MATERIALS AND METHODS

Equipments

Instruments for characterization of composite membranes

3.1 Fourier Transforms Infrared Spectroscopy, FTIR (Perkin Elmer FTIR spectrum GX)

3.2 Nuclear Magnetic Resonance Spectroscopy, NMR

3.3 Thermo Gravimetric analysis, TGA (STD 2960 Simultaneous DSC-TGA)

3.4 Differential scanning calorimetry, DSC (STD 2960 Simultameous DSC-TGA)

3.5 Scanning electron microscopy, SEM (Jeol JSM-56002v)

3.6 Instron mechanical testing machine (Hounsfield H50KS)

Chemical Substances

1. Chemicals for synthesis of sulfonated poly(arylene ether sulfone)

1.1 Poly (arylene ether sulfone), PPSU (Solvay Radel-R®)

1.2 Chloroform (BDH AnalaR®)

1.3 Toluene (Carlo Erba)

1.4 Fuming sulfuric acid 65% SO_3 (Merck)

1.5 Methanol (Carlo Erba)

2. Chemicals for Membrane preparation

2.1 N,N-Dimethylacetamind, DMAc (Carlo)

2.2 Phosphotangstic acid, PWA

2.3 Zeolite, ZSM-5

3. Chemicals for ion exchange capacity

3.1 Sodium chloride (Carlo Erba)

3.2 Sodium hydroxide (Merck)

3.3 Phenolphthalein

Methods

1. Synthesis of sulfonated poly (arylene ether sulfone)

The 30 g of poly(arylene ether sulfone) (PPSU) was dissolved in 300 ml of chloroform at ambient temperature in a 3-necked round bottom flask with an overhead mechanical stirrer. The solution was cooled to 2°C. The mixture of fuming sulfuric acid (15 ml) and chloroform (150 ml) was added. The reaction was allowed for 15 min. before being terminated by addition of fivefold of methanol in the reaction mixture. The precipitated sulfonated poly(arylene ether sulfone) (SPPSU) was washed several times with methanol and dried at 60°C in a vacuum oven.

2. Membrane casting

SPPSU membrane and composite membranes were prepared by solution casting using DMAc as a solvent. In this work, two different kinds of composite membranes, PWA mixed with SPPSU and PWA mixed with ZSM-5 and SPPSU, were of interest, and thus SPPSU/(PWA)-a% and SPPSU/(PWA/ZSM-cd)-a% were used to represent types of composite membrane accordingly. The percentage of weight of inorganic to the weight total of the membrane was substituted with a. For the SPPSU/(PWA/ZSM-cd)-a% composite membranes, c and d were used to represent the ratio of PWA and ZSM-5 that is 3 to 7 in this work.

For preparation of SPPSU/(PWA) membranes containing 9, 15, and 30 wt. % of PWA in SPPSU, the sulfonated polymer was first dissolved in DMAc and then an appropriate weight of PWA was added. The mixture was treated by an ultrasonic probe for 15 minutes, and was casted on a glass plate.

Membranes containing 5, 15, and 25 wt. % of PWA/ZSM-5 in SPPSU were prepared as following: the SPPSU was dissolved in DMAc. Next ZSM-5 was added into the solution and it was mixed by an ultrasonic probe. The PWA was then added into the solution and mixed by an ultrasonic probe. The mixture solution was casted onto a glass plate.

For the drying process, a vacuum oven was used, and all the samples were dried at 60°C for 24 h. The dried membranes were then peeled off from the glass plate and dried under vacuum at 80°C for another 24 h. The membranes were about 20-40 μm thick.

3. Characterization

3.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR was operated to confirm the sulfonate group of the sulfonated polymer. The spectra were measured on Perkin Elmer FTIR spectrum GX using thin polymer membranes.

3.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton (H) Nuclear Magnetic Resonance (H NMR) was used to obtain the chemical composition of the polymer. H NMR experiments were carried out by using DMSO-d6 as solvent (10%w/v).

3.3 Thermo Gravimetric Analysis (TGA)

Thermo Gravimetric Analysis (TGA) was performed to investigate the thermal stability and weight loss of the membranes by using the heating rate of 10° C/min from 50°C to 1000°C under nitrogen atmosphere and air.

3.4 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) measurements were performed on STD 2960 Simultaneous DSC-TGA at the heating rate of 10°C/min from 50°C to 1000°C under nitrogen atmosphere. The glass transition temperatures (T_g) of the polymers were reported as the midpoint of the step in the second heating run.

3.5 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was used to observe the distribution of inorganic using Jeol JSM-56002v.

4. Ion exchange capacity (IEC)

The titration technique was used to determine the IEC of the membranes. Firstly, the membrane was dried at 60°C for 24 h and measured the weight. The dried membranes in the proton form (H^+) were immersed in 60 ml of 1 M NaCl at 50-60°C for 24 h to exchange the H^+ ions with Na^+ ions. Then, the 60 ml of H^+ ions solution were titrated with a 0.01 N NaOH solution using phenolphthalein as the endpoint indicator.

5. Water uptake

The water uptake indicated the water contained in the membrane by calculating the weight differences between the fully hydrated and dried membranes. Firstly, the membranes were dried in a vacuum oven at 60°C for 24 h and weighed to determine the dry mass. Then, the membranes were immersed in DI water for 24 h, removed from the water, quickly dry-wiped, and immediately weighed to determine the dry mass. The water uptake was calculated by using eq. 1.

$$Water\ Uptake = \frac{(W_{wet} - W_{dry}) \times 100}{W_{dry}} \quad (1)$$

6. Tensile strength

The tensile strength of the membranes was carried out at a load speed of 0.2 mm/min by using Instron mechanical testing machine (Hounsfield H50KS). All of the membranes were initially cut with the area of 10 cm^2 (10 cm x 1 cm). Before test, membranes were stored at 25, 80, 100, and 120°C. In this work only 100 % relative humidity was of interest. The tensile test was carried out at ambient conditions.