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## 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 polybenzimidazole (PA-PBI) membranes are the most promising alternatives to Nafion as proton-conducting electrolytes in proton exchange membrane fuel cells (PEMFCs).<sup>1</sup> Besides the high thermal and mechanical stability, such polymers show high proton conductivity exceeding  $0.1 \text{ S cm}^{-1}$  at  $150 \text{ }^\circ\text{C}$  and low humidification.<sup>2,3</sup> Despite 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<sup>4</sup> and (ii) ensuring an efficient proton transport also by using a lower amount of PA. To achieve this aim, several approaches have been discussed in the literature,<sup>4,5-8</sup> among which the design of composite membranes including nanoscale and/or mesoporous inorganic fillers, when properly functionalised, seems to be particularly encouraging.<sup>2,9,10</sup> PBI composite systems show increased proton conductivity, at the same time maintaining good mechanical and chemical properties.<sup>11</sup> In addition, some fillers, such as imidazole-derivatized silica and  $\text{TiO}_2$ , have beneficial effects in the implementation of the membrane acid retention capacity, as well as on the fuel cell

performances at high temperature.<sup>12,13</sup> An optimal composite membrane must have an extended and uniform polymer/filler interphase, which requires a highly homogeneous dispersion of the particles.<sup>14-16</sup> 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 suitable 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 ( $T > 180 \text{ }^\circ\text{C}$ ). 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 leading to drastic phase inhomogeneity. This phenomenon is particularly frequent in the presence of high filler loadings. As a matter of fact, only PBI-based composites with the filler content lower than 5 wt% were considered suitable as electrolytes in a membrane/electrode assembly.<sup>16,17</sup>

Here we report on an easy and effective method to prepare highly homogeneous PBI composite 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 the solvent amount, carrier gas flow and substrate temperature. Three inorganic fillers were 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  $\text{SiO}_2$  (AeroSil<sup>®</sup> RX50) and commercial micro-sized  $\text{TiO}_2$  (Aldrich). PBI composite membranes with filler loadings up to 50 wt% and a thickness of about  $50 \text{ } \mu\text{m}$  were easily produced. The homogeneity level of the filler dispersion was monitored by means of SEM-EDAX investigations. PBI composite electrolytes were characterised in terms of the PA doping level, proton transport, hydrogen crossover and electrochemical tests on properly assembled cells. The functional properties of

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these composite conducting membranes were compared to those of the 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 an appropriate amount of poly-2,2'-(2,6-pyridine)-5,5'-bibenzimidazole (PBI) in a DMA-sec-butylamine solution including various amounts of the 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 ESI.†

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

In the presence of the filler, the inorganic particles were immediately “fixed” in the polymer matrix preventing settling processes. Fig. 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 ESI† (Fig. S1a) for the sake of comparison.

The films obtained by 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 of the particle dimensions. SEM-EDAX microanalysis was carried out to obtain information on the filler distribution in the polymer. Fig. 2 shows the Si maps for the PBI samples filled with the two types of silica (a and b), and the Ti map for the  $\text{TiO}_2$ -based

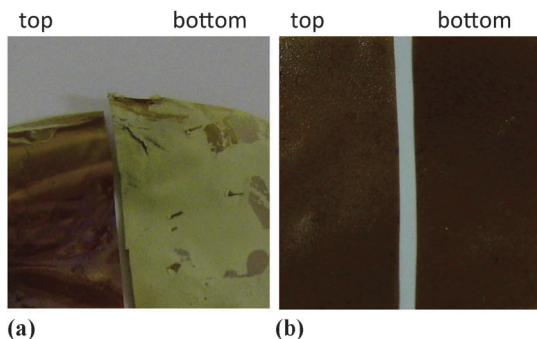


Fig. 1 PBI-composite membranes filled with 30 wt% of SBA-15, produced by casting (a) and spraying (b).

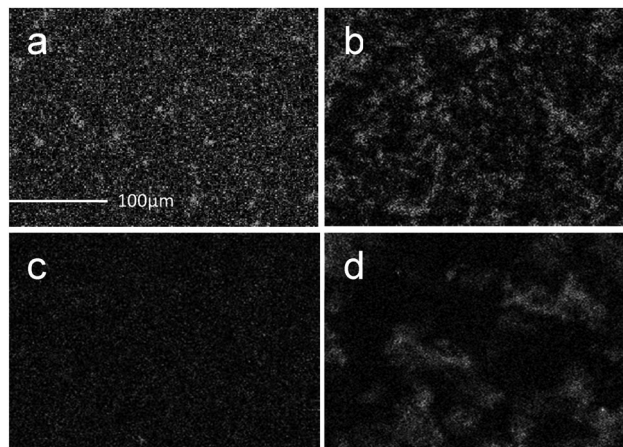


Fig. 2 SEM-EDAX images of the PBI composite membranes with different fillers prepared by spraying: (a) SBA-15; (b) AeroSil®R50; and (c)  $\text{TiO}_2$ . A composite including  $\text{SiO}_2$  nanoparticles (HiSil), obtained by conventional casting, is shown for comparison (d, taken from ref. 19). The bar is the same for all the images.

composite (c). The image of a cast PBI membrane including  $\text{SiO}_2$  nanoparticles (HiSil™) is also reported for the sake of comparison (d).<sup>19</sup> The filler loading is 10 wt% for each investigated system. We can observe that the filler dispersion is quite homogeneous in the case of the sprayed membranes, even in the presence of micro-sized fillers like  $\text{TiO}_2$ , whose particle dimensions range between 1 and 10  $\mu\text{m}$ . A similar quality of dispersion was achieved only in the presence of additives with very high filler/polymer compatibility, such as imidazole-functionalised silica or organically modified clays.<sup>12,18</sup> In contrast, the cast membrane shows large aggregates in the micrometer range, which became larger and more continuous by increasing the silica content.<sup>19</sup>

A more homogeneous filler distribution in the PBI composite membranes seems to greatly affect the proton transport. Fig. 3 shows the conductivity vs. relative humidity (RH%) curve 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. relative humidity for the unfilled system are available in the ESI† (see Fig. S1b). All the sprayed films showed similar conductivity, independent of the filler microstructure, chemical nature and particle size. Values between 20 and 100  $\text{mS cm}^{-1}$  were measured at 120 °C in the explored humidity range (0–70 RH%). Conductivity values exceeding 70  $\text{mS cm}^{-1}$  were obtained at low moisture levels, and this aspect is very encouraging considering that such targets are hardly achieved by Nafion and Nafion-like membranes under similar operating conditions (120 °C and below 40 RH%).<sup>20</sup>

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

By comparing the three systems obtained by spraying with those obtained by casting, we observed that the conductivity of the sprayed membranes is improved by more than one

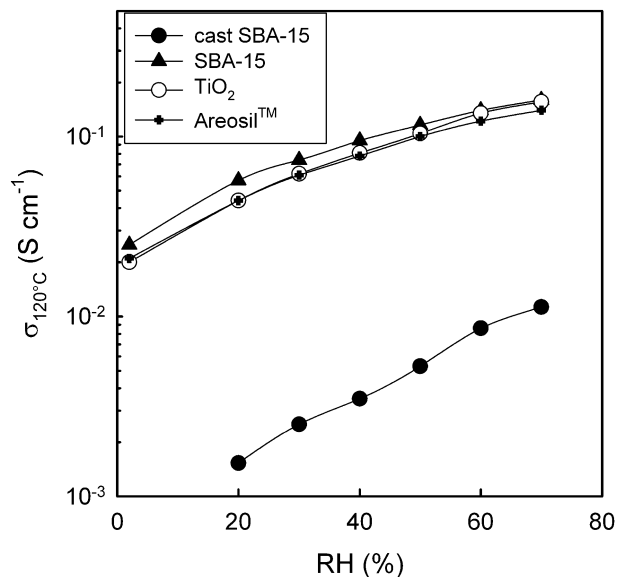


Fig. 3 Conductivity at 120 °C vs. RH% of the PBI-based composite membranes filled with different inorganic solids (10 wt%) and prepared by the spraying method. The results of a cast PBI membrane with 10 wt% SBA-15 is also reported for comparison.

order-of-magnitude over the whole RH range.  $\sigma_{120\text{ }^\circ\text{C}}$  values of  $2.5\text{ mS cm}^{-1}$  and  $80\text{ mS cm}^{-1}$  were, for instance, measured at 30% RH in the 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 the case of cast membranes. Fig. 4 shows, as an example, the conductivity values vs. the SBA-15

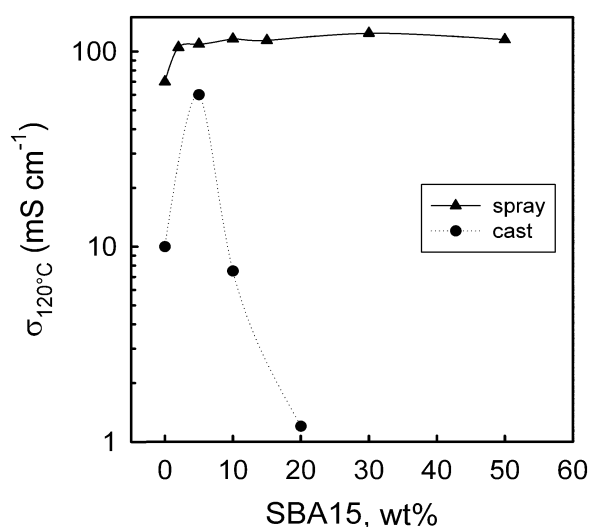


Fig. 4 Conductivity at 120 °C and RH = 50% of the PBI-based composite membranes filled with different amounts of SBA-15, prepared by spraying (triangle) and casting (circles). The values of the cast electrolytes are taken from ref. 10.

content in PBI-based composites prepared by casting (circles) and by spraying (triangles).

The proton conductivity behaviour of the two electrolytes is drastically different. The sprayed membranes did not show the conductivity maximum. The conductivity increases with respect to the unfilled system also for small amounts of SBA-15, reaching a plateau at about  $0.1\text{ S cm}^{-1}$  for silica contents of 10 wt%.<sup>10</sup> In contrast, in the 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 at a high filler concentration, as evidenced in Fig. 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 the spraying procedure, were also characterised in terms of fuel cell performances (see ESI†). Fig. S2 (ESI†) shows the polarization curves of the three investigated systems, collected at 150 °C in the absence of humidification. The two silica-based composites showed a similar open circuit voltage, OCV, of 0.9 V and very promising power density and voltage values at  $200\text{ mA cm}^{-2}$ , namely  $350\text{ mW cm}^{-2}$  and 600 mV, respectively. In contrast, the cell including the  $\text{TiO}_2$ -based membrane showed worst performances with the peak of power density not exceeding  $150\text{ mW cm}^{-2}$ . These results are likely due to the large  $\text{TiO}_2$  particle dimensions, ranging between 1 and  $10\text{ }\mu\text{m}$ , which do not affect the proton transport, as already discussed before, but clearly have a negative impact on the electrochemical interface.<sup>13</sup> Measurements of impedance spectroscopy on MEAs (see Fig. S3, ESI†) show, in fact, a remarkably higher (roughly twice) cathodic resistance in the case of the cell including PBI- $\text{TiO}_2$  membranes with respect to the other composite systems. This confirms the results of Lobato *et al.*, who reported successful electrochemical performances only in the case of MEAs with PBI composite electrolytes containing loadings of micro-sized titania not higher than 2 wt%.<sup>13,16,17</sup>

The presence of cracks or pinholes, eventually caused by the dispersion of inorganic particles, was checked by means of measurements of  $\text{H}_2$  permeability, which is a key parameter in the test protocols for the evaluation of the cell durability.<sup>21,22</sup> Fig. S4, ESI† shows the gas permeation coefficients,  $k_{\text{H}_2}$ , of the sprayed composite membranes, determined in the temperature range 70–150 °C. As expected, a linear trend is observed for each electrolyte.  $k_{\text{H}_2}$  values of  $\sim 1.5 \times 10^{-15}\text{ mol cm}^{-1}\text{ s}^{-1}\text{ Pa}^{-1}$  at 150 °C are calculated for all the composite membranes. These values are comparable to those found for the unfilled systems (*i.e.*,  $1.54 \times 10^{-15}\text{ mol cm}^{-1}\text{ s}^{-1}\text{ Pa}^{-1}$  at 150 °C)<sup>8</sup> and they are also remarkably lower than those recently obtained by Li *et al.* in the case of PBI-based membranes filled by organically modified clays.<sup>18</sup> This suggests that the presence of well-distributed fillers in composite membranes preserves the low gas permeability typical of the PBI-based membranes. The activation energies for hydrogen permeation were estimated to be  $16.4\text{ kJ mol}^{-1}$  in the case of SBA-15,  $13.9\text{ kJ mol}^{-1}$  for

Aerosil<sup>®</sup> and 9.4 kJ mol<sup>-1</sup> for TiO<sub>2</sub>-based composite membranes. A higher  $E_{a,H_2}$  of about 21 kJ mol<sup>-1</sup> was reported for Nafion membranes in the temperature range between 25 and 80 °C under fuel cells conditions.<sup>23</sup>

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 preparation of very homogeneous composite films, independent of the filler microstructure and chemical nature. With respect to casting, it offers the following benefits: (i) good free-standing performances, even in the presence of high filler loadings (at least up to 50 wt%), (ii) the absence of particle aggregation and precipitation, (iii) thickness homogeneity better than 98%, and (iv) an improved filler/polymer interface, even in the case of fillers with particle sizes of several microns. All these features form the basis of a proton conductivity enhancement of more than one order-of-magnitude with respect to what is obtained in the 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

- DOE Fuel Cells Technical Plan, Hydrogen and Fuel Cells Programs (2012), [www.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel\\_cells.pdf](http://www.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf), accessed February 2014.
- Q. Li, J. O. Jensen, R. F. Savinell and N. J. Bjerrum, *Prog. Polym. Sci.*, 2009, **34**, 449.
- J. A. Asensio, E. M. Sanchez and P. Gomez-Romero, *Chem. Soc. Rev.*, 2010, **39**, 3210.
- E. Quartarone and P. Mustarelli, *Energy Environ. Sci.*, 2012, **5**, 6436.
- S. Subianto, *Polym. Int.*, 2014, **63**, 1134.
- A. Carollo, E. Quartarone, C. Tomasi, P. Mustarelli, F. Belotti, A. Magistris, F. Maestroni, M. Parachini, L. Garlaschelli and P. P. Righetti, *J. Power Sources*, 2006, **160**, 175.
- S. Angioni, D. C. Villa, S. Dal Barco, E. Quartarone, P. Mustarelli, C. Tomasi and P. P. Righetti, *J. Mater. Chem. A*, 2014, **2**, 663.
- D. C. Villa, S. Angioni, S. Dal Barco, P. Mustarelli and E. Quartarone, *Adv. Energy Mater.*, 2014, **4**, 1031949.
- E. Quartarone, P. Mustarelli, A. Carollo, S. Grandi, A. Magistris and C. Gerbaldi, *Fuel Cells*, 2009, **9**, 231.
- E. Quartarone, A. Magistris, P. Mustarelli, S. Grandi, A. Carollo, G. Z. Zukowska, J. E. Garbaeczyk, J. L. Nowinski, C. Gerbaldi and S. Bodoardo, *Fuel Cells*, 2009, **9**, 349.
- V. Di Noto, M. Piga, G. A. Giffin, E. Quartarone, P. P. Righetti, P. Mustarelli and A. Magistris, *Phys. Chem. Chem. Phys.*, 2011, **13**, 12146.
- P. Mustarelli, E. Quartarone, S. Grandi, A. Carollo and A. Magistris, *Adv. Mater.*, 2008, **20**, 1339.
- F. J. Pinar, P. Canizares, M. A. Rodrigo, D. Úbeda and J. Lobato, *RSC Adv.*, 2012, **2**, 1547.
- Z. Chen, B. Holmberg, W. Li, X. Wang, W. Deng, R. Munoz and Y. Yan, *Chem. Mater.*, 2006, **18**, 5669.
- E. Quartarone, P. Mustarelli and A. Magistris, *Solid State Ionics*, 1998, **110**, 1.
- J. Lobato, P. Canizares, M. A. Rodrigo, D. Úbeda and F. J. Pinar, *J. Power Sources*, 2011, **196**, 8265.
- J. Lobato, P. Canizares, M. A. Rodrigo, D. Úbeda and F. J. Pinar, *J. Membr. Sci.*, 2011, **369**, 105.
- D. Plackett, A. Siu, Q. Li, C. Pan, J. O. Jensen, S. F. Nielsen, A. A. Permyakova and N. J. Bjerrum, *J. Membr. Sci.*, 2011, **383**, 78.
- P. Mustarelli, A. Carollo, S. Grandi, E. Quartarone, C. Tomasi, S. Leonardi and A. Magistris, *Fuel Cells*, 2007, **7**, 441.
- H. Zhang and P. K. Shen, *Chem. Rev.*, 2012, **112**, 2780.
- A. D. Modestov, M. R. Tarasevich, V. Ya. Filimonov and N. M. Zagudaeva, *Electrochim. Acta*, 2009, **54**, 7121.
- Y. Oono, A. Sounai and M. Hori, *J. Power Sources*, 2012, **210**, 366.
- S. S. Kocha, J. D. Yang and J. S. Yi, *AIChE J.*, 2006, **52**, 1916.