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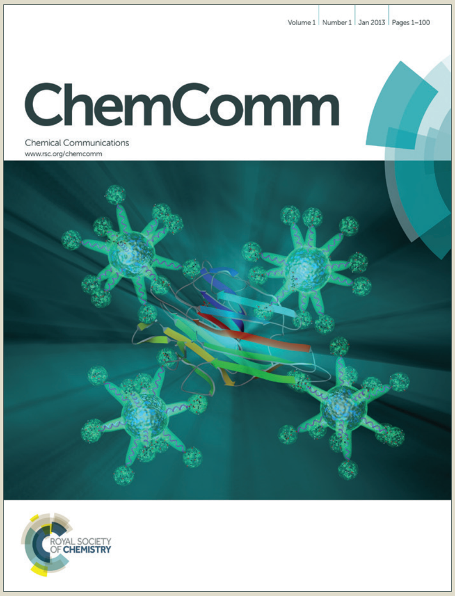

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Communication

Facile and green assembly of nanocomposite membranes for fuel cells

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We report on a facile spray deposition method, which allows obtaining nanocomposite membranes for high-temperature polymer fuel cells characterized by high homogeneity and excellent proton conductivity. The proposed method is also green, as it requires much smaller amounts of solvents with respect to standard casting.

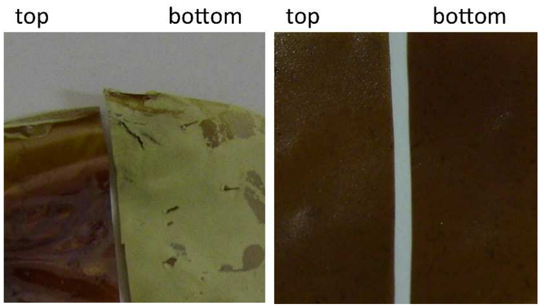
Phosphoric Acid-doped Polybenzymidazole (PA-PBI) membranes are the most promising alternative to Nafion as proton-conducting electrolytes in proton exchange membrane fuel cells (PEMFCs) [1]. Besides the high thermal and mechanical stability, such polymers show high proton conductivity exceeding 0.1 S cm^{-1} at 150°C and low humidification [2-3]. In spite of these benefits, however, some important drawbacks still need to be overcome. One of these is the leaching out of the free fraction of phosphoric acid absorbed by the membrane, which is responsible for the high proton transport. PA loss with time causes membrane degradation as well as a dramatic drop in conductivity, which severely limits cell durability. Possible strategies to improve the membrane functional stability point towards: i) the enhancement of the permanent proton conductivity of the PBI-based membranes, i.e. the conductivity retained after the loss of the free acid [4]; ii) ensuring an efficient proton transport also by using a lower amount of PA. To this aim, several approaches have been discussed in literature [4, 5-8], among which the design of composite membranes including nanoscale and/or mesoporous inorganic fillers, in case properly functionalised, seems to be particularly encouraging [2, 9, 10]. PBI composite systems show increased proton conductivity, at the same time maintaining good mechanical and chemical properties [11]. In addition, some fillers, as imidazole-derivatized silica and TiO_2, have beneficial effects in the implementation of the membrane acid retention capacity, as well as the fuel cell performances at high temperature [12, 13]. An optimal composite membrane must have an extended and uniform polymer/filler interphase, which requires a highly homogeneous dispersion of the particles.[14-16] The preparation method of the composite membrane is, therefore, a crucial step to obtain reproducible and optimal electrolytes for stable fuel cells. The standard method to produce free-standing polymeric films is casting a solution of the polymer matrix onto a proper substrate. In the particular case of PBI-based systems, the typical solvents used for casting (dimethylacetamide, DMA and dimethylsulfoxide, DMSO) have high vapour pressure and boiling point (T>180°C). In order to obtain a good free-standing film, therefore, several days in the oven at high temperature are generally required. However, this is often not enough to completely remove the solvent, and membranes with bad mechanical properties may be obtained. Moreover, the fillers have time to partially aggregate and precipitate so leading to drastic phase inhomogeneity. This phenomenon is particularly frequent in presence of high filler loadings. As a matter of fact, only PBI-based composites with filler content lower than 5 wt% were considered suitable as electrolytes in a membrane/electrode assembly[16, 17].

Here we report on an easy and effective method to prepare highly homogeneous composite PBI membranes for application as electrolytes in high temperature (HT)-PEMFCs. This procedure is based on the spraying of a filler-polymer ink onto a hot-plate, properly optimised in terms of solvent amount, carrier gas flow and substrate temperature. Three inorganic fillers have been tested in order to check the versatility of such a film-forming procedure, which differ in the chemical nature, microstructure and morphology, namely mesoporous silica (SBA-15), nanosized SiO_2 (AeroSil®RX50) and commercial micro-sized TiO_2 (Aldrich). PBI composite membranes with filler loadings up to 50 wt% and thickness of about 50 µm were easily produced. The homogeneity level of the filler dispersion was checked by means of SEM-EDAX investigations. PBI composite electrolytes were characterised in terms of PA doping level, proton transport, hydrogen crossover and electrochemical tests on properly assembled cells. The functional properties of these composite conducting membranes were compared to those ones of systems prepared by means of the standard casting, in order to verify the actual benefits of our alternative deposition technique.

Following our approach, the composite membranes were fabricated by spraying an ink obtained by dissolving a proper amount of poly-2,2'-(2,6-pyridine)-5,5'-bibenzimidazole (PBI) in a DMA/secbutylamine solution including various amounts of filler (up to 50 wt%) under N_2 flow onto a hot plate (150°C) in a ventilated chamber. The films were peeled out, washed and finally doped with PA. Similar doping levels, *DL*~170%, determined as the ratio between the weight of the adsorbed PA and that of the pristine polymer, were obtained for all the investigated composites. More details on materials and methods are available in the Supporting Info.

With respect to the casting technique, the spraying method showed several advantages. First of all, a very low amount of solvent (2 w_{pol}/w_{solv}%) was used contrary to that one typically required in case of casting (0.5 w_{pol}/w_{solv}%). Consequently, the solvent instantly evaporated and free-standing membranes, free from pinholes and cracks, were easily obtained in few minutes. By modulating the polymer/solvent ratio, very thin membranes could be easily obtained (thickness less than 40 μm) with thickness homogeneity better than 98%.

In presence of filler, the inorganic particles were immediately “fixed” in the polymer matrix preventing settling processes. Figure 1 shows, as an example, two composite membranes filled with 30 wt% of SBA-15, prepared by casting (a) and spraying (b), respectively. The image of the unfilled PBI system is reported in the supplementary info (Fig.S1a) for the sake of a comparison.



(a) **(b)**

Fig. 1: PBI-composite membranes filled with 30 wt% of SBA-15, produced by casting (a) and spraying (b).

The films obtained from spraying are homogeneous on the macroscale and show a very smooth surface. In contrast, the cast membrane is strongly corrugated and one side of the film is almost white. This clearly suggests that the SBA-15 particles aggregated and subsequently precipitated during the solvent evaporation. Very good results in terms of filler dispersion were also observed for all the inorganic fillers used in the preparation of the PBI composite membranes, independent on the particles dimensions. SEM-EDAX microanalysis was carried out to obtain information on the filler distribution in the polymer. Figure 2 shows the Si maps for the PBI samples filled with the two types of silica (a-b), and the Ti map for the TiO_2-based composite (c). The image of a cast PBI membrane including SiO_2 nanoparticles (HiSil^{TM}) is also reported for the sake of comparison (d)[19]. The filler loading is 10 wt% for each investigated system. We can observe that the filler dispersion is quite homogeneous in case of the sprayed membranes, even in presence of micro-sized fillers like TiO_2, whose particle dimensions range between 1-10 μm. A similar quality of dispersion was reached only in presence of additives with very high filler/polymer compatibility, such for instance imidazole-functionalised silica or organically modified clays [12,18]. In contrast, the cast membrane shows large aggregates in the micrometer range, which became larger and more continuous by increasing the silica content [19].

A more homegeneous filler distribution in the PBI composite membranes seems to greatly affect the proton transport. Figure 3 reports the conductivity vs. the relative humidity (RH%) for the sprayed composites containing 10 wt% of fillers. The Figure also reports the conductivity values of a cast membrane with a similar content of SBA-15. The conductivity values vs. the relative humidity for the unfilled system are available in the Supplementary Info (see Fig.S1b). All the sprayed films showed similar conductivity, independent on the filler microstructure, chemical nature and particle size. Values between 20 and 100 mS cm^{-1} were measured at 120°C in the explored humidity range (0-70 RH%). Conductivity values exceeding 70 mS cm^{-1} were obtained at low moisture levels, and this aspect is very encouraging if considering that such targets are hardly reached by Nafion and Nafion-like membranes under similar operating conditions (120°C and below 40 RH%) [20].

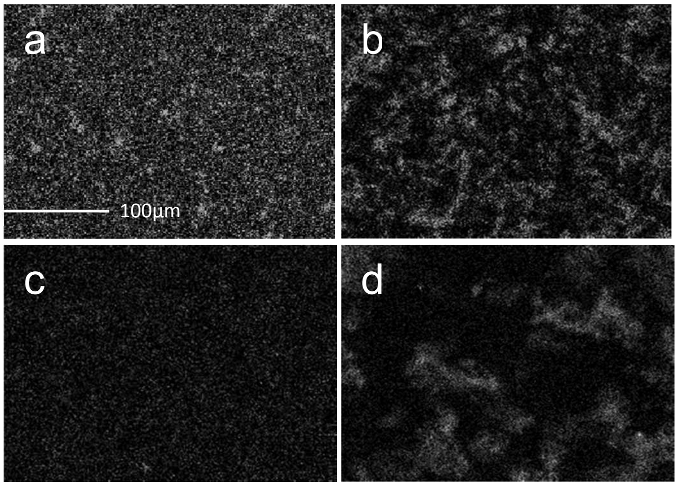


Fig. 2. SEM-EDAX images of the PBI composite membranes with different fillers prepared by spraying: (a) SBA-15; (b) AreoSil®R50; (c) TiO_2. A composite including SiO_2 nanoparticles (HiSil), obtained by conventional casting, is shown for comparison (d, taken from ref.19). The bar is the same for all the images.

However, the most relevant result is indeed concerned with the remarkable differences in proton transport observed between the cast and the sprayed membranes.

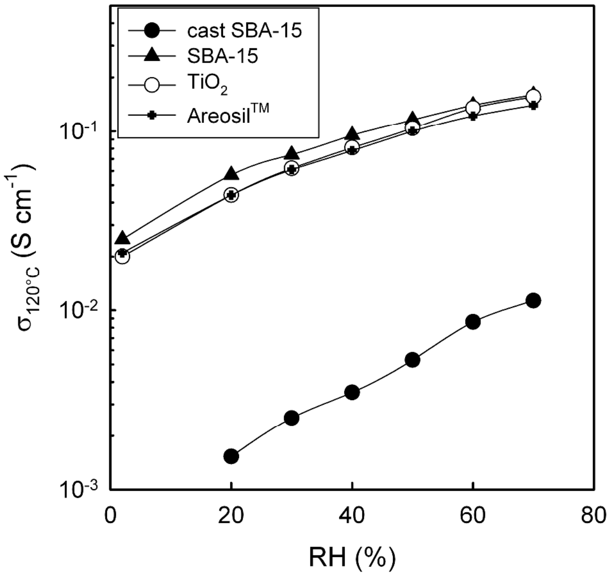


Fig. 3: Conductivity at 120°C vs. RH% of the PBI-based composite membranes filled with different inorganic solids (10 wt%) and prepared by spraying method. The results of a cast PBI membrane with 10 wt% SBA-15 is also reported for comparison.

By comparing the three systems obtained by spraying with that one by casting, we observe that the conductivity of the sprayed membranes is improved by more than one order-of-magnitude over the whole RH range. $\sigma_{120°C}$ of 2.5 mS cm^{-1} and 80 mS cm^{-1} were, for instance, measured at 30% RH in case of cast and sprayed PBI composites, respectively. This difference must be attributed to the improved filler distribution ensured by the spraying technique.

Furthermore, by means of this method, it is possible to disperse large amounts of particles in the polymer (up to 50 wt%) without any worsening of the mechanical performances and of conductivity, as generally observed in case of cast membranes. Figure 4 shows, as an example, the conductivity vs. SBA-15 content in PBI-based composites prepared by casting (circles) and by spraying (triangles).

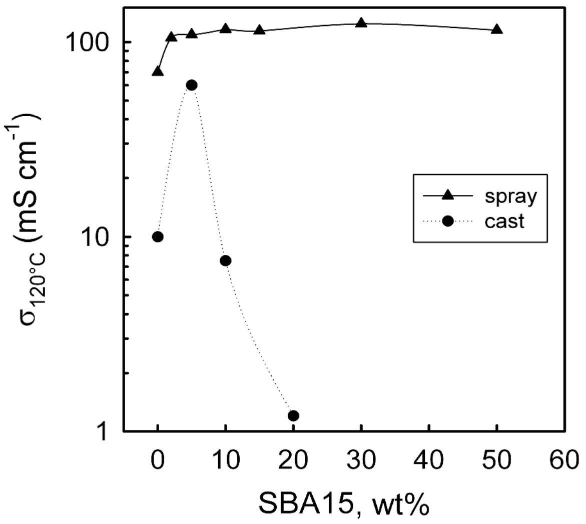


Fig. 4: Conductivity @120°C and RH=50% of the PBI-based composite membranes filled with different amounts of SBA-15, prepared by spraying (triangle) and casting (circles). The values of the cast electrolytes are taken from ref. 10.

The proton conductivity behaviour of the two electrolytes is drastically different. The sprayed membranes did not show conductivity maximum. The conductivity increases with respect to the unfilled system also for small amounts of SBA-15, reaching a plateau at about 0.1 S cm^{-1} for silica contents of 10 wt% [10]. In contrast, in case of the cast membrane, the conductivity is peaked at 5 wt% of SBA-15, but a dramatic drop of about 2 orders-of-magnitude is observed for higher filler amounts. The worsening of the transport properties is reasonably related to the particle segregation phenomena occurring in presence of high filler concentration, as evidenced in Figure 1. Even the proton conductivity of the unfilled membranes is improved by the preparation method, probably because of a better phase homogeneity.

The PBI-based composite membranes, produced by means of spraying procedure, were also characterised in terms of fuel cell performances (see Supporting Information). Figure S2 shows the polarization curves of the three investigated systems, collected at 150°C in absence of humidification. The two silica-based composites showed similar open circuit voltages, *OCV*s, of 0.9 V and very promising values of power density and voltage at 200 mA cm^{-2}, namely 350 mW cm^{-2} and 600 mV, respectively. In contrast, the cell including the TiO_2-based membrane showed worse performances with a peak of power density not exceeding 150 mW cm^{-2}. This result should be likely related to the large TiO_2 particle dimensions, ranging between 1 and 10 μm, which do not affect the proton transport, as already discussed before, but clearly negatively play on the electrochemical interface[13]. Measurements of impedance spectroscopy on MEAs (see Figure S3) show, in fact, a remarkably higher (roughly twice) cathodic resistance in case of the cell including PBI-TiO_2 membranes with respect to the other composite systems. This confirms the results of Lobato et al., who reported successful electrochemical performances only in case of MEAs with PBI composite electrolytes containing loadings of micro-sized titania not higher than 2 wt% [13, 16, 17].

The presence of cracks or pinholes, eventually caused by the dispersion of inorganic particles, was checked by means of measurements of H_2 permeability, which is a key parameter in the test protocols for the evaluation of the cell durability [21,22]. Figure S4 shows the gas permeation coefficients, k_{H2}, of the sprayed composite membranes, determined in the temperature range 70°-150°C. As expected, a linear trend is observed for each electrolyte. k_{H2} values of ~ 1.5 × $10^{□□□}$ mol cm^{-1} s^{-1} Pa^{-1} at 150°C are calculated for all the composite membranes. These values are comparable to what found for the unfilled systems (namely 1.54× $10^{□□□}$ mol cm^{-1} s^{-1} Pa^{-1} at 150°C) [8] and they are also remarkably lower than those ones recently obtained by Li. et al. in case of PBI filled by organically-modified clays [18]. This suggests that the presence of well-distributed fillers in composite membranes does preserve the low gas permeability typical of the PBI-based membranes. The activation energies for hydrogen permeation were estimated to be 16.4 kJ mol^{-1} in case of SBA-15, 13.9 kJ mol^{-1} for Areosil® and 9.4 kJ mol^{-1} for TiO_2-based composite membranes. Higher $E_{a.H2}$ of about 21 kJ mol^{-1} were reported for Nafion membranes in the temperature range between 25 and 80° C under fuel cells conditions [23].

In conclusion, we reported a spraying technique as a powerful method, alternative to conventional casting, to produce optimal PBI-composite membranes for HT-PEMFCs. This facile and fast approach allowed preparing very homogeneous composite films, independent on the filler microstructure and chemical nature. With respect to the casting, it offers the following benefits: i) good free-standing performances, even in presence of high filler loadings (at least up to 50 wt%), ii) absence of particle aggregation and precipitation, iii) thickness homogeneity better than 98%; iv) improved filler/polymer interface, even in case of fillers with particle sizes of several microns. All these features are at the basis of a proton conductivity enhancement of more than one order-of-magnitude with respect to what obtained in case of cast composite membranes. Spraying is also a cheap and green methodology, which could be easily scaled-up for industrial applications.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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