

Appendix A



Journal Publications

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A Flexible Solid State EDLC From a Commercially Prepared Multiwalled Carbon Nanotubes and Hybrid Polymer Electrolytes

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Abstract

An electrochemical symmetric capacitor with a modest energy and power densities has been fabricated using a commercially prepared carbon nanotubes as electrode and hybrid solid polymer electrolyte. This integrated separator and electrolyte layer is made up of a filter paper, a polyvinyl alcohol (PVA) doped with phosphoric acid at three different concentrations. The electrode material consisted of 90 % of the said carbon nanotubes and 10 % of Poly (Vinylidene Fluoride-Co-Hexafluoropropylene) (PVdF-HFP). Three cells were then assembled as follows; cell-A (N90PVdF-HFP10 |H50| N90PVdF-HFP10), cell-B (N90PVdF-HFP10 |H60| N90PVdF-HFP10) and cell-C (N90PVdF-HFP10 |H70| N90PVdF-HFP10). These as-assembled symmetric supercapacitor with an optimal mass ratio was able to be operated reversibly over a wide voltage range of 0.0–3.0 V, depending on the cell-type. Overall, the supercapacitor fabricated from cell A exhibits excellent rate capability with a capacitance, energy and power densities of 163.66 Fg⁻¹, 822.00 Jg⁻¹ and 5.38 Jg⁻¹s⁻¹ respectively, and long-term cycling stability of 5000 cycles.

Keywords: multiwalled carbon nanotubes, Differential Scanning Calorimetry (DSC) Analysis, Cyclic Voltammetry (CV), Charge Discharge (CD), Hybrid Solid Polymer Electrolyte (HSPE)

1. Introduction

The disproportionate usage of fossil fuels in order to earn a living and meet energy requirements has grossly affected the globe, causing climatic change due to the dramatic increase in the CO₂ emission (i.e. Global warming). Hence, in order to decrease our current dependence on environmentally harmful fossil fuels, the society has to move toward pursuing sustainable and renewable resources. At the moment, researchers and academia have focused their watch lights on renewable energy production from solar energy and wind energy, even though, these natural energies are subject to the climatic conditions. So, it is very imperative to devise a means of storing electricity when it is available and retrieving it when needed (Li & Wei, 2013).

Electrochemical energy storage systems are considered to be one of the environmentally friendly alternative energy and power sources. Among them, Supercapacitors are good example of such electrochemical energy storage systems which have higher power densities (Dubal & Rudolf, 2013) than batteries, fast charging and discharging rates, long cycle life, (Stepniak & Ciszewski, 2010). Hence, they are commercially used in electronic markets, (Bittner et al., 2012; Wu et al., 2012), hybrid electric vehicles, (Shi et al., 2013) and other number of applications.

Although conducting polymers and transition metal oxide provide higher specific capacitance than electrochemical double layer capacitors (EDLCs), their poor rate capability, high cost and low conductivity, their academic and industrial usages become limited. The excellent chemical and physical properties of carbon materials such as high conductivity, relatively low cost, high surface area, excellent temperature stability, and good corrosion resistance make them valuable candidates for the electrodes of EDLCs, which holds true especially, for graphene and carbon nanotubes (CNTs), which possess the largest theoretical and experimental surface area (Wang et al., 2013 (a)). In view of the above, therefore, this work is aimed at presenting a flexible solid state EDLC using CNTs as an electrode material and hybrid polymer electrolytes serving as a separator and electrolyte.

2. Methodology

2.1 Electrolytic Materials

The main electrolytic materials used here are; the H_3PO_4 , PVA and Whatman filter paper. The H_3PO_4 (>85 wt. % in water, molar mass of 98.00 gmol^{-1} , product, number of 1502-80) was purchased in aqueous form from R & M marketing, Essex, UK brand, while the PVA (molecular weight; 89,000-98,000, 99 + % hydrolyzed) was purchased from Sigma Aldrich. Both H_3PO_4 and the powdered PVA were directly used as-received without further treatment or purification. An aqueous solution of PVA was then prepared by mixing the PVA with distilled water in the ratio of approximately 1:10 by volume. This solution is mechanically agitated by magnetic stirring at $60\text{ }^\circ\text{C}$ 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 70:30, 60:40 and 50:50 wt. %.

The choice of the aforementioned percentage weights was borne out of assurance that, their respective conductivities are quite promising even at room temperature. We have since reported this development severally in (Hashim et al., 2012; Hashim et al., 2014; Sa'adu et al. (a), 2014; Sa'adu et al. (b), 2014) for a hybrid polymer electrolytes at a concentration combinational ratio of 70:30 wt. %. After the mixture cools down to a room temperature, the resulting homogenous solution of PVA/ H_3PO_4 was cast over a plastic Petri dish. This was performed, after a cellulose filter paper (Whatman brand) was cut into a $6\text{ cm} \times 5.5\text{ cm}$ (to a size that fit into the Petri dish) and soaked into the segment of the said solution. The period between the casting of the samples on the Petri dish and its drying took about 28 days.

2.2 Electrode Materials and Cell Assembly

The powdered MWCNTs with the following specifications; content of 0.71 wt.%, an outer diameter of $> 50\text{ nm}$, length of $10\text{-}20\text{ }\mu\text{m}$, purity and Ash are both $>95\text{ wt.}\%$, and $<1.5\text{ wt.}\%$, respectively, Surface area of $>40\text{ m}^2\text{g}^{-1}$ and Conductivity of $>10^2\text{ Scm}^{-1}$ was obtained locally from Malaysian market (with material code SM 2/2/102). The binder used was P(VdF-HFP) (average molecular weight of $\sim 400,000$; Mn of $\sim 130,000$ 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), 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, and to be used as a binder for fabrication of cells.

The cells for double layer capacitor were fabricated from a mixture of 90 wt.% of a commercially prepared multiwalled carbon nanotubes (CPNMWCNTs) and 10 wt.% of P(VdF-HFP), mixed inside a 20 ml of the acetone. 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 . At the later stage, the dried sample was then further subjected to heat in an oven for overnight at a temperature of $100\text{ }^\circ\text{C}$. Afterward, the solid films were obtained and then further cut into $2\text{ cm}^2 \times 3\text{ cm}^2$ 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 . Using a Perspex of about $5\text{ cm} \times 4\text{ cm}$, the cell was set up by sandwiching two electrodes with the electrolyte and assembled in an innovative supercapacitor tester.

XRD spectra were obtained with an XRD (Philip X'Pert XRD with $\text{Cu K}\alpha$ radiation of wavelength $\lambda=1.54056\text{ \AA}$ for 2θ angles between 10° and 80°) that used $\text{Cu K}\alpha$ radiation ($\lambda=1.5406\text{ \AA}$) operating at 40 kV and 30 mA . Furthermore, the surface morphologies of all films were investigated via FESEM (SU 8030 a family member of SU 8000; Resolution capability of $1.0\text{ nm} / 15\text{ kV}$, $1.3\text{ nm} / 1\text{ kV}$ and abling magnification of $80\times$ to $2,000,000\times$). CD analysis and CV were respectively carried out using a newer battery charger which has been interfaced to a computer called "e-machines" (model: ET1850, Rating: $100\text{-}127/220\text{-}240\text{ Vac}$, $6/3.15\text{ A}$ ($6/3, 15\text{ A}$), $60/50\text{ Hz}$) and Gamry instrument Framework. The following symmetric capacitor cells were assembled;

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

3. Results and Discussions

3.1 Microstructure Characterizations

The microstructure of the samples of this work was examined using XRD and FESEM. The spectra of the X-ray in these samples were obtained from an XRD; a Philip X'Pert XRD model with Cu K α radiation of wavelength $\lambda=1.54056 \text{ \AA}$ for 2θ angles between 10° and 80° that used Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 30 mA.

The XRD analysis of the N90PVdF-HFP10 electrode is shown in Figure 1. As seen in that figure, all diffraction peaks can be observed and the major diffraction peaks of the CPNMWCNTs can also be clearly seen. The broad diffraction peaks that appeared at 43° and 56.1° can be indexed to the presence of MWCNT, while an additional sharp peak at $2\theta=26^\circ$ is due to the embedding of the graphitic CNTs (Wang et al., 2013b). Thus, the intensity of the peak observed, could correspond to the high concentration of the as-prepared carbon electrode (Dong et al., 2007; Hashim & Sa'adu, 2014) of the as-prepared carbon electrode. While the first diffracted peak at the left hand side at $2\theta=20.7^\circ$ correspond to crystalline peaks of PVDV (Stolarska et al., 2007). Similar XRD results were obtained by (Li et al., 2010; Stolarska et al., 2007).

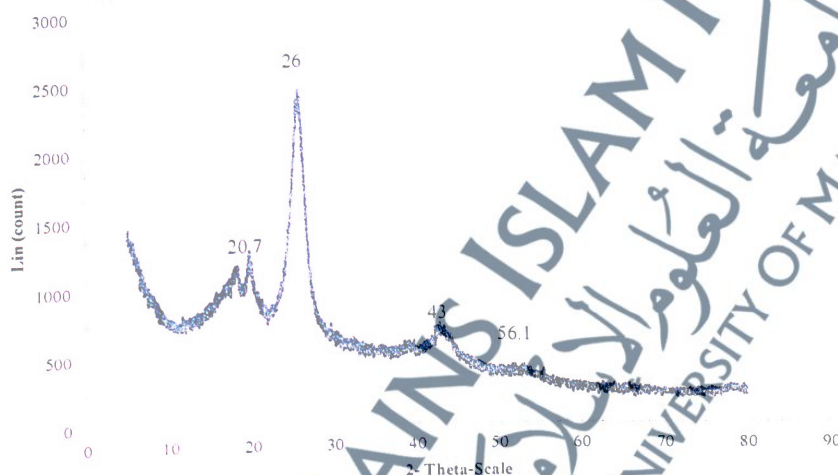


Figure 1. XRD Analysis of CPNMWCNTs

3.2 Thermogravimetric Analysis

Using thermal analyzer in the scale-range of 50°C to 1000°C under nitrogen gas (N_2) flow at a heating rate of $10^\circ\text{C min}^{-1}$ on a METTLER, STAR[®] SW 10.00, the analysis of the temperature stability of the sample were investigated. We have used similar techniques in our previous work (Hashim et al., 2014). The thermal stability of the samples was discerned in Figure 2. The Figures were (a); 0 wt. % sample (Background) (b); pure CPNMWCNTs (c) N90PVdF-HFP10 – Single scale (d); N90PVdF-HFP10 – Double scale. At first, we analyzed background heating in order clear any ruminant residue and for re-calibration. From the traces of Figure (b) it can be seen that, pure CPNMWCNTs suffered its major loss of just 3.1362 % occurring at 596.56°C leaving a residue of 94.3867 %. However, when 10 wt. % of the binder was added to the as-prepared sample, the results dramatically change, especially when compared with those of the functionalized CNTs. Figure 2 (b and c), provided the thermal stability results. In this case, the two losses were discovered. The initial loss of 4.1008 % of the total samples occurs at 108.54°C , then the second and major loss was 60.1150 % occurred at 745.83°C .

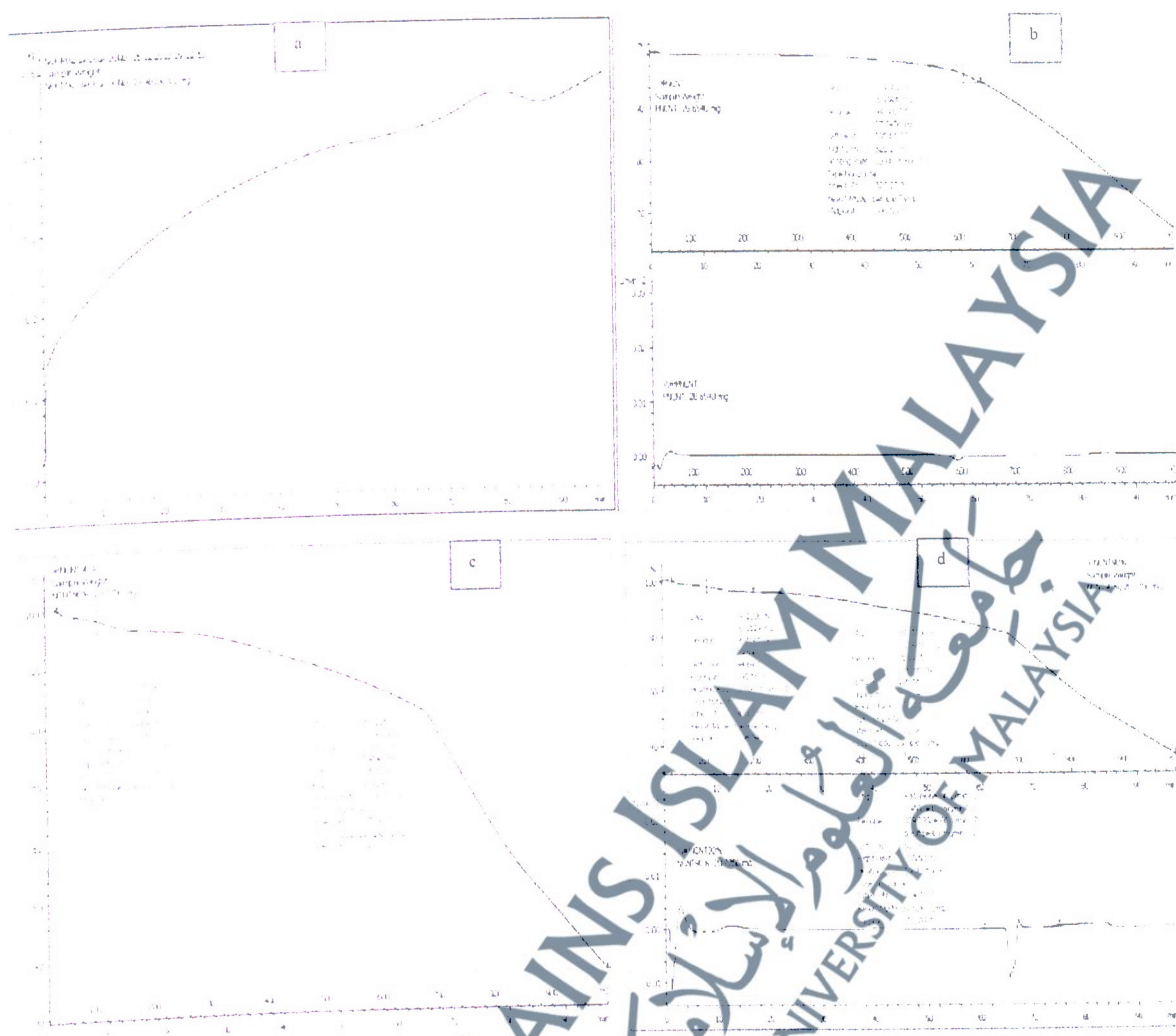


Figure 2. TGA of the electrode at (a); 0 wt. % sample (Background) (b); pure CPNWCNT (c) N90PVdF-HFP10 – Single scale (d); N90PVdF-HFP10 – Double scale.

3.3 Electrochemical Behavior

The electrochemical behaviors of CPNWCNTs were investigated by the cyclic voltammetry (CV) and charge-discharge (CD) measurements using two-electrode system. Figure 3 reveals the CV of Cell –A (N90PVdF-HFP10 |H50| N90PVdF-HFP10) at scan rates of 10, 50 and 100 mV, within a voltage window of 0.0-3.0 V) and 50 mV (for a voltage window of 1 V). It can be discerned that the resulting CV curves of the cell at a scan rate of 50 mV and within 0.0-1 V- voltage window, displayed leaf-like and mirror-symmetric indicating a modest ideal supercapacitive behavior for the CPNWCNTs. The specific capacitance of the electrode materials was obtained based on the total mass of the two electrodes in the symmetric capacitor by integrating the CV curves in that Figure using the equation;

$$C_{sp} = \frac{2i}{sm} \quad (1)$$

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

From the calculation, it could be obtained that, the specific capacitance is 154.1 Fg^{-1} , 28.8 Fg^{-1} , and 17.7 Fg^{-1} for scan rates of 10, 50 and 100 mV, respectively. The decrease in specific capacitance of 154.1 Fg^{-1} - 17.7 Fg^{-1} is an indication of the existing relationship between capacitance and scan rate and this could either be attributed to the slow transfer of ions on the electrode electrolyte interface (Shu et al., 2013).

Furthermore, Figure 4 displays the CV of Cell-B (N90PVdF-HFP10|H60| N90PVdF-HFP10) at scan rates of 10, 50 and 100 mV, (for a voltage window of 3 V) and 50 mV (for a voltage window of 1 V). The specific capacitances obtained in this cell were 93 Fg^{-1} , 36 Fg^{-1} and 26 Fg^{-1} for scan rates of 10, 50 and 100 mV respectively. While Figure 5 shows the CV of Cell -C (N90PVdF-HFP10 |H70| N90PVdF-HFP10) at scan rates of 10, 50 and 100 mV, (for a voltage window of 3 V) and 50 mV (for a voltage window of 1 V). These results gave a balance and modest capacitance and can be considered as better than that of cells A and B. The capacitance recorded here are 112.4 Fg^{-1} , 40.0 Fg^{-1} and 32.0 Fg^{-1} for scan rates of 10, 50 and 100 mV respectively. Table 1 summarizes the results of the capacitance obtained in all the three cells and Figure 6 (a) summarizes the capacitance performance in the combined graph of capacitance against the scan rates for cells A, B and C.

One of the criteria in supercapacitor's fabrication and application is its ability to endure long-term cycling stability. In this respect, the cycling endurance measurement over 5000 cycles for all the cells (Figure 6 (b)) was conducted using the CD test at the working voltage of 1.5 V. The figure displayed the graph of the resulting capacitance retention as a function of cycling number. Of note, compared to cells A and B, cell-C (N90PVdF-HFP10 |H70| N90PVdF-HFP10) exhibits the best cycling stability with about 80 % capacitance of its initial value after 5000 cycles.

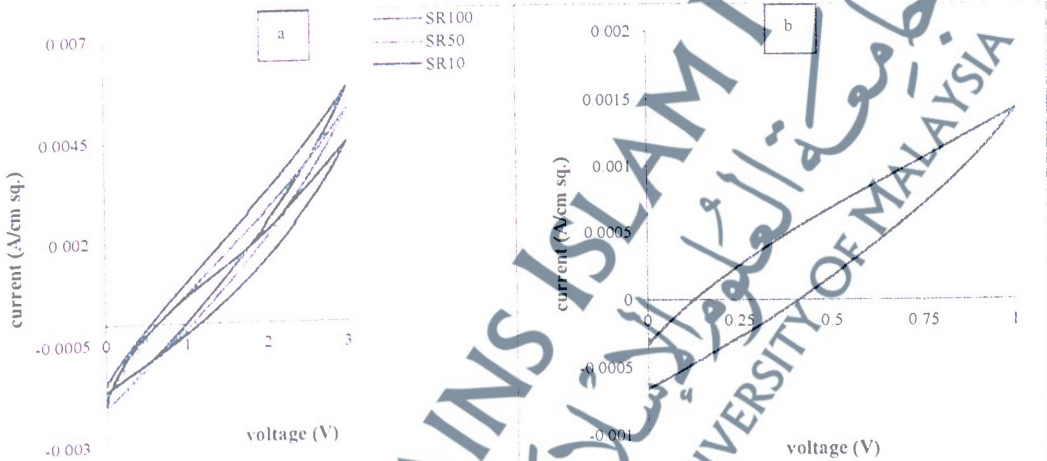


Figure 3. CV of Cell-A (N90PVdF-HFP10 |H50| N90PVdF-HFP10) at (a); scan rates of 1, 50 and 100 mV, 3 V-voltage window (b); scan rate of 50 mV; 1 V – voltage window

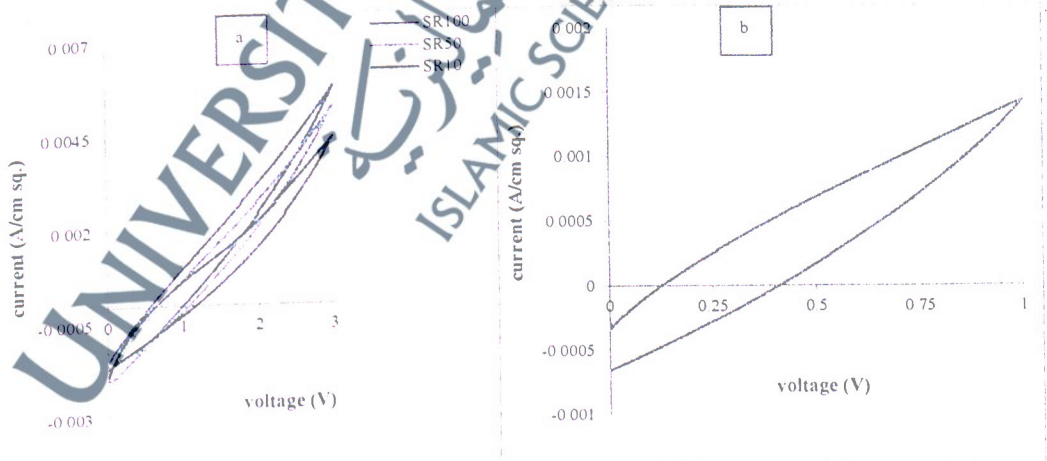


Figure 4. CV of Cell -A (N90PVdF-HFP10 |H60| N90PVdF-HFP10) at (a); scan rates of 1, 50 and 100 mV, 3 V-voltage window (b); scan rate of 50 mV; 1 V – voltage window

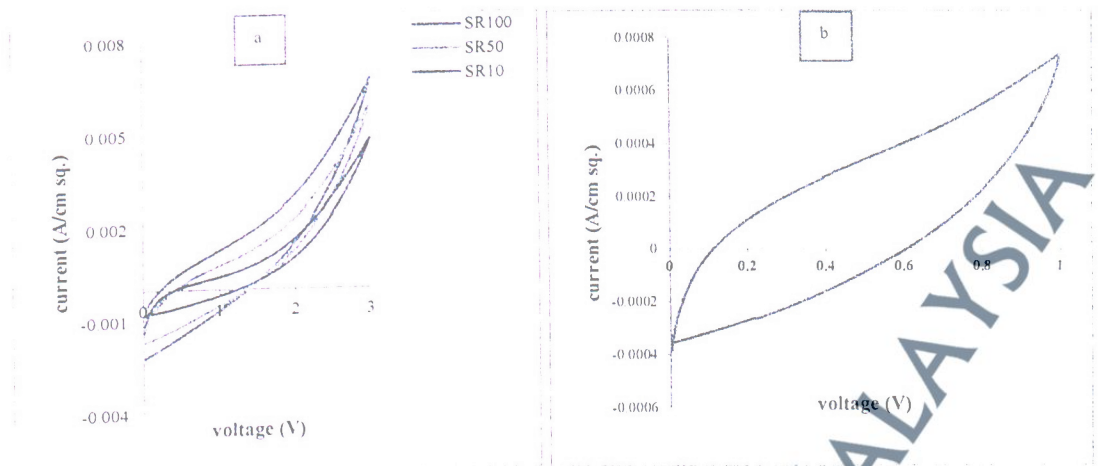


Figure 5. CV of Cell-A (N90PVdF-HFP10 |H70| N90PVdF-HFP10) at (a); scan rates of 1, 50 and 100 mV, 3 V-voltage window (b); scan rate of 50 mV; 1 V – voltage window

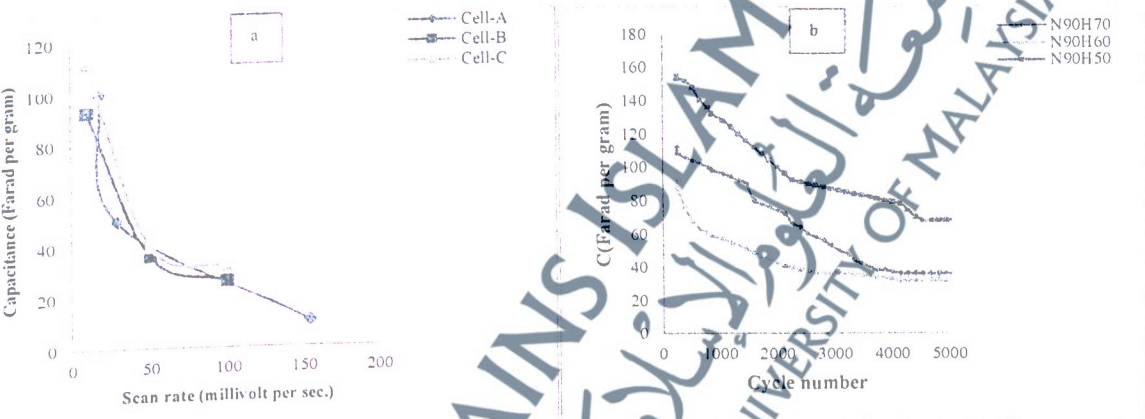


Figure 6. (a); combined graphs of capacitance against the scan rates for cells A, B and C. (b); combined cyclic performances of cells A, B and C

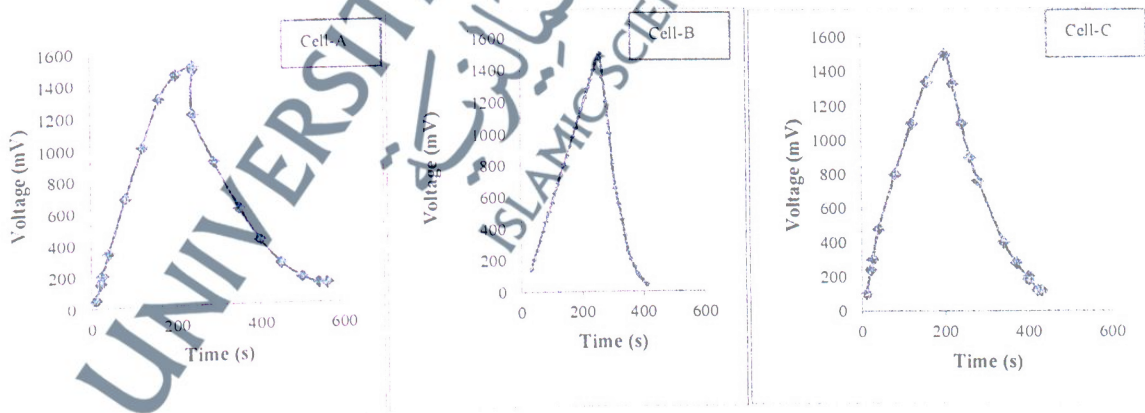


Figure 7. CD graphs of (a); Cell-A (b); Cell-B and (c); Cell-C

Table 1. Performance of supercapacitor by the CV

Cells	Working voltage (V)	Capacitance value of different scan rates (Fg^{-1})		
		100 mV	50 mV	10 mV
A-N90H50	3	17.7	28.8	157.1
B-N90H60	3	26.0	36.0	93.0
C-N90H70	3	32.0	40.0	112.4

Table 2. Performance of supercapacitor by the CD

Cells	Working voltage (V)	C_d (Fg^{-1})	ESR ($\Omega \text{ cm}^2$)	Energy density (Jg^{-1})	Power density ($\text{Jg}^{-1}\text{s}^{-1}$)
A- N90H50	1.5	16.4-163.0	3.0-30.0	82.0-822.0	0.1-5.4
B-N90H60	1.5	8.9-89.3	0.1-1.0	44.7-448.4	1.3-5.3
C-N90H70	1.5	14.0-139.0	0.2-1.5	140.0-700.0	0.8-8.4

Galvanostatic CD is considered one of the complimentary procedure of recording CD relatives at constant-current that is normally employed to practically test supercapacitors and batteries. In a theoretical sense, for a constant capacitor device with less effect on high internal resistance, the constant-current charge and discharge relations are straight lines with $+1/c$ and $-1/c$ respectively (Niu et al., 2006). In view of the above, the capacitance, power and energy densities were also investigated using the galvanostatic CD test. In Figure 7, the CD graphs of (a); Cell-A (b); Cell-B and (c); Cell- C were all depicted at a working voltage of 1.5 V and at three different current densities i.e. 10, 20 and 100 mA. The effective capacitance, power and energy densities were also calculated. In cell-A, the discharged capacitances obtained were 16.36 Fg^{-1} , 32.73 Fg^{-1} and 163.66 Fg^{-1} respectively at an applied current density of 100, 20 and 10 mA; the calculated energy and power densities are $82.21 \text{ Jg}^{-1}/1.27 \text{ Jg}^{-1}\text{s}^{-1}$, $164.40 \text{ Jg}^{-1}/2.52 \text{ Jg}^{-1}\text{s}^{-1}$ and $822.00 \text{ Jg}^{-1}/5.38 \text{ Jg}^{-1}\text{s}^{-1}$ at the aforementioned current densities. For the cell-B, the discharged capacitances obtained were 8.89 Fg^{-1} , 17.80 Fg^{-1} and 89.28 Fg^{-1} respectively at an applied current density of 100, 20 and 10 mA; the calculated energy and power densities are $44.70 \text{ Jg}^{-1}/1.26 \text{ Jg}^{-1}\text{s}^{-1}$, $89.40 \text{ Jg}^{-1}/2.52 \text{ Jg}^{-1}\text{s}^{-1}$ and $448.40 \text{ Jg}^{-1}/12.55 \text{ Jg}^{-1}\text{s}^{-1}$ at the said current densities. Finally, the resulting discharge capacitance of the cell-C are: 13.95 Fg^{-1} , 27.90 Fg^{-1} and 139.50 Fg^{-1} respectively at an applied current density of 100, 20 and 10 mA; power/energy densities are $70.06 \text{ Jg}^{-1}/0.84 \text{ Jg}^{-1}\text{s}^{-1}$, $140.12 \text{ Jg}^{-1}/1.67 \text{ Jg}^{-1}\text{s}^{-1}$ and $700.16 \text{ Jg}^{-1}/8.37 \text{ Jg}^{-1}\text{s}^{-1}$ at the aforementioned current densities. Normally, the dwindle in capacitance could be as a result of the dissolution of the active materials in the electrolytes, mechanical faults of the electrode (e.g. Expansion, agglomeration and so on) and the imbalance of the two electrodes which can cause instability of the electrode potential (Wang et al., 2013). Hence, the discharged capacitance decreases with the increase in current density, which could be as a result of the low penetration of ions into the inner region of the pores due to fast potential changes.

4. Conclusion

We demonstrated a novel of a high-performance symmetric supercapacitor based on CPNMWCNTs sandwiched with the hybrid solid polymer electrolyte. Of the three cells assembled, the optimized N90PVdF-HFP10 [H50] N90PVdF-HFP10 (cell A) symmetric supercapacitor stands better to be operated reversibly in a wide potential window as high as 3.0 V and delivers a high capacitance, energy and power densities of 163.66 Fg^{-1} , 822.00 Jg^{-1} and $5.38 \text{ Jg}^{-1}\text{s}^{-1}$ respectively, and long-term cycling stability of 5000 cycles. With the increasing demands on energy storage systems with high energy and power densities, therefore, these results afford a convenient and efficient way to construct supercapacitors based on CPNMWCNTs electrode materials.

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Supercapacitor Based On a Commercially Prepared Hydroxyl Multiwalled Carbon Nanotubes With Hybrid Polymer Electrolyte

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Abstract

This paper reports on the development of three pieces of supercapacitor cells for portable applications such as mobile and wearable energy storage. In a primary embodiment, the three developed supercapacitors cells, each, consist of two flexible electrodes fabricated on thin metal base substrates. The electrode, mainly a commercially prepared multiwalled hydroxyl carbon nanotubes (CPHMWCNTs), sandwich a hybrid solid polymeric separator doped with an appropriate ionic material acting as an electrolyte. The integrated separator and electrolyte layer was made of filter paper, a polyvinyl alcohol (PVA) doped with phosphoric acid at three different concentrations. The Three cells were then assembled and leveled as cell-A (C90PVdF-HFP10 [H50] C90PVdF-HFP10), cell-B (C90PVdF-HFP10 [H60] C90PVdF-HFP10) and cell-C (C90PVdF-HFP10 [H70] C90PVdF-HFP10). The evaluations of these three different electrodes and their substrate materials allowed for selection of a combination of active material and suitable percentage concentrations that yielded optimal supercapacitor performance. From the overall results of the electrochemical analysis of cyclic voltammetry (CV), cell-B delivered higher capacitance of $86.60.10 \text{ Fg}^{-1}$ which was higher than the capacitance obtained by cell-C (65 Fg^{-1}) and even doubling the capacitance obtained by cell-A (42.1 Fg^{-1}). Whereas the charge-discharge (CD) tests carried out in the cells reveals that, even at the lower voltage window of 1.5 V, cell-B delivered better than cells A and C with a balanced and better discharge capacitance of 119.0 Fg^{-1} and higher energy/power densities of $597.0 \text{ Jg}^{-1}/12.6 \text{ Jg}^{-1}\text{s}^{-1}$ and very low internal resistance.

Keywords: supercapacitor, hydroxyl multiwalled carbon nanotubes, Differential Scanning Calorimetry (DSC) Analysis, cyclic voltammetry (CV), charge-discharge (CD), hybrid solid polymer electrolyte (HSPE)

1. Introduction

In every country across the globe, energy has become an issue of national security, especially with the current rise in the global economy (Dubal et al., 2013), the exhaustion of fossil fuels and increasing environmental pollution. Meeting the energy demands in an environmentally sustainable manner is currently the most important technological challenge facing the society. Energy storage devices can efficiently store electricity generated from renewable sources, such as solar, water, wind, thermoelectric, fuel cells, for reuse at many different scales. Therefore, energy storage devices, such as batteries and supercapacitors, have become a key to society (Shi et al., 2013).

Supercapacitor also known as Electrochemical Capacitor (EC) or ultracapacitor (Hashim et al., 2014; Inagaki et al.(a), 2014; Hashim & Khair, 2011; Burke, 2009) affords new, eco-friendly and low-cost energy storage device for progressive civilization and growing ecological agencies (Dubal et al., 2014), their characteristics comprising a combination of high power density (Wu et al., 2013) and a balanced or reasonable energy density (Dubal et al., 2013) with fast response time and almost infinite life cycleability (Zhao et al., 2011) can complement other storage devices such as batteries, conventional capacitors and fuel cells. Hence, the above properties make them suitable for use in many applications ranging from applications related to portable electronic devices (Perera et al., 2013) UPS, to a hybrid motor vehicles (Inagaki et al.(b), 2014; Qian et al., 2013).

In Electrochemical Double Layer Capacitors (EDLCs), the charge is stored electrostatically at the electrode-electrolyte interface, so, as a result of this storage mechanism, these devices can be charged and discharged within a blink of seconds (Bockenfeld et al., 2013; Gund et al., 2013; Jiang et al., 2013). Electrodes based on carbon nanotubes (CNTs) deliver an impressive power and energy due to their high surface area, high conductivity and

consequently, when functionalized, these electrodes, can deliver up to an optimum level of power and energy densities (Jiang et al., 2013). Hence, this study focused on the fabrication of supercapacitor based on commercially prepared hydroxyl multiwalled carbon nanotubes (CPHMWCNTs). Functionalized supercapacitors are believed to have some key features due to the functionalization processes that occurs in the CNTs chain. The widening of the pore sizes of the CNTs (when functionalized) will result in their improvement for the electrolyte infiltration and ion diffusion throughout the electrode. Other features include the wettability, excellent capacitance, and good charge-storage properties (Van Hooijdonk et al., 2013). Stability for long term storage is one of the merits of the functionalized CNTs (Capek, 2009).

2. Methodology

2.1 Electrolytic Materials

Three different polymer electrolytes which also served as the separators were prepared as follows; The H_3PO_4 (>85 wt.% in water, molar mass of 98.00 gmol^{-1} , 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. Both H_3PO_4 and PVA were used as-received without further treatment or purification. An aqueous solution of PVA was then 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 70:30, 60:40 and 50:50 wt. %.

These percentage weights were shown to have promising conductivities even at an ambient temperature. We have reported this development in (Hashim et al., 2012) for a hybrid electrolyte at a combination of 70:30 wt. %. After the mixture cools to a room temperature, the resulting homogenous solution of PVA/ H_3PO_4 was cast over a plastic Petri dish. This was done after a cellulose filter paper (Whatman brand) was cut into a $6 \text{ cm} \times 5.5 \text{ cm}$ (sizes that fits into the Petri dish) and soaked into each of the aforementioned solutions. The above mixture took roughly four weeks before it dries. Thereafter, the resulting flexible hybrid solid polymer electrolyte (HSRE) that is peeled off from the Petri dish was used as the separator.

2.2 Electrode Materials and Cell Assembly

The Hydroxyl MWCNTs with the following specifications; -OH content of 0.71 wt.%, an outer diameter of $> 50 \text{ nm}$, length of $10\text{-}20 \mu\text{m}$, purity and Ash are both $>95 \text{ wt.}\%$, and $<1.5 \text{ wt.}\%$, respectively, Surface area of $>40 \text{ m}^2\text{g}^{-1}$ and Conductivity of $>10^2 \text{ Scm}^{-1}$ was purchased locally in Malaysia (with material code MH8 11/202). The binder used was P(VdF-HFP) (average molecular weight of $\sim 400,000$; Mn of $\sim 130,000$ pellets; product number of 427160) was purchased from Sigma Aldrich. P(VdF-HFP) copolymer was found to meet all the requirements for use as a binder or even a polymer host in supercapacitor fabrication due to its electrochemical stability and performance, processability, and safety. Again, this co-polymer contains amorphous domains (HFP) which is capable of trapping large amounts of liquid electrolytes, and crystalline regions (VdF) which provide chemical stability and sufficient mechanical integrity for the processing (Lim et al., 2012). Moreover, P(VdF-HFP) is proven to have strong electron withdrawing, unique arrangement and high dielectric constant (Kim et al., 2013).

Therefore, the double layer capacitor was made with a mixture of 90 wt. % of the CPHMWCNTs and 10 wt.% of P(VdF-HFP), mixed inside a 20 ml of the acetone. The slurry was then cast onto the Aluminum foil and allowed to dry for about two hours at room temperature. Prior to that, an applicator was used to polish the slurry with the view to leveling it and obtaining a desired thickness which was around 0.127 mm . The dried sample was then further dried in an oven for about 12 hours at a temperature of 100°C . Afterward, the solid films were obtained and were further cut into $2 \text{ cm}^2 \times 3 \text{ cm}^2$ 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 around 0.224 g . Using a Perspex of about $5 \text{ cm} \times 4 \text{ cm}$, the cell was set up by sandwiching two electrodes with the electrolyte and assembled in an innovative supercapacitor tester.

XRD spectra were obtained with an XRD (Philip X'Pert XRD with $\text{Cu K}\alpha$ radiation of wavelength $\lambda=1.54056 \text{ \AA}$ for 2θ angles between 10° and 80°) that used $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 30 mA . The surface morphologies of all firms were investigated via FESEM (SU 8030 a family member of SU 8000; Resolution capability of $1.0 \text{ nm} / 15 \text{ kV}$, $1.3 \text{ nm} / 1 \text{ kV}$ and abling magnification of $80\times$ to $2,000,000\times$). Charge-discharge (CD) and cyclic voltammetry (CV) analysis were respectively carried out using a newer battery charger which has been interfaced to a computer called "e-machines" (model: ET1850, Rating: $100\text{-}127/220\text{-}240 \text{ Vac}$, $6/3.15 \text{ A}$ ($6/3, 15 \text{ A}$), $60/50 \text{ Hz}$) and Gamry instrument Framework (version 5.61). The following symmetric capacitor cells were assembled;

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

3. Results and Discussions

3.1 Microstructure Characterizations

In order to examine the microstructure of the samples in this work, XRD, and FESEM were used. The spectra of the X-ray in these samples were obtained from an XRD; a Philip X'Pert XR) model with Cu K α radiation of wavelength $\lambda=1.54056 \text{ \AA}$ for 2θ angles between 10° and 80° that used Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 30 mA. The XRD analysis of the H90PVdF-HFP10 electrode is depicted in Figure 1. As seen from this figure, all diffraction peaks can be observed and the major diffraction peaks of the CPHMWNTs can also be seen clearly. The first two peaks that appeared at in $2\theta= 26^\circ$ and $\theta= 43^\circ$ which matched with (002) and (101) respectively indicate the presence of the embedded graphite CNT, while the last peak on the right side at $2\theta= 56.1^\circ$ might also be considered as part of the CNT. Thus, the intensity of the peak observed, could correspond to the high concentration of the as-prepared carbon electrode conductivity (Dong et al., 2007). Furthermore, at the left hand side of the trace, there appeared a diffraction peak at $2\theta=20.1^\circ$ which correspond to the crystalline peaks of the PVDF (Stolarska et al., 2007). Similar XRD results were obtained by (Li et al., 2010).

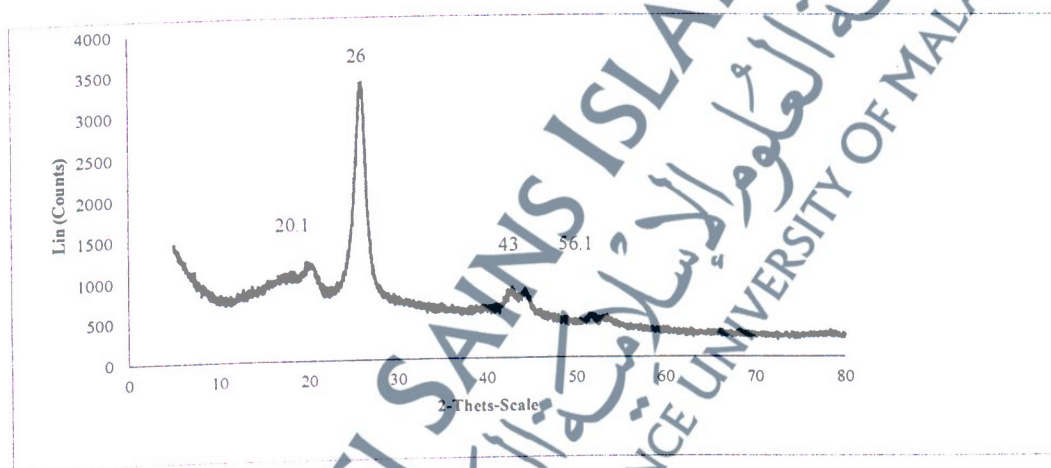


Figure 1. XRD Analysis of CPHMWNTs

FESEM images for the as-prepared electrode and the HSPE are shown in the Figures 2-7. The morphological structure is necessary for the required electrochemical performance of the cell in order to facilitate the electrolyte penetration and ion diffusion in the electrode. Thus, Figure 2, depicts the FESEM images of sample electrode with 90 % of the CPHMWNTs. This sample exhibits similar regular, entangled and smooth surface morphology with the outer diameter of $\sim 28 \text{ nm}$ and lengths of several micrometers. Although, few larger tubes are cited in the FESEM structure, this indicates that, the original MWCNT has been functionalized, since the normal sizes does not exceed 50 nm. Detail structures can be seen more clearly in Figure 3, where the FESEM images of CPHMWNTs were taken at different magnifications of (a); 3.6 mm x 50 k (1 μm) (b); 3.6 mm x 100 k (500 nm) and (c); 3.6 mm x 150 k (300 nm). However, in Figure 4 the FESEM images of HSPE containing 50 wt. % of both PVA and H_3PO_4 at a magnification of (a); 3.5 mm x 35 LM (1.00 mm) (b); 3.5 mm x 150 LM (300 μm) and (c) 3.5mm x 300 LM (100 μm) were all shown. Displayed in the images is the entangling nature of the surface of the sample which was due to the incorporation of the filter paper. Except in a few spots, all over the surface of the polymer looks unique as the Watman filter paper was coated with composites of both PVA and H_3PO_4 .

The same is applicable to Figure 5. Whereas, Figure 6, depicts FESEM images of HSPE with the content of 70 wt. % of H_3PO_4 , 30 wt. % of PVA and at a magnification of (a); 3.5 mm x 35 LM (1.00 mm) (b); 3.5 mm x 150 LM (300 μm) and (c) 3.5mm x 300 LM (100 μm). There are some obvious changes in the surface morphology. Several places spotted seem to have openings almost everywhere, which indicates few flaws in the coating which may

result in lower capacitance. Moreover, Figure 7 depicts the FESEM images of C90PVdF-HFP10 electrode overlapped on HSPE containing 60 wt. % of the H_3PO_4 and 40 wt. % of PVA at the magnifications of $\times 45\text{ k}$ ($1.00\text{ }\mu\text{m}$). This image was also taken at an angle of 30° in order to examine the edge contact at the electrode and electrolyte and to deduce the required thickness needed during the sandwiching of the electrolytes between the electrolytes to avoid high resistance.



Figure 2. FESEM images of sample with 90 % CPHMWNTs showing average diameters of the pore sizes at the magnifications of $4.2\text{ mm} \times 150\text{ k}$



Figure 3. FESEM images of CPHMWNTs showing H90PVdF-HFP10 electrode at a magnifications of (a); $3.6\text{ mm} \times 50\text{ k}$ ($1\text{ }\mu\text{m}$) (b); $3.6\text{ mm} \times 100\text{ k}$ (500 nm) and (c); $3.6\text{ mm} \times 150\text{ k}$ (300 nm)



Figure 4. FESEM images of HSPE containing 50 wt. % of both PVA and H_3PO_4 at a magnification of (a); $3.5\text{ mm} \times 35\text{ LM}$ (1.00 mm) (b); $3.5\text{ mm} \times 150\text{ LM}$ ($300\text{ }\mu\text{m}$) and (c); $3.5\text{ mm} \times 300\text{ LM}$ ($100\text{ }\mu\text{m}$)

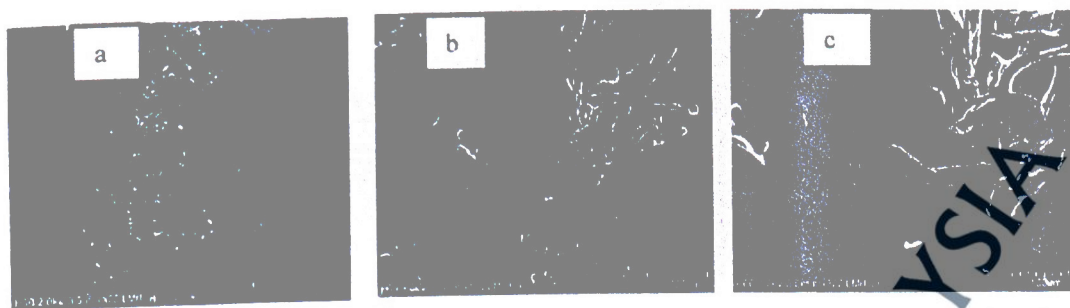


Figure 5. FESEM images of HSPE containing 60 wt. % of H_3PO_4 , 40 wt. % of PVA at a magnification of (a); 3.5 mm x 35 LM (1.00 mm) (b); 3.5 mm x 150 LM (300 μm) and (c); 3.5 mm x 300 LM (100 μm).

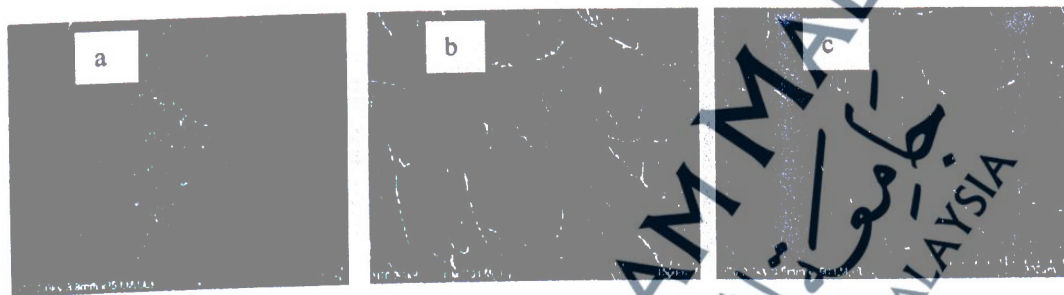


Figure 6. FESEM images of HSPE containing 70 wt. % of H_3PO_4 , 30 wt. % of PVA at a magnification of (a); 3.5 mm x 35 LM (1.00 mm) (b); 3.5 mm x 150 LM (300 μm) and (c); 3.5 mm x 300 LM (100 μm).



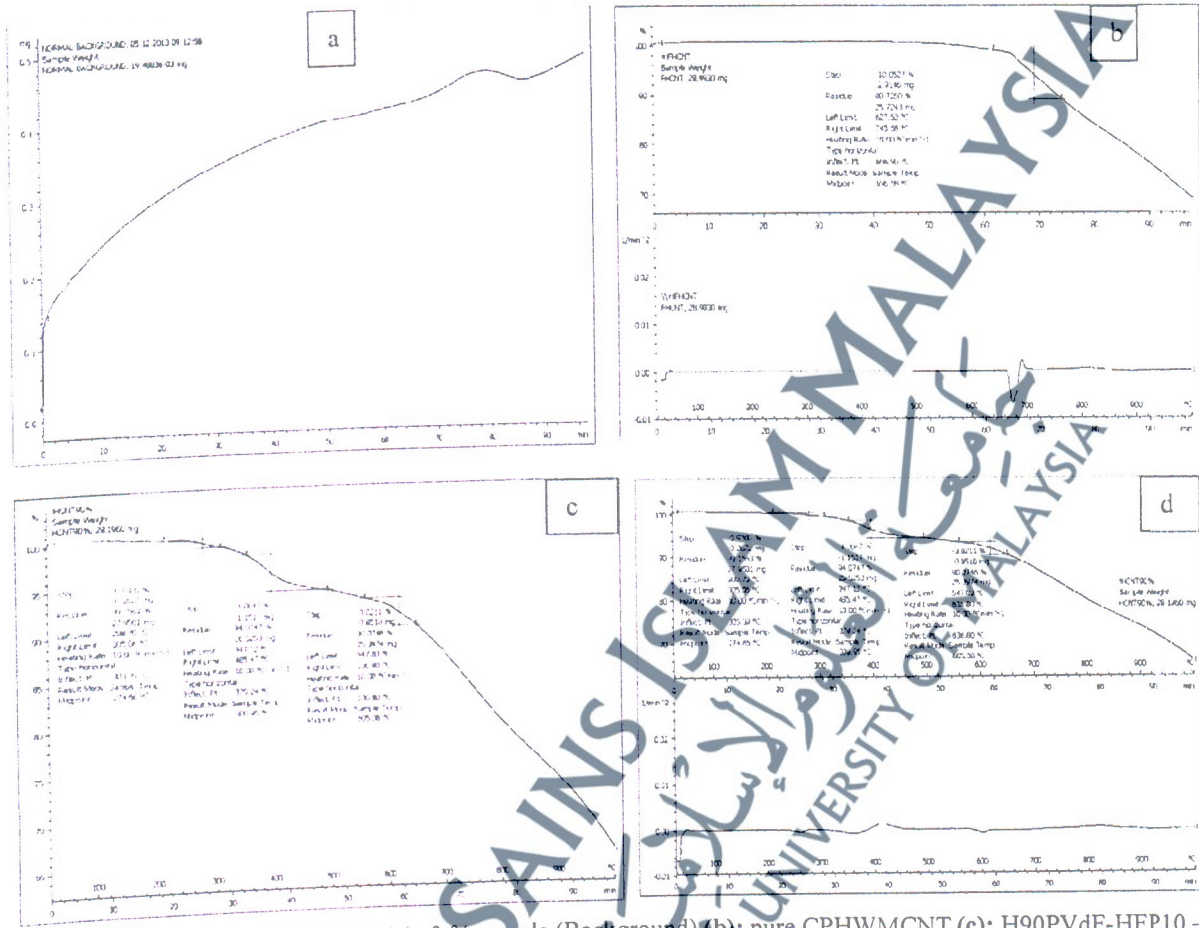
Figure 7. FESEM images of H90PVdF-HFP10 electrode overlapped on HSPE containing 60 wt. % of H_3PO_4 and 40 wt. % of PVA at the magnifications of x 100 k (500 nm) and an angle of 30°

3.2 Thermogravimetric Analysis (TGA)

The analysis of the temperature stability of the sample was investigated by thermal analyzer in the scale-range of 50°C to 1000°C under nitrogen gas (N_2) flow at a heating rate of $10^\circ\text{C min}^{-1}$ on a METTLER, STAR[®] SW 10.00. We have used similar techniques in our previous work (Hashim et al., 2014). The thermal stability of the samples was discerned in Figure 8. The Figures were (a); 0 % sample (Background) (b); pure CPHMWNTs (c) H90PVdF-HFP10 – Single scale (d); H90PVdF-HFP10 – Double scale.

At the starting, we analyzed background heating, in order to clear any ruminant residue and to enable the re-calibration of the analyzer. From the traces in Figure 8 (b) it can be observed that, the pure CPHMWNTs has the major loss of just 10.0522 % occurring at 696.58°C leaving a residue of 88.7270 %. Basically, this results show that pure MWNTs have very good thermal stability and consequently, good in application of electrochemical devices. While in Figure 8 (b and c), it can notice that, when the active material (i.e. the binder) was added into a single electrode, three losses were recorded. The initial loss of 0.9300 % of the total samples occurs at 274.66°C ,

then the second loss of 4.0847 % occurred at 388.95 °C and the highest loss of 7.1 % was noticed at 605.36 °C. This shows that incorporating a binder (of negligible quantity) into the pure CPHMWCNTs does not affect the conductivity supercapacitor.



3.3 Electrochemical Behavior

The electrochemical behaviors of CPHMWCNTs were investigated by the CV and CD measurements. CV measurement was firstly performed to evaluate the electrochemical potential window and adequately quantify the specific capacitance of the electrodes in these cells using two-electrode system. Figure 9 reveals the CV of Cell –A (H90PVdF-HFP10 | H₂O | H90PVdF-HFP10) at (a); scan rates of 10, 50 and 100 mV, within a potential window of 0.0 – 3.0 V and (b); scan rate of 50 mV; within a potential window of 0.0 – 1.0 V. From the resulting CV curves, it can be discerned that, the CV of the cell at a scan rate of 50 mV and 1 V- voltage shows a rectangular shape and mirror-symmetric, indicating an ideal supercapacitive behavior for CPHMWCNTs. We then calculated the specific capacitance of the electrode materials obtained in the two-electrode system by integrating the CV curves in that Figure. However, the CV curves are rather in leaf-like symmetric in shape, when the voltage was extended to 3.0 V, indicating a closely ideal capacitive behavior. The specific capacitance was obtained to be 42.0 Fg⁻¹, 15.0 Fg⁻¹, and 11.1 Fg⁻¹ for the scan rates of 10, 50 and 100 mV, respectively. These results prove that there is a strong correlation between capacitance value and the scan rate. The decrease in specific capacitance of 42.0 Fg⁻¹ to 11.1 Fg⁻¹ could either be attributed to the slow transfer of ions on the electrode electrolyte interface (Shu et al., 2013) or due to the un-uniformity of the coated filter paper by the electrolyte as vindicated in the FESEM analysis, it also suggests an improved performance of supercapacitor at the decreasing scan rates. Noting from the CV from the cell at the scan rate of 50 mV above, the potential window is quite stable for this electrode,

we can, as a consequence, envision that, an operating cell with 1.5 V can be more stable especially when assembled in a three-electrode system.

Furthermore, Figure 10 also shows CV of Cell-B (H90PVdF-HFP10|H60| H90PVdF-HFP10) at various scan rates of (a); 10, 50 and 100 mV; 3 V- voltage window, and (b); 50 mV; 1 V – voltage window. The specific capacitances obtained in this cell were 88.6 Fg^{-1} , 32.6 Fg^{-1} and 22.7 Fg^{-1} for scan rates of 10, 50 and 100 mV respectively. These results almost double that of cell-A which might be attributed to the increase in ionic conductivity in the polymer electrolyte of the HSPE. While Figure 11 depicts a CV of Cell –C (H90PVdF-HFP10 H70| H90PVdF-HFP10) at (a); scan rates of 1, 50 and 100 mV, 3 V- voltage window, and (b); scan rate of 50 mV, 1 V – voltage window. These CV curves result in a balance and modest capacitance value and is considered better of compare to the capacitance of cells A. The capacitance recorded here are 65.0 Fg^{-1} , 36.6 Fg^{-1} and 29.3 Fg^{-1} for scan rates of 10, 50 and 100 mV respectively. Table 1 gave a summary results of the capacitance obtained in all the three cells. Figure 12 (a) summarizes the capacitance performance in the combined graph of capacitance against the scan rates for cells A, B

One important criterion in supercapacitor's fabrication and application is its ability to have long –term cycling stability. In this respect, the cycling endurance measurement over 5000 cycles for all the cells (as shown in Figure 12 (b)) was conducted using the CD test at the working voltage of 1.5 V. This figure shows the resulting capacitance retention as a function of cycling number. It can be seen that of all the three cells, only cell-B (H90PVdF-HFP10 |H60| H90PVdF-HFP10) exhibits the best cycling stability with about 68 % capacitance of its initial value after 5000 cycles.

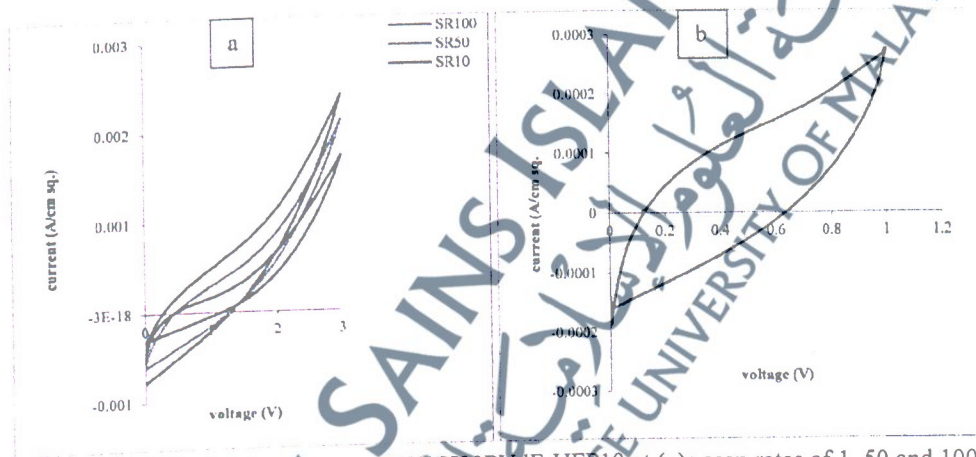


Figure 9. CV of Cell –A (H90PVdF-HFP10 |H50| H90PVdF-HFP10 at (a); scan rates of 1, 50 and 100 mV, 3 V- voltage window (b); scan rate of 50 mV; 1 V – voltage window

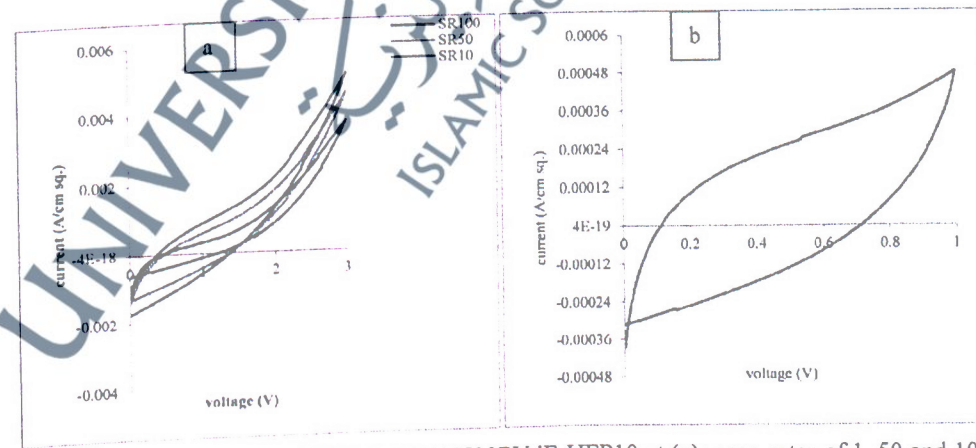


Figure 10. CV of Cell –A (H90PVdF-HFP10 |H60| H90PVdF-HFP10 at (a); scan rates of 1, 50 and 100 mV, 3 V- voltage window (b); scan rate of 50 mV; 1 V – voltage window

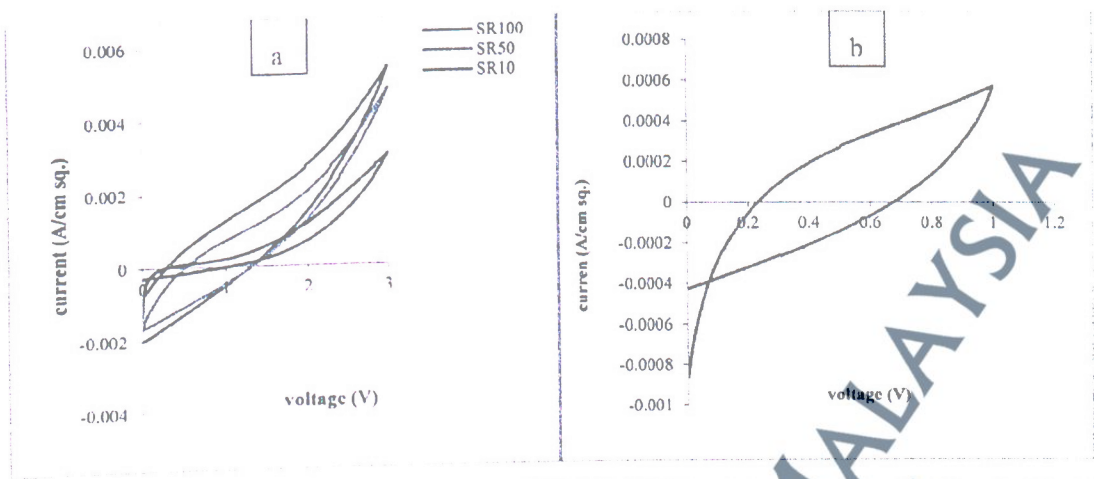


Figure 11. CV of Cell -A (H90PVdF-HFP10 |H70| H90PVdF-HFP10 at (a); scan rates of 1, 50 and 100 mV, 3 V-voltage window (b); scan rate of 50 mV; 1 V - voltage window

Table 1. Performance of Supercapacitor by the CV

Cells	Working voltage (V)	Capacitance value of different scan rates (Fg ⁻¹)		
		100 mV	50 mV	10 mV
A-H90H50	3	11.1	15.0	42.1
B-H90H60	3	22.7	32.6	86.6
C-H90H70	3	29.3	36.6	65.0

Table 2. Performance of Supercapacitor by the CD

Cells	Working voltage (V)	C _d (Fg ⁻¹)	ESR (Ω cm ²)	Energy density (Jg ⁻¹)	Power density (Jg ⁻¹ s ⁻¹)
A- H90H50	1.5	8.9-89.3	2.6-26.0	44.7-448.4	0.04-4.7
B-H90H60	1.5	11.9-119.0	0.1-1.0	59.8-597.0	1.20-12.6
C-H90H70	1.5	8.9-89.3	5.0-50.0	44.7-448.4	0.03-0.3

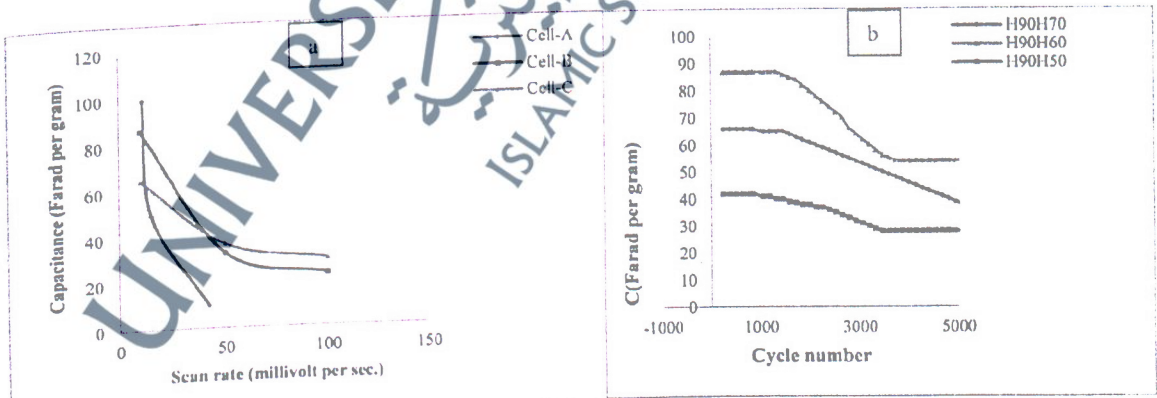


Figure 12. (a); combined graphs of capacitance against the scan rates for cells A, B and C. (b); combined cyclic performances of cells A, B and C

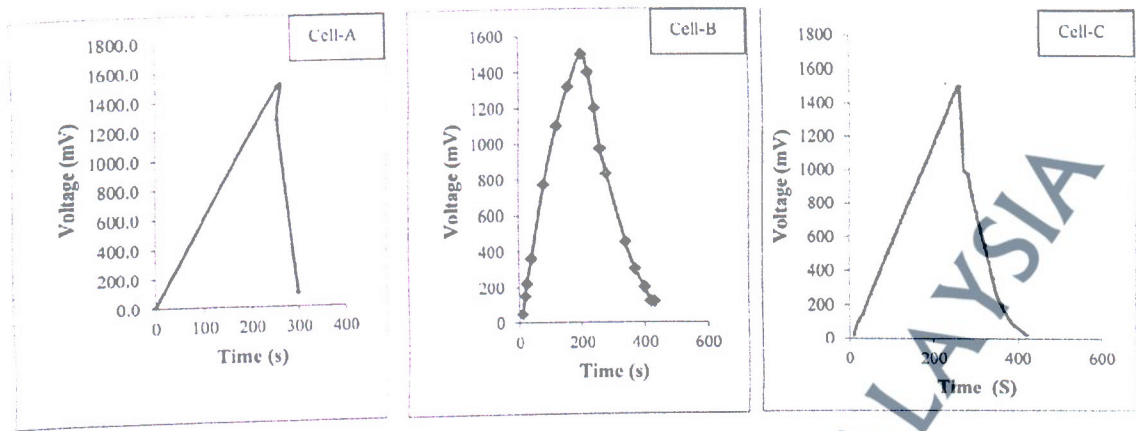


Figure 13. CD graphs of (a); cell- A (b); cell- B and (c); cell- C

The galvanostatic CD test is considered a better alternative and arguably quantitative method to evaluate the supercapacitive nature of an electrode material compared to the CV measurement (Shu et al., 2013), the capacitance of the cells was measured using this technique. The CD graphs of (a); Cell-A (b); Cell-B and (c); Cell- C were all depicted at a working voltage of 1.5 V and at three different current densities i.e. 10, 20 and 100 mA in Figure 13. The effective capacitance, power and energy densities were calculated and the following results were obtained. In cell-A, the discharged capacitances were calculated to be 8.90 Fg^{-1} , 17.80 Fg^{-1} and 89.28 Fg^{-1} respectively at an applied current density of 100, 20 and 10 mA; the calculated energy and power densities are $44.70 \text{ Jg}^{-1}/0.05 \text{ Jg}^{-1} \text{ s}^{-1}$, $89.41 \text{ Jg}^{-1}/0.10 \text{ Jg}^{-1} \text{ s}^{-1}$ and $448.40 \text{ Jg}^{-1}/4.66 \text{ Jg}^{-1} \text{ s}^{-1}$ respectively, for the same above mentioned current densities. While in cell-B, the discharged capacitances obtained were 11.9 Fg^{-1} , 23.8 Fg^{-1} and 119.0 Fg^{-1} respectively at an applied current density of 10, 20 and 100 mA; the calculated energy and power densities are $59.8 \text{ Jg}^{-1}/0.04 \text{ Jg}^{-1} \text{ s}^{-1}$, $119.5 \text{ Jg}^{-1}/0.08 \text{ Jg}^{-1} \text{ s}^{-1}$ and $597.0 \text{ Jg}^{-1}/12.55 \text{ Jg}^{-1} \text{ s}^{-1}$ at the said current densities. And finally cell-C has the following results for the capacitance; 8.89 Fg^{-1} , 17.80 Fg^{-1} and 89.28 Fg^{-1} respectively at an applied current density of 10, 20 and 100 mA; power/energy densities are $44.70 \text{ Jg}^{-1}/0.02 \text{ Jg}^{-1} \text{ s}^{-1}$, $89.41 \text{ Jg}^{-1}/0.05 \text{ Jg}^{-1} \text{ s}^{-1}$ and $448.40 \text{ Jg}^{-1}/0.25 \text{ Jg}^{-1} \text{ s}^{-1}$ at the aforementioned current densities. The discharged capacitance decreases with the increase in current density was noticed in each of the resulting discharging capacitance of the cells, which could be as a result of the low penetration of ions into the inner region of the pores due to fast potential changes. Generally, the fade in capacitance could be as a result of dissolution of the active materials in the electrolytes, mechanical faults of the electrode (such as expansion, agglomeration) and imbalance of the two electrodes which can cause the instability of the electrode potential (Wang et al., 2013).

4. Conclusion

This research demonstrated the fabrication of a CPHMWCNTs used as an electrode for high performance supercapacitors using HPSE which function as an electrolyte and a separator. Three cells were successfully fabricated which were leveled as cell-A (H90PVdF-HFP10 |H50| H90PVdF-HFP10, cell-B (H90PVdF-HFP10 |H60| H90PVdF-HFP10 and cell-C (H90PVdF-HFP10 |H70| H90PVdF-HFP10) with changes in the separator. The XRD analysis depicts the peaks of the sample electrode C90PVdF-HFP10 appearing at $\theta = 26^\circ$ and $\theta = 43^\circ$ which might be as a result of the hexagonal structure of (002) and (101) respectively, this also an indication that the carboxyl multiwalled CNT have high conductivity. Again, a wider diffraction at $\theta = 20.1^\circ$ which correspond to crystalline peaks of PVDF. TGA traces shows that, the pure CPHMWCNTs experienced a major loss of just 10.0522 %, occurring at 696.58°C leaving a residue of 88.7270 %, which also prove that pure MWCNT have very good thermal stability and consequently, good, in application for electrochemical devices. From the overall of the electrochemical analysis of CV results, cell-B delivered higher capacitance of 86.6 Fg^{-1} which doubles the capacitance obtained by cell-A (42.1 Fg^{-1}). In CD analysis with much lower voltage window of 1.5 V, cell-B delivered better capacitance than cells A and C, delivering a balanced and a better discharge capacitance of 119.0 Fg^{-1} with higher energy/power densities of $597.0 \text{ Jg}^{-1}/12.6 \text{ Jg}^{-1} \text{ s}^{-1}$ and lowest in terms of internal resistance.

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A Noble Conductivity Studies and Characterizations of PVA-Orthophosphoric-Filter Paper Electrolytes

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Abstract

The nobility of solid polymer electrolyte (SPEs) has made them a subject of interest, especially in the arena of science and technology, and most importantly as they are used as separators in industries and by researchers for the assembly of some "few battery types" and supercapacitors. This paper, highlights the nobility of the hybrid solid polymer electrolyte (HSPE), particularly at room temperature such that, it can be used as an electrolyte as well as a separator in supercapacitor fabrication. The hybrid SPEs were produced from the composition of polyvinyl alcohol (PVA) and Phosphoric acid (H_3PO_4), where the PVA samples were kept constant while the phosphoric acid concentration was varied at 0, 10, 20, 30, 40, 50, 60, and 70 wt. %. XRD results show that, the crystallinity decreases as the acid concentration increases and consequently, there is an enhancement in the amorphicity of the samples responsible for the process of ion transport. This characteristic behavior was confirmed by the analysis of the differential scanning calorimetry results. FESEM result pictured the entangling nature of the combined samples. High conductivity of $1.67 \times 10^{-3} \text{ Scm}^{-1}$ was recorded for the HSPE at the composition of 70:30 wt. %. It was also noticed that, the bulk modulus, R_b of the HSPE (5.73 Ω) at the aforementioned composition decreases with the increase in concentration.

Keywords: hybrid solid polymer electrolyte (HSPE), polyvinyl alcohol (PVA), phosphoric acid (H_3PO_4), Electrochemical Impedance Spectroscopy (EIS), Differential Scanning Calorimetry (DSC) Analysis

1. Introduction

The invention of polymer electrolyte by Fenton and co-workers (Gu et al., 2000; Kumar & Sundari, 2010; Zhang et al., 2006; Yang, 2004; Ragavendran et al., 2004; Tripath et al., 2012; Ulaganathan et al., 2012; Kuo et al., 2013; Yang et al., 2013; Noor et al., 2010) and Armand (Ragavendran et al., 2004; Zhang et al., 2006) marked exactly three decades (1973) in the year 2013, and ever since then, there has been continuous breakthrough in the research of polymer electrolyte. Three classifications of polymer electrolyte systems have been identified recently. These include, (i) Polyelectrolytes (PEs): - which have independent ion-generating groups chemically bond to the macromolecular chain and presence of counter-ion in order to maintain the electroneutrality of the salt. These types of polymers have low conductivity of about 10^{-10} – $10^{-15} \text{ Scm}^{-1}$ in dry conditions, but in the presence of dielectric solvent such as water, their conductivities do improve (Ulaganathan et al., 2012). (ii) Solvent Swollen Polymer Electrolytes (SSPE): - In SSPE, solvents, both aqueous and non-aqueous swells the host polymer live PVA. So, the dopant ionic solutes such as H_3PO_4 is hosted in the swollen lattice thereby permitting the motion of ions in the solvent swollen region of the polymer host. Their conductivity depends on the concentration of the solvent in the region that is being swollen (Ulaganathan et al., 2012). And lastly (iii) the Solvent Free Polymer Electrolytes (SFPE): These are polymer salt complex, which is formed by complexes between salts of alkali metals and polymer containing solvating hetroatoms, example; O, S and N (Ulaganathan et al., 2012). The complexation between poly ethylene oxide (PEO) and alkali metal salts is a good example of SFPE. SFPE are sub-classified into three also. They are; (a) Solid Polymer Electrolytes (SPEs), (b) Gel Polymer Electrolytes (GPEs), and (c) Composite polymer electrolytes (CPEs) (Kuo et al., 2013; Tripath et al., 2012). GPEs can be simply regarded as plasticizers incorporated polymer-salt complex (Ulaganathan et al., 2012). They are therefore consisted of a liquid electrolytes immobilized in a polymer matrix (Hashmi, 2013a) and exhibits high ionic conductivity (10^{-3} to 10^{-4} Scm^{-1} at ambient temperature) and can be obtained by either loading of a liquid electrolyte in a microporous matrix or by increasing the viscosity of a liquid electrolyte through the addition of a soluble polymer until gel consistency

is achieved or by mixing a liquid electrolyte with monomers of relatively low molecular weight, then curing the mixture by other means, such as UV polymerization, thermal polymerization and electron beam radiation polymerization. They are criticized for having weak mechanical strength and poor interracial properties (Qiu et al., 2004; Hashmi, 2013b). In CPEs, they are normally prepared by addition of high surface inorganic fillers like SiO_2 , MgO , TiO_2 and alike so as to improve the mechanical strength and stiffness of the complex systems (Ulaganathan et al., 2012). Furthermore, SPE is thin films with ionic conductivity when especially an alkali salt dissolves in polymer matrix. SPE have drawn great attention in the development of science and technology of lithium secondary batteries. SPEs have several advantages over liquid, gel or even composite electrolytes in that, it has process ability, flexibility, light weight, elasticity and transparency (Zhang et al., 2006), desirable shape moldability, being free from leakage, mechanical strength, better stability especially in high temperature, and high specific energy and power (Lim et al., 2012). Furthermore, use of solid polymer electrolyte can negate the need for a separator and be amendable to low cost manufacturing technologies (Qiu et al., 2004). Some of the applications of SPE are in Batteries, fuel cell, supercapacitors and other electrochemical devices (Sawada et al., 2000) and other electrochemical devices (Sotta et al., 2010).

Works published particularly on the hybrid polymer electrolyte characterizations are quite minimal. Most of the publications focused on the characterizations of pure solid polymer electrolyte such as those in Prajapati et al. (2010) and Ahmad Khair and Arof (2010). It's in light of the above that, this paper tries to offer a step by step approach on the conductivity studies of the this hybrid polymer so as to determine the specialties peculiar to it, in comparison with the pure solid polymer electrolyte and to ascertain the suitability composition for the usage in the supercapacitor fabrication which is the main target of our future work. Hence, careful measures have been put in place to ensure that, every detail characteristic of the active materials, especially of the PVA (its molecular weight and its percentage hydrolysis), the type of the acid used and even the filter paper brand were taken into considerations

2. Experimental

2.1 Preparation of the Composite PVA Electrolytes

The hybrid solid polymer electrolytes (HSPEs) experimental preparation was discussed elsewhere by us, in Hashim et al. (2012), Hashim et al. (2014) and by Jiang et al. (2013). We also show how effective they are when used as separators and electrolytes in the supercapacitor fabrication. The HSPEs were prepared using 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. On the other hand, H_3PO_4 (>85 wt.% in water, molar mass of 98.00 g/mol, 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. 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 the HSPE to be obtained. (This mixture has been summarized in Table 1). The mixing is done in a drop-wise manner with magnetic stirring at 60 °C for about one hour until it completely turns to homogeneous solution.

The mixture is then allowed to cool down to an ambient temperature. The resulting homogeneous 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. The longer curing period is connected to its high molecular weight and consequently more hydrolyzed. 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 as shown in Figure 1. The resulting polymer film was then put in the plastic bags for safe keeping, and to avoid contamination from surrounding, for further property analysis

3. Result and Discussion

3.1 Conductivity and Chemical Composition Analysis

The Conductivity measurements of the different percentage ratio of PVA- H_3PO_4 of HSPE films were carried out using an impedance method that was highlighted by Ahmad Khair and Arof (2010). The hybrid solid polymer films were sandwiched between a stainless steel, ion-blocking liked measuring device (otherwise known as a probe), each of surface area 2 cm² in radio, in a spring-loaded glass holder. The impedance measurements were carried out by using Electrochemical Impedance Spectroscopy (EIS) testing machine named HIOKI 3532-50 LCR

FESEM Machine



FESEM Machine – An enlarged upper part.

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Hi-Tester which was interfaced to a computer. The frequency range of the device was 50 Hz - 1 MHz, and simultaneously calculating both real and imaginary impedance.



Figure 1. Showing a prepared HSPE

Table 1. Table Showing the Overall Formation of the HSPE Preparation

Coding	Measured Quantity PVA in Distilled Water (g)	Measured Quantity of H ₃ PO ₄ (g)	Ratio of PVA to H ₃ PO ₄
H0	2	0	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

The sample exhibits Debye characteristics, and then the plots of the negative imaginary impedance versus the real impedance on the graph should be able to display a semicircle-like shape (Ahmad Khair & Arof, 2010). From the Equation 1, we calculated the electrical conductivity of the samples;

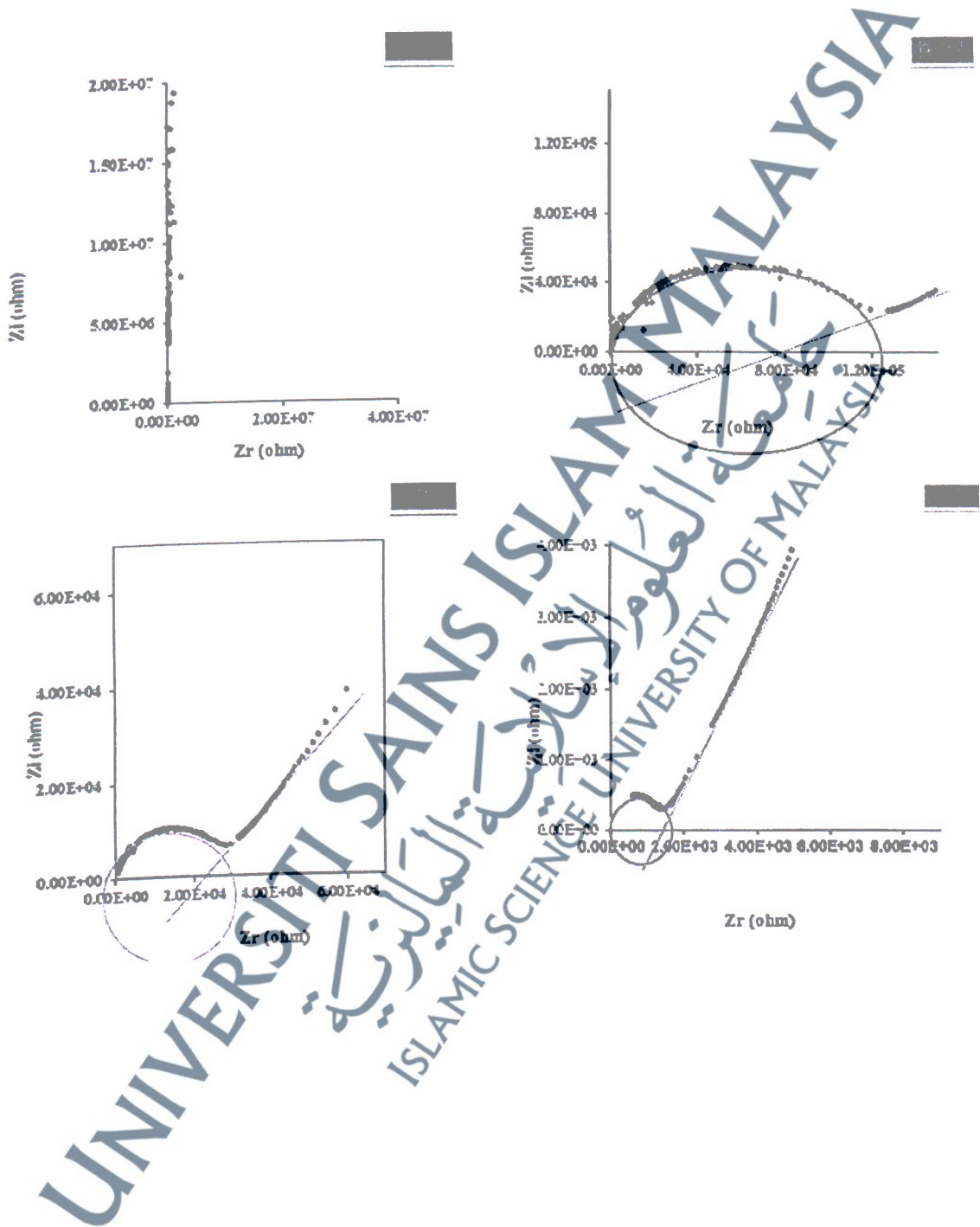
$$\sigma = \frac{l}{R_b A}$$

(2)

Where σ is the conductivity l , R_b and A are respectively the thickness, bulk modulus and area of the samples. The thickness of the sample was measured twice at different positions of the polymer films and an average was taken using digital micrometer.

Figure 2 (a-h) shows impedance plots of a sample of the HSPE containing 0, 10, 20, 30, 40, 50, 60, and 70 wt. % ratio of the H₃PO₄ at room temperatures respectively. The manifestation of semicircle in the 10 wt. %, might be as a result of the presence of the immobile polymer chain that could be found in the filter paper itself. In this case also, it was observed that, the R_b value decreases with the increase in concentration. The calculated values of the R_b are 1.15×10^9 , 1.15×10^6 , 1.00×10^6 , 1.50×10^3 , 2.10×10^3 , 4.30×10^1 , 7.37×10^1 and 5.73Ω for 0, 10, 20, 30, 40, 50, 60, and 70 wt. % ratio of the H₃PO₄ respectively. Moreover, Table 1 summarizes the relationship between the acid concentration and the polymer matrix. It was further deduced from the table that, the thickness on each sample, had some impact on the conductivity of the samples. Hence, while the calculated bulk moduli of the HSPE are found to be promising, the thickness of the sample hinders its conductivity. However, in terms of use as separator in

supercapacitor, the use of HSPE proved to be more acceptable and better as it has been reported by us in (Hashim et al., 2014). Furthermore, the highest conductivity was noticed for the HSPE was $1.67 \times 10^{-3} \text{ Scm}^{-1}$ when the H_3PO_4 was increased to 70 wt. % and the lowest conductivity was noticed at $2.25 \times 10^{-11} \text{ Scm}^{-1}$ when the H_3PO_4 percentage was nil.



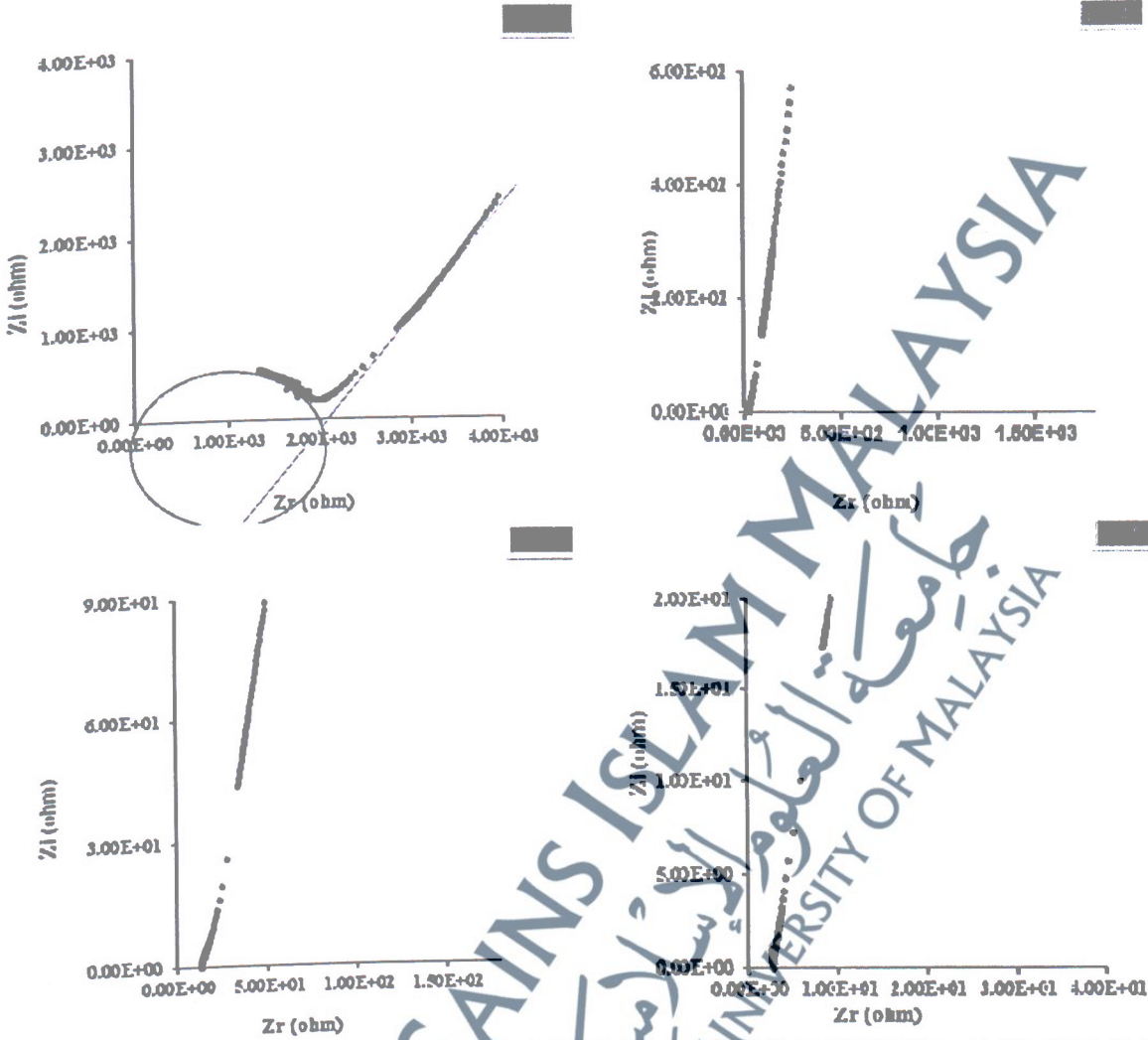


Figure 2. Impedance plots of HSPE containing 0 wt. % (a); 10 wt. % (b); 20 wt. % (c); 30 wt. % (d); 40 wt. % (e); 50 wt. % (f); 60 wt. % (g); 70 wt. % (h); the ratio of the H_3PO_4 at room temperatures

Table 2. Parameters that Determine the Conductivity in HSPE

Coding	PVA: H_3PO_4	l (mm±0.005)	R_b (Ω)	σ (Scm ⁻¹)
H0	100:0	0.01885	1.15×10^9	3.83×10^{-12}
H10	90:10	0.01810	1.15×10^6	1.74×10^{-9}
H20	80:20	0.01620	1.00×10^6	5.16×10^{-9}
H30	70:30	0.01730	1.50×10^3	3.67×10^{-5}
H40	60:40	0.02005	2.10×10^3	3.03×10^{-6}
H50	50:50	0.01980	4.37×10^1	1.47×10^{-4}
P60	40:60	0.02000	7.37×10^1	8.64×10^{-5}
H70	30:70	0.30000	5.73×10^0	1.67×10^{-3}

3.2 Crystal Structure Analysis

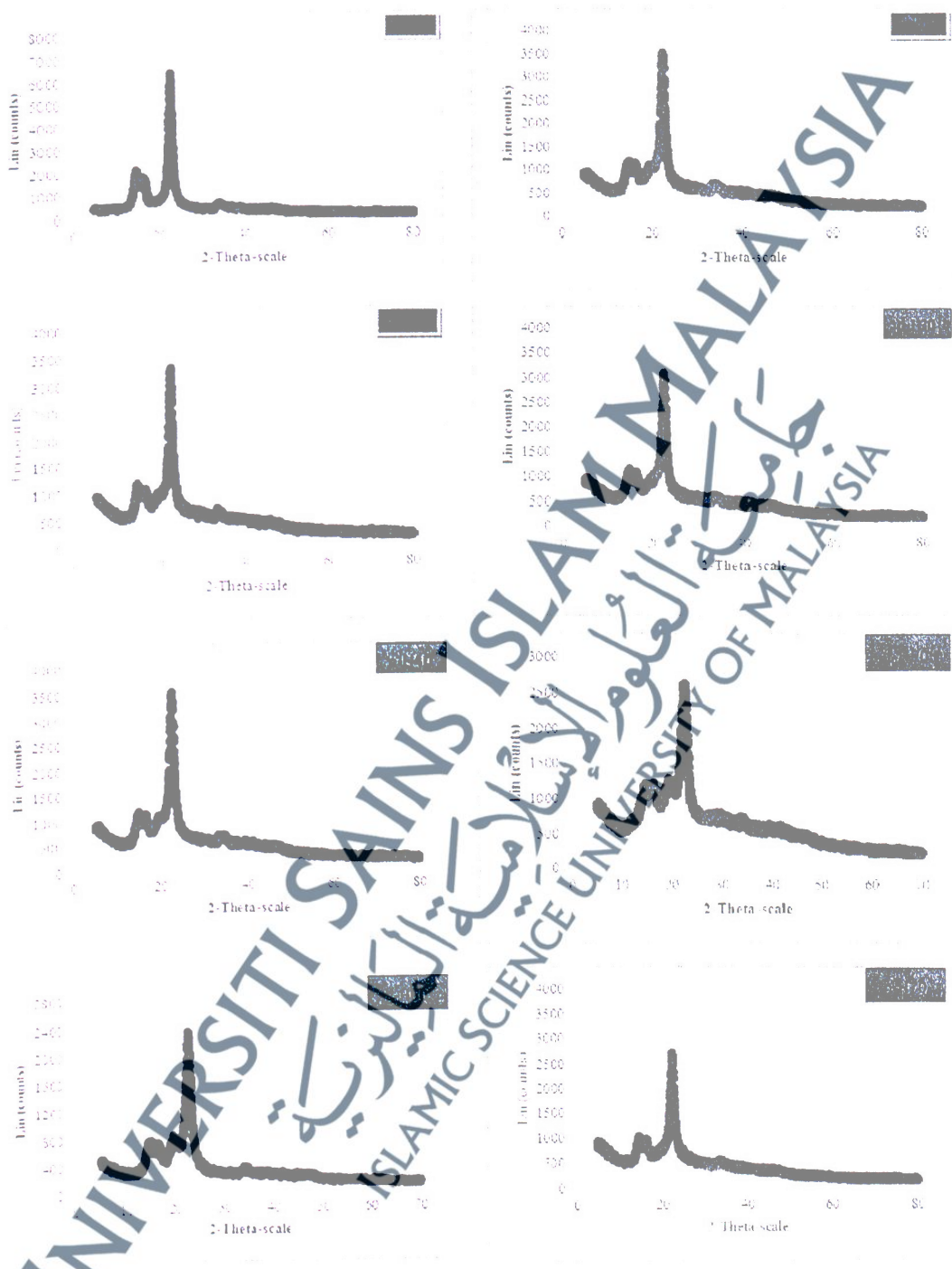


Figure 3. XRD Analysis of HSPE containing 0 wt.% (a); 10 wt.% (b); 20 wt.% (c); 30 wt.% (d); 40 wt.% (e); 50 wt.% (f); 60 wt.% (g); 70 wt.% (h) ratio of the H_3PO_4

The crystal structure analysis of the solid polymer electrolyte films was examined by a Philip X'Pert X-ray diffractometer (XRD) with $Cu K_{\alpha}$ radiation of wavelength $\lambda=1.54056 \text{ \AA}$ for 2θ angles between 10° and 80° . The XRD analysis was carried out on the HSPE films. After the analysis, the following results were obtained.

The analysis of the structure of the HSPE for 0 wt. % (a); 10 wt. % (b); 20 wt. % (c); 30 wt. % (d); 40 wt. % (e); 50 wt. % (f); 60 wt. % (g); 70 wt. % (h) ratio of the H_3PO_4 has been shown in Figure 3 (a-h). From the figure it can be observed that the semi-crystalline peak of the PVA was at $\theta=20^\circ$ which also affirmed the earlier argument put across by (Hashmi, (c), 2013) about the semi-crystal behavior of the PVA. While the border humps by the left shows the inclusion of the acid and that of polymer.

3.3 Field Emission Scanning Electron Microscope (FESEM) Analysis

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 of 80x to 2,000,000x) have been selected. The HSPE films have been examined using different magnifications. The resulting images are shown in Figure 4. In that figure, the FESEM images of HSPE containing 0 wt.% (i); 10 wt.% (ii); 20 wt.% (iii); 30 wt.% (iv); 40 wt.% (v); 50 wt.% (vi); 60 wt.% (vii); 70 wt.% (viii) ratio of the H_3PO_4 was displayed at three different magnifications; 3.5 mm x 35 k, 3.5 mm x 150 k and 3.5 mm x 300 k respectively. Overall, the entangling nature of the images indicates the presence of the compositions in the filter paper. And the cited gross changes of the picture from one sample to another, indicates that, the Whatman filter paper soaked in the prepared compositions of the PVA/ H_3PO_4 liquid electrolyte was not “well-soaked” as such, the some samples show obvious holes.



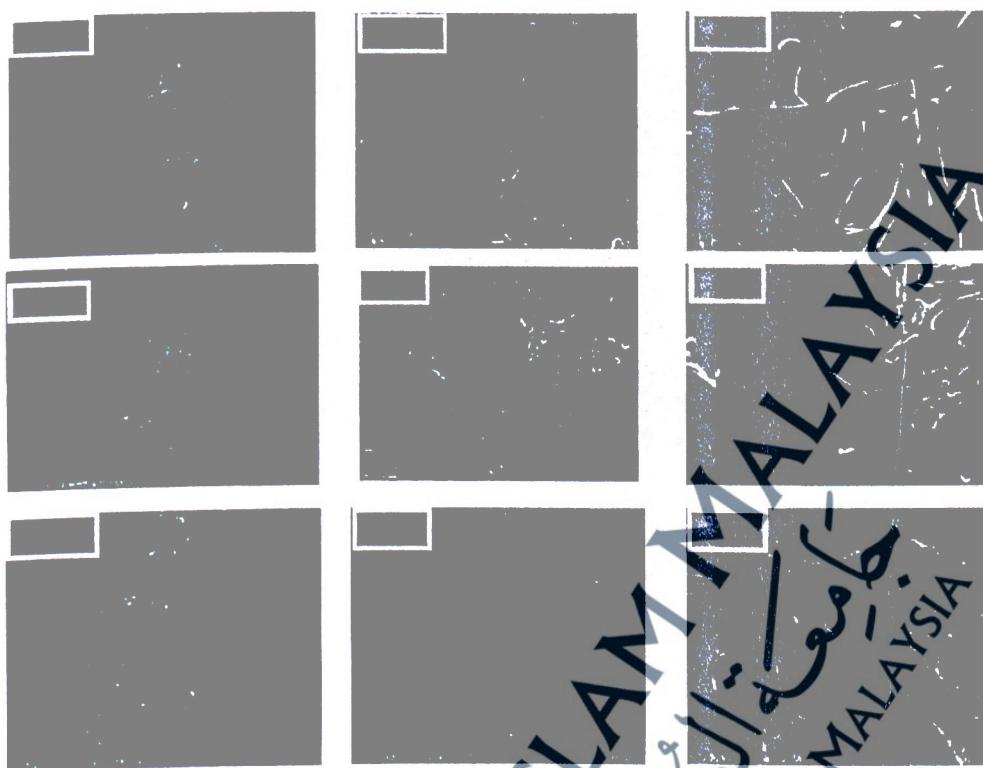


Figure 4. FESEM Images of HSPE containing 0 wt.% (i); 10 wt.% (ii); 20 wt.% (iii); 30 wt.% (iv); 40 wt.% (v); 50 wt.% (vi); 60 wt.% (vii); 70 wt.% (viii); ratio of the H_3PO_4 . The magnification of the images taken were at (i) 3.5 mm x 35 k, (ii) 3.5 mm x 150 k and (iii) 3.5 mm x 300 k

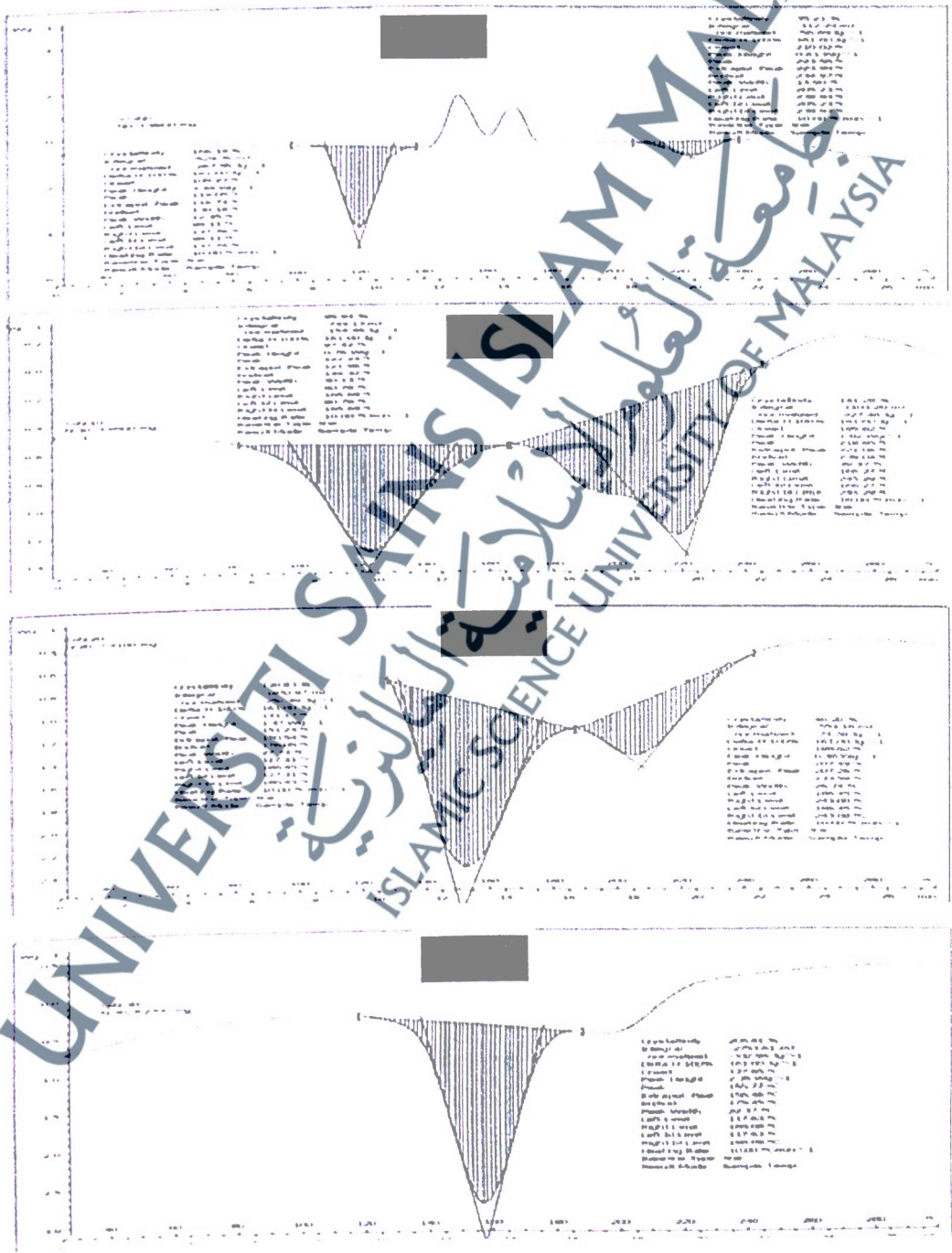
3.4 Differential Scanning Calorimetry Analysis

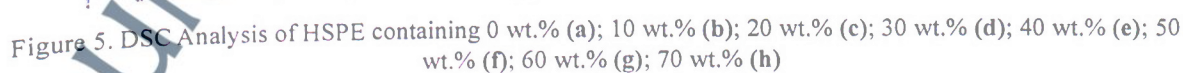
The DSC thermal analysis was carried out using a Mettler Toledo DSC A851 with Star software under N_2 atmosphere with 10 °C/min heating rate from 40 to 300 °C in order to observe the crystalline and semi-crystalline behavior of the whole samples. therefore, various parameters related to thermal properties such as glass transition temperature (T_g), melting temperature (T_m) of crystalline phase of the polymer electrolytes and degree of crystallinity (T_c) can be evaluated from the DSC data and are summarized in Table 3. The samples for DSC measurements were prepared from several tiny rectangular pieces cut from the polymer film to a mass ranging from 7.08 – 19.82 mg for the HSPE. The temperature range studied was –40 to 200 °C. The heating/cooling rate was 10 °C/min.

Table 3. Parameters for the Thermometric Analysis in HSPE

Coding	PVA: H_3PO_4	Mass (g)	Temperature (°C)		
			T_g	T_m	T_c
H0	100:0	7.08	89.43	215.76	165.00
H10	90:10	8.58	125.00	164.81	95.00
H20	80:20	14.63	145.35	172.59	-
H30	70:30	12.08	142.85	68.34	-
H40	60:40	12.08	119.24	159.89	-
H50	50:50	8.65	102.72	117.70	-
H60	40:60	19.82	96.80	150.24	-
H70	30:70	8.80	84.51	111.91	-

Figure 5 shows the DSC analysis result for the HSPE containing 0 wt. % (a); 10 wt. % (b); 20 wt. % (c); 30 wt. % (d); 40 wt. % (e); 50 wt. % (f); 60 wt. % (g); 70 wt. %. From that Figure and the Table 3, one can deduce that, only the H0 which has 100 wt. % of PVA immersed with filter paper immerse in it, gave a T_m value that is closely related to the theoretical value. Others have been down and upward shifting in terms of the T_m . Moreover, we were unable to detect the T_c for all the samples except in H0 and H10. However, since the higher the melting point temperature the more the stability of the molecules therein, pure PVA has more stable molecules than PVA/ H_3PO_4 composite. So, it can be seen that the T_m and T_c values decreases (or even diminishes) as the concentration of the acid increase. This is as a result of the fact that, in homogenized blends, the melting shifts to the lower level (Othman et al., 2011; Guirguis & Moselhey, 2012.). Furthermore, the theoretical glass transition of the PVA alone is about 85 °C while the composite shows down and upwards shifts of this temperature. This could be also be as a result of the gradual increment in the concentration of the acid.





4. Conclusion

The importance of polymer electrolyte in nowadays technology cannot be over emphasized. In this work, we have presented the noble performance of HSPE measured at room temperature and to be used as an electrolyte as well as a separator from the composition of polyvinyl alcohol (PVA) and Phosphoric acid (H_3PO_4), with, the PVA samples

kept constant while varying the phosphoric acid at 0, 10, 20, 30, 40, 50, 60, and 70 wt. % immerse in a filter paper. The HSPE shows an excellent results in term conductivity studies in that, highest conductivity of $1.67 \times 10^{-3} \text{ Scm}^{-1}$ was obtained after the impedance analysis. The XRD analysis reveals the semi-crystalline peak of the PVA at $\theta=20^\circ$ border humps of the left indicating the inclusion of the acid and the crystallinity decreases as the acid concentration increases. Which in turns indicate that, there is an enhancement in the amorphicity of the samples responsible for process of ion transport. This characteristic behavior was confirmed from the analysis of the differential scanning calorimetry results. FESEM result pictured the entangling nature of the combined samples as result of the presence of the filter paper.

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Design, Fabrication and Characterization of a Commercially Prepared Carboxyl Multiwalled Carbon Nanotubes With a Hybrid Polymer Electrolytes

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Abstract

We reported the fabrication of three different supercapacitor cells using a commercially prepared carboxyl multiwalled carbon nanotubes (CPCMWNTs) as electrode, and hybrid solid polymer electrolytes (HSPE) of different electrical conductivities as separators. The Three cells were then constructed and leveled as cell-A (C90PVdF-HFP10 |H50| C90PVdF-HFP10), cell-B (C90PVdF-HFP10 |H60| C90PVdF-HFP10) and cell-C (C90PVdF-HFP10 |H70| C90PVdF-HFP10). Numbers of analysis, such as FESEM, XRD, TGA and electrochemical analysis were carried out on both the commercial CNT and that of the electrolytes. From the overall results of the electrochemical analysis of cyclic voltammetry (CV), cell-B delivered higher capacitance of 60.10 Fg⁻¹ doubling that of cell-A, and tripling cell-C. Whereas the charge-discharge (CD) tests carried out in the cells reveals that even at the lower voltage window of 1.5 V, cell-A delivered slightly better than that of B and C with a balanced and good discharge capacitance of 86.06 Fg⁻¹ and higher energy/power densities of 432.22 Jg⁻¹/8.37 Jg⁻¹s⁻¹ and less internal resistance. All the cells were able to deliver a modest capacitance at a voltage window of 3V.

Keywords: supercapacitor, hybrid solid polymer electrolyte (HSPE), carboxyl multiwalled carbon nanotubes. Differential Scanning Calorimetry (DSC) analysis, cyclic voltammetry (CV), charge discharge (CD)

1. Introduction

Experts in the energy and its usage have identified the recognition of energy, pattern of consuming energy (Paul et al., 2012), the role of industry structure and its values as an energy paradigm change of the globe, with many of them, suggesting and developing a new paradigm, which occurred as a result of the complicated problems such as petroleum exhaustion, environmental pollution, greenhouse effect and climate change. They, however, forecasted that, the future energy paradigm will include concepts that diminishing wasteful energy, enriching the lifestyle and not burdening the environment (Iwama et al., 2012). All these, is in order to pave away to the few prominent energy storage devices such as batteries and most importantly "Supercapacitor" which could be one among the most efficiently used sustainable paradigm which also could tackle the current paradigm (Choi et al., 2012; Dubal et al., 2012).

Supercapacitors, also known as ultracapacitors (Inagaki et al., 2014a; Hashim & Khiar, 2011; Burke, 2009) or power capacitors, store electrochemical energy by accumulating the charge from electric double layer, which is caused by electrostatic attraction. In this case, the capacity of the supercapacitor is proportional to the electrode surface, i.e., the electrochemically active surface, where, how much ions are attracted, (Gund et al., 2013; Jiang et al., 2013). Electrochemical Double Layer Capacitors (EDLCs) are possible to be fully charged and discharged in seconds. Although their energy density (about 5–10 Whkg⁻¹) is lower than in batteries or fuel cells, higher power density (10 Whkg⁻¹) can be reached in a short time (Choi et al., 201). The most attractive advantage of EDLCs is a high power capability (Ayad et al., 2011; Domingo-Garcia et al., 2010; Snook et al., 2011;) with the fast charge/discharge rate (Zheng et al., 2012; Choi et al., 2012). Moreover, most of the EDLCs are safer against short circuit than batteries in terms of the possibility of self-ignition. They do not contain any hazardous or toxic materials (Aravinda et al., 2013a; Aravinda et al., 2013b) and have the durability during long CD cycles.

Basically supercapacitors can be represented by two distinct mechanisms describing them: (i) EDLC and (ii) Pseudocapacitor. EDLCs store the charge electrostatically following a reversible adsorption-desorption cycles of electrolyte ions onto active electrode materials. These active materials might not only be electrochemically stable, but also have accessible large surface area and with no any Faradaic reaction at EDLC electrode. The surface storage mechanism allows very fast energy uptake and delivery, and better power performance. However, the physicochemical process and electrode polarization in EDLC are not enough to apply high energy devices. On the other hand, pseudocapacitors, undergoes reversible Faradaic reactions. Chemically modified carbon materials, (Inagaki et al., 2014 b; Inagaki, 2012; Inagaki et al., 2014 c; Inagaki et al., 2014d; Inagaki et al., 2014 e), metal oxide, (Choi et al., 2012; Paul et al., 2012) and conducting polymers (Hsieh et al., 2012; Choi et al., 2012; Paul et al., 2012) are used as electrodes. In case of pseudocapacitors, the stability for charge-discharge (CD) cycling is relatively poor, though, their energy densities are relatively high compared to EDLCs. Furthermore, the response time is longer than EDLCs, because it takes longer time to move electrons during the redox reaction (Choi et al., 2012). Although supercapacitors can be regarded as "still evolving" into the area of ever more energy containing and powerful devices, they have since been able to address the increasing needs of electronic (cell phones, digital cameras, etc. (Probstle et al., 2002), industrial (uninterruptible power supplies, grid conditioning, windmills, cranes, etc.) (Payman et al., 2008; Wu et al., 2012) and in the sectors of transportation/automotive (trains, busses, cars) (Shi et al., 2013; Tran et al., 2013; Wu et al., 2013; Inagaki et al., 2014). Although supercapacitors have higher capacity than batteries and capacitors, it may present disadvantage of high raw material cost and process difficulty. However the application of thin film processes to the fabrication of the supercapacitors might overcome the above disadvantage. As a result, supercapacitors in thin film form (and using solid and flexible electrolyte) (Wang et al., 2013) are gaining increasing interest in the field of lightweight, ultrathin energy management devices for wearable electronics (Dubal et al., 2012). So far most of the current supercapacitors uses liquid electrolyte which could have side effect on the environment in terms of its hazards; the housing of the cell after the sealing of the electrolyte could also be another issue (Wang et al., 2013), the reason why we chose the former method for the cell fabrication.

Recently, number of researchers have diverted their attentions towards the development of advanced electrode materials, which could replace the most commonly used once (such as Activated Carbon (AC)), by mainly using Carbon Nanotubes (CNTs) networks or graphene as flexible electrodes, for high-performance flexible supercapacitors. CNTs, especially MWCNTs have high inherent conductivity, flexibility, chemical and mechanical stability, and larger surface area polarizability (Paul et al., 2012), and can operate within the voltage window of 3 V or more. Furthermore, their predominant exohedral surface favors the quick accumulation and transport of electrolyte ions so as to increase the performance of quick charge and discharge under high currents (Zheng et al., 2012). This will be vindicated in our cell construction and fabrication highlighted in this paper. In order to reduce the toxic effect to the environment and its inhabitants, (Dumortier et al., 2006) functionalized CNTs were selected for this purpose. Functionalized CNTs are said to be stable for long-term storage, are soluble in aqueous solution, have low toxicity, (Capek, 2009), while increasing more reactivity at their surface walls (Prato et al., 2007; Mittal, 2011). Most importantly, when CNTs are functionalized, their pore sizes will be widened up, thereby increasing the chances of ionic penetration at the electrode-electrolyte interface of fabricated supercapacitor (Van Hooijdonk et al., 2013).

2. Experimental

2.1 Electrolytic Materials

Hybrid Solid Polymer Electrolyte (HSPE) was prepared from a percentage ratio of 70:30, 60:40 and 50:50 wt. % respectively of PVA and H_3PO_4 with cellulose filter paper immersed into it. The H_3PO_4 (>85 wt.% in water, molar mass of 98.00 g/mol⁻¹, product, number of 1562-80) 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. Both H_3PO_4 and PVA were used as-received without further treatment or purification. An aqueous solution of PVA was then 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 70:30, 60:40 and 50:50 wt. % as mentioned above. After the mixture cools to a room temperature, the resulting homogenous solution of PVA/ H_3PO_4 was cast over a plastic Petri dish. This was after a cellulose filter paper (Whatman brand) was cut into a 6 cm x 5.5 cm and soaked in a segment of the aforementioned solution. The above mixture took roughly four weeks before it dries. After which it can be able to peel off was used as the separator and at the same time as the HSPE.

2.2 Electrode Materials and Cell Assembly

The carboxyl multiwalled CNTs with the following 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} was purchased locally in Malaysia (with material code MC8/21/20). The binder used, was P(VdF-HFP) (average molecular weight of $\sim 400,000$; Mn of $\sim 130,000$ pellets; product number of 427160) was purchased from Sigma Aldrich. So, the double layer capacitor was made with a mixture of 90 wt. % of the CPCMWNTs and 10 wt. % of P(VdF-HFP), mixed inside a 20 ml of the acetone. The slurry was then cast onto to the Aluminum foil and allowed to dry for about two hours at room temperature. Prior to that, an applicator was used to polish the slurry with the view to leveling it and obtaining a desired thickness which was around 0.127 mm. The dried sample was then further dried in an oven for about 12 hours at a temperature of 100°C . Afterward, the solid films were obtained and were further cut into $2\text{ cm}^2 \times 3\text{ cm}^2$ 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 around 0.224 g. Using a Perspex of about 5 cm x 4 cm, the cell was set up by sandwiching two electrodes with the electrolyte and assembled in an innovative supercapacitor tester (see Figure 1).



Figure 1. Cross-section of the fabricated supercapacitor cells in our laboratory

The surface morphologies of all films 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 abluf magnification of 80x to 2 000 000x). XRD spectra were obtained with an XRD (Philip X'Pert XRD with $\text{Cu K}\alpha$ radiation of wavelength $\lambda=1.54056 \text{ \AA}$ for 20 angles between 10° and 80°) that used $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 30 mA. CD analysis and CV were respectively carried out by using a newer battery which has been interfaced to a computer called "e-machines" (model: ET1850, Rating: 100-127/220/240Vac, 6/3.15A (6/3,15A), 60/50 Hz) and Gamry instrument Framework (version 5.61).

The following symmetric capacitor cells were assembled

Cells:	Cell A -	C90PVdF-HFP10 H50 C90PVdF-HFP10
	Cell B -	C90PVdF-HFP10 H60 C90PVdF-HFP10
	Cell C -	C90PVdF-HFP10 H70 C90PVdF-HFP10

3. Results and Discussions

3.1 Microstructure Characterizations

As mention earlier, XRD spectra were obtained with an XRD (Philip X'Pert XRD with $\text{Cu K}\alpha$ radiation of wavelength $\lambda=1.54056 \text{ \AA}$ for 20 angles between 10° and 80°) that used $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 30 mA. The XRD analysis of the C90PVdF-HFP10 electrode is depicted in Figure 2. As seen from

this figure, all the diffraction peaks can be observed and the major diffraction peaks of the CPCMWNT can also be seen clearly. The XRD peaks that appear in $\theta = 26^\circ$ and $\theta = 43^\circ$ might be as a result of the hexagonal structure of (002) and (101) respectively, which indicates that the carboxyl multiwalled CNT have high conductivity (Dong et al., 2007). In addition, there appeared a wider diffraction at $\theta = 20.1^\circ$ which correspond to crystalline peaks of PVDF (Stolarska et al., 2007). This also results proved well with the same result of the XRD obtained by many researchers such as (Li et al., 2010; Stolarska et al., 2007).

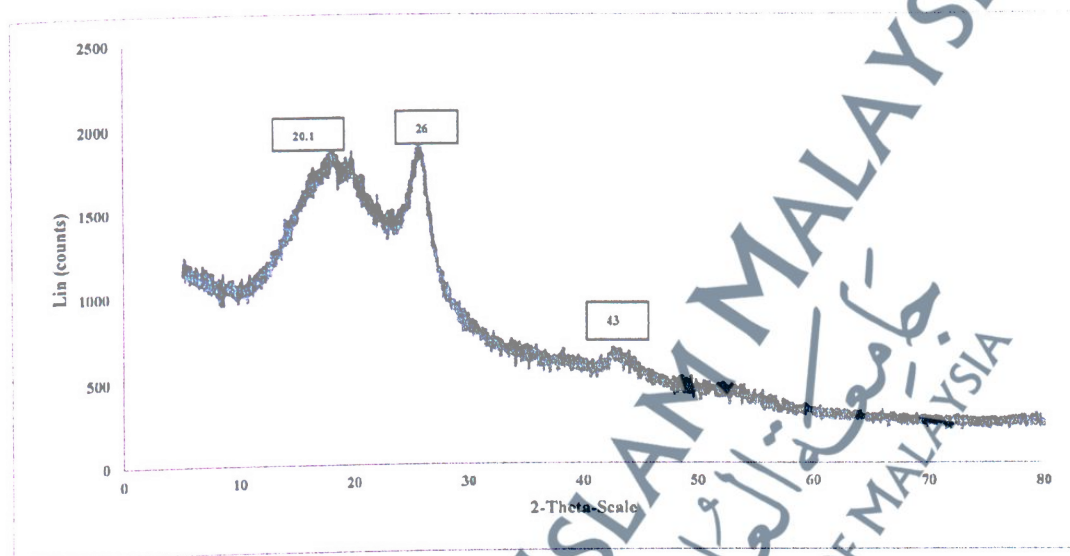


Figure 2. XRD Analysis C90PVdF-HFP10 electrode

In Figure 3 (a, and b), FESEM images of 100 % CPCMWNTs sample electrode with 90 % CPCMWNTs and 10 wt.% of P(VdF-HFP) were shown. Pure CPCMWNT exhibits regular, entangled and smooth surface morphology with an average outer diameter of ~ 30 nm and length of several micrometers. The few larger tubes that were cited in the FESEM structure indicate that the original MWNT has been oxidized thereby resulting in the enlargements of the tubes. However, the FESEM image in Figure 3 (b), although was clearer, but it's not as in Figure 3 (a), which is as a result of the addition of 10 % binder into the composition of the electrode. This could be seen even more clearly in Figure 4, where the FESEM images of CPCMWNTs were taken at different magnifications of (a); 3.6 mm x 50 k (1 μ m) (b); 3.6 mm x 100 k (500 nm) and (c); 3.6 mm x 150 k (300 nm).

On the hybrid polymer electrolytes parts, Figure 5, first show the FESEM images of HSPE containing 50 wt. % of both PVA and H_3PO_4 at a magnification of (a); 3.5 mm x 35 LM (1.00 mm) (b); 3.5 mm x 150 LM (300 μ m) and (c) 3.5mm x 300 LM (100 μ m). The entangling nature of the surface of the image was a clear indication of the presence of the filter paper. Except in a few spots, all over the surface of the polymer look unique as the Watman filter paper was coated with composites of both PVA and H_3PO_4 . The same can also be said to Figure 6. However, in Figure 7 where the FESEM images of HSPE with the content of 70 wt. % of H_3PO_4 , 30 wt. % of PVA and at a magnification of (a); 3.5 mm x 35 LM (1.00 mm) (b); 3.5 mm x 150 LM (300 μ m) and (c) 3.5mm x 300 LM (100 μ m). There appear some obvious changes in the surface morphology. Several places spotted seem to have openings almost everywhere, indication of flaws in the coating. This could result in obtaining a lower capacitance as, the contact between the electrode and the electrolyte could only lead to leaving wider pore sizes that are not in good contacts to each other. Lastly, Figure 8 depicts the FESEM images of C90PVdF-HFP10 electrode overlapped on HSPE containing 60 wt. % of H_3PO_4 , 40 wt. % at the magnifications of x 45 k (1.00 μ m). The image was taken at an angle of 30° in order to see the boarder where the electrode and electrolyte interface. Here it can be deduced that, the thinner the electrode the better, so, thicker electrodes will only result in higher internal resistance.

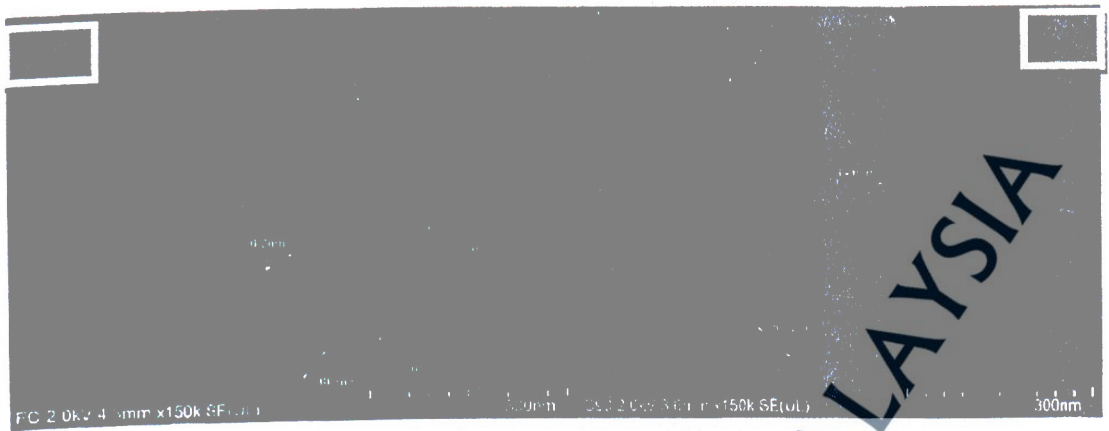


Figure 3. FESEM images of 100 % CPCMWNTs (a); and (b); sample with 90 % CPCMWNT and 10 wt. % of P (VdF-HFP) showing average diameters of the pore sizes. The magnifications of the two samples were 4.3 mm x 150 k and 3.6 mm x 150 k respectively



Figure 4. FESEM images of CPCMWNTs showing C90PVdF-HFP10 electrode at a magnifications of (a); 3.6 mm x 50 k (1 μ m) (b); 3.6 mm x 100 k (500 nm) and (c); 3.6 mm x 150 k (300 nm)



Figure 5. FESEM images of HSPE containing 50 wt. % of both PVA and H_3PO_4 at a magnification of (a); 3.5 mm x 35 LM (1.00 mm) (b); 3.5 mm x 150 LM (300 μ m) and (c); 3.5mm x 300 LM (100 μ m)

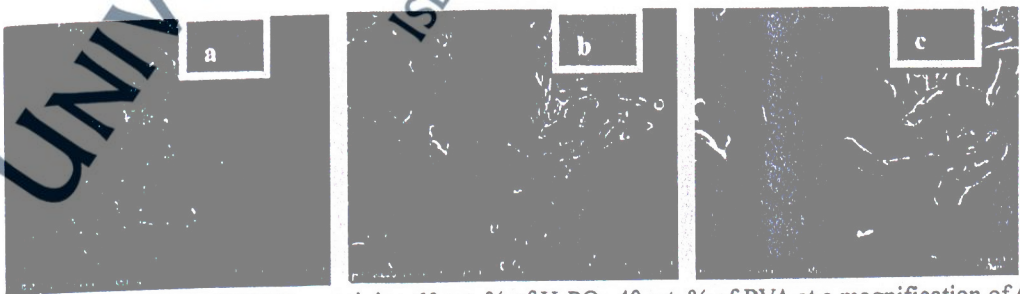


Figure 6. FESEM images of HSPE containing 60 wt. % of H_3PO_4 , 40 wt. % of PVA at a magnification of (a); 3.5 mm x 35 LM (1.00 mm) (b); 3.5 mm x 150 LM (300 μ m) and (c); 3.5mm x 300 LM (100 μ m).

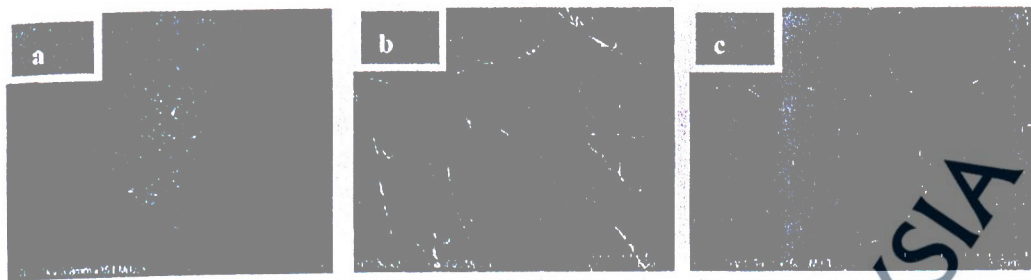


Figure 7. FESEM images of HSPE containing 70 wt. % of H_3PO_4 , 30 wt. % of PVA at a magnification of (a); 3.5 mm x 35 LM (1.00 mm) (b); 3.5 mm x 150 LM (300 μm) and (c); 3.5 mm x 300 LM (100 μm)

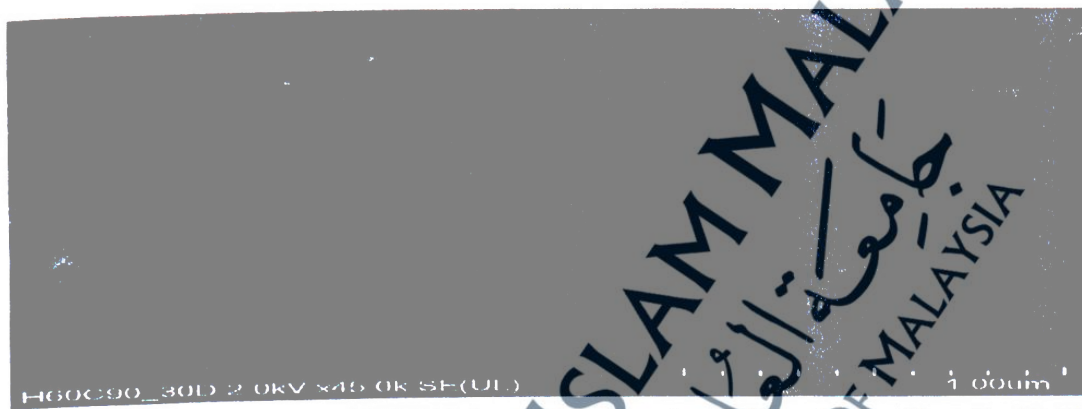


Figure 8. FESEM images of C90PVdF-HFP10 electrode overlapped on HSPE containing 60 wt. % of H_3PO_4 , 40 wt. % at the magnifications of x 45 k (1.00 μm) and an angle of 30°

3.2 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) was carried out on the scale-range of 50°C to 1000°C under nitrogen gas (N_2) flow at a heating rate of $10^\circ\text{C min}^{-1}$ on a METTLER, STAR[®] SW 10.00 thermal analyzer in line with our previous work (Hashim et al., 2014). The thermal stability of the samples was discerned in Figure 9. The Figure were (a); 0 % sample (Background) (b); pure CPCWMCNT (c) C90PVdF-HFP10 – Single scale (d); C90PVdF-HFP10 – Double scale.

Before beginning the experiment a background heating was conducted in order to pave way with any ruminant residue and for re-calibration. Trace in Figure 9 (b) shows that, the pure CPCWMCNT experience a major loss of just 11.0719 % occurring at 611.76°C leaving a residue of 87.9109 %. This result shows that, the pure MWCNT have very good thermal stability and consequently, good in application for electrochemical devices. While in Figure 9 (b and c), it can be noticed that, when the active materials were all incorporated in a single electrode, three losses were then recorded. The initial loss of 2.5224 % of the total samples occurs at 307.24°C , then the second loss of 5.9640 % was observed at 449.5°C and the highest loss of 11.629 % was noticed at 708.84°C . This shows that, the introduction of active material to the pure CPCWMCNT will work well in the supercapacitor fabrication process.

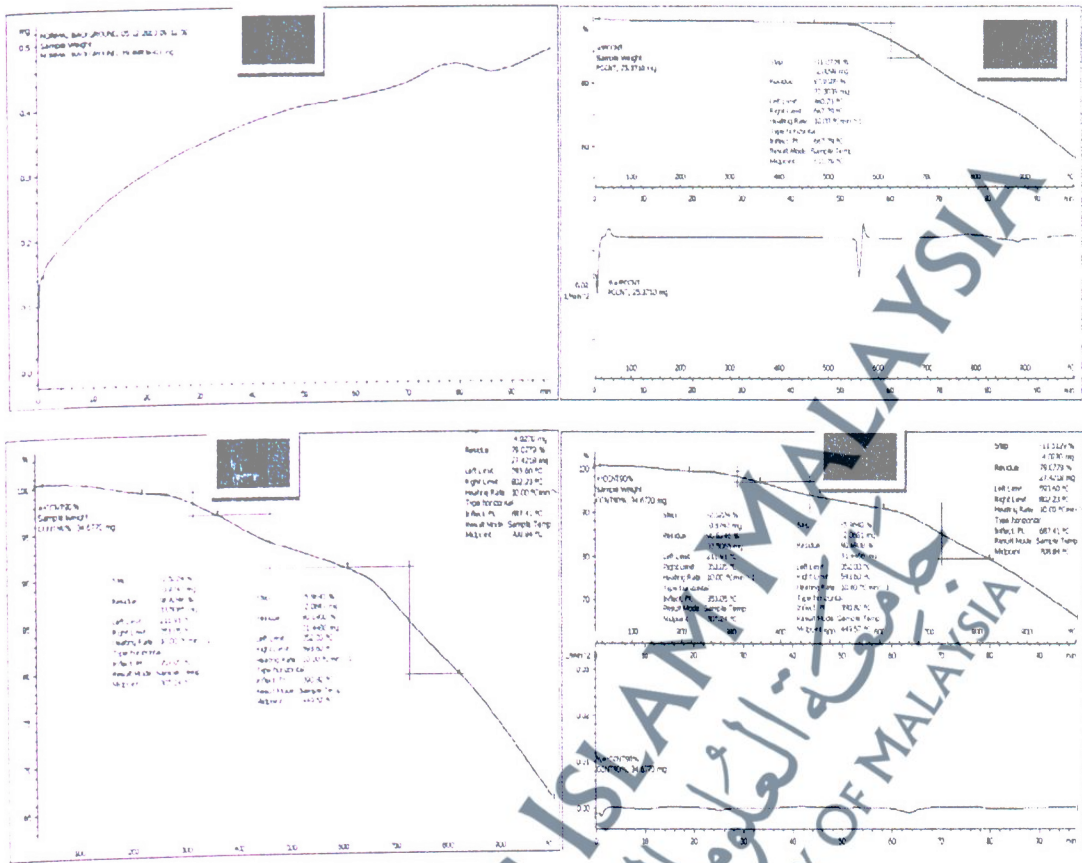


Figure 9. TGA of the electrode at (a); 0 % sample (Background) (b); pure C90PVdF-HFP10 - Single scale (d); C90PVdF-HFP10 - Double scale

3.3 Electrochemical Behavior

The electrochemical behaviors of C90PVdF-HFP10 were investigated by cyclic voltammetry (CV) and CD measurements using two-electrode system. Figure 10 shows a CV of Cell -A (C90PVdF-HFP10 | H50 | C90PVdF-HFP10) at (a); scan rates of 10, 50 and 100 mV; 3 V- voltage window (b) scan rate of 50 mV; 1 V - voltage window. It can be discerned that at a scan rate of 50 mV and 1 V- voltage window, the EDLC curve look more rectangular in shape. The specific capacitance of the electrode materials obtained in the two-electrode system was calculated by integrating the CV curves in Figure using the formula;

$$C_{sp} = \frac{2i}{Sm} \quad (1)$$

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

It could be obtained that the specific capacitance is 30.1 Fg⁻¹, 13.5 Fg⁻¹, and 11.2 Fg⁻¹ for scan rates of 10, 50 and 100 mV, respectively. This gives an explanation of the relationship between the capacitance and scan rate. The specific capacitance decreases from 30.1 Fg⁻¹ to 11.2 Fg⁻¹ which could be attributed to the slow transfer of ions on the electrode electrolyte interface (Shu et al., 2013). It can also be due to the un-uniformity of the coated filter paper by the electrolyte as vindicated in the FESEM analysis.

Furthermore, Figure 11 also shows CV of Cell -B (C90PVdF-HFP10 | H60 | C90PVdF-HFP10) at (a); scan rates of 1, 50 and 100 mV, 3 V- voltage window (b) scan rate of 50 mV; 1 V - voltage window. The specific capacitances obtained in this cell were 60.1 Fg⁻¹, 28.0 Fg⁻¹ and 21 Fg⁻¹ for scan rates of 10, 50 and 100 mV respectively. These results almost double that of cell-A which might be attributed to the increase in ionic conductivity in the polymer electrolyte of the HSPE. And Last but not the least, is the Figure 12, depicting the CV of Cell -C (C90PVdF-HFP10 | H70 | C90PVdF-HFP10) at; (a) Scan rates of 1, 50 and 100 mV, 3 V- voltage window, (b) Scan

rate of 50 mV; 1 V – voltage window. This result represent weakest of all the three cells with the lowest capacitance delivery of 24.0 Fg^{-1} , 5.6 Fg^{-1} and 2.9 Fg^{-1} obtained for the scan rates of 10, 50 and 100 mV respectively. It can be recalled that FESEM analysis of HSPE of this cell shows the poorest coating of the electrolyte as a result very high internal resistance recorded. Table 1 gave a summary report of the capacitance obtained in all the three cells and Figure 13 (a) summarize the capacitance performance in the combined graph of capacitance against the scan rates for Cells A, B and C while Figure 13 (b) revealed the cyclic performances of cell-A (C90PVdF-HFP10 |H50| C90PVdF-HFP10), cell-B (C90PVdF-HFP10 |H60| C90PVdF-HFP10) and cell-C (C90PVdF-HFP10 |H70| C90PVdF-HFP10). Cell-B show a more stable capacitance at about 35 Fg^{-1} up to 5000 cycles, however, both cell-A and C were shown to maintain their cycleabilities at around 10 Fg^{-1} only. This degradation is attributed the high internal resistance that both the cells exhibited.

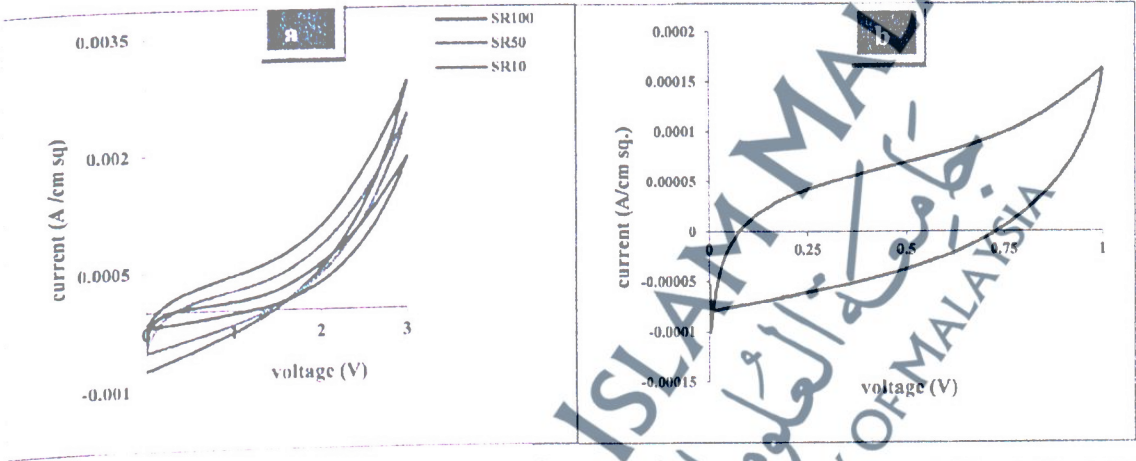


Figure 10. CV of Cell –A (C90PVdF-HFP10 |H50| C90PVdF-HFP10) at (a); scan rates of 1, 50 and 100 mV, 3 V-voltage window (b); scan rate of 50 mV; 1 V – voltage window

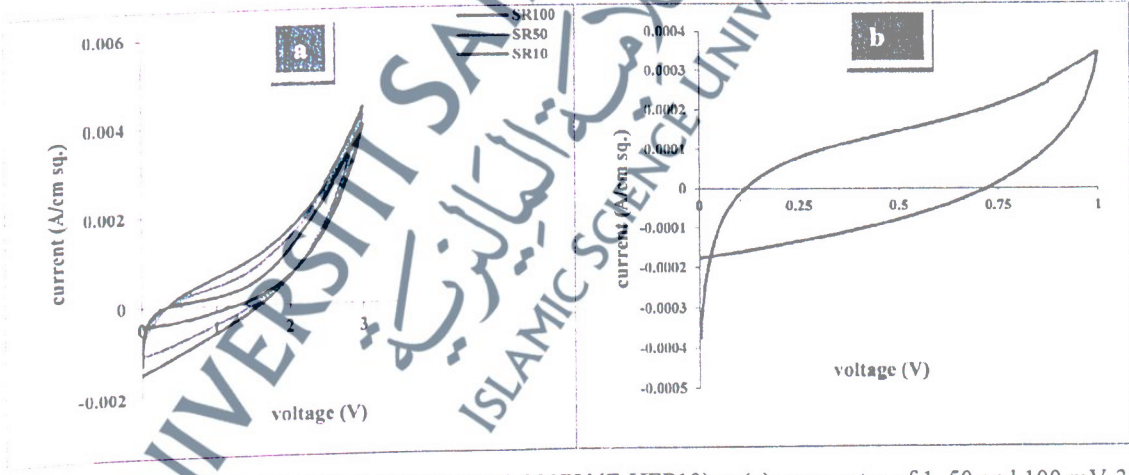


Figure 11. CV of Cell –B (C90PVdF-HFP10 |H60| C90PVdF-HFP10) at (a); scan rates of 1, 50 and 100 mV, 3 V-voltage window (b); scan rate of 50 mV; 1 V – voltage window

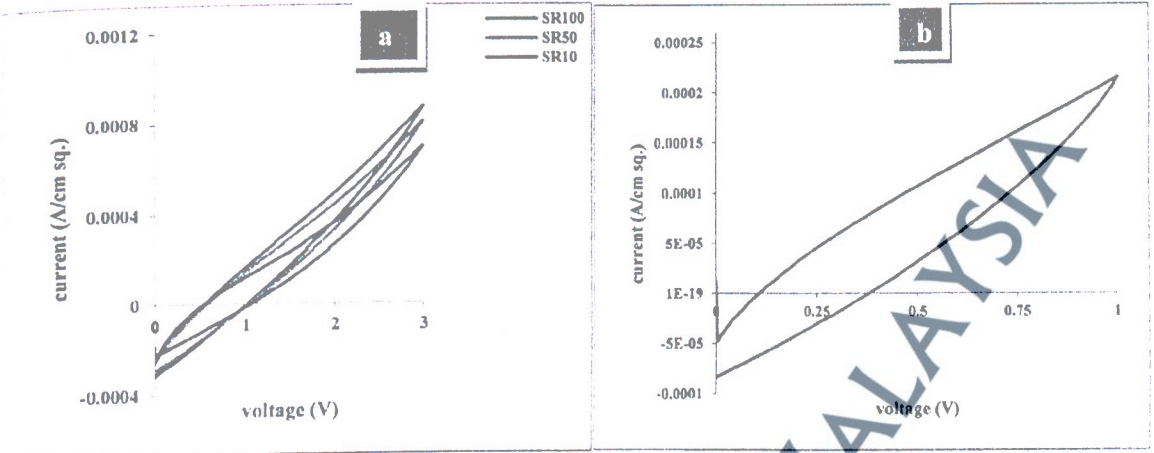


Figure 12. CV of Cell -C (C90PVdF-HFP10 |H70| C90PVdF-HFP10) at (a); scan rates of 1, 50 and 100 mV, 3 V-voltage window (b); scan rate of 50 mV; 1 V -voltage window

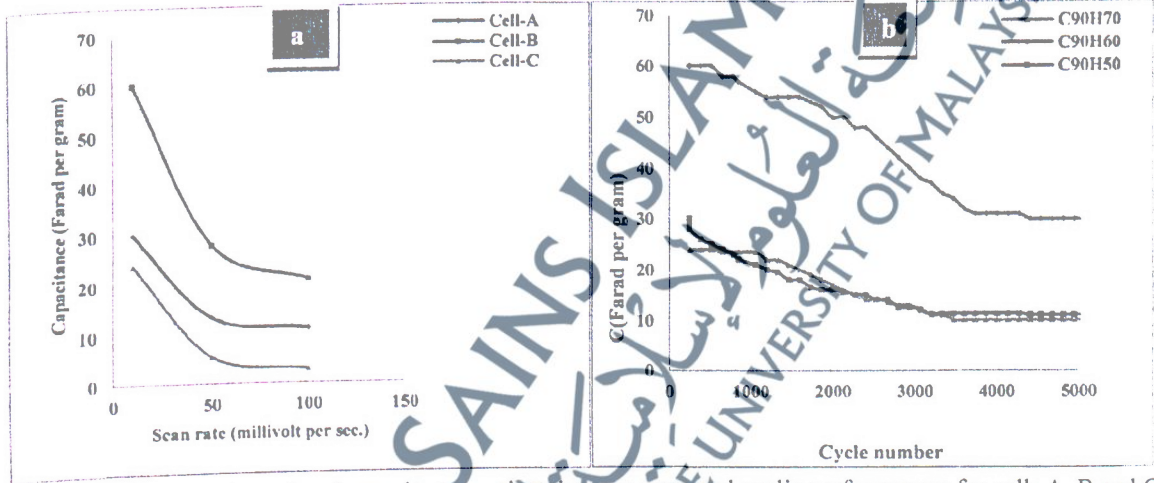


Figure 13. Combined graphs of capacitance against the scan rates and cyclic performances for cells A, B and C

Table 1. Performance of Supercapacitor by the CV

Cells	Working Voltage (V)	Capactance value of Different scan rates (Fg ⁻¹)		
		100 mV	50 mV	10 mV
A-C90H50	3	11.2	13.5	30.1
B-C90H60	3	21.0	28.0	60.1
C-C90H70	3	2.9	5.9	24.0

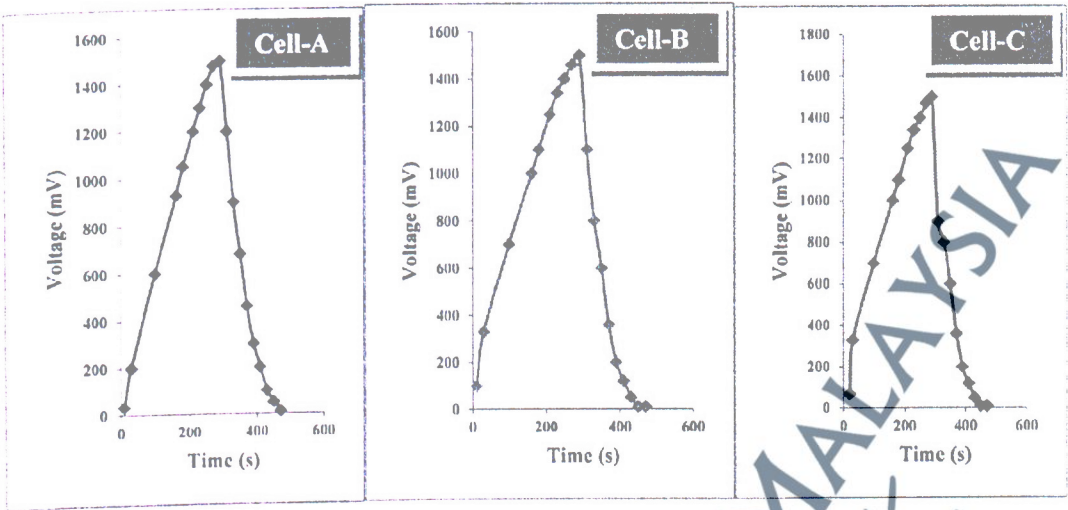


Figure 14. CD graphs of (a); Cell-A (b); Cell-B and (c); Cell- C

Table 2. Performance of Supercapacitor by the CD

Cells	Working Voltage (V)	C _d (Fg ⁻¹)	ESR (Ωcm ²)	Energy Density (Jg ⁻¹) (Jg ⁻¹ s ⁻¹)	Power Density
A-C90H50	1.5	8.6-86.1	0.15-1.5	43.2-432.2	0.8-8.4
B-C90H60	1.5	7.7-76.7	0.2-2.0	38.8-385.3	0.6-6.3
C-C90H70	1.5	8.9-89.3	6.6-66.0	44.7-448.4	0.02-0.1

The galvanostatic CD test is considered to be an alternative and arguably better quantitative method to evaluate the supercapacitive nature of an electrode material compared to the CV measurement (Shu et al., 2013). In this respect, we determined the capacitance of the supercapacitor cell yet, using this method. In Figure 14, the CD graphs of (a); Cell-A (b); Cell-B and (c); Cell- C were all depicted at a working voltage of 1.5 V and at three different current densities i.e. 10, 20 and 100 mA. In addition to effective capacitance, power and energy densities were also calculated using Equations 2, 3 and 4.

For effective capacitance,

$$C_e = i \frac{\Delta t}{\Delta V} \tag{2}$$

Where i is the applied current and Δt and ΔV are the changes in time and current respectively. For energy and power of the capacitance, we use the following Eqs.;

$$E = \frac{1}{2m} CV^2 \tag{3}$$

$$P = \frac{V^2}{4mESR} \tag{4}$$

ESR denotes equivalent series resistance, m is the mass of the electrode and V represents the applied voltage (or voltage window). In cell-A, the discharged capacitances obtained were 8.60 Fg⁻¹, 17.71 Fg⁻¹ and 86.06 Fg⁻¹ respectively at an applied current density of 100, 20 and 10 mA; the calculated energy and power densities are 43.20 Jg⁻¹/0.84 Jg⁻¹s⁻¹, 86.42 Jg⁻¹/1.67 Jg⁻¹s⁻¹ and 432.22 Jg⁻¹/8.37 Jg⁻¹s⁻¹ at the said current densities. In cell-B, the discharged capacitances obtained were 7.67 Fg⁻¹, 15.35 Fg⁻¹ and 76.72 Fg⁻¹ respectively at an applied current density of 100, 20 and 10 mA; the calculated energy and power densities are 38.77 Jg⁻¹/0.63 Jg⁻¹s⁻¹, 77.54 Jg⁻¹/1.26 Jg⁻¹ s⁻¹ and 385.31 Jg⁻¹/6.28 Jg⁻¹ s⁻¹ at the said current densities. And finally cell-C has the following

results for the capacitance; 8.89 Fg^{-1} , 17.80 Fg^{-1} and 89.28 Fg^{-1} respectively at an applied current density of 100, 20 and 10 mA; power/energy densities are $44.70 \text{ Jg}^{-1}/0.02 \text{ Jg}^{-1}\text{s}^{-1}$, $89.41 \text{ Jg}^{-1}/0.04 \text{ Jg}^{-1}\text{s}^{-1}$ and $448.40 \text{ Jg}^{-1}/0.19 \text{ Jg}^{-1}\text{s}^{-1}$ at the said current densities. From the overall results, it can be observed that, the discharged capacitance decreases with the increase in current density, which could be as a result of the low penetration of ions into the inner region of the pores due to fast potential changes.

3. Conclusion

In this work, we have explored the noble of CPCWMCNT used as an electrode for high performance supercapacitors using HPSE as a separator. Three cells were constructed and leveled as cell-A (C90PVdF-HFP10 |H50| C90PVdF-HFP10), cell-B (C90PVdF-HFP10 |H60| C90PVdF-HFP10) and cell-C (C90PVdF-HFP10 |H70| C90PVdF-HFP10) with changes in the separator. The XRD peaks of the sample electrode C90PVdF-HFP10 appeared in $\theta = 26^\circ$ and $\theta = 43^\circ$ which might be as a result of the hexagonal structure of (002) and (101) respectively, which also indicates that the carboxyl multiwalled CNT have high conductivity. Again, a wider diffraction at $\theta = 20.1^\circ$ which correspond to crystalline peaks of PVDF. TGA traces shows that, the pure CPCWMCNT experience a major loss of just 11.0719 %, which occurred at 611.76°C leaving a residue of 87.9109 %, which also shows that, the pure MWCNT have very good thermal stability and consequently, good in application for electrochemical devices. This result, even gets better when the active material was added. From the overall results for the electrochemical analysis of the CV, cell-B delivered higher capacitance of 60.10 Fg^{-1} doubling that of cell-A, and tripling cell-C. Also in CD analysis with much lower voltage window of 1.5 V, cell-A delivered slightly better than B and C with a balanced and better discharge capacitance of 86.06 Fg^{-1} with higher energy/power densities of $432.22 \text{ Jg}^{-1}/8.37 \text{ Jg}^{-1}\text{s}^{-1}$ and lowest in terms of internal resistance.

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Conductivity Studies and Characterizations of PVA-Orthophosphoric Electrolytes

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Abstract

Solid polymer electrolyte (SPEs) has drawn great attention nowadays, particularly in the field of science and applied science, specifically, those used as separators in industries and researchers for the assemblage of some "classified batteries" and super capacitors. In this report, we present the grandeur of this SPE (pure type), particularly at room temperature, such that, it can be applied as an electrolyte as well as a separator in supercapacitor fabrication. The SPEs were produced from the composition of polyvinyl alcohol (PVA) and Phosphoric acid (H_3PO_4), such that, the PVA samples were kept constant while the phosphoric acid was varied at 0, 10, 20, 30, 40, 50, 60, and 70 wt. %. After the experimentation, the pure polymers show excellent results in term conductivity, in that, it has recorded a conductivity as high as $2.56 \times 10^{-3} \text{ Scm}^{-1}$ at the compositions of 70 wt. %. Aside that, we also observed that, the bulk moduli (R_b) value decreases with the increase in concentration, with pure solid polymer electrolyte (PSPE) recording 2.5Ω at the highest composition of 70 wt. %.

Keywords: Pure solid polymer electrolyte (PSPE), polyvinyl alcohol (PVA), Phosphoric acid (H_3PO_4), Electrochemical Impedance Spectroscopy (EIS).

1. Introduction

The year 2013 marked the complete three decades (1973) of the invention of polymer electrolyte by Fenton and co-workers (Gu et al., 2000; Kumar & Sundari, 2010; Zhang et al., 2006; Yang, 2004; Ragavendran et al., 2004; Tripath et al., 2012; Ulaganathan et al., 2012; Kuo et al., 2013; Yang et al., 2013; Noor et al., 2010) and Armand (Ragavendran et al., 2004; Zhang et al., 2006). Ever since then, research on polymer electrolyte has become very elaborate.

Research has shown that, there are three classifications of polymer electrolyte systems, namely (i) Polyelectrolytes (PEs): - which have an independent ion-generating groups chemically bond to the macromolecular chain and presence of counter-ion in order to maintain the electroneutrality of the salt. In dry conditions, they have low conductivity of about $10^{-10} - 10^{-15} \text{ Scm}^{-1}$ but in the presence of dielectric solvent such as water, there conductivities do improve (Ulaganathan et al., 2012). (ii) Solvent Swollen Polymer Electrolytes (SSPE): - In SSPE, solvents, both aqueous and non-aqueous swells the host polymer. Thus, the dopant ionic solutes such as H_3PO_4 is hosted in the swollen lattice thereby permitting the movement of ions in the solvent swollen region of the polymer host. Their conductivity depends on the compactness of the solvent in the region that is being puffed up (Ulaganathan et al., 2012). And lastly (iii) the Solvent Free Polymer Electrolytes (SFPE): These are polymer salt complex, which is formed by complexes between salts of alkali metals and polymer containing solvating hetroatoms, example; O, S and N (Ulaganathan et al., 2012). The complexation between poly ethylene oxide (PEO) and alkali metal salts is a good example of SFPE. SFPE are sub-classed into three also. They are; (a) Solid Polymer Electrolytes (SPEs), (b) Gel Polymer Electrolytes (GPEs), and (c) Composite polymer electrolytes (CPEs) (Kuo et al., 2013; Tripath et al., 2012).

GPEs can be only considered as plasticizers incorporated polymer-salt complex (Ulaganathan et al., 2012). They are therefore consisted of a liquid electrolytes immobilized in a polymer matrix (Hashmi, (a), 2013) and exhibits high ionic conductivity (10^{-3} to 10^{-4} Scm^{-1} at ambient temperature) and can be obtained by either loading of a liquid electrolyte in a microporous matrix or by increasing the viscosity of a liquid electrolyte through the addition of a soluble polymer until gel consistency is achieved or by mixing a liquid electrolyte with monomers of relatively low molecular weight, then curing the mixture by other means, such as UV polymerization, thermal

polymerization and electron beam radiation polymerization. They are criticized for having weak mechanical strength and poor interracial properties, (Qiu et al., 2004; Hashmi, (b), 2013). In CPEs, they are normally prepared by addition of high surface inorganic fillers like SiO₂, MgO, TiO₂ and alike so as to improve the mechanical strength and stiffness of the complex systems (Ulaganathan et al., 2012).

SPE is a thin film that has ionic conductivity, especially, when an alkali salt dissolves in polymer matrix. SPE have drawn great attention in the development of science and technology of lithium secondary batteries. SPEs have several advantages over liquid, gel and even composite electrolytes in that, it has process ability, flexibility, light weight, elasticity and transparency (Zhang et al., 2006), desirable shape moldability, being free from leakage, mechanical strength, better stability especially in high temperature, and high specific energy and power (Lim et al., 2012). Furthermore, use of solid polymer electrolyte can negate the need for a separator and be amendable to low cost manufacturing technologies (Qiu et al., 2004). Some of the applications of SPE are in Batteries, fuel cell, supercapacitors and other electrochemical devices. (Sawada et al., 2000) and other electrochemical devices (Sotta et al., 2010).

Although number of works have been carried out on the characterizations of SSPE like those of Prajapati et al., (2010) and Ahmad Khair & Arof, (2010), this piece tries to offer a tone by step approach on the conductivity studies of this transparent polymer in order to ascertain the suitability composition for the usage in the supercapacitor fabrication which is the main target of our future work. Thus, careful measures have been put in place to ensure that every detail characteristic of the active materials, especially of the PVA – its molecular weight and its percentage hydrolysis – were taken into considerations.

2. Experimental

2.1. Preparation of the Composite PVA Electrolytes

The pure solid polymer electrolyte (PSPE) which can also be served as separators in supercapacitors fabrications have their laboratory preparations discussed elsewhere by us, in Hashim et al., (2012), Hashim et al., (2014) and by Jiang et al., (2013). But for the purpose of elaboration; the active materials comprise of H₃PO₄ and PVA. The H₃PO₄ 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. H₃PO₄ (>85 wt. % in water, molar mass of 98.00 g/mol, 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. Both H₃PO₄ 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. H₃PO₄ 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 the PSPE to be obtained (this has been summarized in Table 1).

In order to vary the percentage of the H₃PO₄ used, the following formula was used;

$$\frac{n}{n+2} \times 100\% = x\% \quad (1)$$

Where x is the percentage of acid require (0, 10, 20, 30, 40, 50, 60, and 70 % wt), and n is the value of H₃PO₄ 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 homogeneous solution (transparent in this case). The mixture is then allowed to cool down to an ambient temperature. The resulting homogeneous solution of PVA/H₃PO₄ 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/H₃PO₄ solution solidifies onto the Petri dish and upon curing for about 3 – 4 weeks at room temperature. This is due to its high molecular weight and consequently more hydrolyzed. 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 enumerated above and as shown in Figure 1. The resulting polymer film was then put in the plastic bags for safe keeping, and to avoid contamination from surrounding, for further property analysis.

3. Result and Discussion

3.1. 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-H₃PO₄ an impedance method which also was highlighted by Ahmad Khair and 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 cm² in radius, in a spring-loaded glass holder.

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 device was 50 Hz - 1 MHz, and simultaneously calculating both real and imaginary impedance.



Figure 1. Showing a prepared and flexible PSPE

Table 1. Table Showing the Overall Formation of the PSPE Preparation

Coding	Measured Quantity PVA in Distilled Water (g)	Measured Quantity of H ₃ PO ₄ (g)	Ratio of PVA to H ₃ PO ₄
P0	2	0	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

The sample exhibits Debye characteristics, and then the plots of the negative imaginary impedance versus the real impedance on the graph should be able to display a semicircle-like shape (Ahmad Khair & Arof 2010). From the Eq. 2, we calculated the electrical conductivity of the samples;

$$\sigma = \frac{l}{R_b A} \tag{2}$$

Where σ is the conductivity itself, l and A are respectively the thickness and area of the samples. The thickness of the sample was measured twice at different positions of the polymer films and an average was taken using digital micrometer.

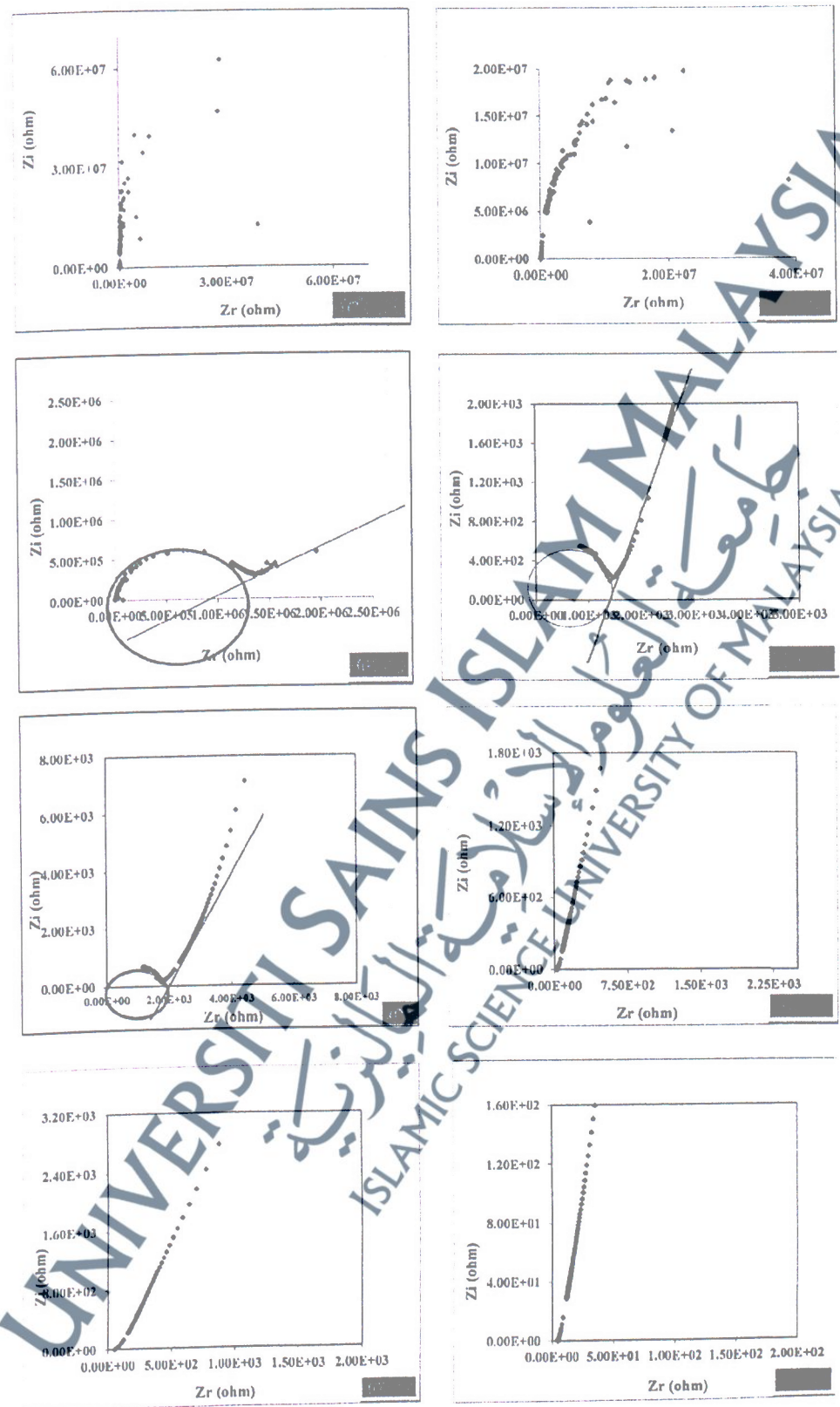


Figure 2. Impedance plots of PSPE containing 0 wt.% (a); 10 wt.% (b); 20 wt.% (c); 30 wt.% (d); 40 wt.% (e); 50 wt.% (f); 60 wt.% (g); 70 wt.% (h) ratio of the H_3PO_4 at room temperatures

Figure 2 (a-h) shows the impedance plots of a sample of the PSPE containing 0, 10, 20, 30, 40, 50, 60, and 70 wt. % ratio of the H_3PO_4 at room temperatures respectively. For the sample with 0 and 10 wt.% of the H_3PO_4 , it can be observed that the point of the graph was dispersed, which clearly indicates the meager or absent of acid in this sample.

The semicircles found on the Figure of the samples containing 20, 30 and 40 wt.% could however be connected with the impact of the introduction of the percentage acid and consequently the immobile polymer chain begins to emerge.

As the acid concentration continues to increase, so the conductivity, thereby making the semicircle disappear, which is an indication that, ions that move around the polymer matrix made resistive component of the polymer electrolytes to exist. (Ahmad Khair & Arof, 2010; Ulaganathan et al., 2012).

The calculated R_b for all the eight samples above were obtained from the frequency intercepts on each and every plotted graph. We also observed that, the R_b value decreases with the increase in concentration. The calculated values of the R_b are 1.15×10^8 , 8.00×10^4 , 2.40×10^4 , 1.70×10^3 , 2.10×10^3 , 1.93×10^1 , 1.26×10^1 and 2.58Ω for 0, 10, 20, 30, 40, 50, 60, and 70 wt.% ratio of the H_3PO_4 respectively. The highest conductivity of PSPE sample was observed at $2.56 \times 10^{-3} \text{ Scm}^{-1}$ when the H_3PO_4 was increased to 70 wt.% while the lowest conductivity of the sample was noticed at $2.25 \times 10^{-11} \text{ Scm}^{-1}$ where the H_3PO_4 percentage was nil. Full details about the average values of the conductivity of PSPE is summarized in Table 2. On a general note, it can be said that, the sample of PSPE performed wonderfully well in terms of both bulk resistance calculation and the conductivity as a whole.

As mentioned earlier, that conductivity is dependent on the concentration of the H_3PO_4 . Table 2 provided us with the information that, there is a relationship between the acid concentration and the polymer matrix. In addition to that, it also be deduce from the table that, the thickness on each sample, also had some impact on the conductivity of the samples. Hence, because of the thinner nature of the films in PSPE, the conductivity seems to be very promising.

Table 2. Parameters that Determine the Conductivity in PSPE

Coding	PVA: H_3PO_4	l (mm $\pm$ 0.005)	R_b (Ω)	σ (Scm^{-1})
P0	100:0	0.00910	1.15×10^8	2.25×10^{-11}
P10	90:10	0.00630	8.00×10^4	7.20×10^{-8}
P20	80:20	0.01100	2.40×10^4	1.46×10^{-7}
P30	70:30	0.05400	1.70×10^3	1.01×10^{-5}
P40	60:40	0.00585	2.10×10^3	8.87×10^{-7}
P50	50:50	0.00745	1.93×10^1	1.23×10^{-4}
P60	40:60	0.02615	1.26×10^1	6.61×10^{-4}
P70	30:70	0.02070	2.58×10^0	2.56×10^{-3}

3.2 Crystal Structure Analysis

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 $\lambda=1.54056 \text{ \AA}$ for 2θ angles between 10° and 80° . The XRD analysis was carried out on the PSPE films. After the analysis, the following results were obtained. The analysis of the structure of the PSPE for 0 wt.% (a); 10 wt.% (b); 20 wt.% (c); 30 wt.% (d); 40 wt.% (e); 50 wt.% (f); 60 wt.% (g); 70 wt.% (h) ratio of the H_3PO_4 was shown in Figure 3.

It can be observed from the semi-crystalline peak of the PVA ($\theta=20^\circ$) which also affirmed the argument put across by (Hashmi, (c), 2013) about the semi-crystal behavior of the PVA. The addition of H_3PO_4 causes the decrease in the degree of the crystallinity and consequently the increase in the amorphicity of the material and its conductivity.

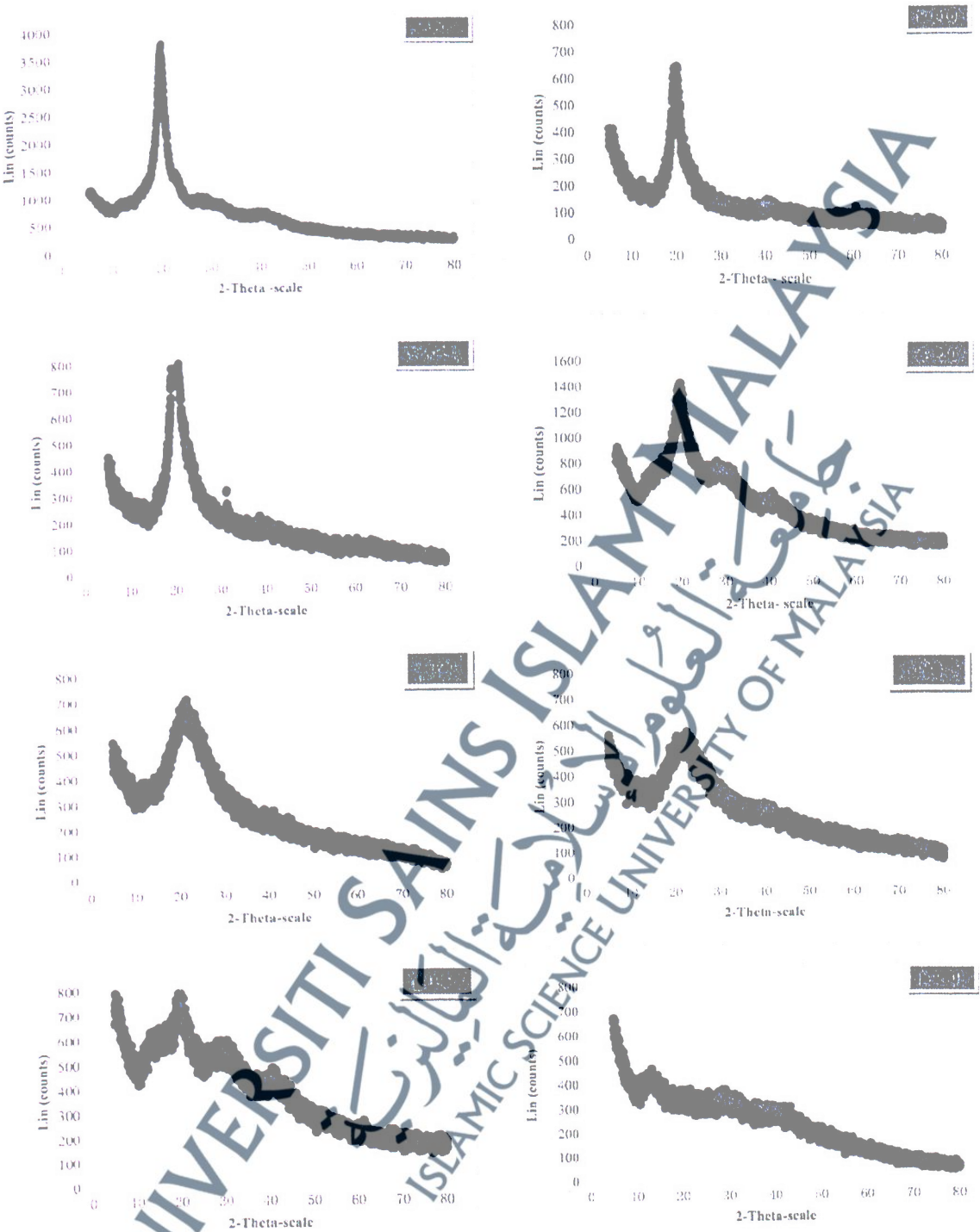


Figure 3. XRD Analysis of PSPE containing 0 wt.% (a); 10 wt.% (b); 20 wt.% (c); 30 wt.% (d); 40 wt.% (e); 50 wt.% (f); 60 wt.% (g); 70 wt.% (h) ratio of the H_3PO_4 and (i) A combined graph containing all the percentages.

3.4 Differential Scanning Calorimetry Analysis

The DSC thermal analysis was carried out using the DCS machine (Mettler Toledo DSC A851 with Star software) under N_2 atmosphere with 10 $^{\circ}C/min$ heating rate from 40 to 300 $^{\circ}C$ in order to observe the crystalline and semi-crystalline behavior of the whole samples, therefore, various parameters related to thermal properties such as

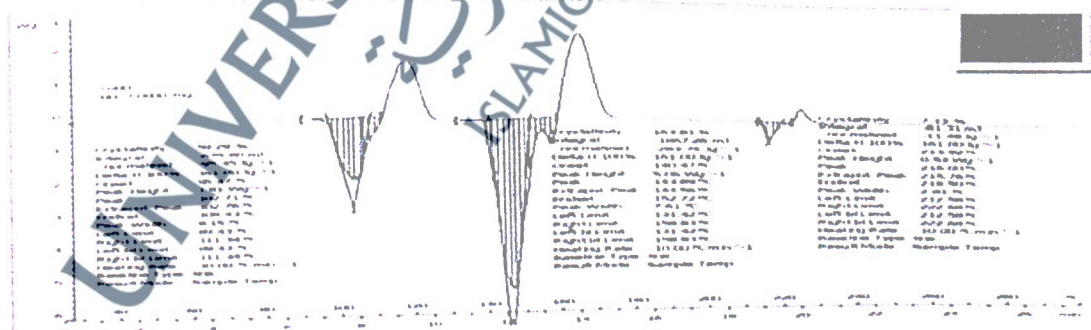
glass transition temperature (T_g), thermal transition (T_m) of crystalline phase of the polymer electrolytes and degree of crystallinity (T_c) can be evaluated from the DSC data. Samples for DSC measurements were prepared from several tiny rectangular pieces cut from the polymer film to a mass ranging 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.

Table 3. Parameters for the Thermometric Analysis in PSPE

Coding	PVA: H_3PO_4	Mass (g)	Temperature (°C)		
			T_g	T_m	T_c
P0	100:0	1.98	98.11	223.56	152.00
P10	90:10	4.48	80.78	221.06	166.27
P20	80:20	7.41	127.31	207.26	186.45
P30	70:30	8.27	117.63	156.46	-
P40	60:40	15.12	116.89	155.00	-
P50	50:50	13.53	101.13	164.59	160.05
P60	40:60	19.48	63.28	160.00	150.00
P70	30:70	24.40	79.41	129.09	79.41

Figure 4 shows the DSC analysis result of PSPE containing 0 wt.% (a); 10 wt.% (b); 20 wt.% (c); 30 wt.% (d); 40 wt.% (e); 50 wt.% (f); 60 wt.% (g); 70 wt.%. From the Figure and Table 3 it can be seen that, the first three samples show a very good T_m with an endothermic peak of slightly above 200 °C (i.e. 233.56, 221 and 207.26 for P0, P10 and P20 respectively) which indicates the huge percentage weight of PVA is present here. Noting the theoretical value of the thermal transition of the pure PVA as 230 °C, this result is closely related to that, and was in agreement with that of (Jelinska et al., 2010; Agrawal, 2004; Othman et al., 2011). However, probably due to the presence of chemical content, or intermolecular interaction (Mudigoudra et al., 2012) form among PVA and H_3PO_4 , the thermal transition starts to decrease with the increase in temperature.

The higher the melting point temperature the more the stability of the molecules therein, as such, pure PVA has more stable molecules than PVA/ H_3PO_4 composite. So, it can be seen that the T_m and T_c decreases (or even diminishes) as the concentration of the acid increase. This is a known fact that, in homogenized blends, the melting shifts to the lower level (Othman et al., 2011; Guirguis & Moselhey, 2012.). The other unusual humps cited in especially P0 and P60 could be as a result of the presence of the moisture inside the samples. Also the theoretical glass transition of the PVA alone is about 85 °C while the composite shows down and upwards shifts of this temperature. This could not be unconnected with the gradual increment in the concentration of the acid.





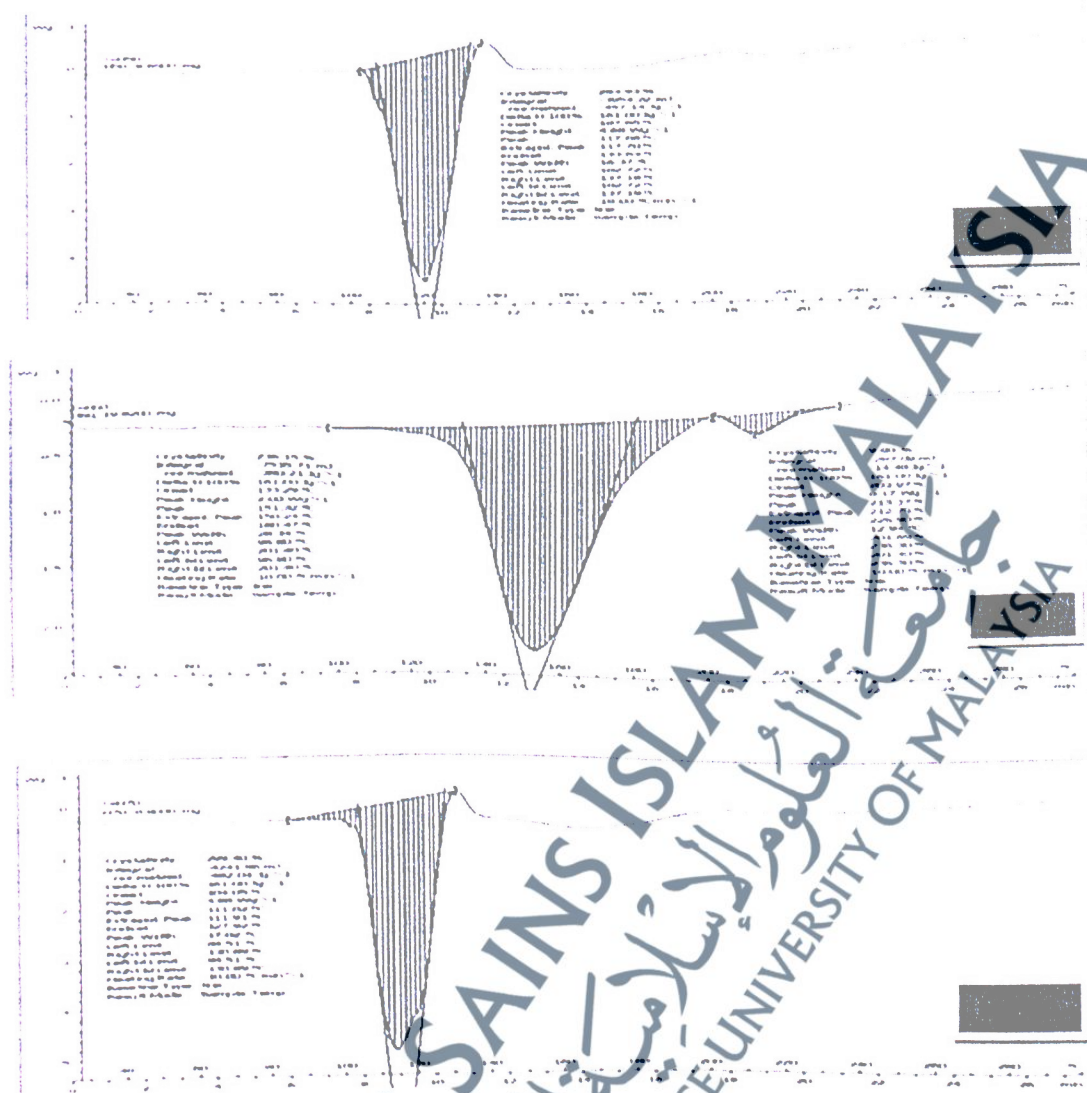


Figure 4. DSC Analysis of Solid (S) Solid Polymer electrolyte containing 0 wt.% (a); 10 wt.% (b); 20 wt.% (c); 30 wt.% (d); 40 wt.% (e); 50 wt.% (f); 60 wt.% (g); 70 wt.% (h)

4. Conclusion

In this study, we have introduced the noble of the pure solid polymer electrolyte at room temperature used as an electrolyte as well as a separator from the piece of PVA and H_3PO_4 such that, the PVA samples were kept constant while the phosphoric acid was varied at 0, 10, 20, 30, 40, 50, 60, and 70 wt. %. The PSPE results in higher conductivity of $2.56 \times 10^{-4} \text{ Scm}^{-1}$, at the compositions of 70 wt. %, in addition to that, we also observed that, the bulk modulus B_b decreases with the increase in concentration, recording $2.5 \text{ } \Omega$ at the highest composition of 70 wt. %. The XRD analysis reveals the semi-crystalline peak of the PVA at $\theta=20^\circ$ border humps of the left indicating the inclusion of the acid and the crystallinity decreases as the acid concentration increases. This result was confirmed by the DSC analysis.

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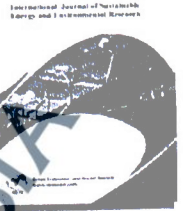
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SUPERCAPACITORS BASED ON ACTIVATED CARBON AND POLYMER ELECTROLYTE

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ABSTRACT

The supercapacitors are characterized by faster discharge rate and easy for maintenance. Their demand is predicted to be most extensive in frequency regulation applications. The other area for significant growth is in regenerative braking for grid-connected light rail systems. In this research we fabricated a Supercapacitor using a commercially prepared Activated carbon which was sized to an area of 1 cm² and combinations of two electrolytes solutions; polymer electrolyte polyvinyl alcohol (PVA) and Phosphoric acid (H₃PO₄) assembled in an innovative supercapacitor tester. The result indicates a relatively high efficiency of about 90 % and also exhibited long cyclability of life time under different voltage windows.

Key Words: Supercapacitor; activated carbon; charge-discharge; cycle-voltammetry.

INTRODUCTION

The current pursue for energy sustainability have made electrochemical supercapacitors or ultracapacitors (1-5) as devices of utmost importance owing to their superior characteristics unmatched by other charge storage devices. Such characteristics include; high power densities (6-15), at relatively high energy densities (less than that of lithium ion batteries (2)) and long cycle life (1, 3, 4, 6, 7) and also broader range of working temperature(11), high coulombic efficiency (high reversibility), environmental friendliness (no heavy metals used) (2, 3).

This paper is aimed at introducing yet another easy but effective method of fabricating an optimized supercapacitor which is being incorporated with activated carbon and solid polymer electrolyte (SPE).



MATERIAL AND METHODS

Commercial activated carbon (Carbon 50) of reasonable pore-size distribution was selected for this study. The electrodes were pressed from a combination of 70 wt% of activated carbon and 30 wt% of polyvinylidene fluoride (PVDF). A 20mL of acetone was added to the mixture in order for the solution to be easily blended in the laboratory blender. The resulting mixture of electrode was then poured in aluminium foil with a measured thickness of 2.5µm and then dried in an oven for 14 hours at 100 °C.

The polymer electrolyte was prepared from 2 gram of polyvinyl alcohol in a 50 mL of distilled water and then stirred at 70 °C for 8 hours. Phosphoric acid (H₃PO₄) was then added to the aforementioned solution at different percentage rate (10 %-50 %) in a multiple of 10 until a desired percentage is reached and achieved (i.e. 50 %), this was due to the optimal conductivity ascertained. The sample was then dried for 14 days at room temperature.

Two electrodes of 1cm² sizes were built in a newly modified Teflon Swagelok-like type system with steeled current collector. A 4 cm² of the already prepared polymer was used as the separator inside the Teflon Swagelok-like type system. The gravimetric capacitance C expressed in Farad (F) per gram of carbon material was estimated by a galvanostatic charge-discharge (C-D) at constant current of 1mA using Multichannel charge-discharge machine (MCCD)

THEORY AND CALCULATION

As a background, the capacitance is defined as the ratio of charge (positive) stored Q to the applied voltage V;

$$C = \frac{Q}{V} \tag{3.1}$$

For a conventional capacitor, C is directly proportional to the surface area A of each electrode and inversely proportional to the distance between the electrodes.

$$C = \epsilon_0 \epsilon_r \frac{A}{D} \tag{3.2}$$

Where $\epsilon_0 \epsilon_r$ are constant of proportionality, ϵ_r as dielectric constant or “permittivity” of free space and ϵ_0 as the dielectric constant of the insulating material between the electrodes. So, the discharge capacitance of the unit cell was calculated from the equation given below

$$C = \frac{2(I \times \Delta t)}{M \times \Delta V} \tag{3.3}$$



Where C is the specific capacitance, I is the discharge current, M is the weight of the electrode and ΔV and Δt are voltage variation in time (with exception of IR drop) and discharge time respectively.

RESULT AND DISCUSSION

Figure (1) shows both galvanostatic charge discharge and cyclic voltammetry curves of the supercapacitor with polymer electrolyte. Using Gamry instruments (Fig. d), in the cyclic voltammetry (Fig a-c), the scan rates were set to be the same (10m V/s) but different voltage window and cycles. In Fig (a) it can be shown that the cyclability of the supercapacitor is very perfect even though the maximum current was set to only 0.5 mA and 1 V voltage window, but still the perfection of the curve was satisfactorily good when the current was increase to 1 mA (as in Fig b). The electrochemical properties of the cell can therefore be considered as good looking at the effectiveness in the cyclability such as that in Fig (c) with 10 cycles.

Multichannel charge-discharge (MCCD) machine (Fig.e) was used to analyze and calculate the capacitance of the 1 cm² supercapacitor. From the profile of the Figures (g and h), the inverse V-shape of the curve with less internal resistance and voltage increment with time indicate the efficiency of the supercapacitor. The charging and discharging capacity of the supercapacitor was calculated to be 34.7 F/g and 38.39 F/g respectively. While the efficiency of the charging and discharging capacity of the supercapacitor were 81 % and 97.9 % respectively. The value of the capacitor was calculated to be 0.152 F.



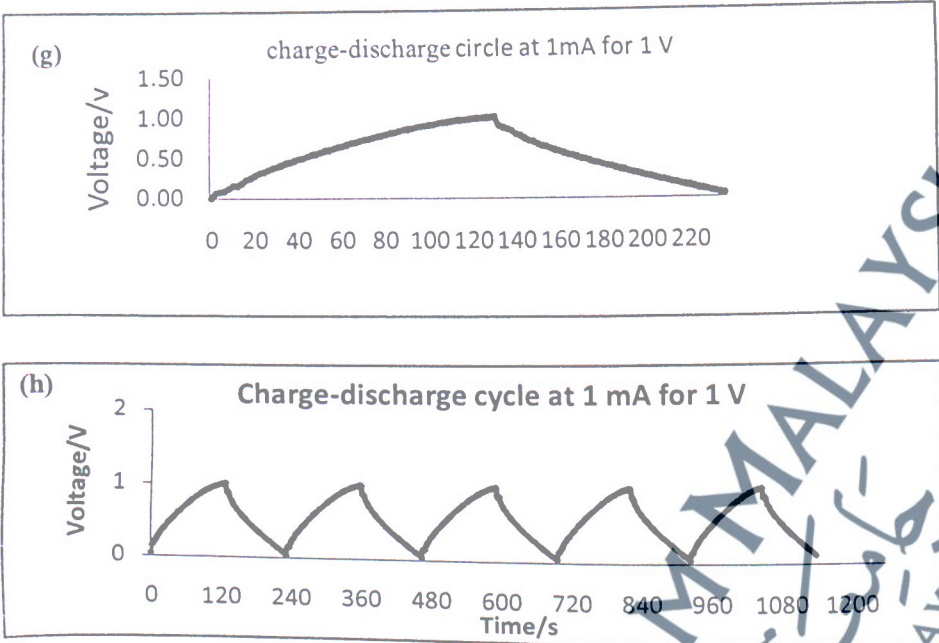


Fig.1. cyclic voltammetry using Gamry instrument software at (a) Maximum current of 0.5 mA and scan rate of 10 mV/s, 1 cycle and voltage window of 1V (b) 1 mA, 1cycle and 1V(c) 0.5 mA, 1 V and 10 cycles (d) Gamry instrument (e) MCCD (f) 1 cm² electrode (g & h) C-D at voltage window of 1 V for 2 minutes at different cycles.

CONCLUSION

Supercapacitor has been fabricated from a commercial activated carbon (carbon 50) and polymer electrolyte from polyvinylidene fluoride (PVDF and Phosphoric acid (H_3PO_4)) into a newly designed Teflon Swagelok-like type system used for testing the capacitance of the supercapacitor. From the aforementioned discussions, it can be seen that the fabricated supercapacitor was able to achieve an average efficiency of 89.6 % for both charging and discharging. Though the capacity value was low, this can be achieved by enhancing the quality of the polymer electrolyte and reducing the thickness of the electrode.

ACKNOWLEDGEMENTS

The corresponding author wish to acknowledge the assistance and contributions of management of Faculty of Science and Technology USIM under which ERGS grant (USIM/ERGS-FST-52-50111) has been provided for the purpose of this research.



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Appendix B

Seminar and Conferences





ULTRA-CAPACITOR

A BATTERY-ALTERNATIVE



SIC2012
STUDENT INNOVATION COMPETITION

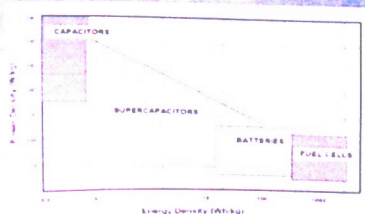
This innovation focuses on two issues; firstly we try to show the major distinctions between Ultra-capacitor (supercapacitor) and a Battery in terms of energy delivering and power density using two softwares; Multi Channel Charge-discharge (MCCD) and Gamry Instruments secondly we fabricated a Supercapacitor using commercially prepared Activated carbon and polymer electrolyte. The result indicated a relatively high surface area supercapacitor and also exhibited long cyclability of life time more than that of Battery of the same proportion

ABSTRACT

Ultracapacitors also known as supercapacitor or even electrochemical double layer (EDLC) is an electrochemical capacitor with relatively high energy density. Their energy density is typically hundreds of times greater than conventional electrolytic capacitors, they also have much high power density compared to Batteries or fuel cells. The supercapacitors are characterized by fast discharge rate and easy for maintenance. Their demand is predicted to be most extensive in frequency regulation applications. The other area for significant growth is in regenerative braking for grid-connected light rail systems [1]

BACKGROUND

THE DIFFERENCES!

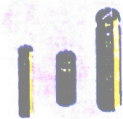


Ragone plot of energy storage devices, adapted from [2]

THE TAXONOMY OF ULTRACAPACITORS



BETWEEN ULTRACAPACITORS AND BATTERIES



- High power density
- Shorter charging times
- Longer cycle life and broader range of working temperature
- Environmental friendliness (no heavy metals used)[1][3]



- Low power density though its energy density is relatively high
- Longer charging times
- Shorter life cycle
- Not environmental friendly because of ions inside such as Lithium ion

HOW IT IS BUILD..



Source: Prof. Kazuhiko Naoi, Institute of Synthetic Science and Technology, Tokyo University of Agriculture and Technology, Advances in Capacitors and Hybrid Power Sources in Japan, presented in DOE Basic Energy Science Workshop, 3-4 March 2007

APPLICATIONS



OUR INNOVATION..



SUMMARY

- PROCESS 1
sample preparation
- PROCESS 2
Sample Characterization and EDLC Fabrication
- PROCESS 3
EDLC Characterization and Capacitance Enhancement
- PROCESS 4
Writing the result

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STUDENT INNOVATION COMPETITION (SIC 2012) ©
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SUPERCAPACITOR

A FUTURE BATTERY ALTERNATIVE



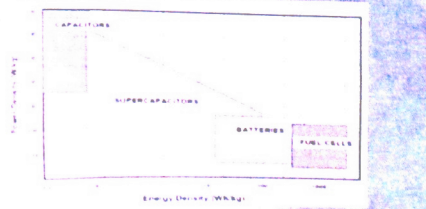
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BACKGROUND

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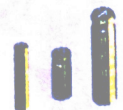


Ragone plot of energy storage devices, adapted from [2]

THE TAXONOMY OF ULTRACAPACITORS



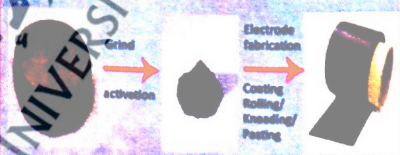
BETWEEN ULTRACAPACITORS AND BATTERIES



- High power density
- Shorter charging times
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HOW IT IS BUILD..



Source: Prof. Katsuhiko Mori, Institute of Symbolic Science and Technology, Tokyo University of Agriculture and Technology. Recent Advances in Capacitors and Hybrid Power Sources in Japan presented to DOE Basic Energy Research Workshop, 3-4 March 2002

APPLICATIONS



OUR INNOVATION...



SUMMARY

- PROCESS 1 sample preparation
- PROCESS 2 Samples Characterization and EDLC Fabrication
- PROCESS 3 EDLC Characterization and Capacitance Enhancement
- PROCESS 4 Writing the result

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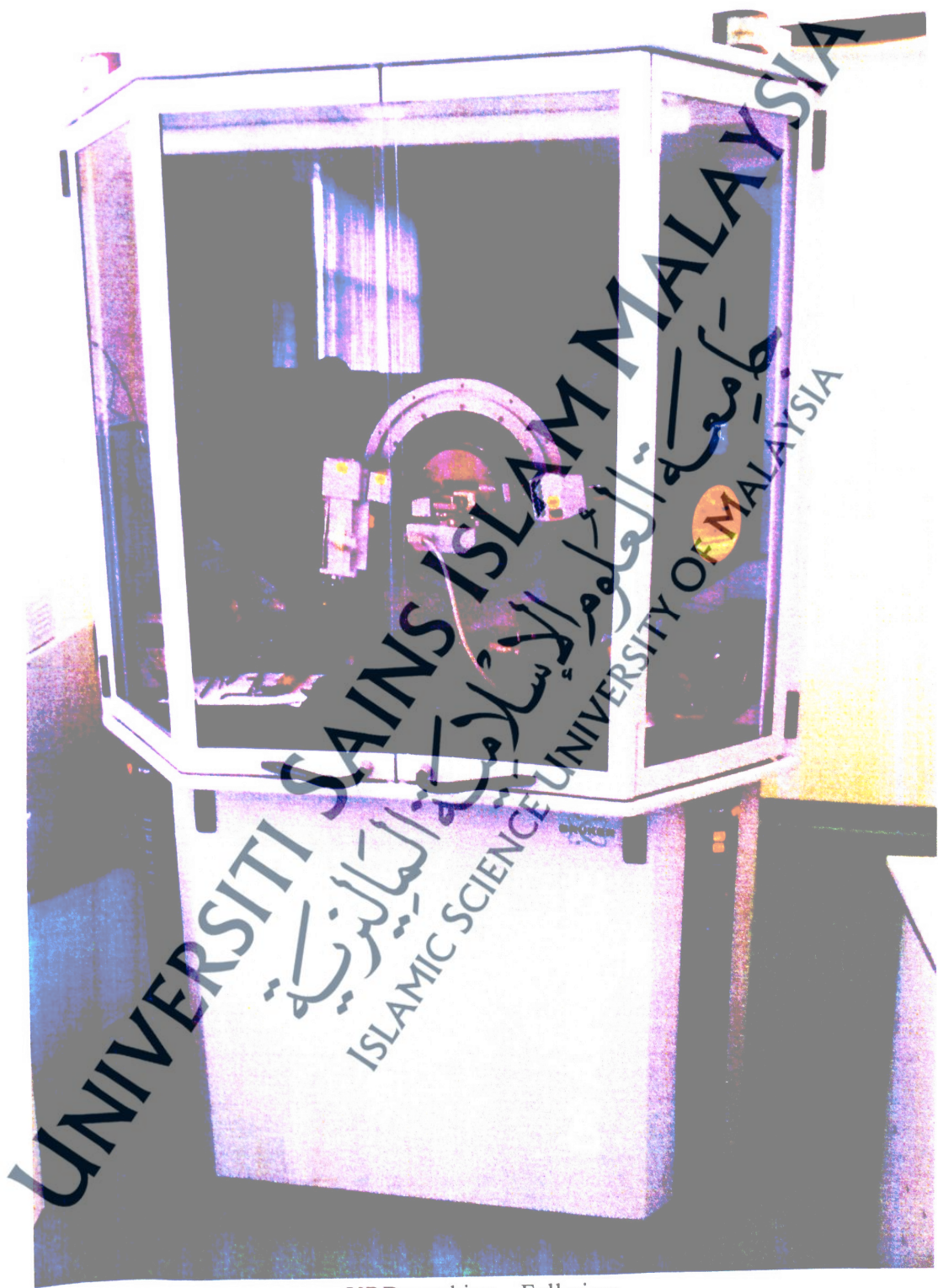
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Appendix C
EIS Device



EIS Device - (a) the Hioki tester and (b) the probe used for EIS measurements.

Appendix D
XRD Machine



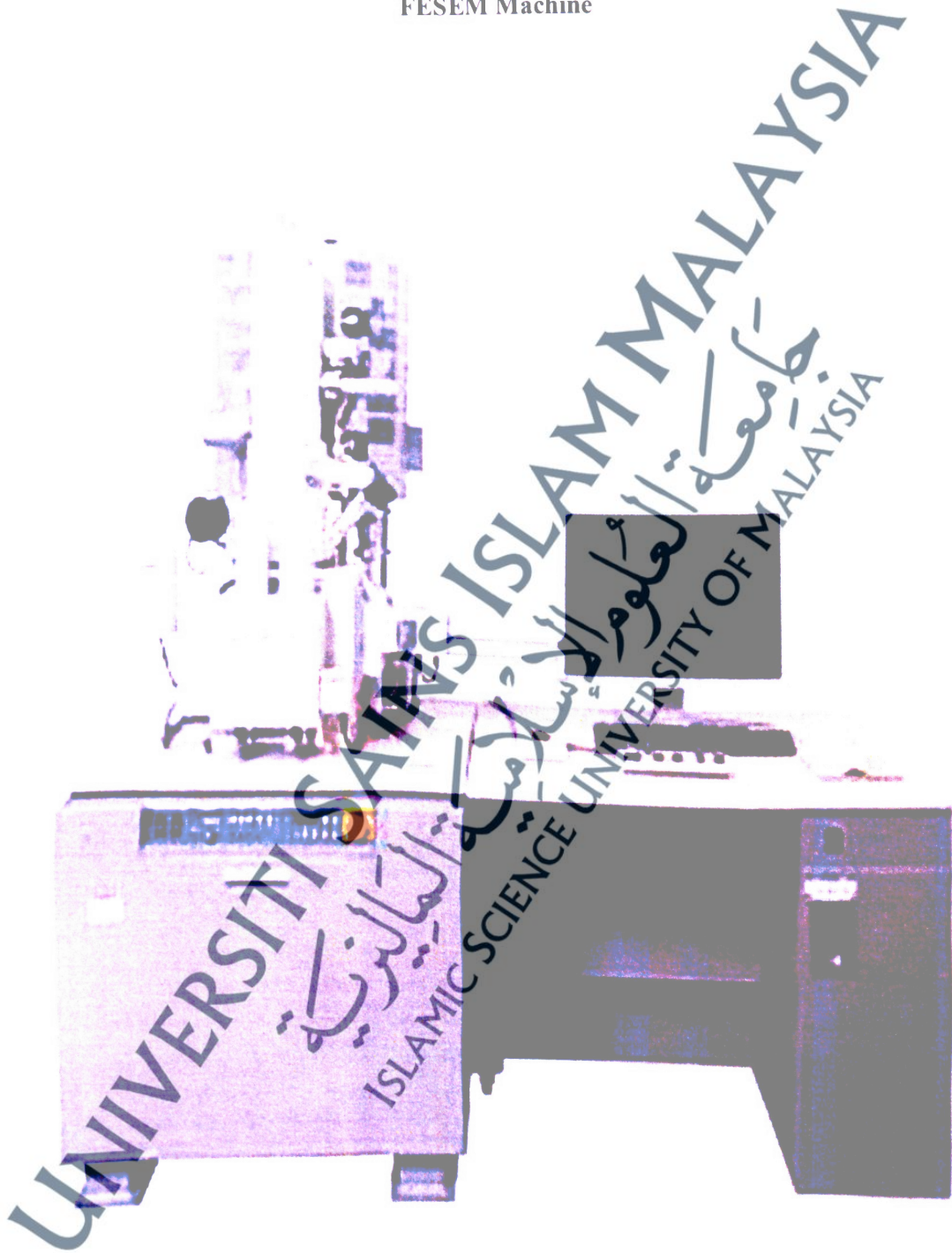
XRD machine – Full view.

XRD Machine



XRD machine – The interior view containing the sample under analysis.

Appendix E
FESEM Machine



FESEM Machine – A complete setting of the FESEM system.