**Poly(ionic liquid)/ionic liquid composite membranes with anions based on fluorosulfonyl derivatives: characterization and CO2/H2 separation**

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**Highlights**

* Poly(ionic liquid)s containing anions based on fluorosulfonyl derivatives were synthesized.
* PIL–IL composite membranes were prepared by solvent casting.
* Pure PILs and ILs and their composites were characterized by different techniques.
* The CO2/H2 separation through the studied PIL–IL membranes was evaluated.

**1. Introduction**

Despite the recognized potential of biohydrogen (bioH2) for sustainable development, there are still issues regarding its production and purification, such as the elimination of CO2, N2, and other impurities (H2O and H2S), so that an enriched H2 stream can be obtained for efficient energy generation [1].

Ionic liquids (ILs) have been used as a successful platform to design novel task-specific materials for CO2 separation [2]. In an effort to improve the CO2 permeability and permselectivity properties of supported ionic liquid membranes (SILMs), we recently reported the CO2/N2 separation performance of different ILs based on the [C2mim]+ cation and different fluorinated-based anions, such as [TFSAM]- or [C4F9SO3]-. The results showed that both [C2mim][TFSAM] and [C2mim][FSI]-based SILMs present remarkable CO2 permeabilities and CO2/N2 permselectivities [3]. However, and considering that the long-term stability and industrial operation of SILMs are still compromised due to the risk of IL draining from the membrane pores, different studies have been unveiling that the use of poly(ionic liquid)s (PILs) and their composites (PIL–IL) is a powerful strategy to design improved CO2 separation membranes [2].

In this work, PIL–IL membranes composed of pyrrolidinium-based PILs with [TFSAM]-, [FSI]- and [TSAC]- anions were prepared by the incorporation of ILs containing the same anions. The composite membranes as well as both PIL and IL components were characterized by different techniques (TGA, DSC, FT-IR and RAMAN) and their CO2/H2 separation performance was evaluated using the time-lag method at biohydrogen production conditions.

**2. Methods**

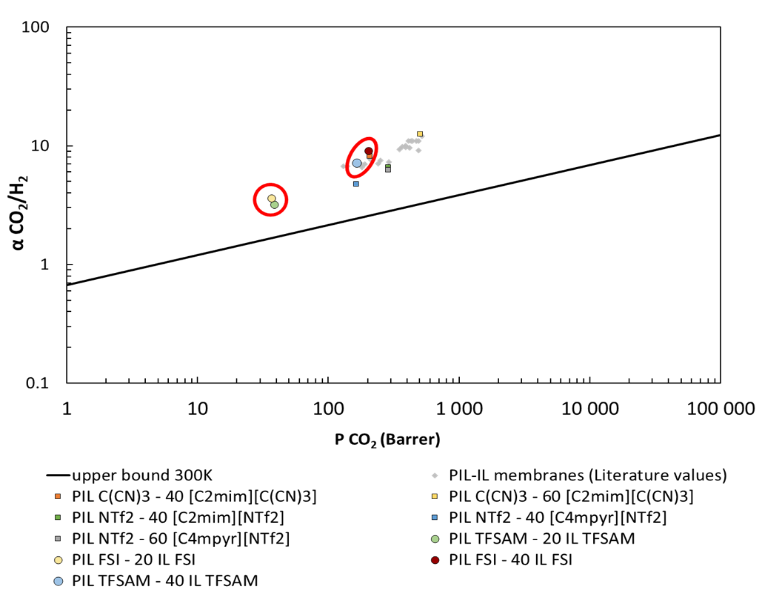
The free-standing PIL–IL membranes were prepared by solvent casting. The 6 (w/v)% solutions were

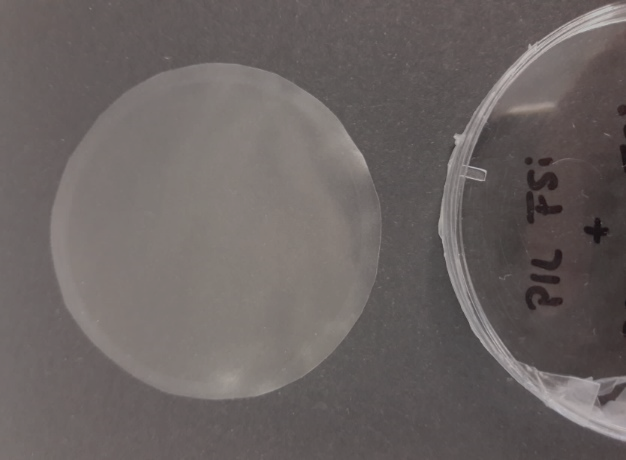
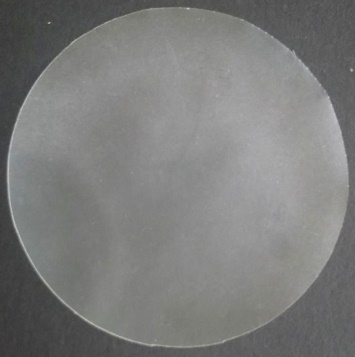
mixed until complete dissolution of the PIL and IL components and then poured into Petri dishes for slow evaporation of the solvent. The gas permeation properties were evaluated using the time-lag method at *T*=35°C and Pfeed of 1 bar.

**3. Results and discussion**

From the thermogravimetric analysis results, and depending of the PIL used, different trends were observed for degradation temperatures of the PIL–IL composites with the addition of free IL, which led to the conclusion that the thermal stability of the studied PIL–IL membranes not always follows a simple mixing rule.

From CO2 and H2 permeation results, and taking into account that it was not possible to prepare PIL–IL composites with more than 40 wt% of free IL incorporated, both PIL TFSAM – 40 IL TFSAM and PIL FSI – 40 IL FSI membranes presented higher CO2/H2 selectivities (Figure 1) compared to the already reported PIL–IL membranes containing the conventional [NTf2]- anion with 60 wt% of free IL.





**20% IL**

**40% IL**

**PIL–IL FSI composites**

**Figure 1.** CO2/H2 separation performance of the PIL–IL membranes studied.

**4. Conclusions**

PILs and ILs containing anions based on fluorosulfonyl derivatives were synthesized and characterized. PIL–IL membranes were prepared to evaluate their CO2/H2 separation performance. In sum, higher CO2/H2 selectivities were obtained for both PIL FSI– 40 [C2mim][FSI] (α = 9.0) and PIL TFSAM– 40 [C2mim][TFSAM] (α = 7.1) compared to those of composites containing the conventional [NTf2]- anion (PIL NTf2 – 40 [C2mim][NTf2] (α = 6.5) and PIL NTf2 – 60 [Pyr14][NTf2] (α = 6.3).

**References**

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