CHAPTER III
METHODOLOGY

In chapter II, a review of the related literature was highlighted in detail. The chapter first, discussed the historical transformation of capacitor to supercapacitor, it then proceeded with the highlights on the basic principles of capacitor. Later, it explained the polymer and it's significant in the fabrication of supercapacitor. Finally the chapter concluded with the review of some selected literatures with regards to polymers/separators and electrode materials used in fabrication of supercapacitor. In this chapter, detail experimental procedures on how the electrolytes and electrode were formed will be discuss.

3.1 Sample Preparation of Composite PVA/H_3PO_4 Electrolytes

Both PSPE and HSPE can also be served as separators in supercapacitors fabrications. The electrolytes were prepared as follows; the active materials comprise of H_3PO_4 and PVA. The H_3PO_4 functions as an ionic liquid, while PVA acts as a polymeric matrix, allowing ionic transport while simultaneously functioning as a separator between the electrodes of the supercapacitor. H_3PO_4 (>85 wt.% in water, molar mass of 98.00 g/mole, product, number of 1502-80) was obtained in aqueous form from R & M marketing, Essex, UK brand, while the PVA (molecular weight; 89,000-98,000, 99+ % hydrolyzed) was obtained from Sigma Aldrich.

The advantage of the aqueous electrolyte is its higher conductance (0.8 S cm^{-1} for H_2SO_4) and the fact that purification and drying processes during production are quite easier compare to other types of electrolytes. Again, aqueous electrolytes are known to be cost effective than organic electrolyte. Both H_3PO_4 and PVA were used as-received without further treatment or purification.

An aqueous solution of PVA is prepared by combining PVA with distilled water in the ratio of 1:10 by volume. This solution is mechanically agitated by magnetic stirring at 60 °C for five hours to thoroughly dissolve the PVA in the distilled water. H_3PO_4 was then mixed with the PVA aqueous solution in the ratio of 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, 40:60 and 30:70 wt.% for PSPE and HSPE (this has been summarized in Tables 3.1 and 3.2).

Table 3.1 Table Showing the Overall Formation of the PSPE Preparation

Coding	Measured quantity PVA in distilled water (g)	Measured quantity of H_3PO_4 (g)	Ratio of PVA to H_3PO_4
P0	2	0.00	100:0
P10	2	0.22	90:10
P20	2	0.50	80:20
P30	2	0.86	70:30
P40	2	1.33	60:40
P50	2	2.00	50:50
P60	2	3.00	40:60
P70	2	4.67	30:70

Table 3.2 Table Showing the Overall Formation of the HSPE Preparation

Coding	Measured quantity PVA in distilled water (g)	Measured quantity of H_3PO_4 (g)	Ratio of PVA to H_3PO_4
H0	2	0.00	100:0
H10	2	0.22	90:10
H20	2	0.50	80:20
H30	2	0.86	70:30
H40	2	1.33	60:40
H50	2	2.00	50:50
H60	2	3.00	40:60
H70	2	4.67	30:70

In order to vary the percentage of the H_3PO_4 used, the following formula was used;

$$\frac{n}{n+2} \times 100\% = x\% \tag{3.1}$$

Where x is the percentage of acid require (0, 10, 20, 30, 40, 50, 60, and 70 wt.%), and n is the value of H_3PO_4 in grams.

The mixing is done in a drop-wise manner with magnetic stirring at 60 °C for about one hour or thereabouts until it completely turns to homogenous solution (transparent in this case).

The mixture is then allow to cool down to an ambient temperature. The resulting homogenous solution of PVA/H_3PO_4 is cast over a plastic Petri dish. Prior to this, the Petri dish was scraped off the dust using a tissue soaked in acetone. The PVA/H_3PO_4 solution solidifies onto the Petri dish and upon curing for about 3 – 4 weeks at room temperature. Prior to that also, a cellulose filter paper (Whatman brand) is cut into a 6 cm x 5.5 cm and soaked in a segment of the aforementioned solution.

The solid layer was easily peeled off from the Petri dish after it dries as a freestanding layer. The thickness of the solid layers formed in this procedure can be controlled depending on the composition that have been mentioned above and also depending on whether it is hybrid (with filter paper) or non-hybrid (without filter paper) (in this case, it was 0.009 – 0.02 mm). The resulting polymer film was then put in the plastic bag for safe keeping and to avoid contamination from the surrounding, for further property analysis.

Fig. 3.1 displayed a prepared solid and hybrid polymer electrolyte before its peel off from the Petri dish.

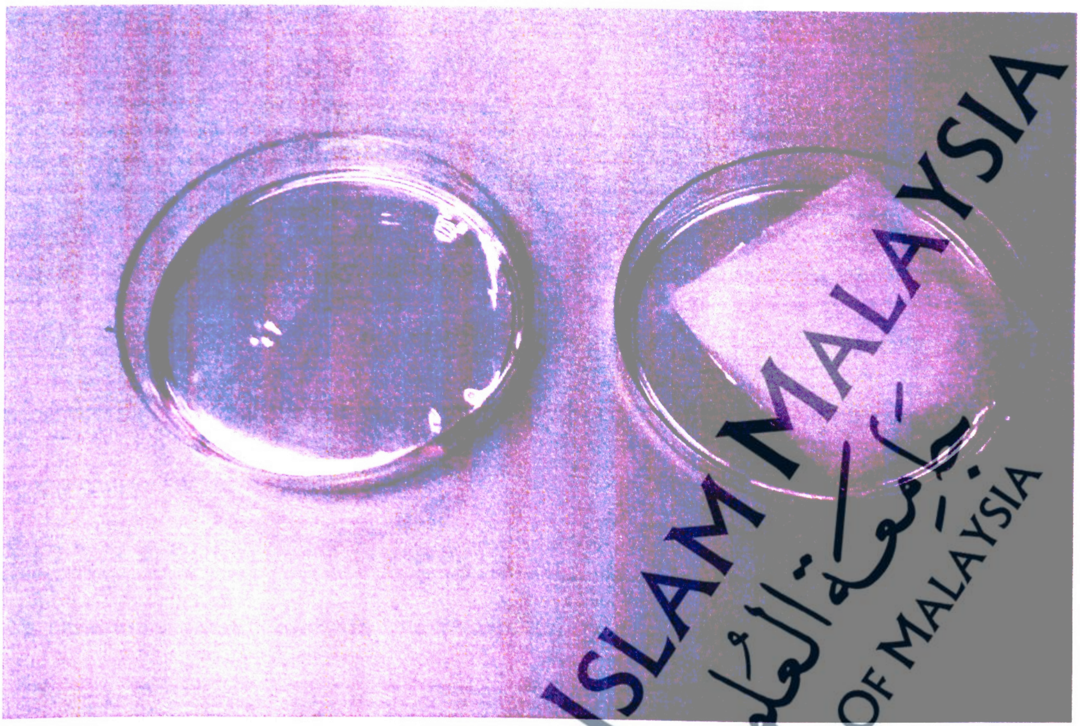

Figure 3.1 pure and hybrid solid polymer electrolytes

3.1.1 Conductivity and Chemical Composition Analysis

Conductivity measurements were carried out on both the solid and hybrid polymer electrolyte films which are also composed of all the different percentage ratio of PVA-H_3PO_4 an impedance method which also was highlighted by Khiar & Arof, (2010). The solid polymer films were sandwiched between a stainless steel, ion-blocking liked measuring device (otherwise known as a probe), each of surface area 2 cm^2 in radius.

The impedance measurements were carried out by using Electrochemical Impedance Spectroscopy (EIS) testing machine named HIOKI 3532-50 LCR Hi-Tester which was connected to the computer. The frequency range of the software was 50 Hz - 1 MHz, and simultaneously calculating both real and imaginary impedance.

The electrical conductivity of both PSPE and HSPE samples were calculated using;

$$i = \frac{t}{R_b A} \tag{3.2}$$

where i is the conductivity of the sample, t, R_b and A are the thickness, the bulk resistance and area of the samples respectively. The thickness of the sample was measured twice at different positions of the polymer films and an average was taken using digital micrometer.

3.1.2 X-Ray Diffraction Analysis

The crystal structure analysis was conducted by XRD. XRD is a powerful and unique technique that can be used to determine the crystalline phases present in the material and to measure the structural properties such as strain state, grain size, epitaxy, phase composition, preferred orientation, and defect structure therein. XRD can also be used to measure the thickness of a thin films and multilayers, and atomic arrangements in amorphous materials (polymer inclusive) and at the interface (Toney, 1992).

The crystal structure analysis of the solid polymer electrolyte films was examined by a Philip X'Pert X-ray diffractometer (XRD) with Cu K_α radiation of wavelength λ=1. 54056 Å for 2θ angles between 10° and 80°. The XRD analysis was carried out on both the PSPE and HSPE films. Furthermore, the degree of crystallinity (%) of the samples using the following equation,

$$CI_n = \frac{100(I_{crys} - I_{amor})}{I_{crys}} \tag{3.3}$$

where CI_n expresses the degree of crystallinity [%] defined by Segal and coworkers, I gives the maximum intensity of the peak corresponding to the plane in the sample at a 2-theta angle of and I_{amo} represents the intensity of diffraction of the amorphous material, which is taken at an angle in the valley between the peaks of all the sample XRD.

3.1.3 Field Emission Scanning Electron Microscope (FESEM) Analysis

Field Emission Scanning Electron Microscope has been reliable and efficient machine used for ultra-high magnification imaging and which produces clearer, less electrostatically distorted images with spatial resolution that could be 3 to 6 times better than conventional SEM. In this analysis, an ultra-high resolution (UHR) FESEM (SU 8030 a family member of SU 8000; Resolution capability of 1.0 nm /15 kV, 1.3 nm/1 kV and abling magnification from 80x to 2,000,000x) have been selected. Both PSPE and HSPE films have been examined using different magnifications.

3.1.4 Differential Scanning Calorimetry Analysis

Differential Scanning Calorimetry, or DSC, is a thermal analysis technique that looks at how a material`s heat capacity (Cp) is changed by temperature. In DSC, a sample of known mass is heated or cooled and the changes in its heat capacity are tracked as changes in the heat flow. This allows the detection of transitions like molten, glass transitions, phase changes, and curing (Guirguis & Moselhey, 2012).

The DSC thermal analysis was carried out using the DCS machine (Mettler Toledo DSC A851 with Star software) under N_2 atmosphere with 10 °C/min heating rate from 40 to 300 °C in order to observe the crystalline and semi-crystalline behavior of the whole samples.

Samples for DSC measurements were prepared from several tiny rectangular pieces, cut from the polymer film to a mass ranging from 1.98 -24.24 mg for PSPE and

7.08 – 19.82 mg for HSPE. The temperature range studied was −40 to 200 °C. The heating/cooling rate was 10 °C/min.

3.2 Sample Preparation of Electrode Materials

Three different types of powdered commercial MWCNTs were selected for this work. These materials are;

(a) Carboxyl, with the specifications; -COOH content of 0.49 wt.%, an outer diameter of > 50 nm, length of 10-20 μm, purity and Ash are both >95 wt.%, and <1.5 wt.%, respectively, surface area of >40 m^2g^{-1} and conductivity of >10^2 Scm^{-1} procured locally from Malaysian market (with material code MC8/21/20),

(b) Hydroxyl, with the specifications; -OH content of 0.71 wt.%, an outer diameter of > 50 nm, length of 10-20 μm, purity and Ash are both >95 wt.%, and <1.5 wt.%, respectively, surface area of >40 m^2g^{-1} and conductivity of >10^2 Scm^{-1}, obtained locally from Malaysian market (with material code MH8 11/202) and

(c) Normal CNTs with the specifications; content of 0.71 wt.%, an outer diameter of 25 nm, length of 10-20 μm, purity and Ash are both >95 wt.%, and <1.5 wt.%, respectively, surface area of >40 m^2g^{-1} and conductivity of >10^2 Scm^{-1}, and was also obtained locally from Malaysian market (with material code SM 2/2/102).

The binder used was P(VdF-HFP) (average molecular weight of ~400,000; Mn of ~130,000 pellets; product number of 427160) was purchased from Sigma Aldrich. Being a co-polymer which possesses dual properties of amorphous domains (HFP), capable of trapping large amounts of liquid electrolytes, and crystalline regions (VdF), P(VdF-HFP) can provide chemical stability and sufficient mechanical integrity for the processing (Lim et al., 2012). Furthermore, its electrochemical stability and performance, processability and safety make them very unique for the usage as a binder in the fabrication of supercapacitor cells.

The cells for the double layer capacitor were fabricated from each of the three aforementioned commercial CNTs. Thus each of;

(i) 90 wt.% of a commercially prepared carboxyl multiwalled CNTs (CPCMWCNTs) and 10 wt.% of P(VdF-HFP),

(ii) 90 wt.% of a commercially prepared hydroxyl multiwalled CNTs (CPHMWCNTs) and 10 wt.% of P(VdF-HFP) and

(iii) 90 wt.% of a commercially prepared normal multiwalled CNTs (CPNMWCNTs) and 10 wt.% of P(VdF-HFP) was mixed inside a 20 ml of the acetone (as shown in Fig. 3.2).

The resulting slurry was cast onto the aluminum foil and was allowed to dry for about two hours at room temperature. Prior to that, an applicator was used to smooth the poured slurry with the view to leveling it and obtaining a desired thickness which was around 0.127 mm (±0.002). At the later stage, the dried sample was then further subjected to heat in an oven for overnight at a temperature of 100 °C. Afterward, the solid films were obtained and then further cut into 2 cm^2 x 3 cm^2 each.

The weights of the films were measured by means of a micro-balance (Santorius, Ax 224) with an accuracy of 0.001 mg. The average weights of two electrode films that make a cell was approximately 0.224 g (±0.002). Using a Perspex of about 5 cm x 4 cm, the resulting cell was set up by sandwiching two electrodes films with a single electrolyte film and finally, assembled in an innovative supercapacitor tester (see Fig. 3.3).

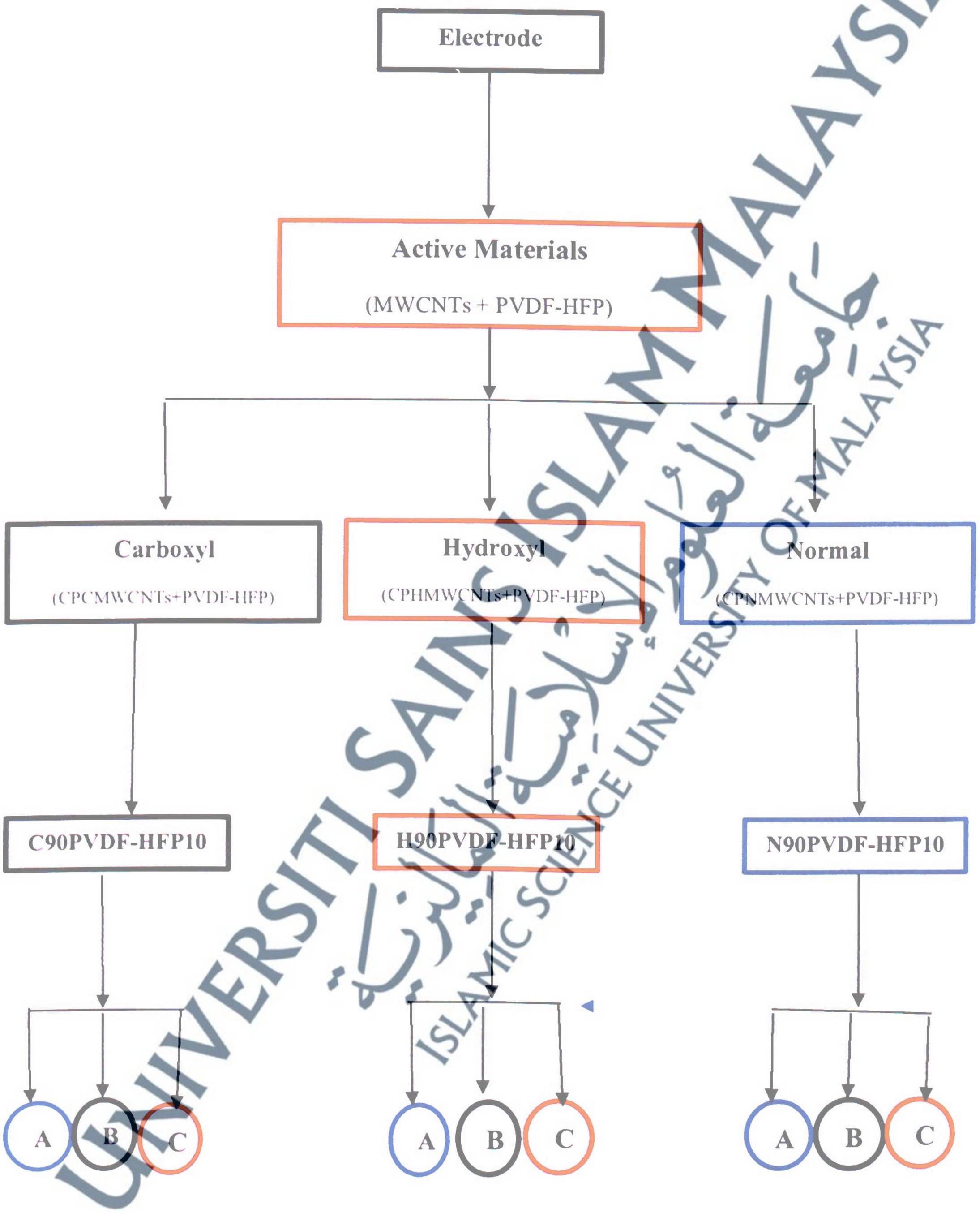

Figure 3.2 A simple chart, showing the sample preparation and cell assembly.

Figure 3.3 Cross-section of the fabricated supercapacitor cells in our laboratory

The following symmetric capacitor cells were assembled;

(a) For CPCMWCNTs;

Cells:
Cell A - C90PVDF-HFP10 | H50 | C90PVDF-HFP10
Cell B - C90PVDF-HFP10 | H60 | C90PVDF-HFP10
Cell C - C90PVDF-HFP10 | H70 | C90PVDF-HFP10

(b) For CPHMWCNTs;

Cells:
Cell A - H90PVDF-HFP10 | H50 | H90PVDF-HFP10
Cell B - H90PVDF-HFP10 | H60 | H90PVDF-HFP10
Cell C - H90PVDF-HFP10 | H70 | H90PVDF-HFP10

(c) For CPCMWCNTs;

Cells:
Cell A - N90PVDF-HFP10 | H50 | N90PVDF-HFP10
Cell B - N90PVDF-HFP10 | H60 | N90PVDF-HFP10
Cell C - N90PVDF-HFP10 | H70 | N90PVDF-HFP10

3.2.1 X-Ray Diffraction Analysis

As mention earlier in the electrolyte preparation, even for the electrode, the XRD spectra were obtained with an XRD (Philip X'Pert XRD with Cu K_α radiation of wavelength λ=1. 54056 Å for 2θ angles between 10° and 80°) that used Cu $K\alpha$ radiation (λ = 1.5406 Å) operating at 40 kV and 30 mA.

3.2.2 Field Emission Scanning Electron Microscope (FESEM)

The surface morphologies of all electrode samples were investigated via FESEM (SU 8030 a family member of SU 8000; Resolution capability of 1.0 nm / 15 kV, 1.3 nm / 1 kV and abling magnification of 80x to 2,000,000x).

3.2.3 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) was carried out on the scale-range of 50 ^{0}C to 1000 ^{0}C under nitrogen gas (N_2) flow at a heating rate of 10 ^{0}C min^{-1} on a METTLER, STAR^e SW 10.00 thermal analyzer in line with our previous work (Hashim et al., 2014).

3.2.4 Electrochemical Behavior

The electrochemical behavior of the cell for the CV analysis and CD were respectively carried out using a newer battery charger which has been interfaced to a computer called "e-machines" (model: ET1850, Rating: 100-127/220-240 Vac, 6/3.15 A (6/3, 15 A), 60/50 Hz) and Gamry instrument Framework. The specific capacitance of the electrode materials obtained in the two-electrode system was calculated by integrating the CV curves using the equation;

$$C_{sp} = \frac{2i}{sm} \qquad (3.4)$$

where i is the current difference, m is the mass of the electrode and s is the scan rate.

However, the effective capacitance obtained from each CD profile is is calculated using the following equation;

$$C_e = i\frac{\Delta t}{\Delta V} \tag{3.5}$$

where C_e stands for effective capacitance, i is the applied current and Δt and ΔV are the changes in time and current respectively. While power and energy densities were obtained using the relations earlier stated in the previous chapter. Moreso, the columbic efficiency is calculated using the following equation;

$$\eta = \frac{t_d}{t_c} \times 100 \tag{3.6}$$

where t_d and t_c represent the time of charging and discharging respectively.

3.3 Chapter Conclusion

This chapter highlighted the experimental procedures for the overall supercapacitor fabrication. Overall, a total of seven cells were set to be fabricated using the three different electrode materials and HSPE. Next chapter, the results and discussion of the already prepared polymer electrolytes and overall cells will be communicated.