CHAPTER 3

EXPERIMENT

This chapter consists of the main four sections including the experiment equipment, the experiment procedure, the material characterizations and the electrochemical test. The first section describes all of the chemical reagent, equipment and the instrument which were used in this research. The second section explains the preparation of NiO nanoparticles and NiO films by using a sparking method. The third section, the systematical characterizations e.g. the structures, morphologies, surface area and optical properties of the nanoparticles and the films were shown. The last section gives a detail of electrochemical test such as CV, GCD and EIS characterization of the samples.

3.1 Experimental equipment

3.1.1 Chemical reagent used in the experiment

1) Absolute ethanol (C_2H_5OH) (99.9%, Merck, German)
2) Acetone (CH3COCH3) (99.9 %, ACI Labscan, Thailand)
3) Absolute ethanol (C_2H_5OH) (99.9%, Merck, German)
4) DEIONIZED Water (Labscan, Thailand)
5) Hydrochloric acid (HCl) (37%, Sigma-Aldrich, German)
6) Potassium Hydroxide (KOH) (85% Sigma-Aldrich, German)

3.1.2 The equipment and instrument

1) Nickel wires (99.98%, 0.25 mm in diameter, Advent Research Material Ltd., Oxford, UK)

2) Sparking machine (Nanomaterials Laboratory, Chiang Mai University, Thailand)

3) Ultrasonic machine (D-78224 Sigen/Htw, Elma, German, Nanomaterials Laboratory, Chiang Mai University, Thailand)

4) Scanning electron microscopy (SEM, JEOL JSM-6335F, Japan, Chiang Mai University, Thailand)

5) Scanning electron microscopy (SEM, Hitachi model SU-8030, Japan, National Metal and Materials Technology Center (MTEC), Thailand)

6) Transmission electron microscopy (TEM, JEOLJEM-2010, Chiang Mai University, Thailand)

7) Raman spectroscopy (RAMAN, Renishaw model Invia, German, National Electronics and Computer Technology Center (NECTEC), Thailand)

8) Atomic Force Microscope (AFM, Nano Scope®IIIa, Veeco Digital Instruments, England, Chiang Mai University, Thailand)

9) UV-Visible Spectrophotometer (UV-vis, Varian Cary 50, USA, Chiang Mai University, Thailand)

10) Brunauer-Emmett-Teller (BET, Autosorb 1 MP, Quantachrome, USA, Chiang Mai University, Thailand)

11) X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, England, Chiang Mai University, Thailand)

12) X-ray diffraction (XRD, Rigaku, TTRAX III, 18kW, Japan, National Metal and Materials Technology Center (MTEC), Thailand

13) μ-Autolab Type III electrochemical work station (ECO-Chemie, Metrohm, Switzerland, National Electronics and Computer Technology Center (NECTEC), Thailand)

14) μ-Autolab Type III electrochemical work station (ECO-Chemie, Metrohm, Switzerland, Chiang Mai University, Thailand).

15) Potentiostat-galvanostat operated by Nova 1.10 software package (ECO-Chemie, Metrohm, PGSTAT302N, Switzerland, National Electronics and Computer Technology Center (NECTEC), Thailand)

16) Microbalance with 5 digit resolution (240A, Precisa, Switzerland, Medical Science Research Equipment Center, Faculty of Medicine, Chiang Mai University).

17) Microbalance with 6 digit resolution (M5P, Sartorius, Germany, Medical Science Research Equipment Center, Faculty of Medicine, Chiang Mai University).

3.2 Experimental procedure

3.2.1 The fabrication of NiO films on flexible Cr/Au coated PET substrates

The schematic illustration of the sparking apparatus for fabrication of NiO films and a diagram strategy of NiO film on flexible Cr/Au coated PET substrates for the electrochemical test are shown in Figure 3.1 and Figure 3.2. Nickel is sparked off between nickel anode and cathode tips under a high applied voltage onto a substrate placed directly below the wires. The sparking machine was equipped with an array of nickel electrodes that would be scanned in one dimension while the substrate would be sliding automatically in another dimension with controllable rates by step motors. The design of sparking system allowed rapid deposition of nanoparticle films over a large area and improved the uniformity and quality of these films. Nickel wires (99.98%, Advent Research Material Ltd., Oxford, UK) with 0.25 mm in diameter were used as the anode and cathode electrodes. Before use, nickel wires were washed with acetone, absolute ethanol, and deionized water in an ultrasound bath for 15 min and then dried by nitrogen gas at room temperature. The wires were cut to form sparking tips and then aligned with a gap between anode and cathode of ~1 mm. The NiO films as working electrodes were deposited by direct sparking from an array of nickel wires at 3 kV and 10 mA onto chromium/gold (Cr/Au) current collector layers on flexible polyethylene terephthalate (PET) substrates. The high applied voltage induced high-temperature arcing plasma in the air gap via field ionization process. Electrons and ions in the plasma bombarded at the two tip surfaces, producing vaporized nickel nanoparticles that were oxidized in air at the high plasma temperature into NiO-NPs and deposited onto underlying substrates. The 50 nm thick Cr and 200 nm thick Au layers were prepared by dc sputtering at an argon pressure of $3x10^{-3}$ mbar and a dc current of 0.2 A. The Cr layer was used as an adhesive layer between Au and PET [179]. The substrate was repeatedly scanned under the arcing electrode to obtain a uniformly thick NiO film. It should be noted that the sparking process parameters were chosen based on the previous studies reported by our group[39], which showed that higher sparking voltage could produce smaller average particle size. In particular, the maximum sparking voltage (3.0 kV) and sample sliding speed (1 cm/min) of the sparking machine were selected to obtain uniform sparked films with very fine nanometer-sized particles and high porosity. The

mass of sparked NiO films was measured by high-precision microbalance with 6 digit resolution (M5P, Sartorius).

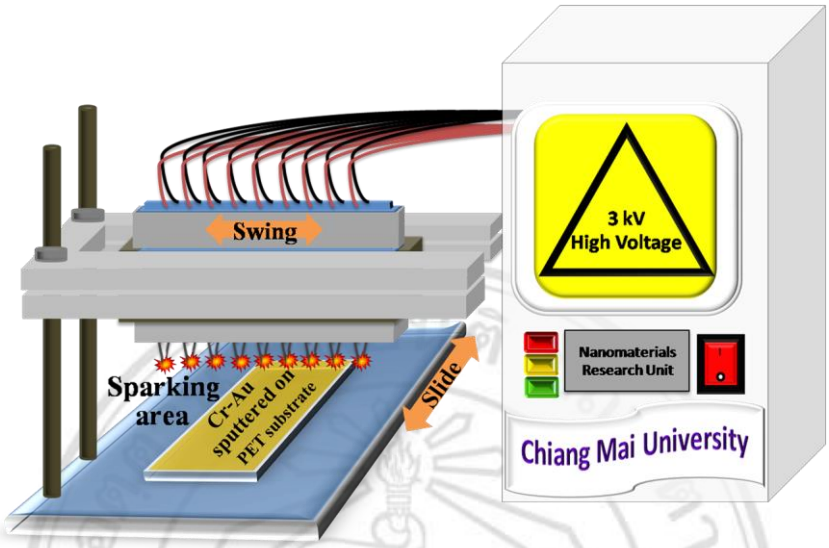

Figure 3.1 Schematic illustration of the sparking system for fabrication of NiO films.

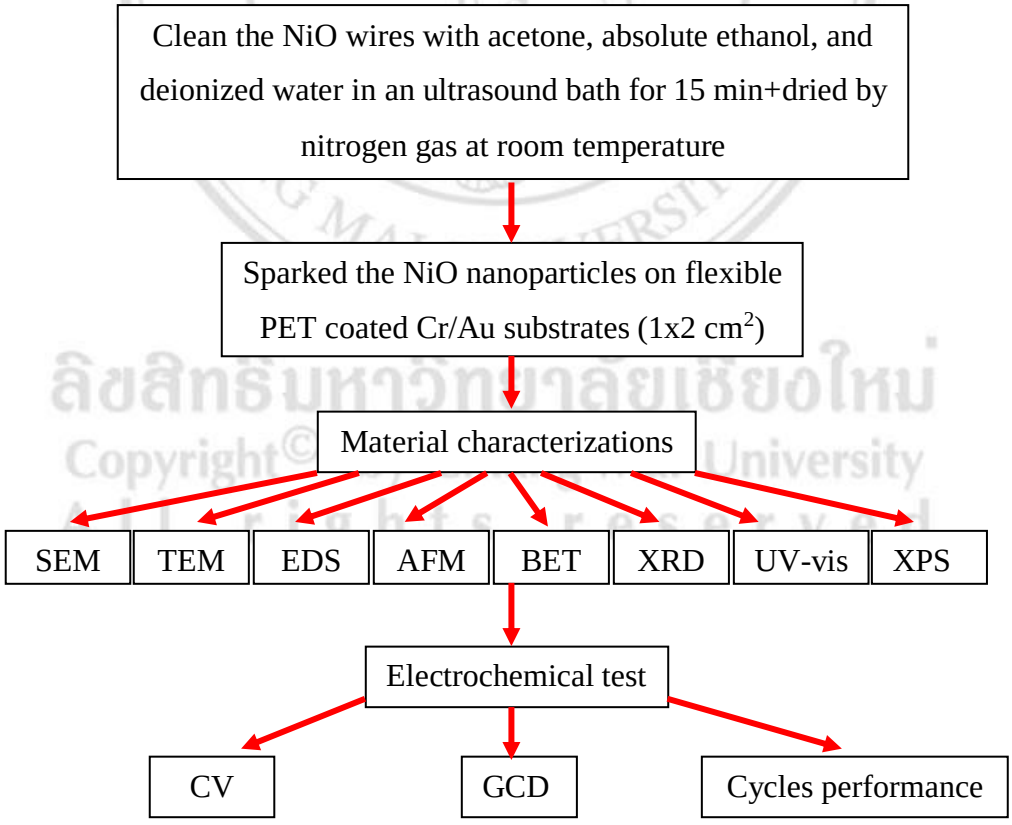

Figure 3.2 A diagram strategy of NiO film on flexible Cr/Au coated PET substrates for electrochemical test.

The film mass was calculated by subtracting the substrate mass measured before NiO film deposition from the final mass measured afterwards. The average mass density of the film was determined from 8 samples (1×1 cm^2) to be 0.0375 mg/cm^2. The NiO electrodes would be characterized for electrochemical energy-storage performances without post-deposition annealing.

3.2.2 The fabrication of NiO films on nickel foam

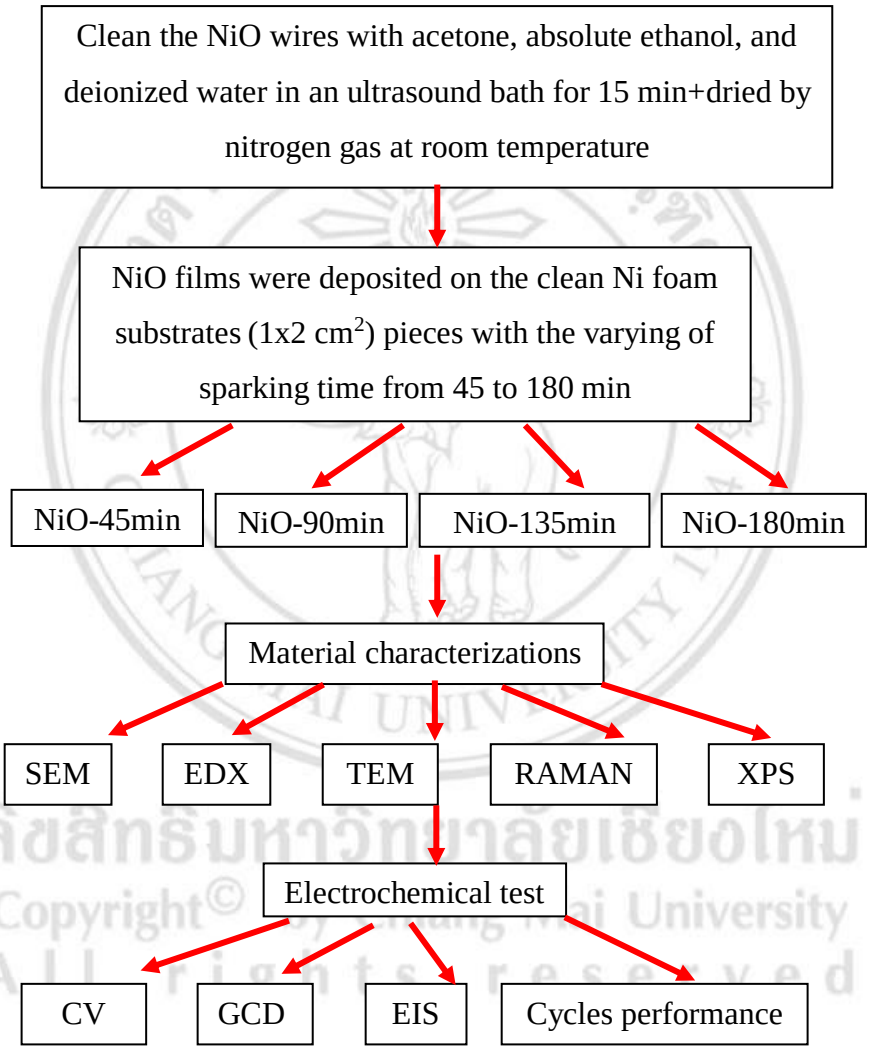

Figure 3.3 A diagram strategy of NiO film on Nickel foam for electrochemical test.

Figure 3.3 is a diagram strategy of NiO film on Nickel foam for the electrochemical test. NiO films were deposited on Ni foam substrates based on the sparking procedure showed in Figure 3.1. In brief, Ni foam substrates were prepared by cutting a 1 mm-thick Ni foam sheet (110 pores per inch) into 1×2 cm^2 pieces, which

were then cleaned in acetone under sonication for 20 min and dried by nitrogen gas. NiO was deposited by direct sparking from an array of 0.25 mm-diameter nickel wires (99.98%, Advent Research Material Ltd, Oxford, UK) at 3 kV and 10 mA onto Ni foam substrates at a fixed substrate-Ni wire spacing of 5 mm. The sparking time was varied from 45 to 180 min with an increment of 45 min. The samples were labeled with the sparking time as NiO-sparking time (45min, 90min, 135min and 180min). The sparking process was repeated on the other side of substrate in order to fully cover the surfaces of Ni foams with NiO. The mass of sparked NiO material was measured by a high-precision microbalance with 5 digit resolution (240A, Precisa). The film mass was calculated by subtracting the substrate mass measured before NiO film deposition from the final mass measured afterwards. The average mass densities of NiO sparked on Ni foams for 45, 90, 135 and 180 min were determined to be 0.15, 0.26, 0.38 and 0.53 mg cm^{-2}, respectively. Then the samples were further analyzed the material characterizations and the electrochemical properties.

3.3 Material characterizations

This part showed details of the material characterizations, which were employed to analyzed the samples. All of techniques comprising field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), atomic force microscope (AFM), Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) nitrogen adsorption measurements, UV-vis spectrophotometer, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (RAMAN) were explained as followed:

3.3.1 Field Emission Scanning Electron Microscope (FESEM)

The FESEM consist of a condensed/accelerated electron beam to focus on a sample. When the primary electron incidents to the sample, it generates secondary and back scattered electrons, which is further detected and is used to create an microscopic images or area mapping. For analyzing morphologies and nanostructures of NiO-NPs and NiO films with a field emission scanning electron microscope (FESEM, JEOL JSM-6335F), the samples were cut and attached on the brass holder with the copper tape prior gold sputtering. Moreover, the NiO films on nickel foam without gold sputtering

were examined using a field-emission scanning electron microscopy (FE-SEM, Hitachi model SU-8030). The instruments were shown in Figure 3.4 and Figure 3.5.

Figure 3.4 Field Emission Scanning Electron Microscope (FE-SEM, JEOL JSM-6335F) including Energy Dispersive X-ray Spectroscopy (EDS).

Figure 3.5 Field Emission Scanning Electron Microscope (FE-SEM, Hitachi model SU-8030) equip with Energy Dispersive X-ray Spectroscopy (EDS).

Figure 3.6 Transmission Electron Microscope (TEM, JEOL JEM-2010).

3.3.2 Transmission Electron Microscope

TEM samples were prepared by drop coating of NiO-NPs dispersion in acetone on a holey carbon/copper grid and TEM (TEM, JEOL JEM-2010) as shown in Figure 3.6 was operated at 200 kV and 108 mA. The selected area electron diffraction pattern (SAEDP) was also recorded to verify the crystal structure of NiO-NPs.

3.3.3 Raman spectroscopy

Raman spectroscopy is a spectroscopic method, which is employed to investigated the rotational, vibrational, and other with a low frequency mode system. It is based on the inelastic scattering, known as Raman scattering. It is operated by using a monochromatic light source, generally use various laser range such as ultraviolet, visible, and infrared. Principledly, the laser hit to the sample, following the electron in the system is excited, leading to the shifting up/down of energy of the laser. Raman spectroscopy give a detail of the structure, chemical bonding, etc. In this study, the chemical bonding of sparked NiO nanostructures on Ni foams were evaluated by Raman spectroscopy (RAMAN, Renishaw model Invia) using the 532 nm laser with 4.9 mW power as shown in Figure 3.7.

Figure 3.7 Raman spectrophotometer (Renishaw model Invia) operated with an argon ion laser.

Figure 3.8 the Atomic Force Microscope (Nano Scope IIIa, Digital Instruments).

3.3.4 Atomic force microscopy (AFM)

The surface topography of NiO films was examined using an atomic force microscope (AFM, Nano Scope IIIa, Digital Instruments, Figure 3.8) equipped with a standard Si tip scanned over an area of 1x1 μm2 in air at room temperature. The

average surface roughness of the film was then calculated from AFM images of 4 different areas on a sample.

3.3.5 UV-Visible Spectrophotometer (UV-vis)

The band gap energy of sparked NiO film was determined by optical absorption spectroscopy using UV-vis spectrophotometer (Varian Cary 50, U.S.A) as shown in Figure 3.9. The UV-vis sample was prepared by sparking of NiO-NPs on a glass substrate and UV-vis spectrum was measured in the wavelength range of ~300-800 nm.

Figure 3.9 UV-vis spectrophotometer (Varian Cary 50, U.S.A)**.**

The value of the band gap (E_g) can be calculated based on the Tauc relation [180], which is given by3.1:

$$\alpha h\nu = A(h\nu - Eg)^n \quad (3.1)$$

Here, α is the absorption coefficient, E_g is the energy band gap, hν is photon energy, A is a constant relative to the materials and n is a characteristic number. n= 1/2 and 2 for direct and indirect band gap transitions, respectively. The energy gap of the sample was estimated by extrapolation of the linear region to the energy intercept.

3.3.6 Brunauer-Emmett-Teller (BET)

The specific surface area and pore size distribution of the film were determined by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) nitrogen adsorption measurements (Autosorb 1 MP, Quantachrome) as shown in Figure 3.10. The samples were outgassed at 60°C for 4 hour before the measurements.

Figure 3.10 Brunauer-Emmett-Teller (Autosorb 1 MP, Quantachrome, USA)

3.3.7 X-ray Diffraction (XRD)

In this research, the crystal structure of NiO films on the flexible PET coated Cr/Au substrates was studied by grazing-incidence X-ray diffraction (GIXRD, Rigaku Ttrax III in Figure 3.11). The Cu-Kα radiation was operated at 50 kV, 300 mA with a scanning speed of 1.5° per minute at a 2θ step of 0.02°. The results were indexed using Joint Committee on Powder Diffraction Standards (JCPDS) files.

3.3.8 X-ray photoelectron spectroscopy (XPS)

Besides, the oxidation state and chemical composition of the sparked NiO film were evaluated by X-ray photoelectron spectroscopy (XPS) using an AXIS Ultra DLD-X-ray photoelectron spectrometer and a monochromatic Al Kα X-ray excitation source. The XPS machine was shown in Figure 3.12.

Figure 3.11 X-ray diffraction (GIXRD, Rigaku Ttrax III).

Figure 3.12 X-ray photoelectron spectroscopy (AXIS Ultra DLD, England)

3.3.8 X-ray photoelectron spectroscopy (XPS)

Besides, the oxidation state and chemical composition of the sparked NiO film were evaluated by X-ray photoelectron spectroscopy (XPS) using an AXIS Ultra DLD-X-ray photoelectron spectrometer and a monochromatic Al Kα X-ray excitation source. The XPS machine was shown in Figure 3.12.

3.4 Electrochemical measurement

The electrochemical energy-storage performances of the NiO films on flexible Cr/Au coated PET substrates were evaluated at room temperature by Cyclic voltammetric (CV) and galvanostatic charge-discharge (GCD) measurements using an μ-Autolab Type III electrochemical work station (ECO-Chemie, Metrohm, Switzerland in Figure 3.13). The electrochemical measurements were conducted in a three-electrode configuration comprising a silver/silver chloride (Ag/AgCl) reference electrode(RE), a platinum (Pt) wire counter electrode (CE), the NiO working electrode (WE) and 1.0 mol l^{-1} KOH electrolyte.

In the part of the NiO films on nickel foams, CV, GCD and electrochemical impedance spectroscopic (EIS) measurements were conducted at room temperature using a computer-controlled potentiostat-galvanostat operated by Nova 1.10 software package (ECO-Chemie, Metrohm, PGSTAT302N, Figure 3.14). All electrochemical measurements were carried out with a three-electrode system in a 3 mol l^{-1} KOH electrolyte. A silver/silver chloride (Ag/AgCl), a platinum (Pt) wire and NiO/Ni foam electrode (1x1 cm^2) were used as the reference, counter and working electrodes, respectively. EIS data were recorded over the frequency range of 10 mHz - 100 kHz with an applied AC voltage of 5 mV and an open-circuit DC potential. The experiments 3-electrodes setup was shown in Figure 3.15.

Figure 3.13 The μ-Autolab Type III electrochemical work station (ECO-Chemie, Metrohm, Switzerland).

Figure 3.14 The Autolab PGSTAT302N (ECO-Chemie, Metrohm, Switzerland)

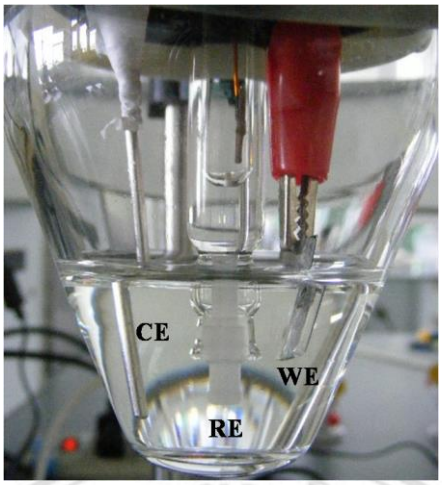

Figure 3.15 The schematic depicting of the 3-electrodes configuration for electrochemical test.