

Unconventional Composite Inorganic Membrane Fabrication for Carbon Emissions Mitigation

Ngozi Nwogu, Godson Osueke, Mamdud Hossain, Edward Gobina

Abstract—An unconventional composite inorganic ceramic membrane capable of enhancing carbon dioxide emission decline was fabricated and tested at laboratory scale in conformism to various environmental guidelines and also to mitigate the effect of global warming. A review of the existing membrane technologies for carbon capture including the relevant gas transport mechanisms is presented. Single gas permeation experiments using silica modified ceramic membrane with internal diameter 20mm, outside diameter 25mm and length of 368mm deposited on a macro porous support was carried out to investigate individual gas permeation behaviours at different pressures at room temperature. Membrane fabrication was achieved using after a dip coating method. Nitrogen, Carbon dioxide, Argon, Oxygen and Methane pure gases were used to investigate their individual permeation rates at various pressures. Results show that the gas flow rate increases with pressure drop. However above a pressure of 3bar, CO₂ permeability ratio to that of the other gases indicated control of a more selective surface adsorptive transport mechanism.

Keyword—Carbon dioxide composite inorganic membranes, permeability, transport mechanisms.

I. INTRODUCTION

Fossil fuels are the principal vector satisfying the global primary energy demand, and will likely stay for next few decades. Even though countless efforts and investments are made by various countries to increase of renewable energy to satisfy the major energy demand and to substitute maintenance and productivity improvements of fossil fuel usage, addressing climate change concerns in future will entail significantly increasing the contributions from carbon recovery from point sources [1]. The accumulation of CO₂ in the atmosphere however constitutes one of the leading contributors to worldwide climate change. In fact, it is accountable for roughly more than 50% of the greenhouse effect [2], [3]. This has subsequently steered up systematic interest in the development of novel approaches for substantially reducing the amount of CO₂ released into the atmosphere from process industry and fossil fuel power plants [2]. Based on existing methods of CO₂ capture, it is well known that CO₂ absorption in amine solvent is the most propagated method on the

industrial scale in natural gas purification and in investigational plants for CO₂ recovery. Specifically, the amine-based solvent absorption incorporating an aqueous monoethanolamine (MEA) solution can be utilized in achieving a reasonable and economical level of CO₂ capture from flue gas. On the other hand, amines are corrosive, inclined to degradation due to the activities of sulphur oxides with high operational energy consumption especially during regeneration [2], [4], [5]. In generally for processes that can be tracked for CO₂ capture from coal-derived power generation include post-combustion capture, pre-combustion capture and oxy-combustion, membranes have numerous advantages over conventional separation methods [2] [6]. In particular, ceramic inorganic membranes for gas separation have been acceptable as a result of its numerous advantages, for instance resistance to chemical and physical degradation, homogenous pore structure, high mechanical strength and resistance at harsh operating conditions, (e.g. elevated temperature and pressure). One encouraging method of achieving an economically viable CO₂ separation from other gas streams involves the development of high-performance CO₂ separation membranes. Coating condition during the fabrication procedure in this circumstance will largely influence the gas separation performance of resulting membrane. This technique has been reported by some researcher in their study [7] [8].

In this work, silica material has been selected as the segment-forming agent giving a thin separation layer for altering the pore structure of an alumina membrane support. The outcome of this process is the fabrication of an unconventional composite inorganic ceramic membrane with high permeation flux and high selectivity to carbon dioxide which are essential requirements for economic exploitation of membrane for carbon capture.

II. EXPERIMENTAL

The unconventional composite membrane was fabricated through the deposition of the silica on a fresh alumina macroporous support. The support has an internal diameter of 20mm, outside diameter 25mm, length of 368mm with 6000nm pore size. Pure gas transport experiments using the unconventional composite ceramic membrane were carried out to investigate individual gas permeation behaviours at different pressures and membrane efficiency.

III. PURE GAS TRANSPORT THROUGH THE COMPOSITE MEMBRANE

Fig. 1 depicts a schematic diagram of the experimental set-up used for gas transport test carried out. The unconventional

N. C. Nwogu is a PhD research student with the Centre for Process Integration and Membrane Technology, School of Engineering, Robert Gordon University, Aberdeen, UK (e-mail: n.c.nwogu@rgu.ac.uk)

G. Osueke is a Senior lecturer with the Department of Mechanical Engineering, Federal University of Technology Owerri, Imo State, Nigeria (e-mail: osueke2009@yahoo.com)

Prof. E. Gobina is a Professor of Chemical Engineering and the Director of Centre for Process Integration and Membrane Technology, School of Engineering, Robert Gordon University, Aberdeen, UK (Corresponding author; Tel: +441224262348; e-mail: e.gobina@rgu.ac.uk).

membrane was held in stainless steel housing. At each end, graphite seals were used to seal the tube side to ensure that good closure is accomplished. The gases used for the permeation test are nitrogen, carbon dioxide, Argon, Oxygen and Methane (with a purity of at least 99.9%) all supplied by BOC (UK).

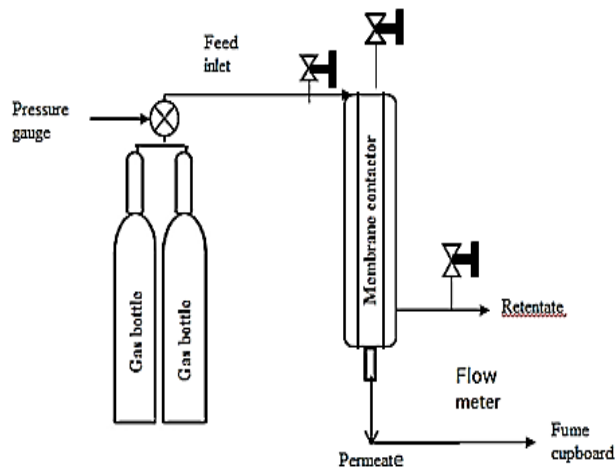


Fig. 1 Gas transport through unconventional composite ceramic membrane at room temperature

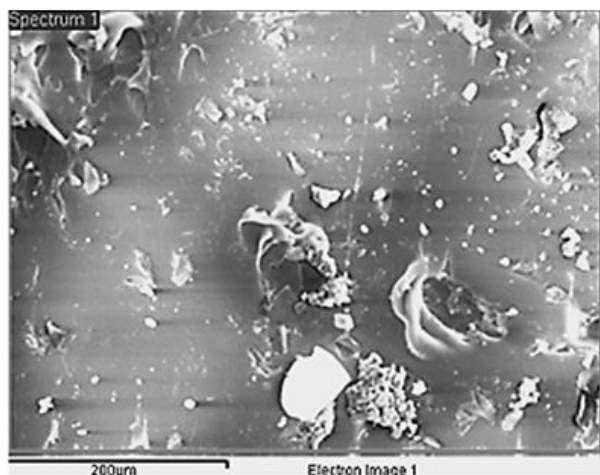


Fig. 2 SEM image of the composite membrane surface

Knudsen separation factor for two gases can be calculated using (1)

$$\alpha_{AB} = \sqrt{\frac{M_B}{M_A}} \quad (1)$$

where α is the ideal Knudsen selectivity for pure gases, M_A , the molecular weight of the more permeating gas and M_B , the molecular weight of the less permeating gas.

IV. MEMBRANE CHARACTERIZATION

The conventional composite membrane morphology was studied with the Zeiss EVO LS10 variable pressure scanning

electron microscope (SEM) while the elemental composition was obtained with the Oxford instrument INCA Energy dispersive x-ray analyzer (EDXA). SEM images of the external surface were obtained for membrane as shown in Fig. 2. The whitish spots and smooth surface indicate the presence of the deposited silica solution for enhanced selectivity and permeability characteristics. The chemical composition of the membrane is shown in Table I. EDXA analysis as presented in Fig. 3 confirms the formation of silica films, indicating the relevant peaks for C, O, Al, Si, Cl and Ti elements. The presence of Si in the film is due to the use of silicon elastomer.

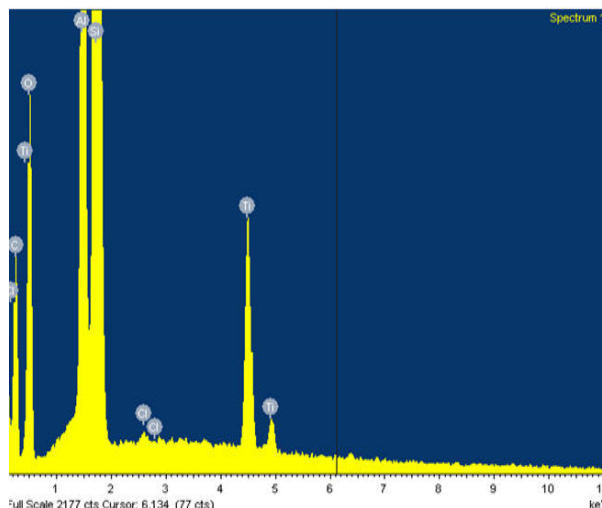


Fig. 3 Chemical composition of the composite membrane using EDXA instrument

TABLE I
CHEMICAL COMPOSITION OF THE UNCONVENTIONAL MEMBRANE

Element	C	O	Al	Si	Cl	Ti
Percentage Weight	31.97	26.74	5.81	32.21	0.08	3.2

V. RESULT AND DISCUSSION

The permeation properties of the pure gases (N_2 , CO_2 , Ar, O_2 and CH_4) through the membrane were measured over a pressure difference range of 1–5 bar gauge. Fig. 4 indicates that the flow rate of the five gases increase with the increase in pressure difference –in the following order: $CO_2 > CH_4 > N_2 > O_2 > Ar$. The change in flow as a function of inverse square root of the molecular weight suggests that Knudsen diffusion is not the dominant transport mechanism for the investigated composite. The transport mechanism for gas permeation was shown to be non- Knudsen, since CO_2 permeated faster than all the gases particularly the lighter ones.

Gas permeance as a function of the feed pressure is presented in Fig. 5. From the plot, very distinct permeation behaviour is observed for CO_2 and CH_4 . As observed, CO_2 permeance increased exponentially with change in pressure, while, CH_4 decreased continuously with rise in pressure. At a pressure of 3bar, CH_4 permeance seems to be stabilized, this may suggest that a change in the transport mechanism may have occurred at that point. A similar trend was observed for

N₂, O₂ and Ar, as there seems to be very slight effect in their permeance with pressure above 3bar. As suggested surface adsorptive transport mechanism remains dominant, although Knudsen flow might set in at a higher pressure.

Tables II-V show the experimental and ideal Knudsen selectivity of CO₂ to the other gases. As can be observed, the outcome of results obtained are very promising since CO₂ permselectivity (ratio of CO₂ flow rates to the other gases at different pressure) is higher than ideal Knudsen selectivity (that is inverse square root of the molecular weight of CO₂ to other gases). Therefore, by a methodological procedure, it has been possible to minimise the detectable cracks through modification. Our results are in harmony with literature [9]-[13].

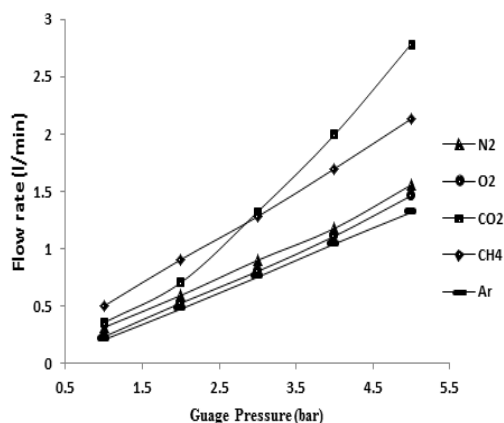


Fig. 4 Single gas flow rate measurement as a function of feed pressure at room temperature

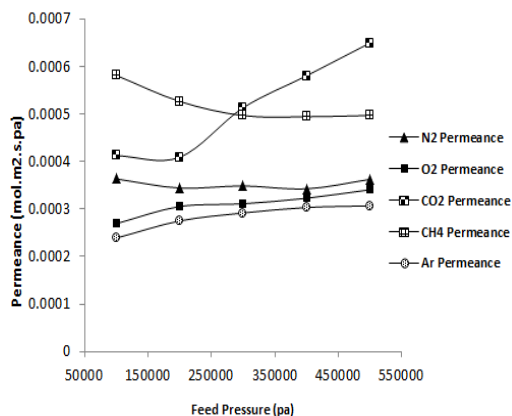


Fig. 5 Single gas permeance measurement as a function of feed pressure at room temperature

TABLE II
CO₂/N₂ SELECTIVITY

Gauge Pressure (bar)	Flow rate of CO ₂ /Flow rate of N ₂ (l/min)	Ideal Knudsen Selectivity
1	1.134615	0.79
2	1.187817	0.79
3	1.471047	0.79
4	1.694728	0.79
5	1.791131	0.79

TABLE III
CO₂/O₂ SELECTIVITY

Gauge Pressure (bar)	Flow rate of CO ₂ /Flow rate of O ₂ (l/min)	Ideal Knudsen Selectivity
1	1.5324675	0.85
2	1.3396947	0.85
3	1.6491885	0.85
4	1.7987365	0.85
5	1.9062927	0.85

TABLE IV
CO₂/CH₄ SELECTIVITY

Gauge Pressure (bar)	Flow rate of CO ₂ /Flow rate of CH ₄ (l/min)	Ideal Knudsen Selectivity
1	0.709419	0.60
2	0.776549	0.60
3	1.032838	0.60
4	1.174425	0.60
5	1.306610	0.60

TABLE V
CO₂/AR SELECTIVITY

Gauge Pressure (bar)	Flow rate of CO ₂ /Flow rate of Ar (l/min)	Ideal Knudsen Selectivity
1	1.134615	0.95
2	1.187817	0.95
3	1.471047	0.95
4	1.694728	0.95
5	1.791131	0.95

VI. CONCLUSION

An unconventional composite inorganic ceramic membrane was prepared by coating a layer of silica material onto a porous alumina substrate. The permeance of the designed composite membranes to N₂, CH₄, O₂, Ar and CO₂ was tested. Coating condition largely influenced the composite membrane performance for CO₂ separation. The SEM and EDXA experiments showed the presence of the dense coating on the membrane surface and the chemical composition respectively. For the composite membrane the CO₂ permeance was about 6.3 x 10⁻⁴ mol/m².sec.pa and CO₂/N₂, CO₂/O₂, CO₂/CH₄ and CO₂/Ar selectivity at 5bar were 1.79, 1.90, 1.30 and 2.12 much which are more than ideal their Knudsen selectivity: 0.79,0.85,0.60 and 0.95 respectively. It was observed that although the alumina support used in this work have not been submitted to any surface finishing procedure, the achieved membrane has potential application in gas separation processes involving CO₂ gas stream. We observed that increasing the pressure feed leads to improved separation ability. This is a very significant result because the high mechanical stabilities of the alumina/titania system allow its use in high pressure applications.

ACKNOWLEDGMENT

The author wishes to express sincere thanks to the Centre for Process Integration and Membrane Technology of Robert Gordon University for procuring the fresh membrane used for the study and to the School of Life Sciences at The Robert Gordon University for SEM and EDXA observations.

REFERENCES

- [1] Herzog H, Golomb D. Carbon capture and storage from fossil fuel use. Encyclopedia of energy. 2004; 1:1-11.
- [2] Iulianelli A, Basile A, Li H, Van den Brink RW. 7 - Inorganic membranes for pre-combustion carbon dioxide (CO₂) capture. In: Basile A, Nunes SP, editors. *Advanced Membrane Science and Technology for Sustainable Energy and Environmental Applications*. Woodhead Publishing; 2011. p. 184-213.
- [3] Zhou Q, Chan C, Tontiwachiwuthikul P. A monitoring and diagnostic expert system for carbon dioxide capture. *Expert Systems with Applications*. 2009; 36(2):1621-1631.
- [4] Choi W, Seo J, Jang S, Jung J, Oh K. Removal characteristics of CO₂ using aqueous MEA/AMP solutions in the absorption and regeneration process. *Journal of Environmental Sciences*. 2009; 21(7):907-913.
- [5] Maneeintr K, Idem RO, Tontiwachwuthikul P, Wee AG. Comparative mass transfer performance studies of CO₂ absorption into aqueous solutions of DEAB and MEA. *Industrial & Engineering Chemistry Research*. 2010; 49(6):2857-2863.
- [6] Adhikari S, Fernando S. Hydrogen membrane separation techniques. *Industrial & Engineering Chemistry Research*. 2006; 45(3):875-881.
- [7] Liu L, Chakma A, Feng X. Preparation of hollow fiber poly (ether block amide)/polysulfone composite membranes for separation of carbon dioxide from nitrogen. *Chemical Engineering Journal*. 2004; 105(1):43-51.
- [8] Ji P, Cao Y, Jie X, Li M, Yuan Q. Impacts of coating condition on composite membrane performance for CO₂ separation. *Separation and Purification Technology*. 2010; 71(2):160-167.
- [9] Gobina E. *Apparatus and Method for Separating Gases*, US Patent 7,048,778, Washington, DC: U.S. Patent and Trademark Office. 23 May 2006.
- [10] Gobina E. *Apparatus and method for separating gases*. U.S. Patent No. 7,297,184. 20 Nov. 2007.
- [11] Middleton D, McCulloch M, Miller P, Normand E, Cassels G, Bullock A, et al. Trial CO₂ measurement and capture system incorporating hybrid inorganic membranes for flue-gas cleaning (Part II). *Membrane Technology*. 2011; 2011(6):7-10.
- [12] Nwogu NC, Gobina E, Kajama MN. Improved carbon dioxide capture using nanostructured ceramic membranes. *Low Carbon Economy*. 2013; 4(03):125.
- [13] Nwogu N, Kajama M, Okon E, Shehu H, Gobina E. Testing of Gas Permeance Techniques of a Fabricated CO₂ Permeable Ceramic Membrane for Gas Separation Purposes. 2014.