



CHAPTER III EXPERIMENTAL

3.1 Materials

Titanium (IV) butoxide, niobium (V) chloride and antimony (V) chloride were purchased from Aldrich Chemical Co. Inc.(USA). Glacial acetic acid and methanol were purchased from Lab-Scan Company Co.Ltd. Epotec[®] epoxy resin and Epotec[®] curing agent were supplied from Aditya Birla Chemicals (Thailand) Ltd. (Epoxy Division) All chemicals were used as received.

3.2 Instruments

3.2.1 Fourier Transform Raman Spectrometer

The Raman spectrum was measured by a laser Raman Spectrometer (Renishaw-1000) at an output power of 200mW of 1064 nm Nd:YAG laser.

3.2.2 X-Ray Diffraction (XRD)

Characterization of crystal structure of products 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 α 1 radiation ($\lambda = 1.54 \text{ \AA}$) 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 K β filter. The goniometer parameters were divergence slit = 1° (2 θ); scattering slit = 1° (2 θ); and receiving slit = 0.3 nm. Sample was spread on a glass slide. A scan speed of 5° (2 θ)/min with a scan step of 0.02° (2 θ) was used during a continuous run in the 20° to 80° (2 θ) range.

3.2.3 Scanning Electron Microscope(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 JEOL JSM-6400 scanning electron microscope (SEM) and the doped Nb and Sb species were identified by LINK ISIS series 300 for energy dispersive X-ray (EDX) analysis.

3.2.4 Transmission Electron Microscope (TEM)

Transmission electron microscopy (TEM) was carried out using a Model H-7650 Transmission Electron Microscope apparatus, operating at 100 kV with a 0.204 nm point resolution.

3.2.5 Thermo gravimetric Analysis (TGA)

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

3.2.6 Surface Area and Pore Size Measurement

Nitrogen adsorption-desorption isotherms at 77 K were obtained using Thermo Finnigan, Sorptomatic 1990 from Quanta Chrom 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 and the Horvath-Kawazoe approach for micropore determinations.

3.2.7 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 x 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 five samples.

3.2.8 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,

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

3.2.9 A Frequency Response Analyzer (FRA), Impedance Spectroscopy

The proton conductivity of films samples was measured by four-probe electrochemical impedance spectroscopy (EIS) using a Solartron 1260 frequency response analyzer and a Solartron 1287 potentiostat. The outer electrodes are connected to the working and counter electrodes on the 1287 potentiostat, and the two inner electrodes are connected to the reference electrodes.

3.2.10 Electrochemical Fuel Cell Test Station

Electrochemical fuel cell test station were carried out to evaluate the potential use as electrolyte in PEMFC. Electrochemical tests were carried out in a 25 cm² commercial single cell supplied by Electrochem connected to a Fuel Cell Technologies work station. Membrane-electrode-assemblies with the different membranes were tested in a range of 25°C < T < 100°C in humidified.

3.3 Methodology

3.3.1 Sol-gel Processing of Antimony-modified Titania Ceramics

Titanium (IV) butoxide (Ti(OC₄H₉)₄) was dissolved in the mixture between methanol/acetic acid ratio at room temperature with continuous stirring. The ratios of methanol/acetic acid were varied. In a different beaker, 3 wt.% antimony (V) chloride (SbCl₅) was dissolved in methanol and gradually mixed with TiO₂ sol. After we find optimum condition to form gel at room temperature, the gel was calcined at temperature about 500 °C, 3 hours. Antimony-modified titania particles were ground into powder and then sieved by mesh#325. TiO₂ powder was also prepared in order to use it as reference to compare with other. The ceramic powder was characterized using TEM, SEM, Raman, XRD/EDX and TGA. The surface area and pore size distribution were also measured using Nitrogen sorption.

3.3.2 Sol-gel Processing of Antimony and Niobium-modified Titania Ceramics

Titanium (IV) butoxide (Ti(OC₄H₉)₄) was dissolved in the mixture between methanol/acetic acid ratio at room temperature with continuous stirring. The ratios of methanol/acetic acid were varied. In different beakers, 3 wt.% Niobium (V) chloride was dissolved in methanol and 0-3 wt.% antimony (V) chloride (SbCl₅) was

dissolved in methanol in the other one and then gradually mixed with TiO₂ sol respectively. After we find optimum condition to form gel at room temperature, the gel was calcined at temperature about 500 °C, 3 hours. Antimony and niobium-modified titania particles were ground into powder and then sieved by mesh#325. TiO₂ powders were also prepared in order to use it as reference to compare with other. The ceramic powders were characterized using TEM, SEM, Raman, XRD/EDX and TGA. The surface area and pore size distribution were also measured using Nitrogen sorption.

3.3.3 Preparation of Ceramic Membranes by the Spin Coating Technique

Epoxy resin, hardener and 70 wt.% ceramic powder were mixed together and then the thin film was prepared by spin coating technique at room temperature. The thickness of thin film was adjusted by varying the speed of spin coating and the coating time. The mould was then transferred in a vacuum oven for initial curing process at temperature of 35 °C for 1 h to evacuate the entrapped air. Based on the visual observation and the homogenous color of sample, minimum sedimentation occurred in the sample. The mixture was then placed into the oven for curing process followed by cooling at room temperature. The dispersion of ceramic particles was observed by using SEM. The ceramic membranes were tested in order to evaluate the potential use as electrolyte in PEMFCs at high temperature by using TGA, Impedance spectroscopy, Water uptake and Electrochemical fuel cell test station. Moreover, Lloyd Universal Testing machine were carried out to measure the mechanical properties of the thin films.

3.3.4 Membrane Electrode Assembly Preparation and Accelerated Fuel Cell Life Test

The loading of Pt/C catalyst on the anode and cathode are 0.25 mg Pt cm⁻², respectively. Two electrodes with effective area 25 cm² were hot-pressed to one piece of membrane to form a MEA. The MEA was mounted in a single cell with stainless steel end plates and stainless steel mesh flow field as current collectors. The accelerated fuel cell life tests were performed via the open-circuit voltage (OCV)

test. During the OCV tests, H_2 and air with saturated humidity were fed to the anode and the cathode, respectively.