DELIVERABLE

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D3.6 - CO_2 selective membranes

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1. Executive Summary

Task 3.4 of project BeingEnergy refers to the preparation and characterization of membranes and membrane modules for selective removal of CO_2. The goal was to produce and characterize polymer / ionic liquids membranes. Various ionic liquids were to be prepared and accessed. At M32 it was intended to report on high temperature CO_2 selective membranes (milestone MS05) concerning CO_2 permeability and the CO_2/H_2 selectivity.

This work characterizes four suitable polymeric ionic liquid-based membranes for low temperature methanol steam reforming (MSR) application, for CO_2 removal. Polymeric ionic liquids were prepared with 40 wt.% and 20 wt.% of free ionic liquid (samples PIL1-40IL1 and PIL2-20IL2) and without free ionic liquid (PIL1 and PIL2). PIL1-40IL1 and PIL2-20IL2 composite membranes present high CO_2 diffusivity and sorption and negligible H2 diffusivity and sorption. For PIL1-40IL1 CO_2 permeance was higher than H_2 permeance. On the other hand, PIL1 and PIL2 present higher permeances for H_2 rather than for CO_2. Therefore, it can be presumed that free IL compounds may enhance the CO_2 permeance.

Taking into account the comments and recommendations of the Mid-Term Review of the project (FCH-JU 2014 D2612), task 3.4 (Preparation and characterization a membrane and membrane module for selective CO_2 removal) was reassessed. Considering the limited improvements regarding the development and characterization of CO_2 selective membranes and the complexity of the hybrid MSR reactor, no further efforts will be made regarding task 3.4.

2. Developed work

2.1 Introduction

Methanol steam reforming (MSR) is being used to supply high temperature polymer membrane fuel cells (HT-PEMFC). Methanol reforming is endothermic while HT-PEMFC produces heat; if the two devices are run at the same temperature, ca. 180 °C – 190 °C, energy integration becomes possible. Also, at lower reforming temperature less CO is produced and catalyst is more stable. At this low temperature MSR needs a significantly more active catalyst. Despite the recent efforts for developing such catalyst, the best result up to now is a catalyst ca. 2x more active than catalyst by BASF. Other approach is the selective removal of hydrogen or carbon dioxide from the reaction medium [1]. For high methanol conversions the backward reaction becomes relevant and removing hydrogen from the reaction medium stops the backward reaction increasing the overall effective reaction kinetics [2]. Though attractive, this strategy hides the high-energy consumption needed for driving hydrogen out of the reactor – using either a pump or water vapour sweep gas. For CO_2 removal, air can be used as sweep gas (ca. 400 ppm CO_2,). Despite palladium membranes work quite well for hydrogen removal there is no membrane for removing selectively CO_2 at MSR conditions [2]. Preliminary results show that supported polymeric ionic liquid-based membrane selective for CO_2 can work at 180 °C improving the reaction kinetics of the MSR and decreasing the production of CO. When the HT-PEMFC feed is changed from pure hydrogen to direct reformate feed, the stoichiometric hydrogen increases ca. 30 %. This work characterizes four suitable polymeric ionic liquid-based membrane for low temperature steam reforming.

2.2 Experimental

- Adsorption tests

Adsorption isotherms for carbon dioxide were performed applying the volumetric method. This method is fundamentally based on pressure variation of the relevant gas after an expansion. By the knowledge of pressure decrease and assuming ideal gas behaviour for the system, it is possible to determine the concentration of adsorbed solute. Composite membranes were prepared based on polymeric ionic liquids (PILs) with chemically compatible ionic liquids (ILs). One of the composites is made of PIL1 and 40% of ionic liquid (PIL1-40IL1) and the other is made of PIL2 and 20% of ionic liquid (PIL2-20IL2).

- Permeation experiments

Tubular ceramic supports preparation

The preparation of tubular ceramic supports included firstly the blending of porous ends of Al2O3 to nonporous Al_2O_3 tubes through a sealing with glass sealant at 1150 ºC. The supports have a mean pore size of 200 nm (located in the outer part of the tube), an external diameter of 10 mm and a length of 70 mm. An effective length of approximately 50 mm was left for dip-coating. After this procedure, the membranes were dip coated with yttrium zirconia stabilized (YSZ) solution using a vacuum pump. The YSZ coated on the membranes was dried in a rotating oven at 40 ºC for 4 h. The membranes were then coated with the selective solution and were dried also at 40 ºC for 24 h.

Permeation measurement

The permeation tests on the produced supported PIL membranes were performed by probing the target pure gases, namely CO_2 and H_2. The gases in study were introduced in the shell side at 500 – 100 kPa feed pressure (Horiba Stec, model UR7340) and the permeated flow rate at room pressure was determined by one of three flowmeters (Bronkhorst, ranges: 0–10, 0– 100, 0–1000 and 0-10000 mLNmin-1).

2.3 Results and discussion

Figures 1 and 2 show carbon dioxide adsorption equilibrium isotherms for PIL1-40IL1 and PIL2-20IL2. Both composite membranes adsorb carbon dioxide, although the adsorption capacity is reduced. The kinetic parameters for both samples are shown in Table 1. At 0.5 bar and 100 ºC and 200 ºC the diffusivity of PIL1-40IL1 is very fast and at 1 bar PIL2-20IL2 is also very high. Diffusivities were obtained from the uptake curves for polymers PIL1-40IL1and PIL2-20IL2 – Table 1.

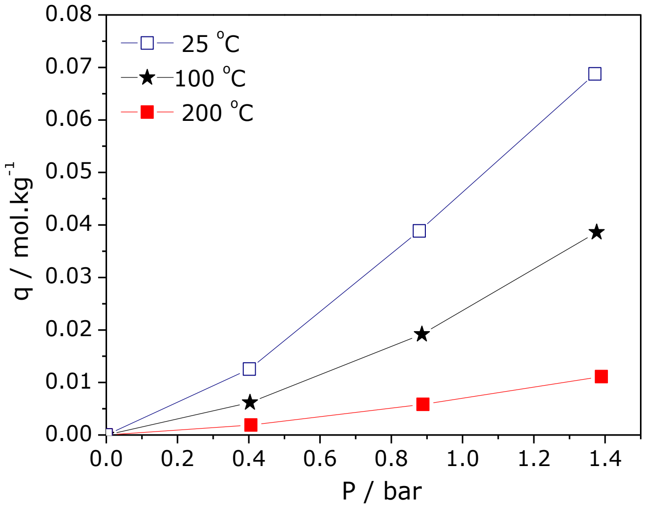

Figure 1 - CO_2 adsorption equilibrium isotherms for PIL1-40IL1 at 25 ºC, 100 ºC and 200 ºC (lines were added for readability).

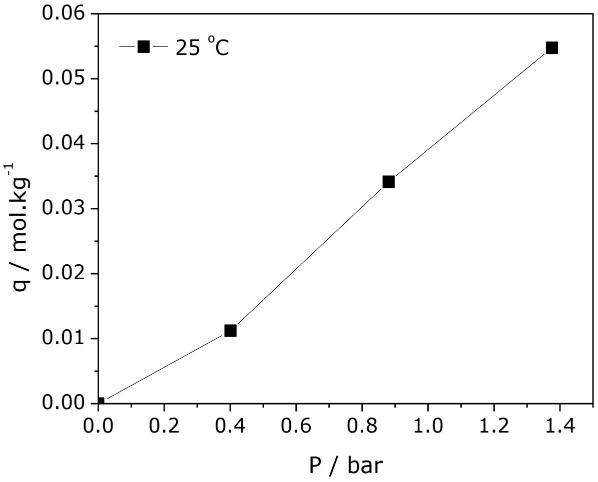

Figure 2 - CO_2 adsorption equilibrium isotherms for PIL2-20IL2 at 25 ºC (lines were added for readability).

Table1 - Kinetic parameters obtained for PIL1-40IL1 and PIL2-20IL2 at 25 ºC, 100 ºC and 200 ºC

Temperature / ºC	Sample	Pressure / bar	CO_2 Diffusivity / s^{-1}
25	PIL1-40IL1	0.5	2.63×10^{-4}
100			1.73×10^{-3}
200			1.05×10^{-3}
25	PIL2-20IL2	1.0	1.38×10^{-3}

Permeation tests were also performed on polymeric ionic liquid-based membranes in order to obtain pure CO2 and H2 permeances. Tables 2, 3 and 3 show the permeances and ideal selectivity as function of feed pressure for PIL1-40IL1, PIL2 (without YSZ calcination) and PIL1 (without YSZ), respectively.

Table 2 - Permeance for PIL1 – 40IL1, at feed pressure of 500 kPa.

Temperature / ºC	Permeance / $mol.m^{-2}.s^{-1}.Pa^{-1}$		Ideal selectivity CO_2 / H_2
	CO_2	H_2	
25	1.47×10^{-9}	8.89×10^{-11}	> 16.5
50	2.07×10^{-9}	8.89×10^{-11}	> 23.3
100	3.57×10^{-9}	1.35×10^{-9}	2.6
150	5.42×10^{-9}	2.49×10^{-9}	2.2
200	7.62×10^{-9}	4.06×10^{-9}	1.9

Table 3 - Permeance for PIL2 (without YSZ calcination), at feed pressure of 500 kPa.

Temperature / ºC	Permeance / $mol.m^{-2}.s^{-1}.Pa^{-1}$		Ideal selectivity CO_2 / H_2
	CO_2	H_2	
25	8.89×10^{-11}	5.72×10^{-10}	> 6.4
50	8.89×10^{-11}	5.54×10^{-10}	> 6.2
100	8.89×10^{-11}	1.55×10^{-9}	> 17.5
150	3.21×10^{-8}	1.15×10^{-7}	3.6
200	3.55×10^{-7}	8.51×10^{-8}	4.2

Table 4 - Permeance for PIL1 (without YSZ), at feed pressure of 500 kPa.

Temperature / ºC	Permeance / $mol.m^{-2}.s^{-1}.Pa^{-1}$		Ideal selectivity H_2 / CO_2
	CO_2	H_2	
25	1.55×10^{-7}	4.28×10^{-7}	2.8
50	1.09×10^{-7}	3.30×10^{-7}	3.0

From Tables 2, 3 and 4 it can be concluded that permeance increases with temperature [3]. It can also be concluded that PIL1-40IL1, PIL1 and PIL2 show facilitated transport due to the heavy presence of amino functional groups, which makes CO_2 to be faster. Polymer membrane 40IL1 shows the best performance. The ideal selectivity decreases abruptly as temperature increases. Low selectivities are then obtained even for low temperatures indicating that the membrane broke. This may happen since the ceramic support has very large pores and does not support properly the polymer membrane.

3. Conclusions

This work characterizes four suitable polymeric ionic liquid-based membranes for low temperature MSR for CO_2 removal. Polymeric ionic liquids were prepared with 40 wt. % and 20 wt. % of free ionic liquid (samples PIL1-40IL1 and PIL2-20IL2) and without free ionic liquid (PIL1 and PIL2). PIL1-40IL1 and PIL2-20IL2 composite membranes present high CO2 diffusivity and sorption and negligible H2 diffusivity and sorption. Permeances were also determined for PIL1-40IL1, PIL2 (without YSZ calcination) and PIL1 (without YSZ). Analysing the obtained permeances it was concluded that PIL1-40IL1 shows the highest CO_2/H_2 selectivity. However, PIL1 and PIL2 present higher permeances for H_2 rather than for CO_2. Therefore, it can be presumed that free IL impregnating the polymer membrane enhance the CO_2 permeance.

Task 3.4 was reassessed to respond to the comments and recommendations of the Mid-Term Review of the project (FCH-JU 2014 D2612). Considering that the development and characterization is still undergoing and the limited advances up to M32, no further efforts will be made regarding the task 3.4. This innovative task will be considered in the frame of other projects. The future work will include CO_2 and H_2 permeance measurements for concentrated PIL1/2-40IL1/2 selective solutions dip coated with YSZ solution.

Bibliography

[1] N. Katiyar, S. Kumar, S. Kumar, Comparative thermodynamic analysis of adsorption, membrane and adsorption-membrane hybrid reactor systems for methanol steam reforming, International Journal of Hydrogen Energy 38 (2013) 1363-1375.

[2] A. Iulianelli, P. Ribeirinha, A. Mendes, A. Basile, Methanol steam reforming for hydrogen generation via conventional and membrane reactors: A review, Renewable and Sustainable Energy Reviews 29 (2014) 355–368.

[3] S. C. Rodrigues, R. Whitley, A. Mendes, Preparation and characterization of carbon molecular sieve membranes based on resorcinol–formaldehyde resin, Journal of membrane science 459 (2014) 207-216.