

CHAPTER III

EXPERIMENTAL

3.1 Materials

The starting materials are titanium tetraisopropoxide (TTIP), poly vinylpyrrolidone (PVP), carbon black, ethyl alcohol, and acetic acid.

Titanium tetraisopropoxide (TTIP) 97% was purchased from Sigma-Aldrich Chemical Company and used as received. It was kept in dry environment prior to use to prevent moisture adsorption.

Poly vinylpyrrolidone (PVP), $M_w \approx 1,300,000$ and 10,000 were purchased from Sigma-Aldrich Chemical Company and used as received.

Carbon black (particle size ~ 29 nm.) were supplied by the East Asiatic Public and used as received.

Ethyl alcohol 98% and acetic acid were purchased from Sigma-Aldrich Chemical Company and used as received.

3.2 Electrospinning Apparatus

The schematic diagram of the electrospinning apparatus used in this work is shown in Figure 3.1. The components of the apparatus and their functions are described as follows.

- A high voltage power supply (ES30PN, Gamma High Voltage Research Inc., Ormond Beach, Florida) is used to generate either positive or negative DC voltage up to 30 kV, with very low electrical current of 166 microamperes.
- A 5 ml syringe is used as a container for electrospinning solutions. The syringe makes of plastic and is set in vertical orientation.

- A stainless steel needle (guage number 20 and the outside diameter of 0.90 mm) is used as a nozzle and as an electrode to conduct the electrical energy from the power supply to the solution. The tip of the needle is cut into a flat shape and the length of the needle is 2 cm.
- Aluminum foil is used as a ground collector which is covered on the plastic stand.

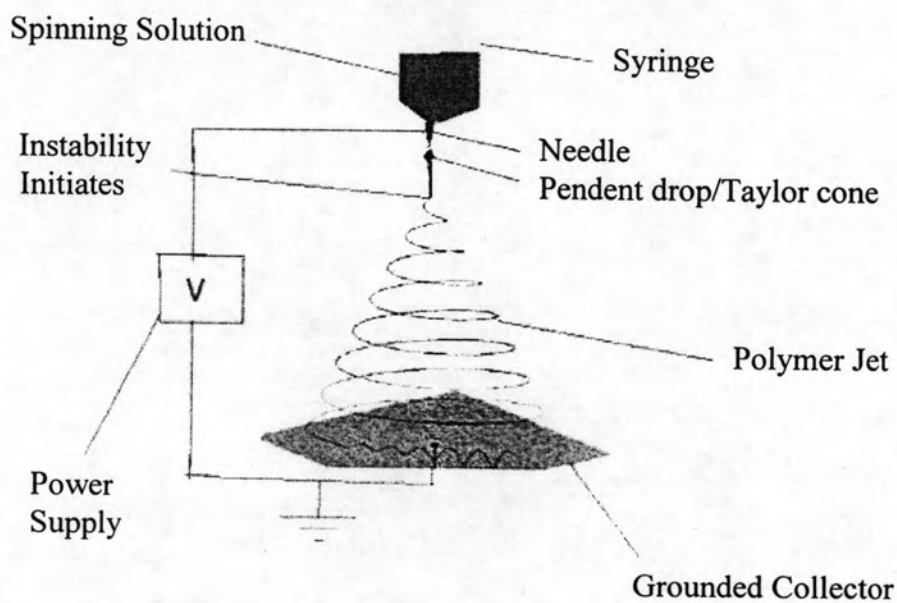


Figure 3.1 Experimental set up for electrospinning process.

3.3 Procedures

3.3.1 Preparation of Spinning Solution

In a typical procedure, 1.5 g of titanium tetraisopropoxide (TTIP) was mixed with 3 ml of acetic acid and 3 ml of ethanol. The solution was rest for 10 min before being added into the mixture of polyvinylpyrrolidone (PVP, $M_w \approx 10,000$ or 1,300,000) and 7.5 ml of ethanol. The concentration of the PVP solution was varied between 13 and 35 wt.% and the resulting mixture was constantly stirred for 10 min. PVP used was a mixture of high-molecular weight PVP (M_w of 1,300,000) and low-molecular weight PVP (M_w of 10,000) in the predetermined ratio. However, it should be noted that most experiments employed only high-molecular weight PVP. The final mixture was constantly stirred for another hour. The as-prepared solution was referred to as the spinning solution.

For some experiments whereas carbon black was employed as source of carbon, the TTIP solution was prepared in the same manner as described earlier. However, the PVP solution was replaced by the mixture of PVP ($M_w \approx 1,300,000$), carbon black and 7.5 ml of ethanol. The concentration of the PVP in the solution was 13 wt.%, while the amount of carbon black was adjusted to achieve $\text{TiO}_2\text{:C}$ ratio of 1:2. The final mixture was constantly stirred for one hour.

3.3.2 Spinning of the TiO_2 /PVP Composite Fibers

The spinning solution was immediately loaded into a plastic syringe. A blunt-ended 20-gauge stainless steel needle was used as the nozzle. The emitting electrode from a Gamma High Voltage Research ES30PN power supply capable of generating DC voltages up to 30 kV was attached to the needle. The grounding electrode from the same power supply was attached to a piece of aluminum foil which was used as the collector plate and was placed approximately 7 cm below the tip of the needle. Upon the application of a high voltage ranging between 9 and 22.5 kV across the needle and the collective plate, a fluid jet was ejected from the nozzle. As the jet

accelerated towards the collector, the solvent evaporated, leaving only ultrathin fibers on the collector. The obtained fibers were left exposed to moisture for approximately 1 day to allow complete hydrolysis of TTIP.

3.3.3 Pyrolysis of TiO_2/PVP Composite to form $\text{TiO}_2/\text{Carbon}$ Composite

For this step, the composite fibers were put into alumina trays (40 mm \times 30 mm \times 5 mm deep). Then, these trays were placed in the uniform temperature zone of a horizontal tubular reactor which is an alumina tube (50 mm inside diameter \times 1.2 m long) placed inside a high temperature furnace (Carbolite-STF 15/--/180). For comparison purposes, the composite gel (i.e. the spinning solution that had not been electrospun) was also placed in the reactor. Samples were heated to 600°C under heating rate of 10°C/min in argon atmosphere and hold for 3 h. The flow rate of argon was fixed at 0.9 l/h (measured at room temperature). The schematic diagram of this system is shown in Figure 3.2.

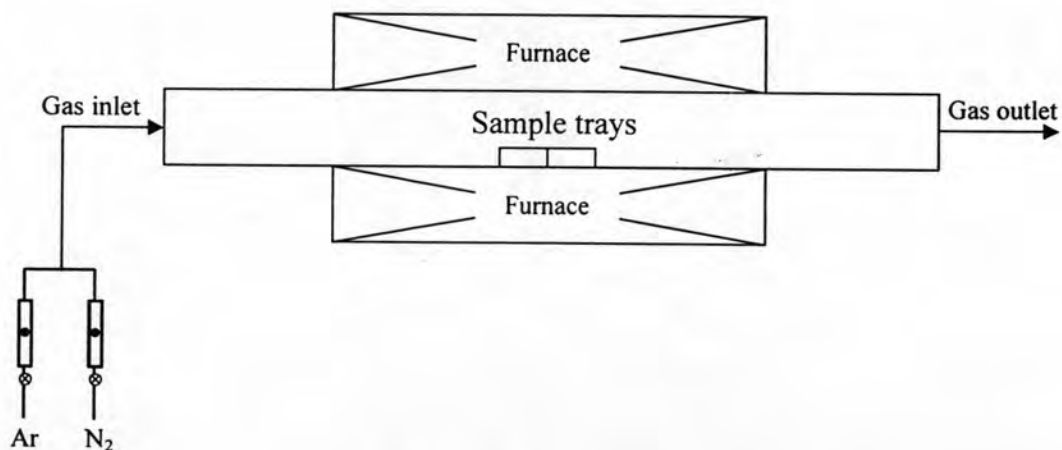


Figure 3.2 Schematic diagram of the tubular flow reactor system

3.3.4 Calcination of the TiO₂/Carbon Composite Fibers

In some experiments where the effect of carbon content in the composite fibers was investigated, the pyrolyzed fibers were intentionally oxidized to partially remove parts of their free carbon. The fibers were subjected to heat treatment in stagnant air at temperature in the range between 350 and 400°C for 5 or 10 min by using box furnace. The samples were heated up from the room temperature at the rate of 10°C/min.

3.3.5 Carbothermal Reduction and Nitridation of the TiO₂/Carbon Composite

The carbothermal reduction and nitridation was employed to convert TiO₂/carbon composite into titanium nitride. For this step, the pyrolyzed samples or the calcined samples were put into alumina trays (25 mm × 15 mm × 5 mm deep) and placed in the uniform zone of the horizontal tubular flow reactor (Figure 3.2). The samples were heated up to desired reaction temperature in the range of 1,300 to 1,400°C with constant heating rate of 10°C/min under constant flow of argon with the flow rate of 0.9 l/h. After the system had reached the prescribed temperature, the argon was replaced by, nitrogen gas which was fed into the reactor at the same flow rate as argon. The system was kept at this condition for 0-6 h.

3.4 Sample Characterizations

3.4.1 X-ray Diffractometry (XRD)

The crystalline phase of the products were identified by a Siemens D5000 X-ray diffractometer. The measurements were carried out by using Ni-filtered $\text{CuK}\alpha$ radiation and operated in the 2θ range of 10-80 degree at the scan step of 0.02 degree.

3.4.2 Scanning Electron Microscopy (SEM)

The surface morphology and size of the resulting electrospun TiO_2 /PVP composite fibers, TiO_2 /carbon composite fibers and nitrated products were observed by a JSM 5800 Scanning Electron Microscopy (SEM), which operated at 20 kV, at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. Samples were coated by thin film of gold prior to the analysis.

3.4.3 Thermogravimetric and Differential Thermal Analysis (TG-DTA)

The as-spun titania fibers, TiO_2 /carbon composite fibers and nitrated products were subjected to the thermogravimetric and differential thermal analysis (Diamond Thermogravimetric and Differential Thermal Analyzer, TG-DTA, Perkin-Elmer) to determine the carbon content in the sample, as well as their thermal behaviors.

3.4.4 Transmission Electron Microscope (TEM)

The morphology of an individual grain in the samples was observed on a JEOL JEM-2100 Analytical Transmission Electron Microscope, operated at 80-200 keV at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University and JSM 6301 & EDS Analytical Transmission Electron Microscope at National Metal and Materials Technology Center, Thailand. The crystallographic information was also obtained from the selected area electron diffraction (SAED) analysis performed in the same instrument.

3.5 Evaluation of the Reaction Conversion

The nitrided products were analyzed by powder X-ray diffraction (XRD) as described earlier. Peak areas, background noise, and separation of overlapped peaks were determined by fitting the diffraction patterns using the Pseudo-Voight function (McCusker et al. 1999) in the Xfit-Koalariet software package from the Collaborative Computational Project number 14 (CCP14). Then, the mass fraction of each phase as well as the conversion from titania to titanium nitride were calculated based on the calculation method proposed by Jovanovic and Kimura (1994), using the integrated intensity of (110) and (211) peaks of titania in rutile phase and those of (111), (200) and (220) peaks of titanium nitride, as follow:

$$\frac{I_{TiN}(111) + I_{TiN}(200) + I_{TiN}(220)}{I_{Rutile}(110) + I_{Rutile}(211)} = K_{TiN/Rutile} \frac{W_{TiN}}{W_{Rutile}} \quad (3.1)$$

and
$$W_{TiN} + W_{Rutile} = 1 \quad (3.2)$$

where $I_{\delta}(hkl)$ signifies the integrated intensity of the hkl reflection of phase δ , and W_{δ} is the mass fraction of corresponding phase δ in a mixture. The linear regression

calibration constant, $K_{TiN/Rutile}$ was evaluated to be 0.7127. Details of the evaluation are shown in the Appendix E.

From measured mass composition, the overall conversion of titania, X , was calculated as:

$$X = \frac{1 - W_{Rutile}}{1 + \left(\frac{M_{TiN}}{M_{Rutile}} - 1 \right) W_{Rutile}} \quad (3.3)$$

where M_{TiN} and M_{Rutile} are the molar masses of titanium nitride and titania, and $(M_{TiN}/M_{Rutile})-1 = -0.2252$ is a converting factor.

An example of X-ray diffraction pattern of synthesized product and the calculation are also given in Appendix F.