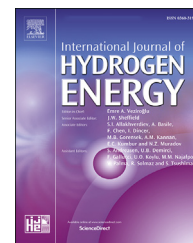


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Stability investigation of polyPOSS-imide membranes for H₂ purification and their application in the steel industry

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HIGHLIGHTS

- Exposure of the polyPOSS-imide membrane to 300 °C increases the H₂ permeance.
- Long-term hydrothermal stability of polyPOSS-imide membranes proven.
- Membranes were operated over a period of 1000 h.
- Process evaluation for implementation in the steel industry performed.

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ABSTRACT

In the present work, the high-temperature and long-term hydrothermal stability of novel polyPOSS-imide membranes for high-temperature hydrogen separation is investigated. The polyPOSS-imide membranes are found to exhibit an appropriate stability up to 300 °C. Above this temperature the membrane selectivity rapidly decreases, which is seemingly related to changes in the molecular structure coupled to silanol condensation forming siloxane groups. Surprisingly, the exposure of the membrane to temperatures of up to 300 °C even increases the H₂ permeance together with the selective feature of the polyPOSS-imide layer. Subsequently, the long-term hydrothermal stability of the polyPOSS-imide membranes was investigated over a period of close to 1000 h at 250 °C exposing the membrane to 10 mol% steam in the feed. An increase in H₂/CH₄ selectivity was observed upon water addition, and even though a minor drop was noticed over time during the hydrothermal operation, the selectivity exceeds the initial selectivity obtained in the dry feed atmosphere. After the removal of steam from the feed the performance returns to its original state prior to the exposure to any steam showing an appropriate steam stability of the polyPOSS-imide membranes. A conceptual process design and assessment was performed for application of these membranes involving a combination of carbon reuse and electrification of the steel making process with co-production of hydrogen. The results indicate a CO₂ avoidance of 14%. The CO₂ reduction achieved using

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renewable electricity in the proposed scheme is a factor 2.76 higher compared to a situation where the same renewable electricity would be fed in the electricity grid.

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Introduction

Recent international agreements on CO₂ emission reductions contribute to push the energy sector towards more sustainable and environmental-friendly solutions of energy production. In this perspective, the carbon-free nature of hydrogen makes it the prime candidate for solving future energy challenges. Hydrogen is mainly produced from reforming reactions of steam with fossil feedstocks, with around 50% from natural gas [1]. Approximately 5% of the hydrogen produced worldwide is obtained through water electrolysis. In the transition towards a climate neutral energy management, large-scale hydrogen production by electrolysis of water with electric power from renewable sources would be preferable. However, with increasing but still insufficient and intermittent supply of renewable energy, hydrogen production from fossil fuels combined with CCS deployment is unavoidable for low CO₂ emission hydrogen production on a shorter term. Even for 2050, it is estimated that fossil sources will still account for 58–81% of the hydrogen production [1]. In the recent European Commission long-term vision for a prosperous, modern, competitive and climate neutral economy by 2050 – A Clean Planet for all, the production of low-carbon footprint hydrogen through CCS is indisputable in the *transitional phase* to a low carbon economy [2]. Industrial processes can reduce their emissions largely by using renewable electricity rather than fossil fuel as an energy source, yet they may still rely on fossil feedstocks as a carbon source. Various options exist for obtaining hydrogen as a by-product.

Nowadays, H₂ is thus mainly produced via steam reforming of hydrocarbons but is diluted with large amounts of by-products (CH₄, CO₂, N₂, H₂O) that needs to be removed to reach the required purity for further utilization. Membrane technology offers an attractive alternative to traditional separation processes, where high temperature membranes (T > 200 °C) offer the advantage of large fluxes, thereby reducing the membrane surface area, as well as potential benefits in process integration. Even though Pd-based membranes represent a suitable solution, the identification of cheaper and more abundant materials with feasible fabrication of thin (<1 μm) selective layers remains of high priority. Recently, hyper-crosslinked nanoscale hybrid materials derived from polyhedral oligomeric silsesquioxane (POSS) cages and aliphatic imide bridges (polyPOSS-imide) showed promising performance for H₂ purification applications [3–5]. Ultrathin films (<100 nm) obtained via interfacial polymerization allowed to achieve a high H₂ permeance while the inorganic-organic hybrid nature of the POSS fraction ensures a thermal stability exceeding the one of traditional polymeric membranes [4]. Where the POSS cages in itself are impermeable to gases, different dianhydrides can be used as organic linkers to

tailor the intercage spacing, which enables tuning of gas permeability and selectivity [3,6]. Whereas the materials with short linker dianhydrides show the highest selectivity, the material based on 6FDA dianhydride exhibits the most promising performance in terms of its flux-selectivity behavior in comparison to the other dianhydrides [3]. A diffusivity-controlled selectivity was observed for the 6FDA-modified polyPOSS-imide membrane, which originates from the hyper-crosslinked network characteristics. Even during operation at 300 °C it has been shown that the polyPOSS-imide membrane retains gas selectivities of approximately 5 for H₂/CH₄ and H₂/N₂, while CO₂/CH₄ selectivities of approximately 60 at temperatures below 100 °C were obtained showing as well the applicability of the polyPOSS-imide over a wide range of operating temperatures [3,4].

In a recent study, we have evaluated the potential of these novel polyPOSS-imide membranes for the recovery of H₂ from industrial gaseous streams, more specifically the performance in coke oven gas (COG) streams was investigated [5]. Herein, the mixed gas permeation performance was also reported for the first time for these membranes. Also, aiming at upscaling the membrane fabrication, tubular single channel and multi-channel element membranes were prepared, using commercial POSS nanostructures and 6FDA as precursors [5]. At 300 °C and 10 bar, hydrogen and methane permeance are 2610 and 148 GPU, respectively, resulting in a H₂/CH₄ selectivity of approximately 18. For the same temperature and pressure, the obtained H₂/CO₂ and H₂/N₂ selectivity are 7.6 and 16, respectively. Mixed gas conditions were also investigated, showing minor deviation of the H₂ permeance compared to the ideal case [5]. Also, lower separation factors were obtained in gas mixtures, but such decrease was related to the difference between a material and a module performance, rather than to a real drop of the actual separation efficiency. However, one of the biggest challenges that is faced by all H₂ separation membranes is the lack of chemical stability, and water, sulfur-containing species, and acidic vapors are the most commonly encountered contaminants which must be dealt with. For the polyPOSS-imide membranes such investigation is so far, as to our knowledge, not been reported, whereas uncertainties around membrane stability are normally perceived as one of the largest hurdles for membrane commercialization.

With the aim of evaluating the polyPOSS-imide membranes under conditions that are close to industrial pre-combustion processes, the current work studies the effect of steam on the membrane performance and stability. More specifically hydrothermal cycling and stability of the polyPOSS-imide membranes were evaluated up to 300 °C with up to 10 mol% of steam, with feed pressures up to 8 bar. Membranes were operated over a period of 1000 h. Furthermore, a process evaluation was performed for full scale implementation of polyPOSS-imide membranes in the steel

industry, aiming at using renewable power ultimately to produce export pipeline hydrogen and reduce pulverized coal injection. Key performance indicators were selected to assess the specific emission reductions that can be obtained and to evaluate economic feasibility of defined value chains.

Experimental section

Membrane fabrication

The membranes applied in the current study are prepared in a similar manner as described in our previous work [5], following the procedure reported by Raaijmakers et al. [4], by interfacial polymerization of water soluble octa-ammonium chloride-functionalized POSS 0.9 wt% (Hybrid Plastics) and a 0.075 wt% 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, Sigma-Aldrich) solution in toluene. The partial conversion of ammonium to primary amino groups was achieved by addition of NaOH until the solution reached a pH of 9.9. The γ -alumina tubular supports (mean pore size = 3–5 nm, CTI, France) were pre-wetted with the aqueous POSS solution for 15 min under vacuum, followed by drying for 30 min at room temperature. Subsequently, the 6FDA was brought in contact with the support by simply pouring the dianhydride solution into the lumen side of the support. After 5 min, the solution was removed, and the samples were rinsed with acetone. The membranes were dried for 3 h in air atmosphere and heat-treated for 2 h at 300 °C to achieve the imidization. The reaction scheme and materials molecular structure are reported in the supporting information of the initial study on polyPOSS-imide membranes [4].

In addition to the commercially available ammonium-functionalized POSS material from Hybrid Plastics (HP-POSS), amine-functionalized POSS (HAPS-POSS) is produced by Funzionano AS based on a patented method [7] by a sol-gel process of (γ -aminopropyl)-triethoxy silane. Of commercial reasons we are unable to detail the manufacturing procedure. The HAPS-POSS bearing propyl bridges between the POSS cage, and the amino groups produced at Funzionano AS mimics the molecular core structure of HP-POSS achieved at high pH, as FT-IR spectra from the corresponding intermediated amic acids (before thermal treatment) and the

imides (after thermal treatment) do not show obvious differences in molecular structure [8]. Even though their molecular structure is similar, the HAPS-POSS material may have a larger potential compared to HP-POSS to be used as a reactant in synthesizing polyPOSS-imide membranes on a large scale because of their ability to produce defect-free membranes in a reproducible manner. Also, the pure gas selectivity of membranes made with the HAPS-POSS material is higher than those produced with HP-POSS [8].

Gas permeation performance

The permeation system reported in Fig. 1 was used for the evaluation of the gas permeation properties of the polyPOSS-imide membranes. The tubular samples were placed inside a custom-made membrane module (Swagelok), where Kalrez® 7075 O-rings (stable up to 327 °C) were used to seal the upstream from the downstream side. Mass flow controllers (Bronkhorst High-Tech B.V., The Netherlands) were used to supply the feed gas, and individual flow controllers for each gas allowed for the accurate supply of gas mixtures. The feed pressure was controlled by means of a back-pressure regulator (Bronkhorst High-Tech B.V., The Netherlands). The permeate side of the membrane was always kept at ambient pressure and the permeate flow was measured by means of a mass flowmeter (Bronkhorst High-Tech B.V., The Netherlands). The membrane module was placed inside a furnace (ESTF 100/11, Entech, Sweden). The gas concentration of all the gas streams was measured using a micro-GC (Agilent 490). To allow for the supply and removal of steam, the permeation setup presented in Ref. [5] was equipped with a liquid flow controller (Bronkhorst High-Tech B.V., The Netherlands) and a large condenser for knocking out the permeated water, which also allowed for the measurement of the water transmembrane flux.

The gas permeance of the i -th gas, P_i , is calculated as reported by Equation (1):

$$P_i = \frac{\dot{n}_p \cdot y_{i,p}}{A \cdot \Delta p_i} \quad (1)$$

where $\dot{n}_p$ is the total molar gas flow on the permeate side calculated from the MFM measurement, $y_{i,p}$ is the i -th gas concentration in the permeate side, A is the membrane area and Δp_i is the differential partial pressure of species i between

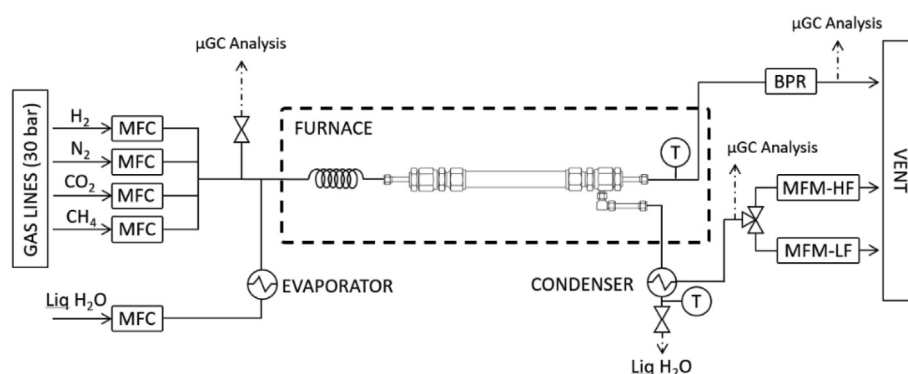


Fig. 1 – Schematics of the gas permeation test system (MFC = mass flow controller; MFM – HF = mass flowmeter high flow, MFM – LF = mass flowmeter low flow; BPR = back pressure regulator; T = temperature sensor).

the feed/retentate and the permeate side (i.e., the driving force). In the case of single gas experiments, the Δp_i is calculated as:

$$\Delta p_i = p_{f,i} - p_{p,i} \quad (2)$$

where the indexes refer to the total pressure on the feed (f) and permeate (p) side, respectively. In the case of mixtures, due to the large permeance and the stage-cut reached in the experiment, the Δp is calculated as its logarithmic mean:

$$\Delta p_i = \frac{(p_{f,in} - p_p)_i - (p_{f,out} - p_p)_i}{\ln(p_{f,in} - p_p)_i - \ln(p_{f,out} - p_p)_i} \quad (3)$$

Where the $p_{f,in}$ and $p_{f,out}$ are the pressure at the feed inlet and outlet, respectively. The selectivity of the membrane is calculated as the ratio between the gas concentration in the permeate (y) and in the feed (x) stream, the separation factor, according to Equation (4):

$$\alpha = \frac{y_i/y_j}{x_i/x_j} \quad (4)$$

where, i is the concentration of the fastest permeating component, while j is the concentration of the slower permeating component. In the case of single gas experiments, the separation factor can be approximated by the permeance ratio as reported in Equation (5), referred to as the ideal selectivity.

$$\alpha_{ideal} = \frac{P_i}{P_j} \approx \lim_{p_p \rightarrow 0} \alpha \quad (5)$$

For each separation experiment, the stage cut (namely also H_2 recovery) was also calculated as the ratio between the gas flow on the permeate and on the feed side of the membrane:

$$stage\ cut = \frac{\dot{n}_p \cdot y_{i,p}}{\dot{n}_f \cdot y_{i,f}} \quad (6)$$

Conceptual process design and evaluation at industrial scale

The polyPOSS-imide membranes can be applied in various CCUS pre-combustion schemes for pure hydrogen production from e.g. natural gas or biomass, involving separation of H_2 from CO_2 , methane or other carbon sources. In this work the technical feasibility of integration of polyPOSS-imide hydrogen selective membranes in the steel industry was assessed by a conceptual process design and modelling. The proposed concept involves a combination of carbon reuse and electrification of the steel making process with co-production of hydrogen. For the assessment, 3 cases were defined: a baseline case without emission reduction, a reference case using “conventional” separation technology, and the case where polyPOSS-imide membranes were implemented as separation technology. The simplified process flow scheme of the studied membrane and reference systems is depicted in Fig. 2, where the emission reduction measures are indicated in green colour. Residual gas from coke ovens, coke oven gas (COG) is sent to a separation section. For the membrane case, this section uses polyPOSS-imide membranes in combination with Pressure Swing Adsorption (PSA) for further purification of the produced hydrogen. Here, gas separation is performed producing a pure hydrogen (H_2) product stream for export as well as a mixed stream of CO_2/CH_4 that is sent to a plasma torch. In the plasma torch, syngas is produced by combined dry/steam reforming making use of renewable electricity. This syngas is used in the blast furnace, resulting in a reduction in the amount of Pulverized Coal Injection (PCI). Following this approach, the COG is not used anymore to cover the heat demand of the steel plant, and this heat needs thus to be replaced with an alternative off-gas, which is the blast furnace gas (BFG). Therefore, the amount of BFG used in the electricity production is reduced, resulting in a lower electricity production in the power plant. Thus, in addition to the renewable electricity use for the plasma torch, to compensate for the lower electricity production, import of renewable electricity is

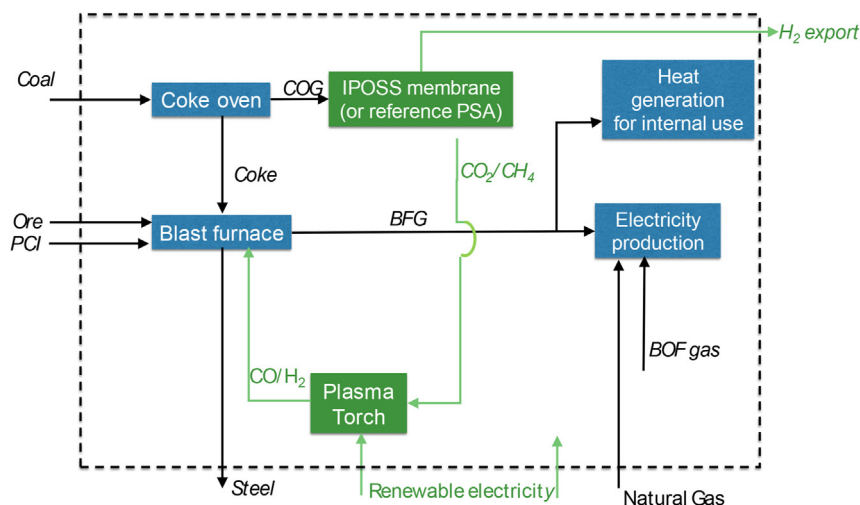


Fig. 2 – Simplified process schematic for the polyPOSS-imide membrane-integrated or reference process.

required to cover the electricity demand of the steel making process. Besides a scheme for CO₂ emission reduction and carbon reuse, the proposed concept is as such also a scheme for partial electrification of the steel making process. The reference case process is identical to the membrane separation case with the difference that H₂ separation is all achieved by a substantially larger PSA unit.

The baseline case information on the feed/product streams were taken from literature [9]. The key data are coal and iron ore inflow, steel production capacity, CO₂ emissions from heat and electricity production, electricity produced, electricity and heat demand of the steel mill and off-gases flow capacity and composition. Table 1 gives an overview of the key data for the baseline case. The data of IEAGHG assumes that the plant is energy neutral, meaning that the gases produced are exactly sufficient to cover the heat and power demand of the plant. For the technical evaluation, mass and heat balances were made using the flow sheeting tool Aspen Plus V10. Standard models were used for the heating, cooling and compression required. Custom models were developed for non-standard equipment such as membranes, PSA, the plasma torch and the blast furnace. The membrane model used was a 1-dimensional cross-flow model using the approach of [10]. Here, the trans-membrane flux for each component *i* is described as a function of the dimensionless membrane length *z* according to Equation (7).

$$J_i(z, T) = P_{0,i} \exp \left[-\frac{E_{act,i}}{RT} \right] [p_{i,f}(z) - p_{i,p}(z)] \quad (7)$$

With $P_{0,i}$ a pre-exponential factor and $E_{act,i}$ the activation energy for permeance for component *i*, *R* the gas constant, *T* the absolute temperature and $p_{i,f}(z)$ and $p_{i,p}(z)$ the local partial pressure of component *i* at the feed and permeate side respectively. Experimental permeance data for the various gaseous components were taken from our previous study [5]. A correction on the total membrane surface area is made for the mass transfer resistance based on comparison of pure gas and mixed gas experiments (+30%). In the calculations the membrane operating temperature was fixed at 250 °C, while an optimization with respect to the feed pressure was performed up to the maximum experimentally evaluated

pressure of 10 bar as the upper feed pressure limit [5]. The plasma torch model was a combined stoichiometric reactor model based on experimental data from Ref. [11]. Relative sizing of the PSA unit was done based on the molar flow rate of hydrogen feed contaminants.

The composition, flow and operating conditions of the COG is given in Table 2.

Pipeline hydrogen is produced at a purity of 99.999% and at pressure of 10 bar. The Key Performance Indicators (KPI's) defined were:

1. CO₂ avoided is defined as the reduction in CO₂ emission per unit of hot metal produced (*e*) of the process with CO₂ capture (e_{clk}) with respect to the baseline process ($e_{clk,ref}$) according to:

$$CO_2 \text{ avoided} = \frac{e_{clk,ref} - e_{clk}}{e_{clk,ref}} \quad (8)$$

Here, the avoided emissions by production of H₂ were also accounted for, using literature data for a state-of-the-art steam methane reforming (SMR) plant. The CO₂ avoided is expressed as a percentage.

2. Green electricity CO₂ reduction potential (GECRP) is a measure of how effectively the renewable electricity is reducing emissions. It is defined as the amount of CO₂ avoided per amount of renewable electricity used in the concept according to:

$$GECRP = \frac{\dot{m}_{CO_2,ref} - \dot{m}_{CO_2}}{\Delta E_{import}} \quad (9)$$

Where $\dot{m}_{CO_2,ref}$ and $\dot{m}_{CO_2}$ are the mass flows CO₂ emitted for the baseline and studied case respectively and ΔE_{import} is the difference between power imported in the studied cases and the baseline case. The GECRP is expressed in kg_{CO2}/GJ_{el} and is compared to feeding the renewable electricity in the electricity grid, using typical CO₂ emissions from the average EU28 electricity mix from 2014 that is 73 kg_{CO2}/GJ_{el}.

Results and discussion

Investigation of polyPOSS-imide membrane stability

In the following section, the stability of the developed polyPOSS-imide membranes is thoroughly investigated. Initially, we report on the temperature stability, followed by experiments targeting hydrothermal cycling. Finally, we report on longer-term stability of the polyPOSS-imide membranes up to 250 °C in the presence of up to 10% of steam at 8 bar during which membranes were operated over a period of up to 1000 h.

Table 1 – Key data for baseline steel mill [9].

Parameter	Value
Hot metal production [Mt/year]	4.0
Coking coal [GJ/t HM]	16.292
PCI coal [GJ/t HM]	5.032
NG for electricity production [GJ/t HM]	0.85
CO ₂ emissions [kg/t of HM]	2094.4
Average daily power output power plant [MW _{el}]	200
Power export [MW]	0

Table 2 – COG composition and flow.

Component [mol%]	CO ₂	CO	N ₂	H ₂	CH ₄	O ₂	H ₂ O	total flow [kNm ³ /h]	p [bara]	T [°C]
	0.94	3.84	5.74	59.54	23.04	0.19	3.15	80	1.1	29

Temperature stability

Fig. 3 shows the polyPOSS-imide membrane performance obtained at 250 °C and 2 bar after exposing the membrane to a temperature pre-treatment of up to 400 °C in air. This temperature pre-treatment is stepwise performed using one single membrane in an external furnace to prevent that the Kalrez O-rings used to seal the membrane are damaged at such high temperature. The temperature was increased to the setpoint with a ramp rate of 5 °C/min and then the final temperature was maintained for 2 h. Between a pre-treatment temperature of 250 and 300 °C, the membrane performance at 250 °C (both in terms of permeance and selectivity) did not show significant changes. Upon treatment at 350 °C, the permeance of all gases increased and especially the less permeable gases were affected to a larger extent: CH₄ and N₂ showed a 6-fold enhancement, whereas H₂ and CO₂ increased by 2.5- and 4-fold, respectively, resulting in a dramatic decrease of the membrane selectivity. Exposure of the membrane to 400 °C had a tremendous impact on the membrane performance: the H₂ permeance increased to a value (15,000 GPU) in the same range of the one reported for the bare alumina support [5]. Simultaneously, the permeance of the other gases increased to an even larger extent, lowering the obtained selectivity to a value of ~4, close to the Knudsen selectivity expected for the alumina-based support.

The performance decline with increasing temperature is seemingly related to the degradation of the polyPOSS-imide material, possibly through further silanol condensation reactions as concluded from the weight loss detected during thermal analysis of the freestanding poly(POSS-amic acid) film [12]. The thermal conversion of poly(POSS-amic acid) is described by 3 distinct exothermic steps releasing different fragments. The initial large weight decrease is observed between 150 and 300 °C. This is related to the conversion of amic acid to imide groups (imidization step) dominated by the loss of water from the material, accompanied by the release of small amounts of CO₂ and aromatic fragments. The second step, roughly between 300 and 400 °C is only because of the loss of water and is coupled to silanol condensation (recombination of silanol groups to form siloxane groups). The last step, between 420 and 600 °C reveals further release of aromatics, CO₂ and water from the material degradation in itself [12]. Based on this information, the polyPOSS-imide membranes are found to exhibit an appropriate thermal stability up to 300 °C.

Hydrothermal stability

To investigate the hydrothermal stability, a HAPS-POSS polyPOSS-imide membrane was exposed to hydrothermal cycling. Fig. 4 shows a comparison of performance obtained at 150 °C after exposure to various high-temperature and humid conditions.

Upon exposure to 300 °C, a 2-fold increase (from 550 to 950 GPU at 10 bar) was observed for the H₂ permeance, as well as in the H₂/CH₄ selectivity. A more limited increase was observed for H₂/N₂, whereas a negligible change was obtained for the H₂/CO₂ selectivity. The subsequent exposure of the polyPOSS-imide membrane to humid conditions at room temperature resulted in a minor decrease in both the H₂ permeance and selectivity over the other gases. It should be noted though that the obtained performance still largely exceeds the original membrane performance. Finally, exposure again to 300 °C for 24 h resulted in a further increase in H₂ permeance (from 950 to 1050 GPU at 10 bar) together with minor changes in the selective features. These results showed a good stability of the polyPOSS-imide to hydrothermal cycling, with a surprising improvement of the separation performance upon exposure to high temperature conditions, pointing at a good thermal stability of the polyPOSS-imide selective layer. The exact reason of the improved separation properties after exposure to 300 °C need to be further investigated, but it can potentially be related to a further thermal imidization of the membrane layer.

Subsequently, the long-term hydrothermal stability of the polyPOSS-imide membranes was investigated over a period of close to 1000 h at 250 °C exposing the membrane to 10% steam. Fig. 5 shows the observed performance as a function of time at varying pressure between 4 and 8 bar.

Despite minor changes at the different pressures because of the differences in the stage-cut (the feed flow rate was kept constant throughout the 1000 h), the H₂ permeance was shown to be stable at unchanged conditions. The selective features of the polyPOSS-imide membrane were found to increase in the presence of water as indicated by the increase in H₂/CH₄ selectivity upon water addition (time = 150 h). Even though a minor drop was observed over time during the hydrothermal operation, the selectivity still exceeds the initial selectivity obtained in the dry feed atmosphere. After the removal of steam from the feed (at time = 480 h) the performance returns to its original state prior to the exposure to any steam showing

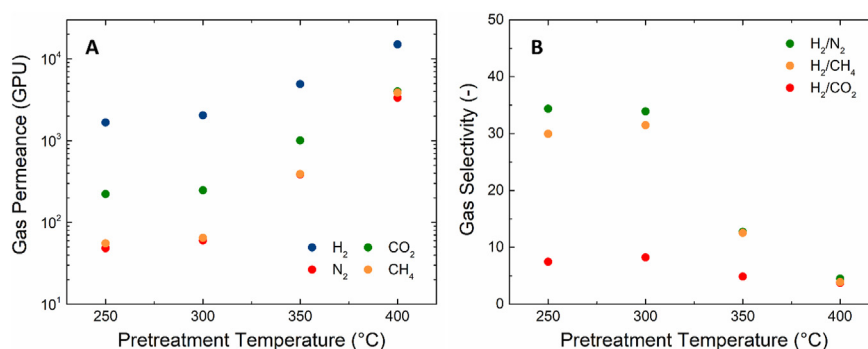


Fig. 3 – Effect of temperature exposure up to 400 °C on the polyPOSS-imide membrane (HP-POSS) performance (a) single gas permeance; (b) ideal gas selectivity.

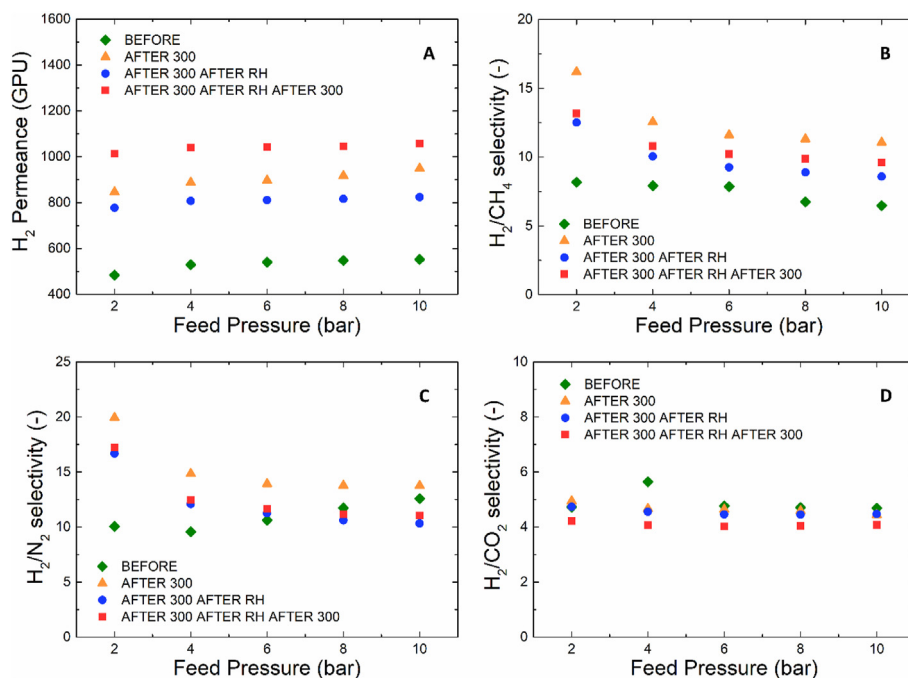


Fig. 4 – PolyPOSS-imide (HAPS-POSS) membrane single gas performance obtained at 150 °C, before and after exposure to respectively 300 °C, humid conditions at room temperature, and again 300 °C, respectively. (a) H₂ permeance; (b) H₂/CH₄ selectivity; (c) H₂/N₂ selectivity; (d) H₂/CO₂ selectivity.

an appropriate steam stability of the polyPOSS-imide membranes. The operation was stopped over a period of approximately 300 h, and during this period the membrane was kept at 250 °C and 2 bar in a N₂ atmosphere. After around 950 h, the membrane operation was started again, and a separation performance similar to the initial one was obtained. These results suggest that, at the operating conditions used in this work, physical aging has a limited effect on the separation performance of polyPOSS-imide membranes.

The average values of H₂ permeance and separation factor obtained at the various operating conditions are reported in Fig. 6. Both the H₂ permeance and separation factor for all the gas pairs of interest is significantly lower compared to the ideal gas selectivity previously shown in Fig. 3b. As reported previously [5], the high H₂ permeance coupled with the relatively large permeation area leads to a significant depletion of the H₂ concentration in the feed side within the module length, while the concentration of the other gases increases, resulting in a lower performance. In addition, concentration polarization at the gas/membrane interface on the feed side can also play a role [13]. For all the reported conditions, a further decrease in H₂ permeance is observed at higher pressure. Such effect is related to the testing conditions and specifically to the higher stage cut obtained at high pressure, due to the fact that the total feed flow (1 L/min) was kept constant throughout the duration of the experiment. As described before, the addition of steam determined a minor drop of the H₂ permeance and a simultaneous increase in the obtained H₂ selectivity of the polyPOSS-imide layer. While the drop in permeance is more evident at low pressure, the increase of the separation factor appears to be independent from the feed pressure. Upon removal of steam from the feed gas, the H₂ permeance showed an increase (from

870 to 955 GPU at 4 bar). Such effect is however reduced at 6 bar and almost negligible at 8 bar. Further exposure to dry and high temperature conditions resulted in a further increase of the H₂ permeance (up to 1085 GPU), with negligible effect the selectivity. This effect is similar to the one reported in Fig. 4. Interestingly, the permeance increase is less notable at higher pressure (6 bar) and almost negligible at 8 bar. This might suggest that because of the increase in stage cut, boundary layers effect starts to dominate the gas transport (especially at 8 bar, where the stage cut is close to 70%), so that minor changes in the membrane characteristics have negligible impact on the overall H₂ permeance [13].

H₂O permeance of polyPOSS-imide membranes

The permeation equipment presented in Fig. 1 allowed also to estimate the H₂O permeance through the polyPOSS-imide membrane by weighing the amount of water present in the condenser after each test and considering the gaseous stream leaving the condenser saturated at the measured temperature. In this manner, the absolute H₂O flux through the membrane could be determined, allowing for the calculation of the H₂O permeance. Fig. 7 shows the results obtained for an HP-POSS membrane at different operating temperatures. The steam content was changed from 5, 9 and 13 mol%, and tests were performed using pure H₂ and a quaternary feed mixture (60% H₂, 10% CO₂, 10% N₂, 20% CH₄). Each experimental condition was run for a few (~3–4 h) hours to ensure steady state. Despite the relatively large water contact angle, 72°, of the polyPOSS-imide layer [4], the H₂O permeance is observed to be always above 1000 GPU within the operating window considered in the study. Such value clearly indicates a permeability closer to H₂ than to the other gases. Therefore, in presence of

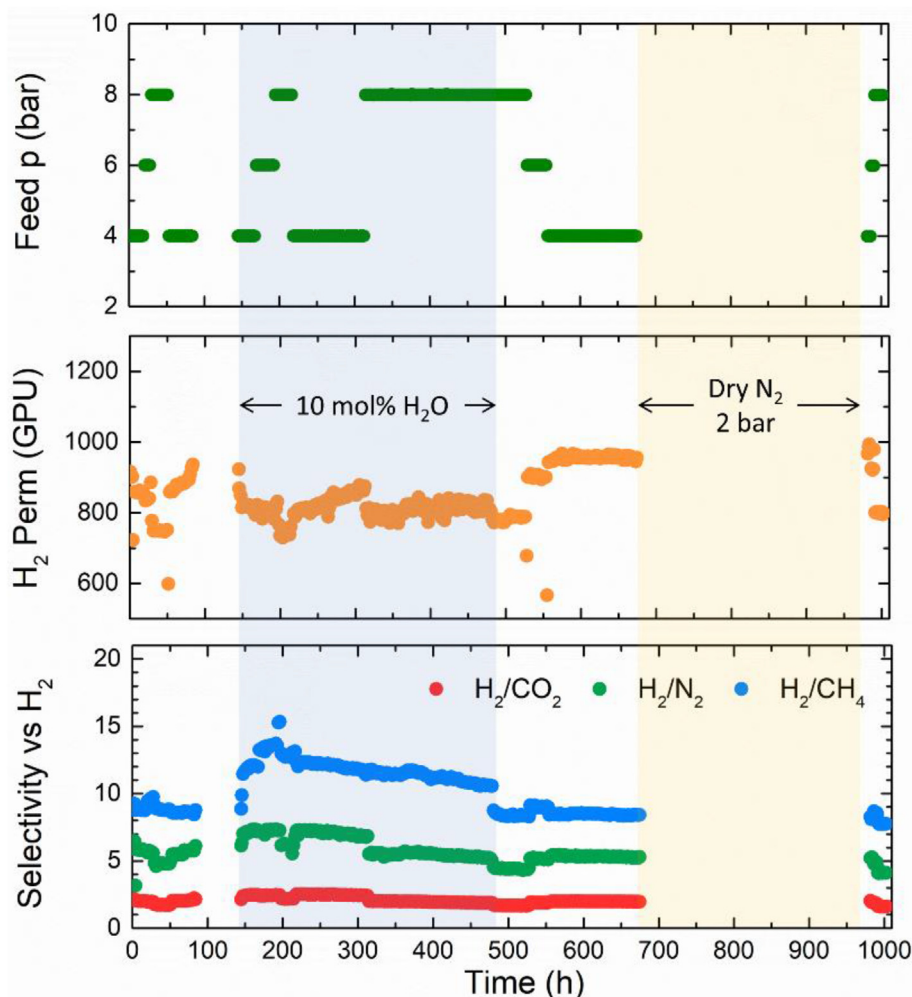


Fig. 5 – Long-term hydrothermal stability of a polyPOSS-imide membrane (HAPS-POSS) applying mixed gas at 10% humidity as feed at 250 °C (total feed pressure 4–8 bar). The stage cut was changing from $37 \pm 4\%$ at 4 bar, to $57 \pm 3\%$ at 6 bar and to $69 \pm 2\%$ at 8 bar.

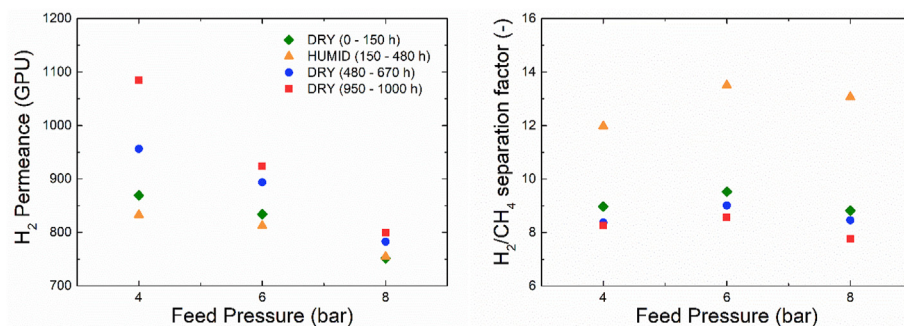


Fig. 6 – Average H_2 permeance and H_2/CH_4 separation factor for the polyPOSS-imide membrane (HAPS-POSS) obtained over the long-term stability test. H_2/CH_4 is reported as reference, but similar trends are observed for H_2/N_2 and H_2/CO_2 .

steam in the feed gas, most of the water can be expected to permeate with H_2 towards the permeate side of the membrane. In addition, as expected from the other gases, also the permeation of H_2O is temperature activated. Finally, minor differences are observed between pure and mixed gas conditions.

H_2O permeance data were also obtained from the long-term stability tests reported in Fig. 5 and the results are reported in Table 3. The values are similar to the one reported in Fig. 7, showing permeances close to the one observed for H_2 rather than to other gases. However, the H_2O permeance observed for the HP-POSS material is slightly higher (~ 3000

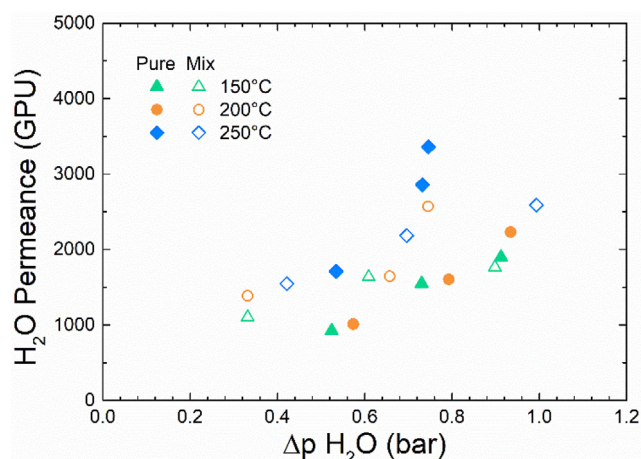


Fig. 7 – H₂O permeance for a polyPOSS-imide membrane (HP-POSS) measured for pure H₂ and mixed gas as feed (Feed pressure 10 bar).

Table 3 – H₂O permeance for the HAPS-POSS membrane tested for long-term stability (H₂O content feed = 10 mol %).

p [bar]	H ₂ O Permeance [GPU]
4	3536
6	2758
8	2290

GPU) compared to the one obtained for the HAPS-POSS. Such behavior can be expected, as the presence of salt [8] in the HP-POSS can lead to higher affinity with H₂O molecules. A decreasing trend with pressure, similar to one observed for H₂, is measured and this might again be related to the stage cut achieved at various pressures.

Conceptual process design and evaluation

A single and two-stage membrane system were evaluated for the integration of the polyPOSS-imide H₂-selective membranes in the steel industry. In the two-stage system the

permeate stream of the first stage is fed to the feed side of the second stage for increasing the purity before feeding it into the polishing PSA. After compression the feed is heated to a temperature of 250 °C. The membrane feed and permeate pressure were optimized to 8 bar and 1 bar, respectively. Compared to the single stage system, the two-stage system gave a H₂ purity increase from 90% to 97%, while the power input increased with a factor 1.6 and the membrane area with a factor 1.4. Since in either case the PSA polishing step cannot be omitted, the one stage membrane process was selected for further evaluation, because this avoids additional costs for the second membrane stage, recompression and heating/cooling steps. The PSA system employed after the membrane system (polishing PSA) was found to be 20% of the size of the PSA system performing the whole separation.

Table 4 lists an overview of the obtained results for three cases considered. The total membrane area required to produce 29 kt/year of export H₂ is 4693 m². The membrane case has a higher H₂ export than the reference case. Since feeding H₂ to the blast furnace has a significant positive effect on the PCI reduction, this additional H₂ export thereby leads to a lower PCI reduction. The resulting CO₂ emission reductions are very similar for the two concepts, as well as the energy use, with only a slightly better performance for the membrane case. The total CO₂ avoided in the membrane case is 1177 kt/year and in reference case 1133 kt/year.

The green electricity CO₂ reduction potential (GECRP) for both the membrane case and reference case cases is higher than the EU28 mix emission factor (which is 73 kg CO₂ per GJ_{el}). This implies that using renewable electricity with the proposed concepts to decarbonise steel production has a higher impact in terms of CO₂ avoidance than feeding the same amount of renewable electricity into the electricity grid where it would reduce emissions associated with the EU28 mix of power generation technologies. This difference is significant, and the amount of CO₂ emissions reduced per amount of GJ of renewable electricity for the membrane case and reference case used is a factor 2.76 respectively 2.53 times higher than when feeding it into the electricity grid. The membrane case has slightly better performance in terms of GECRP. Future economic evaluations can bring further insights in whether the membrane concept would be better in terms of emission reduction costs.

Table 4 – Summary of results for the baseline, reference, and polyPOSS-imide membrane integrated cases.

Parameter	Unit	Baseline	Reference case	Membrane case
Hot metal production	Million t _{hot metal} /year	Constant	Constant	Constant
Coking coal	kg/t _{hot metal} (GJ/t _{hot metal})	Constant	Constant	Constant
PCI	kg/t _{hot metal} (GJ/t _{hot metal})	152 (5.03)	69.51 (2.29)	73.41 (2.49)
Natural gas for electricity production	GJ/t _{hot metal}	Constant	Constant	Constant
Electricity import	MW _{el} (GJ/t _{hot metal})	0	204 (1.48)	202 (1.46)
H ₂ produced	kt/year (GJ/t _{hot metal})	0	24 (0.75)	29 (0.87)
Total energy input	GJ/t _{hot metal}	22.17	20.20	20.17
Energy use reduction	%	n.a	8.9%	9.0%
CO ₂ emissions	kg/t _{hot metal}	2094	1809	1797
CO ₂ avoided %	%	n.a.	13.62%	14.17%
Total CO ₂ avoided/year	kt/year	0	1133	1177
GECRP	kgCO ₂ /GJ _{el}	n.a	192	202

Conclusions

In the current work we report on how steam affects the membrane performance and stability of novel polyPOSS-imide membranes for high-temperature H_2 separation. It is found that these membranes exhibit an appropriate stability up to 300 °C. At an even higher temperature the membrane selectivity rapidly decreases, which is seemingly related to changes in the molecular structure of the inorganic backbone. Surprisingly, the exposure of the membrane to temperatures of up to 300 °C even increases the H_2 permeance together with the selective features of the polyPOSS-imide layer. Long-term hydrothermal stability was shown over a period of close to 1000 h at 250 °C exposing the membrane to 10% steam at pressures between 4 and 8 bar. The application of the polyPOSS membranes in a partial electrification scheme for the steel industry can achieve a CO_2 emission reduction of 14%. This CO_2 reduction is a factor 2.76 higher than if the renewable electricity would be fed in the electricity grid.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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