# Polybenzimidazole/Silica Nanocomposites: Organic-Inorganic Hybrid Membranes for PEM Fuel Cell

Sandip Ghosh, Sudhangshu Maity and Tushar Jana<sup>\*</sup>

School of Chemistry University of Hyderabad Hyderabad, India Tel: (+91) 40 23134808 Fax: (+91) 40 23012460 E-mail: tjsc@uohyd.ernet.in tjscuoh@gmail.com

(\* To whom correspondence should be addressed)

# **Electronic Supplementary Information**

#### Materials.

3, 3', 4, 4'- tetraaminobiphenyl (TAB, polymer grade), 4, 4'-oxybis (benzoic acid) (OBA) and polyphosphoric acid (PPA, 115 %) were purchased from Sigma-Aldrich. Formic acid (FA) (99%) was purchased from Qualigens, India and tetraethylortho silicate (TEOS) was purchased from Merck, India. 3-aminopropyltriethoxy silane (APTES) was purchased from Sigma-Aldrich. All chemicals were used as received.

#### **OPBI** synthesis.

The synthesis of OPBI was carried out by as per our method reported previously.<sup>1</sup> Briefly: equal moles of TAB and OBA were taken into three-neck round bottom flask along with polyphosphoric acid (PPA). The reaction mixture was stirred by using a mechanical overhead stirrer and slow stream of purged nitrogen gas was maintained throughout the reaction. The polymerization was carried out at 190-220°C for approximately 26 hours. The OPBI polymer was isolated, neutralized with sodium bicarbonate, washed thoroughly with water and finally dried in vacuum oven for 48 hours at 100°C. The dried polymer was characterized by measuring the viscosity in concentrated sulfuric acid (98%) by using a Cannon Ubbelohde capillary dilution viscometer (model F725). The synthesized OPBI has an inherent viscosity (I.V.) value of 2.29 dL/g at 30°C. The concentration of the polymer solution for the viscosity measurement was 0.2 g/dL.

#### Synthesis of silica nanoparticle and its surface modification.

Silica nanoparticles were prepared by hydrolysis and condensation of TEOS (10.7 mmol) in ethanol, and in presence of 28% ammonia as catalyst, as described by Stöber et al.<sup>2</sup> First, solution containing appropriate quantities of absolute ethanol, ammonia and deionized water were stirred for 5 minutes to ensure complete mixing. Then a certain amount of TEOS in absolute ethanol was added to the above solution and the reaction was carried out at ambient temperature for 24 hours. The colloidal solution

was separated by centrifugation, and the silica nanoparticles were washed by absolute ethanol for three times, followed by drying in oven at 100°C for 6 hrs. The average size of the silica nanoparticle is ~50 nm as obtained from TEM images. The silica nanoparticles were dispersed in ethanol followed by the addition of APTES (12.9 mmol) as described earlier.<sup>3</sup> The above mixture was stirred for 6 h at reflux conditions. Again the surface modified silica nanoparticles were separated from dispersed solution of ethanol in a similar way as it was done in case of silica particles described above. The average size of the silica nanoparticle is ~90 nm as obtained from TEM images.

#### Spectral characterization.

The FT-IR spectra of the OPBI and its nanocomposite membranes were recorded on a (Nicolet 5700 FT-IR) FT-IR spectrometer. The infrared spectra were obtained in the region 3900-600 cm<sup>-1</sup>. Solid state <sup>13</sup>C CPMAS NMR spectra were obtained on a Bruker AV 400 MHz NMR instrument operating at 100 MHz at a spinning rate of 5 kHz and a contact time of 2 ms.

### X-ray study.

X-ray diffraction was used in this study to investigate the structure of the OPBI nanocomposites. The small angle X-ray diffraction (SAXD) experiment of the OPBI film and its nanocomposites were carried out on a Hecus X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418$ Å) source operated at voltage of 50 kV and 1 mA current and the wide angle X-ray diffraction (WAXD) patterns of the samples were performed in an X-ray generator (Model PW 1729, Philips, Holland) with Cu K $\alpha$  radiation ( $\lambda = 1.5418$ Å) source operated at voltage of 40 kV and 30 mA current in the angular range (20) of 5-40°.

#### Morphology.

The distributions of the silica nanoparticles into the polymer matrix were examined by transmission electron microscope (TEM). For TEM study, a drop of samples prepared from FA was placed on a carbon coated copper (200 mesh) grid, dried and observed through the TEM instrument (FEI Tecnai Model No. 2083) operating at 200kV.

#### Thermal measurement.

Thermogravimeteric analysis is done to explain thermal decomposition behavior. The thermogravimetric analysis of OPBI and its nanocomposites membranes were carried out on a (Netzsch STA 409PC) TG-DTA instrument from 50 to 800°C with a scanning rate of 10° deg/min in the presence of nitrogen flow.

#### Dynamic mechanical study.

Dynamic mechanical analyses (DMA) of all the OPBI nanocomposite membranes were determined using a TA Instrument Mechanical Analyzer (DMA) Q800. The storage modulus, loss modulus, and tan  $\delta$  were measured at a heating rate of 4°Cmin<sup>-1</sup> under a preload force of 0.01N at a frequency of 10 Hz. The samples were annealed at 400°C for 30 min, then kept at 100°C isothermally for 20 min inside the DMA machine, and finally scanned from 100 to 400°C at a heating rate of 4°C/min.

#### Oxidative stability.

The stability of all the OPBI nanocomposite membranes to oxidation was investigated by immersing the membranes into Fenton's reagent (30 ppm FeSO<sub>4</sub> in 30%  $H_2O_2$ ) at 70°C. The oxidative stability was characterized by the expanded time variation up to 100 hours. The membranes were taken out at certain time intervals, dried in vacuum oven at 80°C overnight, and weights were recorded. The

oxidative stabilities of all the membranes were calculated as a weight remained after taking out the membranes from the Fenton's reagent.

#### Doping of OPBI and its nanocomposite membranes with phosphoric acid (PA).

The dried OPBI, OPBI/AMS and OPBI/UMS nanocomposite membranes with the above mentioned loading of silica nanoparticles made from FA were immersed into PA (85%) for 7 days to get free standing PA doped membranes.

#### PA doping level.

The PA doping level of all the OPBI nanocomposite membranes were determined by titrating of a preweighed piece of membrane sample with standardized sodium hydroxide solution with a Metrohm Titrino Titrator. The acid doping levels, expressed as moles of phosphoric acid per mole of PBI repeat unit, were calculated from the equation:

Acid doping level 
$$= \frac{V_{NaOH}C_{NaOH}}{W_{drv}}M_w$$

where,  $V_{NaOH}$  and  $C_{NaOH}$  are the volume and the molar concentration of the sodium hydroxide, respectively.  $W_{dry}$  is the dry polymer membrane weight and  $M_w$  is the molecular weight of the polymer repeat unit respectively. The acid doping level reported here are the average values obtained from three separate values, measured from three similar size membrane samples.

#### Water uptake and swelling ratio.

Water uptake and swelling ratio of the nanocomposite membranes were obtained by immersing the membranes in water for three days. The nanocomposite membranes were thoroughly vacuum dried for three days at 100°C. The length and weight of the membrane were measured. Then the membranes

were immersed in water for three days at room temperature. The wet membranes were quickly wiped to remove the surface water. Again the length and weight of the wet membrane were noted. Water uptake of the membranes were calculated as

Water Uptake = 
$$\frac{W_w - W_d}{W_d} \times 100\%$$

where,  $W_w$  and  $W_d$  are the weights of the wet and dry membranes, respectively. The swelling ratio of the membranes were calculated as

Swelling Ratio = 
$$\frac{L_w - L_d}{L_d} \times 100\%$$

where,  $L_w$  and  $L_d$  are the lengths of the wet and dry membranes, respectively. The water uptake and swelling ratio measurements of the membranes were carried out in triplicate independently with different pieces of membranes to check the reproducibility of the results.

#### Conductivity study.

Proton conductivities of all the nanocomposites membranes of OPBI were measured with a four-point probe technique. The impedance of the membrane was measured with an impedance analyzer by using a Zahner Impedance spectrometer (ZENNIUM PP211) over a frequency range from 1 Hz to 100 kHz. The acid loaded membrane was cut into a rectangular shape and mounted onto the in house built conductivity cell. The membranes were dried at 100°C by heating and holding at 100°C isothermally for 2 hours to remove the water from the membrane. The membrane samples were cooled in a vacuum oven and taken out before conductivity measurement in an effort to keep the samples dry. The conductivities of the samples were obtained from the direct- current potential difference between the two inner electrodes. The conductivity was calculated with the following equation:

$$\sigma = \frac{D}{RBL}$$

where,  $\sigma$  is the proton conductivity (S/cm), D is the distance between the electrodes, and B and L are the thickness and width of the gel sample, respectively. In all cases, R was obtained from the Nyquist plots.

## REFERRENCE

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- 2. W. Stöber and A. Fink, J. Colloi. Interf. Sci., 1968, 26, 62-69.
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**ESI Figure 1.** FT-IR spectra of the AMS, OPBI and OPBI nanocomposite membranes with the indicated AMS loading.



ESI Figure 2: WAXD patterns of OPBI and its composites with different percentage loading of UMS.



**ESI Figure 3:** Photographs of OPBI/AMS and the OPBI/UMS nanocomposite membranes.



ESI Figure 4: SAXS patterns of OPBI and its composites with different percentage loading of UMS.

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**ESI Figure 5.** Nyquist plots of (A) OPBI, (B) OPBI/4 wt% AMS, (C) OPBI/7 wt% AMS, (D) OPBI/10 wt% AMS, (E) OPBI/ 15wt% AMS, (F) OPBI/ 20wt% AMS and (G) OPBI/15 wt% UMS nanocomposites.

Sample	W510°C (%) <sup>a</sup>	$T_{20\%}$ (°C) <sup>b</sup>	W790°C (%) <sup>c</sup>
OPBI	66.76	116	58.74
OPBI/4wt% AMS	73.47	158	66.24
OPBI/7wt% AMS	75.58	205	68.05
OPBI/10wt% AMS	77.09	210	69.86
OPBI/15wt% AMS	77.99	226	70.46
OPBI/20wt% AMS	80.41	249	73.48
OPBI/15wt% UMS	69.46	191	62.35

ESI Table 1. Thermal stability data for all the OPBI nanocomposite membranes with the silica nanoparticles.

<sup>a</sup> Residual weight percentage at 510°C.
<sup>b</sup> Temperature at which 20% weight loss is observed.
<sup>c</sup> Residual weight percentage at 790°C.