Supplementary Info.

Facile and green assembly of nanocomposite membranes for fuel cells

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Materials and Methods

PBI-based composite membranes were prepared with different amounts of inorganic particles (up to 50 wt%). The chosen polymer was poly-2,2'-(2,6-pyridine)-5,5'-bibenzimidazole (PBI-5N), synthetized as described in the following. Three different types of inorganic fillers were used for the preparation of PBI-based composite membranes: a) micrometric mesoporous silica SBA-15; b) micrometric TiO_2; c) micrometric silica Aerosil®RX-50. Table 1 reports some microstructural features of such inorganic particles.

	BET Surface area (m^2/g)	Particles size (μm)	Pores size (nm)
SBA-15	1285	0,1	6-7
Aerosil	42,1	0,1	2-25
TiO_2	-	1-10	-

Table 1: Microstructual properties of the inorganic fillers.

SBA-15 was synthetized by means of standard acid hydrolysis/condensation process, starting from tetraethoxysilane (TEOS) and pluronic as a template in hydrothermal conditions (see Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548). Commercial TiO_2 and Aerosil®RX-50 were purchased from Sigma-Aldrich and Degussa, respectively.

Synthesis of poly-2,2'-(2,6-pyridine)-5,5'-bibenzimidazole (PBI-5N)

Poly-2,2'-(2,6-pyridine)-5,5'-bibenzimidazole (PBI) was prepared by polycondesation of 3,3'-diaminobenzidine(DAB) and 2,6-pyridinedicarboxylic acid (PDA) in polyphosphoric acid (PPA, 85% P_2O_5), as already reported in details elsewhere (Carollo, A.; Quartarone, E.; Tomasi, C.; Mustarelli, P.; Belotti, F.; Magistris, A.; Maestroni, F.; Parachini, M.; Garlaschelli, L.; Righetti, P. *Journal of Power Sources* **2006**, *160*, 175). DAB and PDA were dissolved in PPA and polymerized at 200 ◦C under nitrogen atmosphere for 30 h. After the condensation reaction, the polymer were soaked in distilled water, in order to eliminate any residual of monomer and PPA, and subsequently treated with a saturated K_2CO_3 solution. The polymer was then washed in boiling water overnight, and finally dried under vacuum for 24 h. The PBI inherent viscosity, η, was 0.7 g dl^{-1}.

Synthesis of SBA-15 silica

SBA-15 silica was synthesized by a sol-gel route. A solution of P123 template in HCl 1.9 M was prepared in a Teflon flask, pre-heated at 40°C and mixed to TEOS. The resulting mixture was left under stirring for 20 h at 50 °C and then transferred into a Teflon bottle and heated at 100 °C for 24 h. After cooling at room temperature, the solid product was recovered by filtration, washed with distilled water, and dried in air at ambient temperature. The template was removed refluxing the obtained product with ethanol for 48 h.

Preparation of composite membrane: the spraying method

A proper amount of polymer powder was dissolved in a sealed flask at 120°C in a DMA/sec-butylamine (8:2) solution. Various amounts of filler were added, in the range 2-50 % w/w with respect to the pristine polymer, and the mixture was sonicated for ½ h. The suspension was finally sprayed under N_2 flux onto a hot plate (150°C) in a ventilated special chamber. The obtained film was peeled out from the cooled plate and washed in deionized water overnight. Film thickness of about 50 μm was obtained, with a thickness homogeneity of about 98%.

The composite membranes were then doped in a phosphoric acid (PA) solution (70% w/w) for 24 h and dried at 110°C for 2 h. The doping level (*DL*) was calculated as in the following:

$$DL\ (\%) = \frac{(Wp - Wd)}{Wd} \times 100$$

where W_p and W_d are the weights of the doped and undoped membranes, respectively.

Characterization

The inherent viscosity measurements were carried out by an Ubbelohde viscosimeter at 50°C in sulfuric acid. Scanning electron microscopy images were collected with a variable pressure Scanning Electron Microscope VEGA TS 5136 (Vega- Tescan), equipped with the EDAX microanalysis accessory, using an accelerating voltage of 20 kV.

The proton conductivity was measured by means of the impedance spectroscopy technique, using a frequency response analyser (FRA Solartron 1255), connected to an electrochemical interface (Solartron 1287), over the frequency range 1 Hz-1 MHz at a voltage of 100 mV. The membrane was fixed to a four-points BekkTech conductivity cell, connected to the test stand BekkTech 411 for the humidity and temperature control. The impedance scans were performed at 120°C ranging from 0 to 70% R.H. with a cell back-pressure of 2.5 bar. The films were allowed to equilibrate 1 hour at each moisture level before of the measurements. The impedance spectra were fitted with the ZView 3.0 software (Scribner Associates, Inc.).

The membrane electrode assemblies (MEAs) were prepared by hot pressing two gas diffusion electrodes (GDE HT-ELAT, ETek) at 130°C and 1 ton for 10 minutes. The Pt loading was 0.5 mg cm^{-2} at both the electrodes. The cell active area was 5 cm^2. The electrochemical measurements were performed at 150°C with a BT-552 Membrane Conductivity & Single Cell Fuel Cell Test System (BekkTech LLC). The cell was operated at ambient pressure without external humidification of the feed gas steams. In some cases an overpressure was imposed to the cell. The H_2 and air flow rates were 70 sccm and 300 sccm, respectively.

Hydrogen crossover measurements were carried out in the temperature range 70 -150°C by means of potentiodynamic scans between 0 and 0.7V. The cathode gas flow was switched from air to nitrogen, with a flow rate of 400 sccm at 1 bar, whereas the anode hydrogen flow was set at 200 sccm at the same pressure. The anode was taken as both counter and reference electrode, whereas the cathode served as the working one. A potentiostatic assessment at the voltage plateau (0.3V) was finally performed to measure the current through the fuel cell for 15 minutes at each temperature.

Fig.S1a: Unfilled PBI membrane produced by spraying.

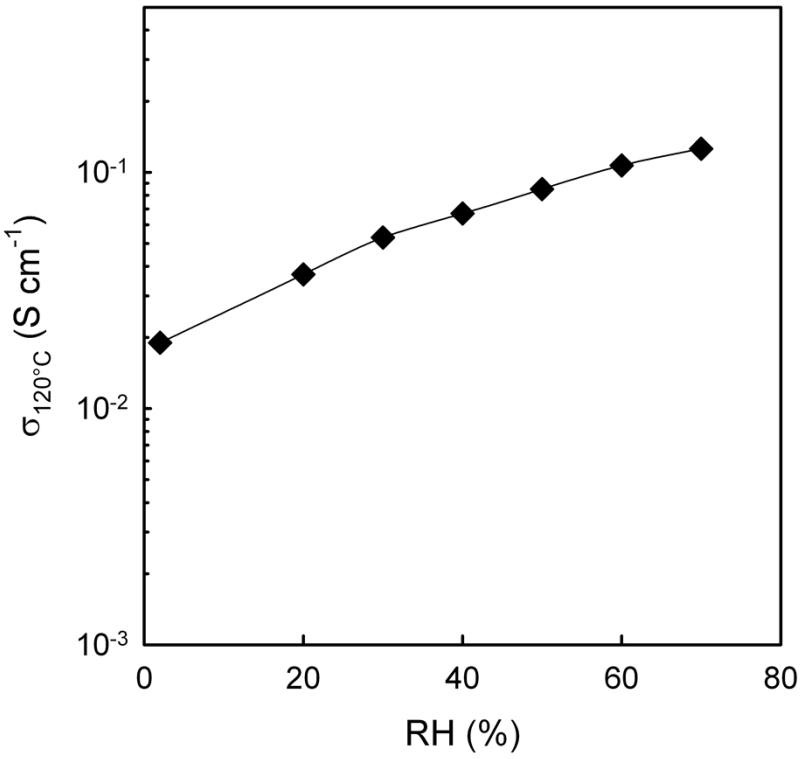
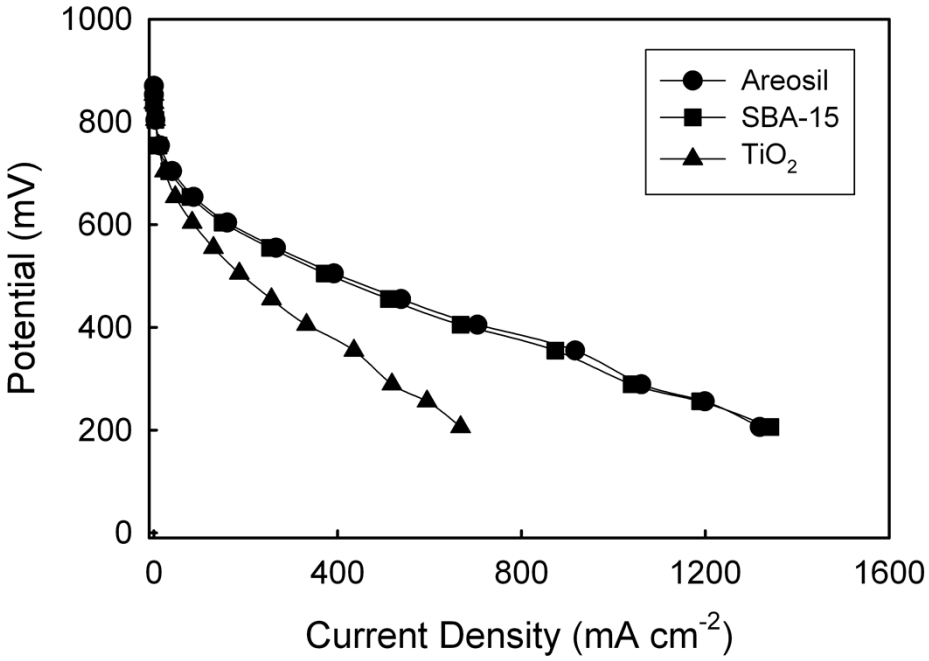
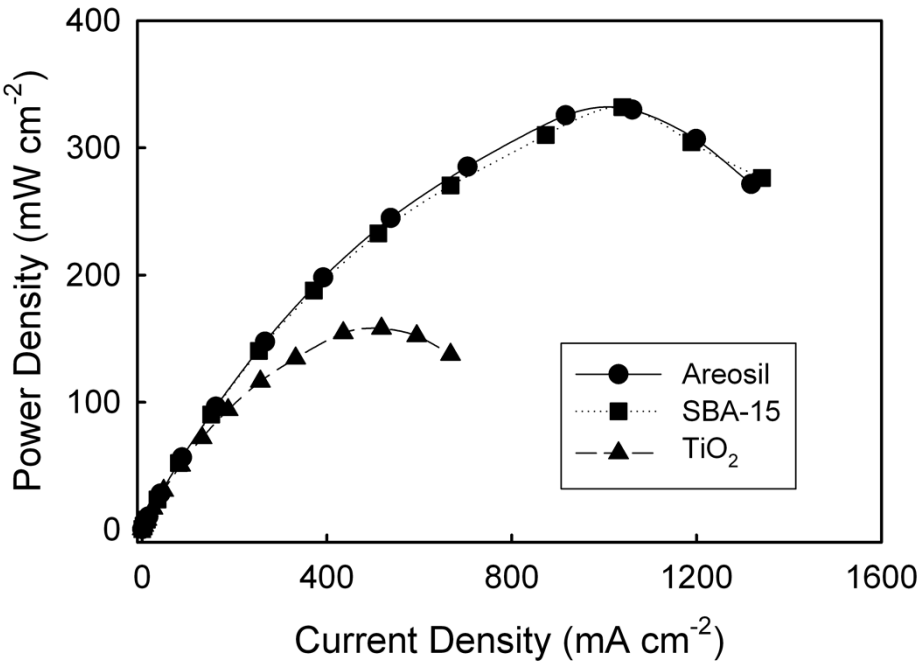


Fig.S1b: Proton conductivity vs Relative Humidity (RH%) of the unfilled PBI membrane produced by spraying.



(a)



(b)

Fig.S2: Polarization (a) and power density (b) curves collected at 150°C without humidification for MEAs including PBI composites as electrolytes (10 wt% of filler).

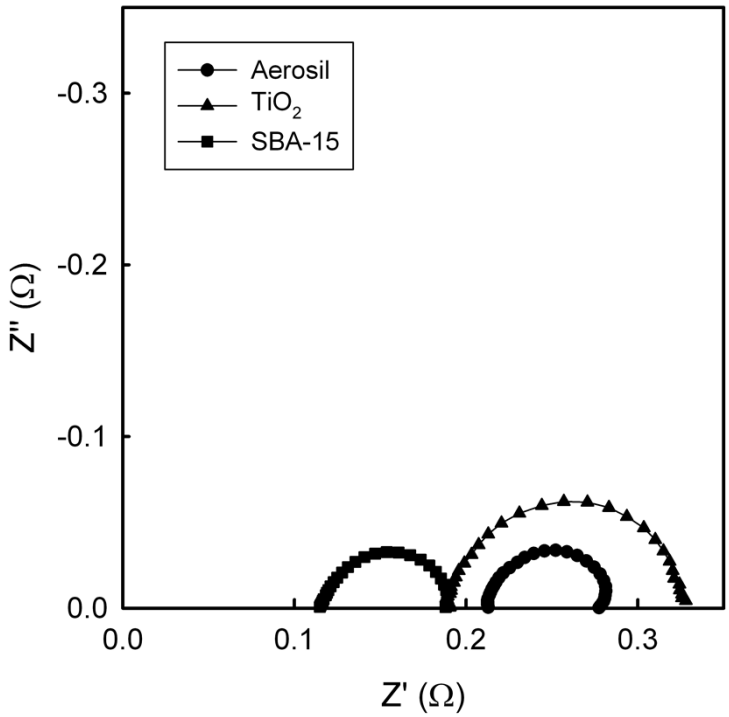


Fig.S3: Impedance Spectra collected at 150°C without external humidification for MEAs including PBI-based composite membranes (10 wt% of filler)

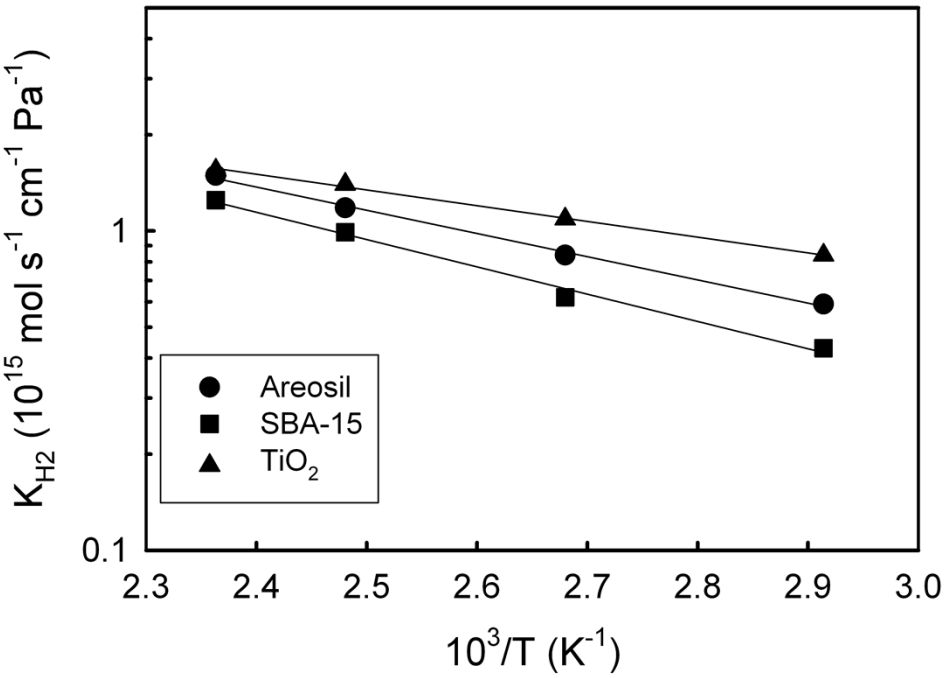


Fig.S4: Arrhenius behavior of the hydrogen permeability coefficients for the PBI-based composite membranes (10 wt% of filler)