

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Materials Used for Coaxial Electrospinning

- Poly (vinyl acetate) (PVAc, MW= 500,000 g/mol) : Aldrich
- Titanium (IV) isopropoxide (Ti(Iso)) : TCI Co., Ltd. (Japan)
- N,N-dimethylformamide (DMF) : Lab-Scan (Asia)
- Acetic acid : Lab-Scan (Asia)
- Mineral oil : Ajax Finechem Pty Ltd.
- Zinc powder (particle size <45 μm) : Merck
- Silver powder (particle size <100 nm) : Aldrich

3.1.2 Materials Used for Hydrothermal Treatment

- Bis(hexamethylene)triamine (BHT) : TCI Co., Ltd. (Japan)
- Zinc nitrate hexahydrate (ZNH) : Lobachemie
- Silver nitrate (AgNO_3) : VWR International

3.1.3 Materials Used for Electrochemical Characterization

- Polyvinylidene fluoride (PVDF) : Aldrich
- N-methyl pyrrolidinone (NMP) : Merck
- Carbon black (CB)
- Lithium hexafluorophosphate (LiPF_6) : Aldrich
- Ethylene carbonate (EC) : Merck
- Dimethyl carbonate (DMC) : Merck

3.2 Equipments

3.2.1 Scanning Electron Microscope (SEM)

Scanning electron microscope equipped with EDX (SEM, a JEOL JSM 5200) was used to study the surface morphology of the synthesized fibers.

3.2.2 Transmission Electron Microscope (TEM)

Transmission electron microscope (TEM; a JEOL JEM 2010) was used to observe high resolution images and selected area electron diffraction patterns of the synthesized fibers.

3.2.3 X-ray Diffraction (XRD)

X-ray diffraction (XRD, PAN analytical X'pert PRO XRD) with Cu $K\alpha$ ($\lambda = 1.54056 \text{ \AA}$) radiation over a range of 2θ angles from 20 to 80° was used to study the crystal structures of the synthesized fibers.

3.2.4 Surface Area Analyzer (Autosorp-1MP)

Surface area analyzer (Autosorb iQ Station 1) was used to measure surface area, pore volume, pore size distribution and the specific surface area of the synthesized fibers.

3.2.5 Attenuated Total Reflectance-Fourier Transform Infrared Spectrometer (ATR-FTIR)

Attenuated total reflectance-Fourier transform infrared spectrometer (ATR-FTIR; Thermo Nicolet Nexus 670) was used to determine functional groups of the synthesized fibers.

3.2.6 Maccor Battery Test System Series 4000

Maccor battery test system series 4000 (New York, USA) was used to measure the charge-discharge characteristics of the cells which was operated over the potential range between 0.0 and 4.2 V at room temperature.

3.3 Methodology

3.3.1 The Effect of Operating Voltage to the Morphology of Synthesized Fibers

3.3.1.1 *Preparation of TiO_2 Fibrous Materials*

3.3.1.1.1 *TiO_2 Hollow Fibers*

TiO_2 colloidal solution was prepared by dissolve 0.7 g of PVAc granules in 4.6 mL of DMF solvent at room temperature with vigorous stirring for 2 h , the polymer content in the solution was 14 wt\% . The PVAc

solution was mixed with 5.2 mL of Ti(Iso) and a few drops of acetic acid until the solution become transparent. The mixture was then stirred for 3 h, so a colloid was attained. Later on, the titanium sol and mineral oil were fed into the two glass syringes of the coaxial electrospinning. A blunt-ended 16-gauge stainless steel needle was used as the nozzle for syringe of shell while the another blunt-ended 24-gauge was used for syringe of core. An Al foil wrapped around a rotating drum (rotational speed: 50 rpm) was employed as the collector. The working distance from the tip of the needle to the surface of the Al foil was fixed at 17 cm. A gamma high-voltage research D-ES30PN/M692 power supply was used to produce a high DC potential. The spinning time was completed uninterruptedly for 6 h.

3.3.1.1.2 Zn/TiO₂ Composite Hollow Fibers

Zn/TiO₂ colloidal solution was prepared by dissolve 0.7 g of PVAc granules in 4.6 mL of DMF solvent at room temperature with vigorous stirring for 2 h. The PVAc solution was mixed with 5.2 mL of Ti(Iso) and a few drops of acetic acid until the solution become transparent and then stir for 3 h. After that, 0.1 g of Zn powder was added to the polymeric solution. The mixture was then stirred for 10 minutes, so a colloid was attained. Later on, the titanium sol and mineral oil were fed into the two glass syringes of the coaxial electrospinning.

3.3.1.1.3 Ag/TiO₂ Composite Hollow Fibers

Ag/TiO₂ colloidal solution was prepared by dissolve 0.7 g of PVAc granules in 4.6 mL of DMF solvent at room temperature with vigorous stirring for 2 h. The PVAc solution was mixed with 5.2 mL of Ti(Iso) and a few drops of acetic acid until the solution become transparent and then stir for 3 h. After that, 0.1 g of Ag powder was added to the polymeric solution. The mixture was then stirred for 10 minutes, so a colloid was attained. Later on, The titanium sol and mineral oil were fed into the two glass syringes of the coaxial electrospinning.

3.3.1.1.4 TiO₂ Fibers

TiO₂ colloidal solution was prepared by dissolve 0.7 g of PVAc granules in 4.6 mL of DMF solvent at room temperature with vigorous stirring for 2 h. The PVAc solution was mixed with 5.2 mL of Ti(Iso) and a few drops of acetic acid until the solution become transparent. The mixture was then stirred for 3 h, so a colloid was attained. Later on, the titanium sol was fed into

the glass syringes of the coaxial electrospinning. A blunt-ended 16-gauge stainless steel needle was used as the nozzle for syringe.

3.3.1.2 Adjusting the Spinning Condition at Various Operating Voltages

The different morphologies of synthesized fibers were obtained after applying high voltage at 15, 17, 19, 21, 23, and 25 kV between the needle and the collector.

For Zn/TiO₂ composite hollow fibers, Ag/ TiO₂ composite hollow fibers, and TiO₂ fibers, they were also produced at the proper spinning condition which obtained after choosing the best results of TiO₂ hollow fibers.

3.3.2 The Effect of Calcination Process to the Crystal Structure of Synthesized Fibers

3.3.2.1 Adjusting the Calcination Condition at Various Time and Temperature

The obtained TiO₂ hollow fibers were initially dried in the oven at 80 °C for 2 days to remove solvent and then calcined in air atmosphere with a heating rate of 5 °C minute⁻¹ at 500 °C for 1,2,3 h, 600 °C for 1,2,3 h, and 650 °C for 1,2,3 h.

For Zn/TiO₂ composite hollow fibers, Ag/ TiO₂ composite hollow fibers, and TiO₂ fibers, they were also initially dried in the oven at 80 °C for 2 days to remove solvent and then calcined in air atmosphere with a heating rate of 5 °C minute⁻¹ at the proper calcination condition which obtained after choosing the best results of TiO₂ hollow fibers.

3.3.3 The Effect of Surface Modification by Hydrothermal Treatment to the Morphology, Weight, and the Average Diameter of Synthesized ZnO/TiO₂ and AgO₂/TiO₂ Composite Hollow Fibers

3.3.3.1 Adjusting the Hydrothermal Treatment Condition under the Fixed Time for 1 Hour at Various Temperatures

3.3.3.1.1 ZnO Outgrowths

The calcined Zn/TiO₂ composite hollow fibers were treated with two chemicals; bis-hexamethylene triamine and zinc nitrate hexahydrate. In process, 1.076 g of bis-hexamethylene triamine and 1.487 g of zinc nitrate

hexahydrate were dissolved in 50 g of distilled water with two individual bottles. Later on, the two solutions were mixed together and 10 mg of the calcined Zn/TiO₂ composite hollow fibers were then added. The mixture was vigorously stirred for 4 h and finally placed inside an autoclave. An autoclave was operated at the fixed time of 1 h at 110 °C, 115 °C, and 120 °C. Then, they were naturally cooled down to the room temperature. The attained products were filtered off, washed with distilled water several times and eventually dried at 60 °C for 12 h in the oven for further characterization.

3.3.3.1.2 Ag₂O Outgrowths

The calcined Ag/TiO₂ composite hollow fibers were treated with two chemicals; bis-hexamethylene triamine and silver nitrate. In process, 1.076 g of bis-hexamethylene triamine and 0.849 g of silver nitrate were dissolved in 50 g of distilled water with two individual bottles. Later on, the two solutions were mixed together and 10 mg of the calcined Ag/TiO₂ composite hollow fibers were then added. The mixture was vigorously stirred for 4 h and finally placed inside an autoclave. An autoclave was operated at the fixed time of 1 h at 110 °C, 115 °C, and 120 °C. Then, they were naturally cooled down to the room temperature. The attained products were filtered off, washed with distilled water several times and eventually dried at 60 °C for 12 h in the oven for further characterization.

3.3.3.2 Adjusting the Hydrothermal Treatment Condition under the Fixed Temperature at 115 °C at Various Times

3.3.3.2.1 ZnO Outgrowths

The calcined Zn/TiO₂ composite hollow fibers were treated with two chemicals; bis-hexamethylene triamine and zinc nitrate hexahydrate. In process, 1.076 g of bis-hexamethylene triamine and 1.487 g of zinc nitrate hexahydrate were dissolved in 50 g of distilled water with two individual bottles. Later on, the two solutions were mixed together and 10 mg of the calcined Zn/TiO₂ composite hollow fibers were then added. The mixture was vigorously stirred for 4 h and finally placed inside an autoclave. An autoclave was operated at the fixed temperature of 115 °C for 0.5, 0.75, and 1 h. Then, they were naturally cooled down to the room temperature. The attained products were filtered off, washed with

distilled water several times and eventually dried at 60 °C for 12 h in the oven for further characterization.

3.3.3.2.2 *Ag₂O Outgrowths*

The calcined Ag/TiO₂ composite hollow fibers were treated with two chemicals; bis-hexamethylene triamine and silver nitrate. In process, 1.076 g of bis-hexamethylene triamine and 0.849 g of silver nitrate were dissolved in 50 g of distilled water with two individual bottles. Later on, the two solutions were mixed together and 10 mg of the calcined Ag/TiO₂ composite hollow fibers were then added. The mixture was vigorously stirred for 4 h and finally placed inside an autoclave. An autoclave was operated at the fixed temperature of 115 °C for 0.5, 0.75, and 1 h. Then, they were naturally cooled down to the room temperature. The attained products were filtered off, washed with distilled water several times and eventually dried at 60 °C for 12 h in the oven for further characterization.

3.4 Characterization

3.4.1 Scanning Electron Microscope (SEM)

The surface morphology and size of the individual synthesized fibers were investigated by scanning electron microscope (SEM) model a JEOL JSM 5200. Before SEM observation, each sample was prepared by placing it on the stub and coating with a thin gold layer for 100 s using JEOL-JFC-1100E ion sputtering device. SemAphore 4.0 software was employed to measure diameters of the obtained fibers in order to get the average diameters from at least five images with at least 100 readings of fiber diameters.

3.4.2 Transmission Electron Microscope (TEM)

The high resolution images and selected area electron diffraction pattern were examined by transmission electron microscope (TEM) model a JEOL JEM 2010. Small amount of interested fibers were added in ethanol, ultrasonicated, and finally dropped onto a carbon-coated 400-mesh Cu grid.

3.4.3 X-ray Diffraction (XRD)

The crystal structures and crystallinity of the synthesized fibers were observed by X-ray diffraction (XRD) model PAN analytical X'pert PRO XRD with Cu K α ($\lambda = 1.54056 \text{ \AA}$) radiation over a range of 2θ angles from 20 to 80°. In the x-ray spectrum, a broad peak indicated the amorphous region, meanwhile the sharp peaks on the broad peak are responsible for the crystalline region. The area under crystalline peaks and amorphous peaks can be used to determine degree of crystallinity. The Scherrer's equation (see Eq. 3.1) was used to determine the crystallite size of crystals outgrowths.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (3.1)$$

In this equation, k is a constant equal to 0.89, λ , the X-ray wavelength equal to 1.54056 \AA , β , the full width at half maximum and θ , the half diffraction angle (Wu, 2004).

3.4.4 Surface Area Analyzer (Autosorb iQ Station 1)

Surface area analyzer (Autosorb iQ Station 1) was used to measure surface area of the synthesized fibers. Prior to analysis, the interested samples were dried at 60 °C in oven to ensure removing moistness of samples.

3.4.5 Attenuated Total Reflectance-Fourier Transform Infrared Spectrometer (ATR-FTIR)

Attenuated total reflectance-Fourier transform infrared spectrometer (Thermo Nicolet; Model: Nexus 670) was used to determine the functional groups of the synthesized fibers.

3.5 Electrochemical Characterization

The charge-discharge characteristics of the cells was studied using Maccor battery test system series 4000 (New York, USA) over the potential range between 0.0 and 4.2 V at room temperature.

3.5.1 Preparation of Materials Used as Anode

The hydrothermally-treated ZnO/TiO₂ composite hollow fibers was employed to use as anode materials together with carbon black (CB) and binder with weight ratio at 2 : 90 : 8, respectively. The poly (vinylidene fluoride) used as binder was dissolved in N-methyl-2-pyrrolidone (NMP) in which the hydrothermally-treated ZnO/TiO₂ composite hollow fibers and pyrolytic carbon could be dispersed. The viscous slurry was coated on Cu foil (as a current collector) by blade coating. Then, it was dried at 80 °C for 24 h in an air oven. The geological area of the anode was 1.0 cm² with a thickness of ~10 μm. In case of the hydrothermally-treated AgO₂/TiO₂ composite hollow fibers and TiO₂ hollow fibers were prepared by the same method as well.

3.5.2 Preparation of Materials Used as Cathode

Cathode materials were prepared by blade coating. LiCoO₂ was mixed with carbon black and PVDF binder at weight ratio of LiCoO₂/CB/PVDF = 85 : 10 : 5 in NMP to form a slurry. The slurry was finally coated on aluminium foil. Later on, it was dried at 80 °C for 24 h in an air oven. The geological area of the cathode was 1.0 cm² with a thickness of ~10 μm.

The prepared electrodes were coupled with an electrolyte of 1 M LiPF₆ dissolved in a 1 : 1 (v/v) mixture of EC-DMC and assembled in a nitrogen-filled glove box (OMNI-LAB system). Meanwhile, WHATMAN paper (GF/F, pore = 0.7 μm) was used the separator.