade-off relation between the permeability and selectivity of the organic polymer materials, settles the fundamental limitation for having highly permeable and selective materials in the same time.

2. 研究の目的

The idea of current research was the separation of the main functions of gas filtration membrane in double layer design employing ultra-thin inorganic separating layer. In order to tune the selectivity of the membranes molecular imprinting and molecular templating as main methods were utilized.

Research target: Development of novel self-supporting gas separation membranes with nano-scale thickness of separation layer able to overcome the performance (selectivity and permeability) of organic polymer membranes.

3. 研究の方法

1. Application of the ultra-thin dense, inorganic, metal oxide films as gas selective separation layer.

2. Utilization of the double layer structure with separated functions where “selectivity” relies on the nano-thin separating layer, supported by highly permeable and robust polydimethylsiloxane (PDMS) layer responsible for membrane physical durability.

3. Employment of the free-standing giant nanomembrane fabrication approach, necessary for precise architecture of the films of nanoscale thickness.

4. Achievement of selectivity by introduction of gas selective compounds into the dense, ultrathin metal oxide film with initial high gas barrier (Fig.1).

Molecular imprinting and molecular templating used for the selectivity tuning in the ultra-thin metal oxide film.

![Fig. 1 Schematic illustration of the proposed gas separation membrane (a) suggests modification of the inorganic oxide material CO₂/N₂ selectivity (b) by addition of the CO₂-phlic molecule (e.g. benzoic acid) to the separation layer which possess site with CO2 affinity (c).](image_url)

4. 研究成果

Current research project was devoted to the development of the double layer composite membrane for efficient separation of carbon dioxide. Polydimethylsiloxane was used as a support layer and phthalic acid (PA) was incorporated titanium dioxide (TiO₂) to form a selective layer. Developed membranes demonstrated unique gas separation performance with higher selectivity separation of carbon dioxide and nitrogen.

Metal oxides (MO) composite layers were fabricated using sol-gel method from alkoxide precursors. TiO₂ layer was modified...
by incorporation of phthalic acid in matrix resulting in CO₂ selective material. Fig. 2a shows the structure of PA incorporated in TiO₂, Fig.2b shows the SEM image of the typical double layer membrane. Uniform inorganic layer with intended nanoscale thickness were successfully fabricated.

![Chemical structure of the CO₂ selective site in the composite PA@TiO₂ layer](image)

**Fig. 2 (a)** Chemical structure of the CO₂ selective site in the composite PA@TiO₂ layer (b) SEM image of the fabricated double layer PA@TiO₂/PDMS membrane.

Nitrogen and carbon dioxide separation performance of the fabricated membranes overcome the parent PDMS and reference TiO₂/PDMS membranes, evidencing successful transfer of CO₂ philicity from molecular level to material. Fig. 3 demonstrates long time performance of PA@TiO₂/PDMS membrane for the separation of the CO₂ and N₂. Gas separation was measured using mixed 1:1 CO₂ and N₂.

![Gas separation performance of the double layer membrane](image)

**Fig.3** Gas separation performance of the double layer membrane.

Selectivity of composite membranes were more than α(CO₂/N₂) >30 that is significantly higher compared to PDMS alone (α(CO₂/N₂) = 11.6 at 25°C).

Figure 4 shows the comparison of the developed membranes (point 2) with state-of-art gas separation materials. In order to evaluate the selectivity and permeability of the PA@TiO₂ layer alone, the resistance model was used and the result is shown as point 3 in the Fig. 4. It is seen that the results for composite layer is lying below the upper bound, however with exceptionally high selectivity (α(CO₂/N₂) > 150) that is far higher than that reported for majority of organic polymers.

![Gas separation performance of the double layer membrane](image)

**Fig.4** Gas separation performance of the double layer membrane (point 2) with reference PDMS (point 1) and several conventional organic polymer materials. Point 3 represents the performance of the selectivity layer alone, calculated using the resistance model.

The mechanism of gases separation was attributed to the abundance of the carboxylic groups originated from the incorporated acids. The mechanism of material selectivity was verified using theoretical calculations (density functional theory).

![Mechanism of gas separation in double layer membrane](image)

**Fig. 5** Mechanism of gas separation in double layer membrane: TiO₂ film enriched with carboxylic acids provides preferential surface diffusion of CO₂ in the pores.
Plausibly, we have succeeded to create CO₂‐philic sites in the composite phthalic acid/titanium dioxide layer. These sites exhibit much higher attractive force for carbon dioxide gas compared to nitrogen and provide the surface diffusion mechanism of gases separation (Fig. 5). As a result we have in fact achieved the translation of the molecular level property (chemical affinity) to the material (high selectivity).

5. 主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

[雑誌論文]（計 5 件）

[学会発表]（計 7 件）
5. Selyanchyn, R., Fujikawa, Metal oxide crosslinked PDMS: new materials with high gas permeability // *Kobe Membrane Symposium*, Kobe, Japan, November-2015


トSelyanchyn, R., Fujikawa, S. Tuning the selectivity of inorganic membranes towards CO₂ using the introduction of CO₂-philic compounds in the membrane matrix, // *Japanese Membrane Symposium 2014*, Kobe University, 27 November 2014

6. 研究組織
研究者番号：26889045