



On the incorporation of protic ionic liquids imbibed in large pore zeolites to polybenzimidazole membranes for high temperature proton exchange membrane fuel cells

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H I G H L I G H T S

- ▶ Synergic combination between H₃PO₄, PBI and IL3 imbibed in NaY.
- ▶ IL3 molecules leached out from NaY crystals contribute to the conduction outperformance.
- ▶ H⁺/H₂ transport selectivity values higher than PBI and hybrid NaY–PBI counterparts.
- ▶ Proof of concept demonstration in H₂/O₂ single cell up to 180 °C under non humidified conditions.
- ▶ I–V improvement performance values over pristine PBI ranging from 20% up to 100%.

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Conducting fillers based on 2-hydroxymethyl trimethylammonium dimethyl phosphate (IL1), *N,N*-dimethyl-*N*-(2-hydroxyethyl) ammonium bis(trifluoromethanesulfonyl)imide (IL2) and 1-*H*-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL3) encapsulated in large pore zeolites (NH₄BEA and NaY) have been added to the PBI casting solution for the preparation of high temperature proton exchange membranes (HTPEMs). The filler loading has been systematically varied from 3% to 20% wt. for all the studied composites. The morphological, physicochemical, and electrochemical properties of the as prepared hybrid doped PBI membranes have been fully characterized. For a given conduction filler, the optimum loading is found to be 3% wt. as inferred from the conductivity measurements at 0.05 water molar fraction. Among the tested, the outstanding electrolyte membranes are those containing IL3–NaY. The exhibited through-plane proton conductivity is 54 mS cm^{−1} at 200 °C for the optimum PBI + IL3–NaY_3%wt hybrid membrane. The so obtained results are explained by the assisted 1-*H*-3-methylimidazolium and bis(trifluoromethanesulfonyl)imide hydrogen bonding type interactions, clearly beneficial for the proton conduction processes. Moreover, the H₂ permeability values for the hybrid electrolyte membranes and pure PBI are quite similar at the examined conditions; indicating the suitability of the preparation procedure in terms of fuel cross-over. The H⁺/H₂ transport selectivity of the optimum IL3–NaY composite membrane clearly outperforms pure PBI and zeolite–PBI counterparts at 50°, 100° and 150 °C. Finally, the optimum composite membranes have been validated in H₂/O₂ single cell under non humidified conditions up to 180 °C as a “proof of concept” demonstration.

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1. Introduction

It is expected that fuel cell systems play a key role and contribute, in a more effective way, to satisfy energy market demands by 2050 [1]. Long-term and breakthrough orientated research is progressively

focused on degradation and lifetime fundamentals related to materials and typical operation environments for all power ranges. In particular, the availability of commercial membrane materials having high proton conductivity almost unaffected by temperature and relative humidity is identified as one of the main bottlenecks preventing the commercialization of FC technologies. The higher operation temperatures in the proton exchange membrane fuel cells (PEMFC) could be accompanied with higher CO tolerance, better reaction kinetics, and simpler water management.

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Commercially available polybenzimidazole (PBI) has been the most extensively studied and used in membranes doped with all sorts of strong inorganic acids for high temperature applications up to 200 °C [2]. By far, the most common approach is phosphoric acid impregnated systems. However, phosphoric acid autodehydration at temperatures above 140 °C is a serious limitation due to the formation of lower conductivity oligomers like pyrophosphoric acid. On the other hand, elution of the water soluble phosphoric acid from the membrane and dilution of the acid in the membrane can occur when the vapor produced at the cathode in the operation process of fuel cells is not eliminated. Among the main strategies to improve the performance and stability of current PBI membranes, the most studied are: i) ionic cross-linking of polymeric acids and polymeric bases; ii) use of covalently cross-linked acids or halides; iii) composite organic-inorganic membranes from PBI and inorganic fillers. Accordingly, a new generation of advanced PBI membranes are currently commercially available (i.e. Celtec®-P1000 MEA from BASF [3] and fupapem® from FuMA-Tech [4]).

In general, the use of composite materials is a clear research path for the development of improved electrolyte membrane materials for high temperature applications. Thus, the inclusion of different inorganic fillers [5–9] to the casting PBI solution (zirconium phosphates, phosphotungstic acid, silico-tungstic acid, zirconium tricarbonylphosphate, polyoxometals, sulfonic silica nanoparticles, titanium oxide) has been already proposed to enhance the conduction performance and fuel cross-over properties of PBI membranes at temperatures above 120 °C. In general, the as prepared composite membranes show higher water uptake, acid doping levels and improved mechanical properties comparing to pristine PBI counterparts. In an attempt to improve interactions at the interface, external surface functionalization of either inorganic [10,11] or organic [12,13] fillers has also been attempted. In particular, novel dense and porous hybrid PBI membranes [14] including microporous ETS-10 titanosilicate type materials have been previously developed by our group for high temperature PEMFC applications. Some of these authors attribute the enhanced performance of composite membranes to the formation of new proton conducting networks that formed along the functionalized filler's surface [12–14].

On the other hand, the deployment of ionic liquids (ILs) as proton transport carriers in the polymer membrane is emerging as an attractive alternative to overcome the operational limitations above 100 °C. These organic salts are able to transport protons due to their acid-base character and their capability to form complex or intermolecular hydrogen bonds [15]. The main challenge hindering the use of ionic liquids as proton conductor in PEMFCs is the phase separation process that takes place between the polymer phase and ionic liquids resulting in inhomogeneous membranes. Nevertheless, conducting polybenzimidazole based systems containing ILs has been already reported by dissolving the polymer and IL in a common solvent and casting the film [16–18]. The pioneer work of Greenbaum et al. [16] demonstrated the feasibility of anhydrous proton solvent H₃PO₄, the protic ionic liquid 1-propyl-3-methylimidazolium dihydrogen phosphate and PBI for operation up to 150 °C. Under completely anhydrous conditions, these novel membranes exhibited conductivities up to 2.04 mS cm⁻¹ at 150 °C. In fact, the incorporation of ionic liquid into H₃PO₄/PBI complex significantly increased the ionic conductivity of the membranes. In a step further, Hsu et al. [18] prepared composite membranes from a fluorine-containing PBI with 1-hexyl-3-methylimidazolium trifluoromethanesulfonate. The ionic liquid based composite membranes shown a significant improvement in thermal stability compared to the H₃PO₄/PBI system and ionic conductivities up to 16 mS cm⁻¹ at 250 °C under anhydrous conditions.

In contrast to published works dealing with PBI-ILs membranes, the electrolyte membrane concept proposed in our previous work

[19] was based on the simplest Supported Ionic Liquid Membrane approach commonly used for Gas Separations. Thus, randomly porous doped PBI membranes (80% in porosity) containing 1-H-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IL3) were tested for high temperature PEMFCs. Through plane conductivity values above 35 mS cm⁻¹ were reported at 160 °C in presence of 0.05H₂O molar fraction. In order to avoid the IL leakage/dragging with time on stream by water reaction molecules, microporous ETS-10 titanosilicate coatings were performed over supported protic ionic liquid membranes. The so obtained microporous layers also reduce fuel cross-over at the expense of higher ohmic polarization.

Unlike previously, the strategy herein proposed to alleviate IL dragging phenomena with time on stream is the IL immobilization in large pore zeolites, which are further deployed as fillers to the PBI casting solution. The encapsulation procedures for different ammonium based protic ionic liquids within the microporous framework of FAU and BEA zeolites have been recently studied [20] in our group to improve the proton conductivity of the filler itself. In general, all the composites exhibited the same conductivity behavior under anhydrous conditions: a gradual increase up to a maximum followed by a conductivity decay. This experimental observation was attributed to the weakly bounded water molecules desorption capable to ionic liquid dragging, and the maximum position was related to the hydrophilicity not only of the zeolitic host but also on the ionic liquid itself. Accounting from these results, the aim of this work is the preparation of hybrid doped PBI membranes based on conducting IL-zeolite fillers with enhanced performance for high temperature PEMFCs applications. Firstly, the influence of the type and amount of composite filler over the phosphoric acid and water uptake values and conduction properties of the as prepared membranes has been systematically analyzed to identify the best combination. Special attention to the membrane casting and doping steps has been carried out to check the potential ionic liquid dragging from the internal microporous surface. Once the outperforming membrane is defined, the second part of this work has been devoted to the characterization of the optimum electrolyte membrane and MEA testing in H₂/O₂ single cell at temperatures up to 180 °C. The H₂ permeability and H⁺/H₂ transport selectivity values have been evaluated and compared with those values exhibited by pure PBI and bare zeolite-PBI counterparts at 50°, 100° and 150 °C.

2. Experimental

2.1. Starting materials

Two types of commercial large pore zeolites were used as ionic liquid hosts: NH₄-BETA (denoted as BEA) supplied by Zeolyst International (Si/Al ratio = 12.5) and Na type zeolite Y (denoted as NaY) from Sigma Aldrich (Si/Al ratio = 1.5). As guest molecules, ionic liquids based on ammonia and imidazolium salts were studied: (2-hydroxymethyl) trimethylammonium dimethyl phosphate (denoted as IL1) purchased from Solvent Innovation, *N,N*-dimethyl-*N*-(2-hydroxyethyl) ammonium bis(trifluoromethanesulfonyl) imide (denoted as IL2), and 1-H-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (denoted as IL3); both supplied by Solvionic [21]. Following the encapsulation procedures already described in previous works [20,22], four different conducting fillers were prepared. Soxhlet extraction to remove the IL excess from the external microporous surface at solvent reflux temperature was performed in all the cases. The main properties of the as prepared composites, including conductivity values at 100 °C as a function of relative humidity, are depicted in Table 1. For the same preparation method and a BEA type zeolite, the IL1 loadings are always higher than IL2

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