Zwitterionic Functionalized Silica Copolymer based Crosslinked Organic-Inorganic Hybrid Membranes for Electrochemical Applications

Tina Chakrabarty, Ajay K. Singh, Vinod K. Shahi^{*}

Electro-Membrane Processes Division, Central Salt and Marine Chemicals Research Institute, Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar-364002 (Gujarat) India Tel: +91-278-2569445; Fax: +91-278-2567562/2566970; E-mail: <u>vkshahi@csmcri.org</u>; <u>vinodshahi1@yahoo.com</u>

S1. Cross-linking density

The cross-linking density, (ρ) of the developed membranes was calculated from the network theory of rubber elasticity using the following equation.

Cross-linking Density (
$$\rho$$
) = $\begin{pmatrix} E'/\\ 3d\phi RT \end{pmatrix}$ (1)

where the modulus, E', was determined from the measurements with a dynamic mechanical analyzer under 10 Hz frequency at 40°C temperature, d is the membrane density, φ is the front factor (where $\varphi = 1$), R is the universal gas constant, and T is the absolute temperature.

S2 Ion-exchange capacity (IEC)

IEC determines the number of exchangeable ionic groups (equivalents) per dry membrane weight. IEC was measured by the classical titration method as reported previously. Membrane samples with known dry weight were equilibrated in 1.0 M HCl for converting all charge sites into the H⁺ form. The membranes were then washed thoroughly with double distilled water to remove the last trace of acid. Then, they were equilibrated in a known volume of 1.0 (M) NaCl for 24 h to replace the H⁺ by Na⁺ ions. The remaining solution was titrated against 0.1 (M) NaOH solution using phenolphthalein as an indicator.

S3 Water uptake, and state water

The swelling ratio (S_w) for ZI membranes was determined by water uptake measurement using following equation (1):

$$S_{w}(\%) = \frac{(m_{s} - m_{D})}{m_{D}} \times 100$$
 (1)

Where m_D is weight of dry membrane and m_s is weight of wet membrane after wipe out surface water by absorbing paper.

State of water freezing water (loosely bound and free water) and non-freezing water (bound water)) in fully swelled membranes were analyzed by DSC studies using a low-temperature measuring head and a liquid-nitrogen-cooled heating element. The state of water was determined by a melting transition in DSC measurements as described elsewhere. The membrane samples were cooled from +25 to -50 °C and then heated at a rate of 2 °C/min up to +50 °C. The peak area of the melt endotherm obtained by integration was used for the estimation of bulk water. The degree of crystallinity of the water, obtained from the heat of fusion of pure ice, 333.5 J/g, was used as a standard. Water mobility during the dynamic deswelling test, determined water retention ability of the prepared membranes, as described earlier.

S4 Dimensional, oxidative and hydrolytic stabilities

Dimensional stability of the membranes were investigated by recording the dimensions of (square pieces) fully dried and refluxed in water at 70 °C for 12 h, membrane samples, described earlier. Dimensional stability is expressed in terms of change in volume fraction (Φ). Oxidative stability was assessed by treating the membrane in Fenton's reagent (3% H₂O₂ containing 3 ppm FeSO₄) at 80 °C for 1 h. Oxidative stability was expressed in terms of weight and ion-exchange capacity loss. For the hydrolytic stability test, a small piece of membrane was boiled in water for 24 h at 140 °C in a pressurized closed vial. The stability was evaluated by the weight and ion-exchange loss for the membrane before and after treatment.



Fig. S1. SEM images (Surface) for Si-70% and Si-50% ZIMs.



Fig. S2. TGA curves for different ZIMs.



Fig. S3. DSC thermograms for different ZIMs.



Fig. S4. DMA curves for different ZIMs at 10° C/min heating rate under N₂ atmosphere; (inset) effect of ZI content on cross-linking density.



Fig. S5. Membrane conductivity vs T^{1} (Arrhenius plot) for different ZIMs in a 100% RH.



Fig. S6. Variation in Electro-osmotic flux for different ZIMs in equilibration with 0.02 M NaCl solution.