CHAPTER III
EXPERIMENTAL

3.1 Materials

Titanium (IV) butoxide, glacial acetic acid, and methyl alcohol were purchased from Italmar. The Poly(vinylidene fluoride) (PVDF) powder samples were supported by Solvay (#1008). N,N-Dimetyl formamide (DMF) and were purchased from Lab Scan. Antimony (V) chloride and polyacrylonitrile (PAN) were purchased from S.M. Chemical. All chemicals are used without further purification.

3.2 Instruments

3.2.1 X-Ray Diffraction (XRD)

Characterization of crystal structure of the samples were obtained from a Rigaku X-ray diffractometer (XRD) system equipped with a RINT 2000 wide angle goniometer and a Cu tube for generating a CuK 1 radiation (= 1.54 A°) was used to obtain the X-ray diffraction patterns at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter was used as the Kβ filter. The goniometer parameters were divergence slit = 1 ° (2θ); scattering slit = 1 ° (2θ); and receiving slit = 0.3 nm. Sample was spread on a glass slide. A scan speed of 5 ° (2θ)/min with a scan step of 0.02 ° (2θ) was used during a continuous run in the 20 ° to 80 ° (2θ) range.

3.2.2 Surface Area and Pore Size Measurement

Nitrogen adsorption-desorption isoterms at 77 K were obtained using Thermo Finnigan, Autosorb-1 from Quantachrome Company. The Brunauer-Emmet-Teller (BET) equation was used to calculate the specific surface area. Pore size distributions were obtained using the Barret-Joyner-Halenda (BJH) model in the range of mesopores.

3.2.3 Field Emission Scanning Electron Microscope (FE-SEM)/Energy Dispersive X-ray (EDX)

The scanning electron micrographs were carried out to identify the microstructure of a sample. The samples were characterized using a Hitachi/S-4800 field emission scanning electron microscope and the doped Sb species were identified by LINK ISIS series 300 for Energy dispersive X-ray (EDX) analysis.

3.2.4 Thermal Gravimetric Analysis (TGA)

Thermo gravimetric Analysis was carried out on a Perkin-Elmer TG-DTA pyres diamond over 30 ° - 900 ° C at a heating rate of 10 ° C/min under nitrogen atmosphere.

3.2.5 Lloyd Universal Testing Machine

Mechanical properties of the thin films were investigated by using a Model LRX Lloyd Universal Testing machine following ASTM D882. The specimen size is 10 mm × 100 mm. The thickness of all films is in the range of 90-120 μm. Gap between grips was set to 50 mm. Draw speed was 12.5 mm/min. All calculations are based on a minimum of three samples.

3.2.6 Water Uptake

Samples of the membrane were soaked in water at 25 ° C for 48 h in turn. After removing the membranes from water, the surface-attached water was quickly removed with a paper towel. Subsequently, the wet weight (W_{wet}) was determined. After drying at 80 ° C in the oven over night, the dry weight (W_{dry}) was determined. The water uptake (%W) was calculated from this equation,

$$\% \text{ water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$

3.2.7 Impedance Analyzer

The impedance of the samples was measured by using impedance analyzer (Hewlett Packard., model 4194A) in impedance (Z) mode, with frequency from 1 kHz to 10 MHz.

3.2.8 Differential Scanning Calorimeter (DSC7)

The glass transition temperature of polyvinylidene fluoride/polyacrylonitrile blend film was measured by using differential scanning

calorimeter 7, DSC 7 (Perkin Elmer) at a heating rate of 10 °C/min. The samples were heated from -50 °C to 150 °C.

3.3 Methodology

3.3.1 PVDF Film Preparation

Poly(vinylidene fluoride) pellets manufactured from Solvay Company (Belgium) (Solef 1008) were used. The fabrications of PVDF film was the solution casting which PVDF pellets were dissolved in DMF solution. The viscous solution was then casted on glass substrate. After the solvent evaporation in a vacuum oven at 60°C for 3 hours, the precursor membranes were washed in distilled water and dried in vacuum to assure the elimination of the solvent.

3.3.2 PVDF/PAN blend Film Preparation

Poly(vinylidene fluoride) powders manufactured from Solvay Company (Belgium) (Solef 1008) and Polyacrylonitrile (PAN) purchased from Aldrich Chemical Co. Inc. (USA) were mixed together in DMF solution. The weight ratio of PVDF/PAN was 9:1. The viscous solution was then casted on glass substrate. After the solvent evaporation in a vacuum oven at 60°C for 3 hour, the precursor membranes were washed in distilled water and dried in vacuum to assure the elimination of the solvent.

3.3.3 Composite Film Preparation

3.3.3.1 Sol-Gel Processing of Antimony-Modified Titania Ceramics

Titanium (IV) butoxide (Ti $(OC_4H_9)_4$) was dissolved in the mixture between methanol/acetic acid ratio at room temperature with continuous stirring. The ratio of methanol/acetic acid was 1:1. In a different beaker, antimony (V) chloride ($SbCl_5$) was dissolved in methanol and gradually mixed with TiO_2 sol. After that, the gel was calcined at temperature about 500 °C for 3 hours. Antimony-modified titania particles was grounded into powder. TiO_2 powder was also prepared as a reference. The ceramic powder was characterized using XRD, SEM, and EDX. The surface area and pore size distribution were also measured using Nitrogen sorption.

3.3.3.2 Preparation of PVDF Composite Membranes by Solution Casting Technique

PVDF powder supplied by Solvay (Solef 1008) was dissolved in dimethyl formamide (DMF) at 60°C. For composite preparation, the ratio of polymer and solvent was 1:10 w/v. Proportionate quantity of Antimony-modified Titania ceramics powder was added in the polymer solution. It was homogenized by magnetic stirrer. The solution was then cast on a glass substrate. After that, the solvent was evaporated at 60°C for 3 hour under vacuum. Following this method, the composite films of 10%, 20%, 30%, 40%, and 50% by weight ceramic were fabricated. The precursor membranes were washed with distilled water and dried in vacuum. The dispersion of ceramic particles was observed by using SEM and EDX-mapping. The composite membranes were tested in order to evaluate the potential use as electrolyte in PEMFCs at high temperature by using TGA, Impedance spectroscopy and Water uptake. Lloyd Universal Testing machine were carried out to measure the mechanical properties of the thin films.

3.3.3.3 Preparation of PVDF/PAN Composite Membranes by Solution Casting Technique

Poly(vinylidene fluoride) powders manufactured from Solvay Company (Belgium) (Solef 1008) and polyacrylonitrile (PAN) purchased from Aldrich Chemical Co. Inc. (USA) were mixed together in DMF solution at 60°C. The weight ratio of PVDF/PAN was 9:1. For composite preparation, the ratio of polymer and solvent was 1:10 w/v. Proportionate quantity of Antimony-modified Titania ceramics powder was added in the polymer solution. It was homogenized by magnetic stirrer. The solution was then cast on a glass substrate. After that, the solvent was evaporated at 60°C for 3 hour under vacuum. Following this method, the composite films of 10%, 20%, 30%, and 40% by weight ceramic were fabricated. The precursor membranes were washed with distilled water and dried in vacuum. The dispersion of ceramic particles was observed by using SEM and EDX-mapping. The composite membranes were tested in order to evaluate the potential use as electrolyte in PEMFCs at high temperature by using TGA, Impedance spectroscopy and Water uptake. Lloyd Universal Testing machine were carried out to measure the mechanical properties of the thin films.