

**OPTIMIZATION OF POLYVINYLPIRROLIDONE (PVP) AS A POTENTIAL AND
SUITABLE BINDER FOR ELECTROCHEMICAL SUPERCAPACITOR**

A thesis submitted to the Department of Materials Science and Engineering
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In partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE

By

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CERTIFICATION

This is to certify that the thesis titled “**OPTIMIZATION OF POLYVINYLPIRROLIDONE (PVP) AS A POTENTIAL AND SUITABLE BINDER FOR ELECTROCHEMICAL SUPERCAPACITOR**” submitted to the Department of Materials Science and Engineering in the African University of Science and Technology (AUST), Abuja, Nigeria for the award of the Master's degree is a record of original research carried out by **GONO, SYLVESTER Z.**

ABSTRACT

Polyvinylpyrrolidone (PVP) is suitable alternative to the polyvinylidene fluoride (PVDF) often used binder in electrode of supercapacitor. The major problem of the PVP is the part it plays in the conductivity of ions in the electrode. As the amount of PVP in the electrode increase above certain critical point the conductivity decrease. In this project, various weight percent of Polyvinylpyrrolidone (PVP) is dissolved different volume of ethanol and mixed with activated carbon to produce the electrode for electrochemical capacitors which shows a maximum specific capacitance of 94.49, 72.30 and 69.37 fg^{-1} respectively. The optimised mass of 0.2 g PVP exhibited good electrochemical performance. With the amount of ethanol and activated carbon constant, increasing the amount of PVP decrease the specific capacitance of the device made of the electrode and 6 M KOH electrolyte.

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DEDICATION

I dedicate this work to the thesis to God, who endowed me with the grace and strength to accomplish this task and Daddy Lauren Nyah McCoy who reawakened my spirit for higher education.

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CHAPTER ONE

INTRODUCTION

1.1 Background to the study

Supercapacitors are energy storage devices with very high capacity and a low internal resistance, that are able to store and deliver energy at relatively higher rates as compared to batteries due to the mechanism of energy storage which involves a simple charge separation at the interface between the electrode and the electrolyte [1, 2]. A supercapacitor comprises of two electrodes, an electrolyte, and a separator which separates the two electrodes electrically. Electrode material is the most important component of a supercapacitor [3, 4]. Some of the benefits of supercapacitors when compared with other energy storage devices are long life, high power, flexible packaging, wide thermal range (-40 to 70 °C), low maintenance and low weight [5]. Supercapacitors can best be used in areas that require applications with short load cycle and high reliability, for example energy recapture sources such as forklifts, load cranes and electric vehicles, power quality improvement [6]. Among the promising applications of supercapacitors is in fuel cell vehicles and low emission hybrid vehicles [7, 8]. Supercapacitors with its unique qualities when used with batteries or fuel cells they can serve as temporary energy storage devices providing high power capability to store energy from braking [9, 10].

Due to its high-power capability a bank of supercapacitors, can bridge the short time duration between a power failure and the start-up of backup power generators. Even though energy density of supercapacitor is greater than that of conventional capacitors; it is considerably lower than batteries or fuel cells. Electrochemical performances of an electrode material strongly rely on factors like surface area, electrical conductivity, wetting of electrode and permeability of electrolyte solutions [11]. Passive components are required in all electronic applications to store electrical energy in volume and weigh as small as possible. The power needed by an application as well as the speed of storage process determines the type of energy storage device to be used. Essentially, when it comes to applications the ones that need faster discharge rate go for capacitor while the slower ones go for batteries. Battery can attain up to 150 Wh/kg of energy density, around 10 times what an electrochemical capacitor is capable of. In terms of power density batteries don't have the capability of reaching the values of electrochemical capacitors.

Batteries hardly reach 200 W/kg which is about 20 times less than the expected electrochemical capacitor performance. Batteries experience weaknesses like rapid decrease in performances due to fast charge discharge cycles or cold environmental temperature, they are expensive to maintain and have a limited lifetime [12].

In general, considering energy storage mechanism, supercapacitors are grouped into three (3) different categories. The first being electrical double layer capacitor (EDLC), in this group capacitance is achieved due to pure electrostatic charge accumulated on the electrode electrolyte interface, this group strongly relies on electrode surface area that is available to electrolyte ions. Second is the pseudocapacitor, in this case a fast and reversible faradic process take place due to electro active species [13, 14]. The third group is hybrid which combines the properties of both EDLC and Pseudocapacitors. Selection of electrode material is of paramount importance in supercapacitors as it determines the electrical properties [15]. Double layer charge storage is a surface process therefore surface property of electrode material greatly influences capacitance of the cell.

1.2 Statement of Problem

For the various electrochemical energy storage (EES) systems, the electrochemical Double later capacitors are considered as one of the promising energy storage devices because of its remarkable features of high energy density, power density, fast charging and discharging rate, long cycling stability and environmentally friendly. This indicates that there is the possibility for Electrochemical Double Layer capacitors to give good results in the next generation of energy storage system. In recent time, Supercapacitors have gained attention due to their vast applications. The limitation of supercapacitors is they have low energy density as compare to that of lithium battery for this reason their electrochemical performances are limited by their electrolytes, electrode materials and their interface interactions.

The selection of binder material must balance a couple of partially diametrical properties. It is especially important to lower the amount of added binder as they are commonly electrically insulating and do not contribute to the charge storage mechanism. In particular, the challenge is to combine chemical stability in the presence of the selected electrolyte, mechanical strength,

and film integrity with little or no detrimental impact on either particle porosity or electrical film conductivity.

1.3. Aim and Objectives of the study

The aim of this work is to probe the optimum amount of PVP that can be used as binder for electrode for electrical supercapacitor application through the following set of objectives:

Dissolving PVP in ethanol and mixing it with activated carbon into a paste.

Electrochemical characterization of the SC devices fabricated using KOH as electrolyte via electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV).

1.4. Scope of study

This work explores the possibility of an optimum amount of PVP that can be used as binder in the electrode of EDLC devices. The work targets the maximizing the conductivity of the ion in the electrodes through optimizing the PVP dissolves in fix amount of ethanol.

1.5. Organization

The five chapters in this project are in the following order.

Chapter one, the introduction.

Chapter two, the literature review

Chapter three, the materials, and methods.

Chapter four, the results, and discussion and

Chapter five consists of a conclusion and recommendation.

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CHAPTER TWO

LITERATURE REVIEW

2.1 WORLD ENERGY CRISIS

Energy has been recognised as an important resource for the satisfaction of human needs. It is the satisfaction of the daily human needs, which cannot be reached without energy that brings relief and accessibility to human life. This shows that every human activity involves one form of energy or the other to be fruitful and prosperous. By suggestion, over seven billion people in the world today need energy to satisfy their needs to survive and live easily. The problem here is that though various energy resources have been discovered, but some are renewable and some are non-renewable. Another misunderstanding associated with this problem is that technologies for the exploration, exploitation and transformation of energy resources in reasonable quantity are only available for non-renewable energy resources. For this reason, the energy developed from non-renewable energy is easily accessible. These non-renewable energy resources had been identified unclean because most of the disaster in the environment come across and suffered today has been ascribed to them due to their carbon content.

Another problem is a divide that exist between nations that own energy resources and those that do not have. The most disappointing part is that the nations that do not have energy resources own the technologies for the exploration, exploitation and transformation of energy resources while nations that have energy resources do not have the technologies for the exploration, exploitation and transformation of energy resources. Almost all the nations that own energy resources belong to the category of nations classified as developing nations while the owners of technologies belong to the category of nations classified as developed nations. While some nations are categorized as developed due to their level of industrialization; high, improved and stabilized economic growth; use of advanced technologies; improved living standard, adherence to human right provisions, other nations with poor living standard; poor and fluctuating economy; low level of industrialization, lack of and/or poor technology infrastructure and low adherence to human rights provisions are categorized as developing nations.

The preceding scenario indicates that developed nations have increased infrastructural facilities and home appliances that require large amount of energy to be powered and maintained

compared to those of developing nations. This deduction shows that demand for energy is higher in developed nations than in developing nations. Since the demand for the use of energy resources is high in the developed nations of the world and they are the owners of the technologies for the exploration, exploitation and transformation of energy resources, they therefore determine the prices they will buy energy resources. When they want the price of energy resource especially oil to be high, they will manipulate it to be high. When they want it to be low, they will manipulate it to fall, just as it is being experienced now in the world. It is this crisis associated with the mode of production, sales and use of energy resources that is referred to as energy crisis.

The struggle to maintain the constant supply of energy resources without falling short of their supply in process of exploring, exploiting and transforming, and utilizing them to achieve social and economic goals.

Energy crisis is therefore any great shortfall in the supply of energy [1]. Energy crisis is seen as “the problem of decreasing oil production and increasing oil prices” [2]. This definition only reflects how the developed nations, suffer economically due to scarcity of energy resources to power their economy. This is because they spend huge amount of money to buy little amount of energy resource from the producers who mainly are from the developing nations of the world. This situation favours the producers like Nigeria whose major source of revenue is oil. In this situation, the producers raise huge amount of money from a small volume of energy resource. They do not only raise huge amount of money to run their economy, but their environment is also almost kept intact because not so much pressure is mounted on it in a bid to produce more oil for the world market. These puzzles call for a balanced definition of energy crisis that takes care of situations in both developed and developing nations of the world. It is in this regard that energy crisis could be alteration of energy balance in the general circulatory system arising from decrease or increase in energy demand with attendant economic and environmental impact. This alteration could lead to either rise or fall in energy price. When a rise in energy price results, the developed nations suffer some form of setbacks in their economic development while developing nations especially the energy producers enjoy a boom in their economy. When a fall in energy price results, the developed nations enjoy a boom in their economy because they have access to

a large amount of energy resource required to power their economy while the producers suffer economic setbacks and environmental degradation because they would produce more energy resource which would only earn them a little amount of money that may not be enough to run their economy. This also mounts pressure on the environment because they would want to produce more energy resources and thus degrading the environment. This situation can summarily see energy crisis as a crisis of interest between the owners of energy resources and owners of technologies used for the exploration, exploitation, and transformation of energy resources. There is also a dimension of fear of exhaustion of conventional energy resources due to their non-renewable nature to energy crisis. This fear was explicitly expressed when it was noted that: Since the energy crisis of the 1970s, we have witnessed the US demand for oil increasing at an alarming rate, the price of oil steadily escalating and an increasingly unstable world's economy, prompted to some degrees by the world's demand for oil, a product which will, at some point in time, cease to be available at any price [2]. From this perspective, energy crisis could be a fear expressed in connection with the dwindling or liquidation rate of world's conventional energy resources arising from their level of demand and usage. This fear has resulted into increased clamour for the development of technologies for harnessing clean, environmentally friendly renewable energy resources, because if oil finishes and there is no other source of energy resource for sustainable living, there will be crisis in human race which will result in loss of lives. Many developed nations have made advanced efforts in this regard. A point worth noting is that energy crisis is not synonymous to poor electric power generation as scholars and commentators/analysts posit, but energy crisis can result into poor electric power generation. In other words, shortage, or lack of access to electricity supply characterises energy crisis. This affects every gamut of national development.

2.2 Electrochemical capacitor: Theory and operation

Capacitors are essential electrical circuit elements that store electrical energy in the order of microfarads and help in filtering. Capacitors have two main applications; one of which is a function to charge or discharge electricity. This function is applied to smoothing circuits of power supplies, backup circuits of microcomputers, and timer circuits that make use of the periods to

charge or discharge electricity. Blocking the flow of direct current is also another function of capacitor. This help filter that extract frequency. This is vital to circuits where excellent frequency characteristics are required. Electrolytic capacitors are next generation capacitors which are commercialized in full scale. They are like batteries in cell construction, but the anode and cathode materials remain the same. They are aluminium, tantalum, and ceramic capacitors where they use solid/liquid electrolytes with a separator between two symmetrical electrodes.

2.2.1 Electrochemical Double Layer Capacitor (EDLCs)

Electrochemical double-layer capacitors (EDLCs) are constructed from two Carbon-based electrodes, an electrolyte, and a separator. Figure 2.1 provides a schematic of a typical EDLC. Like ordinary capacitors, EDLCs store charge electrostatically and there is no transfer of charge between electrode and electrolyte. EDLCs use an electrochemical double-layer of charge to store energy. As voltage is applied, charge accumulates on the electrode surfaces. Following the natural attraction of unlike charges, ions in the electrolyte solution diffuse across the separator into the pores of the electrode of opposite charge. However, the electrodes are engineered to prevent the recombination of the ions. Thus, a double-layer of charge is produced at each electrode. These double-layers, coupled with an increase in surface area and a decrease in the distance between electrodes, allow EDLCs to achieve higher energy densities than ordinary capacitors [3-5]. Because there is no transfer of charge between electrolyte and electrode, there are no chemical changes associated with non-Faradaic processes. For this reason, charge storage in EDLCs is highly reversible, which allows them to achieve very high cycling stabilities. EDLCs generally operate with stable performance characteristics for a great many charge-discharge cycles, sometimes as many as 10^6 cycles. On the other hand, electrochemical batteries are generally limited to only about 10^3 cycles. Because of their cycling stability, EDLCs are well suited for applications that involve non-user serviceable locations, such as deep sea or mountain environments [3-5, 6]. The performance characteristics of an EDLC can be adjusted by changing the nature of its electrolyte. An EDLC can utilize either an aqueous or organic electrolyte. Aqueous electrolytes, such as H_2SO_4 and KOH, generally have lower ESR and lower minimum pore size requirements compared to organic electrolytes, such as acetonitrile. However, aqueous electrolytes also have lower breakdown voltages. Therefore, in choosing between an aqueous or

organic electrolyte, one must consider the trade-offs between capacitance, ESR, and voltage [3-5, 7]. Because of these tradeoffs, the choice of electrolyte often depends on the intended application of the supercapacitor. The subclasses of EDLCs are distinguished primarily by the form of carbon they use as an electrode material. Carbon electrode materials generally have higher surface area, lower cost, and more established fabrication techniques than other materials, such as conducting polymers and metal oxides [3-5, 7]. Different forms of carbon materials that can be used to store charge in EDLC electrodes are activated carbons, carbon aerogels, and carbon nanotubes.

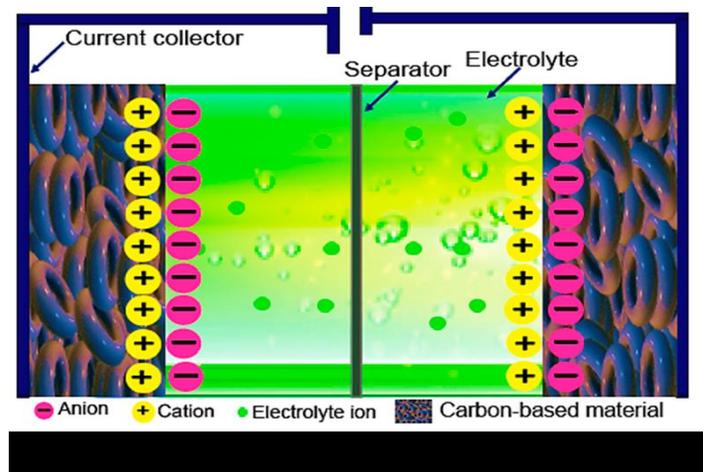


Figure 2.1: Schematic diagram of electrochemical double layer capacitor

2.2.2 Pseudocapacitor

In contrast to EDLCs, which store charge electrostatically, pseudocapacitors store charge faradaically through the transfer of charge between electrode and electrolyte. This is accomplished through electrosorption, reduction-oxidation reactions, and intercalation processes [3, 8-9]. These Faradaic processes may allow pseudocapacitors to achieve greater capacitances and energy densities than EDLCs [10-11]. There are two electrode materials that are used to store charge in pseudocapacitors, conducting polymers and metal oxides. Figure 2.2 provides schematic diagram of pseudocapacitor.

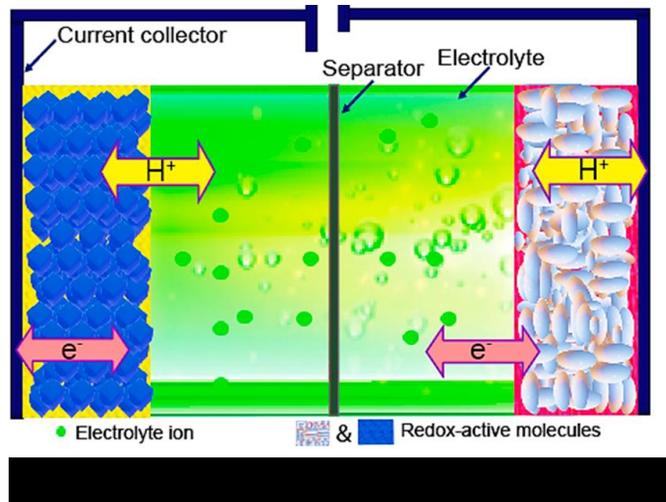


Figure 2.2: Schematic diagram of pseudocapacitor

2.2.3 Hybrid capacitors

Hybrid capacitors have been demonstrated to exhibit a combination of Performance characteristics that formerly was unattainable. They combine the best features of EDLCs and pseudocapacitors together into a unified supercapacitor. Although hybrid capacitors have been explored less than EDLCs or pseudocapacitors, the research that is available suggests that they may be able to outperform comparable EDLCs and pseudocapacitors [12, 13, 14]. As a result, R&D efforts concerning the fabrication of improved hybrid capacitors and the development of more accurate quantitative models of hybrid capacitors have continued to expand [15-22, 23, 24]. Along with the increasing interest in developing high cycle life, high-energy supercapacitors, the tremendous flexibility in tuning the design and performance of hybrid capacitors is leading them to surpass EDLCs as the most promising class of supercapacitors.

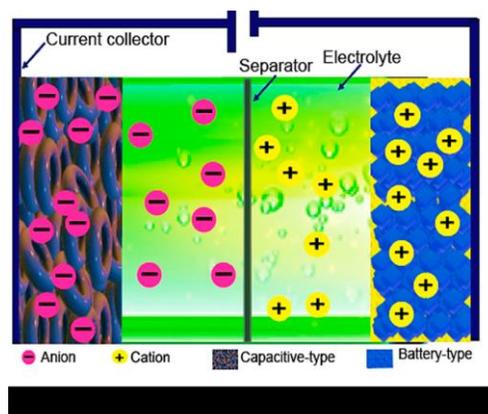


Figure 2.3: Schematic diagram of Hybrid supercapacitors

2.3 Electrochemical testing of cells

Supercapacitors are rapidly being adopted for a wide range of electrical energy storage applications. While supercapacitors can deliver high rates of charge and discharge, they are limited in the amount of energy stored. The capacity of supercapacitors is largely determined by the electrode material and as a result research to improve the performance of electrode materials has dramatically increased. While test methods for packaged supercapacitors are well developed, it is often impractical for the materials scientist to assemble full sized, packaged cells to test electrode materials.

2.3.1 Electrochemical testing of electrode materials in a three (3) and two (2) electrode configurations

A typical supercapacitor unit cell is comprised of two electrodes that are isolated from electrical contact by a porous separator [25]. Electrodes often contain conductive but low surface area additives such as carbon black to improve electrical conductivity. Current collectors of metal foil or carbon filled polymers are used to conduct electrical current from each electrode. The separator and the electrodes are impregnated with an electrolyte, which allows ionic current to flow between the electrodes while preventing electronic current from discharging the cell. A packaged supercapacitor module, depending upon the desired size and voltage, is constructed of multiple repeating unit cells. A test fixture configuration that closely copies the unit cell configuration will more closely match the performance of a packaged cell. Two-electrode test fixtures are either available commercially or can be easily fabricated from two stainless steel plates as shown in Figure 2.4 [28]. Three-electrode electrochemical cells are commonly used in electrochemical research and consist of a working electrode, a reference electrode, and a counter electrode. Three-electrode cells differ from two-electrode test and packaged cells in several important aspects. With the three-electrode configuration, only one electrode, called the working electrode, contains the material being analysed and the applied voltage and charge

transfer across the single electrode is markedly different than with a two-electrode cell configuration. The potential drop across the single electrode/electrolyte interface is controlled with respect to a reference electrode. However the current flow is from the working electrode to the counter electrode. [27].

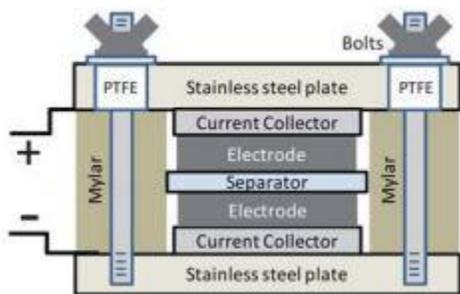


Figure 2.4: Two-electrode test cell configuration [28]

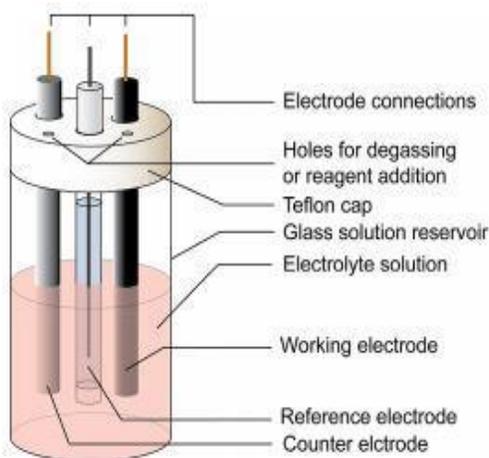


Figure 2.5: Two-electrode test cell configuration [29]

2.3.2 Fabricating of electrode for testing

Methodology for electrode material testing can be grouped into test fixture configuration and measurement procedures. Test fixture configuration includes the test fixture type along with guidelines for electrode mass and thickness, and other cell components including the electrolyte, separator, current collectors, and binder. Measurement procedures include electrochemical measurements and parameters along with the computations to reduce the data to the desired.

2.4 Evaluation of electrode material

To evaluate supercapacitors performance, three essential parameters, cell capacitance C_T , operating voltage V_o , and equivalent series resistance R_{ES} , are often used to assess their energy and power performance, and usually are sufficient for commercial products where the materials, fabrication, and cell design are all fixed. However, the constant probing for novel materials, more advanced manufacturing processes, and new cell designs, additional factors become essential. In fact, there is a rather large group of important factors necessary to paint the whole picture for supercapacitors and an overview of the complex inter-relationship between the different performance metrics, the major affecting factors, and the corresponding test methods is presented in figure 2.6. Several colour schemes are employed in the figure: the three core parameters are highlighted in yellow; the power and energy densities in dark blue; time constant and cycling stability in light orange; all the important affecting factors in light purple; and the corresponding test methods in white. The figure is for illustration purpose and is by no means exclusive in presenting all the factors or detailing the complex multifaceted connections between them. For example, the evaluation method for V_o and the influence of electrolyte materials on specific capacitance are not explicitly presented.

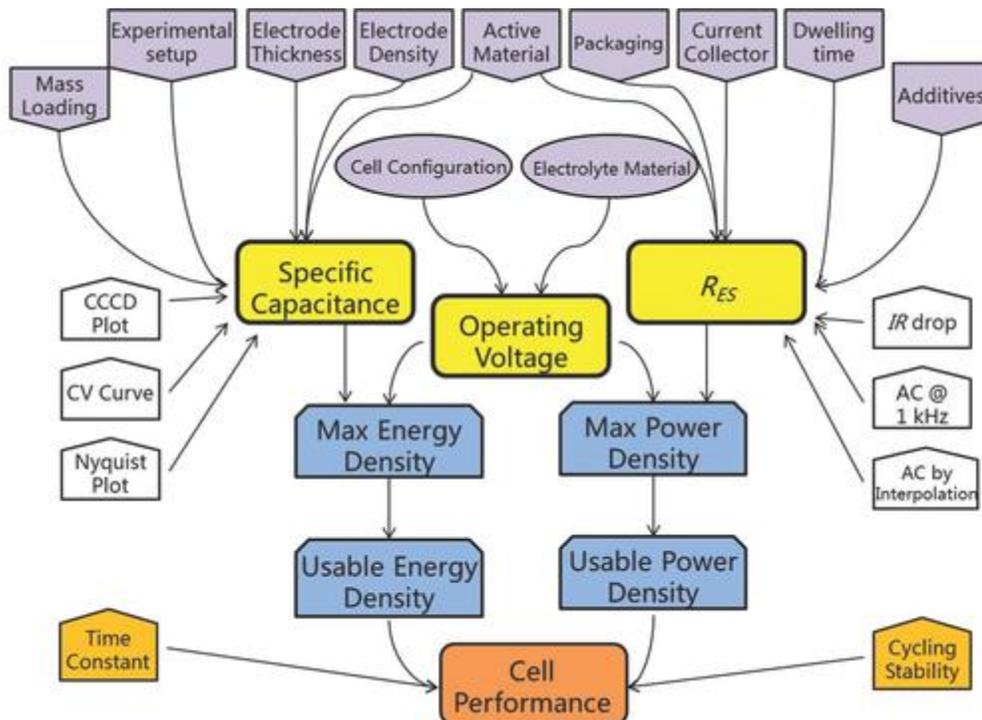


Figure 2.6: An illustration of key performance metrics, test methods, major affecting factors for the evaluation of Supercapacitors [30].

Giving the multiple performance metrics, test methods, and affecting factors shown in Figure 2.6, and the multidimensional relationships among them, contradictions become inevitable in the test results for the same cell measured in different labs, using different methods, and between academia and industry. To understand the causes for such contradictions, some important issues must be addressed.

2.4.1 Cyclic voltammetry (CV) and galvanostatic charge discharge (GCD)

CV testing applies a linearly changed electric potential between positive and negative electrodes for two-electrode systems, or between reference and working electrodes for three-electrode configurations. The speed of the potential change in mV s^{-1} is designated as the sweep rate or scan rate, v , and the range of potential change is called the potential window or operating potential. The instantaneous current during the cathodic and anodic sweeps is recorded to characterize the electrochemical reactions involved. The data are plotted as current (A) vs. potential (V) or sometimes as current (A) or potential (V) vs. time (s). [31]

To examine the charge storage mechanisms of SC materials where EDLC and PC types are separate, CV testing with the three-electrode setup is regarded as the most suitable approach [32,33]. The test results can first be analysed by examining the shape of the CV curves, as for EDLC and most PC materials, the shape of the resulting CV curves is rather rectangular, whereas for some PC materials, pronounced redox peaks may occur in a highly reversible manner [34]. Therefore, it is not sufficient to differentiate EDLC and PC materials by solely observing the shape of CV curves.

A more quantitative and reliable method for interpreting the data from a CV test to extract the contributions from EDL and PC mechanisms separately is by utilizing the knowledge that the instantaneous current induced by the EDL mechanism is proportional to the scan rate, while the semi-infinite diffusion limited cation adsorption at the electrode surface from PC mechanism is proportional to the square root of the scan rate [35,36-42]. However, this approach is limited in its ability to separate the contribution of surface-redox reactions from EDL mechanisms since

they happen roughly on the same time scale [31]. Therefore, more experimental, and theoretical studies are required to address this issue.

CV testing is also suitable in practice to determining the operating voltage or potential window for SC materials by successive adjustment of the reversal potential in a three-electrode system, and the reversibility of the charge and discharge processes can also be studied simultaneously(43,35). In addition, the specific capacitance and energy performance of the SC materials can be obtained via integration of the CV curves. Similar process can also be conducted for SC devices to obtain their total cell capacitance and hence the amount of electricity stored. GCD testing is the most widely used method for the characterization of supercapacitors under direct current (44, 45). It is conducted by repetitive charging and discharging of the SC device or the working electrode at a constant current level with or without a dwelling period (a time period between charging and discharging while the peak voltage V_o remains constant), and normally a plot of the potential (E) vs. time (s) is the output. Choosing a proper level of the constant current is critical to produce reliable and comparable data from a GCD test.

GCD test is regarded as the most useful and precise approach in characterizing supercapacitors devices. All three core parameters of SC devices, C_T , R_{ES} , and V_o , can be tested from it and later used to derive most of the other properties, such as the time constant, power and energy densities, and leakage and peak current. It can also be conveniently used to study the cycling stability of SC devices. Moreover, by using a three-electrode setup, the specific capacitance, reversibility, and potential window for SC materials can also be obtained via GCD test.

2.4.2 Electrochemical impedance spectroscopy (EIS)

EIS testing, also known as the dielectric spectroscopic testing, measures the impedance of a power cell as a function of frequency by applying a low-amplitude alternative voltage (5 mV) superimposed on a steady-state potential. The resulting data are usually expressed graphically in a Bode plot to demonstrate the cell response between the phase angle and frequency, and in a Nyquist plot to show the imaginary and real parts of the cell impedances on a complex plane [46, 47]. In addition to the frequency response and impedance, EIS has also been used to characterize the charge transfer, mass transport, and charge storage mechanisms, as well as to estimate the

capacitance, energy, and power properties [48, 49], Different equivalent circuits and models have been developed to distinguish the contribution of individual structure component in a cell system to the total impedance [50, 51, 52]. When SC devices are tested, the real parts of the complex impedance at selected frequencies are used to represent R_{ES} . However, one needs to keep in mind that this R_{ES} from an EIS test is often much smaller than that derived from the GCD test [53] and is therefore limited in describing the power performance of SC devices.

For SC materials, EIS testing can be used to study the impedance, specific capacitance, charge transfer, mass transport, and charge storage mechanisms involved by executing similar analysis in a three-electrode system.

2.5 Electrode materials

The selection of electrode materials and their fabrication play a crucial role in enhancing the capacitive performance of SCs [54]. Electrodes of SCs must provide thermal stability, high surface area, corrosion resistance, high electrical conductivity, appropriate chemical stability, and suitable surface wettability. They should also be low-cost and environmentally nonthreatening. Besides, their capability of transferring the faradic charge is important to enhance the capacitance performance [55, 56].

In fact, the specific capacitance factor is not only affected by surface area, but also there are other essential parameters including the simple morphology manipulation, including pore size distributions, as well as the pore shape, pore sizes, and their availability for the electrolyte [57,58,59]. Thus, two of the most important requirements for designing an SC device are (i) improving the electrochemically active sites by selecting the electrode materials with a high surface area, and (ii) tuning the pore size and pore shape in the case of graphene nanopore [60], and cylindrical, spherical, and slit in the case of the biomass-derived carbon [61]) of the electrode material to make them suitable candidates which ease the transportation of electrolyte ions [57, 62]. The electrode material having smaller pores over higher capacitance and, thus, higher energy density. However, the smaller the pore size leads to having a higher the equivalent series resistance (ESR), therefore, decreasing the power density. Based on this, the application of the electrode material directs the selection of the materials. For example, for the applications in

which having more peak currents is important, the electrode materials should satisfy the criteria of having greater pores, while for the applications that higher energy density is required, the electrode materials should have smaller pores [63,64]. Furthermore, the suitable size distribution can improve the retention capability, which is the indication of high power density in a supercapacitor device. The elective distribution of micro/mesopores of the electrode material can provide a fast mass and ion transport through a continuous pathway, thus enhance the accessibility of the electrolyte and make an appropriate choice for supercapacitor application [65]. The electrode materials are categorized based on three main classes, including carbonaceous materials, transition metal oxides, and conducting polymers [66].

2.5.1 Conducting polymers (CP)

Conducting polymers have a relatively high capacitance and conductivity, plus a relatively low ESR and cost compared to carbon-based electrode materials [67]. In particular, the n/p-type polymer configuration, with one negatively charge and one positively charged conducting polymer electrode, has the greatest potential energy and power densities; however, a lack of efficient, n-doped conducting polymer materials has prevented these pseudocapacitors from reaching their potential [68, 69]. Additionally, it is believed that the mechanical stress on conducting polymers during reduction-oxidation reactions limits the stability of these pseudocapacitors through many charge-discharge cycles [70, 67, and 71]. This reduced cycling stability has hindered the development of conducting polymer pseudocapacitors.

2.5.2 Transition metal double hydroxide (t-MOH)

Because of their high conductivity, metal oxides have also been explored as a possible electrode material for pseudocapacitors [72-73, 74, 75-76]. The majority of relevant research concerns ruthenium oxide. This is because other metal oxides have yet to obtain comparable capacitances. The capacitance of ruthenium oxide is achieved through the insertion and removal, or intercalation, of protons into its amorphous structure. In its hydrous form, the capacitance exceeds that of carbon-based and conducting polymer materials [75-76]. Furthermore, the ESR of hydrous ruthenium oxide is lower than that of other electrode materials. As a result, ruthenium

oxide pseudocapacitors may be able to achieve higher energy and power densities than similar EDLCs and conducting polymer pseudocapacitors. However, despite this potential, the success of ruthenium oxide has been limited by its prohibitive cost. Thus, a major area of research is the development of fabrication methods and composite materials to reduce the cost of ruthenium oxide, without reducing the performance [72-73, 74].

2.5.3 Carbon Material

Carbon materials in their various forms are the most used electrode materials in the fabrication of supercapacitors. Reasons are due to its (i) high surface area (ii) low cost (iii) availability (iv) established electrode production technologies. The storage mechanism used by carbon materials is electrochemical double layer formed at the interface between the electrode and electrolyte. Hence, the capacitance mainly relies on the surface area accessible to electrolyte ions. Important factors which influence electrochemical performance are specific surface area, pore shape and structure, pore size distribution, surface functionality and electrical conductivity [77-79]. Having a high specific surface area in the case of carbon materials, results in a high capability for charge accumulation at the interface of electrode and electrolyte. When improving specific capacitance for carbon materials, apart from pore size and high specific surface area, surface functionalization must be considered. Examples of carbon materials used as electrode materials are activated carbon, carbon aerogels, carbon nanotubes, graphene etc.

2.5.4 Composite

Composite electrodes integrate carbon-based materials with either conducting polymer or metal oxide materials and incorporate both physical and chemical charge storage mechanisms together in a single electrode. The carbon-based materials facilitate a capacitive double-layer of charge and provide a high-surface-area backbone that increases the contact between the deposited pseudocapacitive materials and electrolyte. The pseudocapacitive materials can further increase the capacitance of the composite electrode through Faradaic reactions [80, 81]. Composite electrodes constructed from carbon nanotubes and polypyrrole, a conducting polymer, have been particularly successful. Several experiments have demonstrated that this electrode is able to achieve higher capacitances than either a pure carbon nanotube or pure polypyrrole polymer-based electrode [82, 80, 81]. This is attributed to the accessibility of the entangled mat structure,

which allows a uniform coating of polypyrrole and a three-dimensional distribution of charge. Moreover, the structural integrity of the entangled mat has been shown to limit the mechanical stress caused by the insertion and removal of ions in the deposited polypyrrole. Therefore, unlike conducting polymers, these composites have been able to achieve a cycling stability comparable to that of EDLCs [80, 81]

2.6 Binders

Binders are a central component for supercapacitor electrode and paramount to a more sustainable and “green” processing of electrodes. The major function of binders is to act as an effective dispersion agent to connect the electrode species together and then steadily adhere them to the current collectors providing excellent contact for electron flow. Polyvinylidene fluoride (PVdF) is the most used binder for electrode materials in supercapacitor due to the excellent electrochemical and thermal stability and good adhesion between the current collectors and electrode films. [82-84]

2.6.1 Non aqueous binder

Non aqueous binders are binders dissolve in organic substance. Polyvinylidene fluoride (PVdF) is the most commonly used binder for electrode of a supercapacitor and lithium battery due to the excellent electrochemical and thermal stability and good adhesion between the current collectors and electrode films.[82-84] Noticeably, using PVdF binder requires the most common organic solvent of N-methyl-2-pyrrolidone (NMP) which is expensive, volatile, combustible, toxic, and has poor recyclability [85]

2.6.2 Water- base binder

Binders that are processed using water seem to perform significantly better than non aqueous binder [86]. However, aqueous characteristics are not the only attractive components to these binders; multifunctional binders, such as ammonium polyphosphate can also block diffusion of parasitic species and even act as a flame retardant in supercapacitor [87]. Other binders are also naturally produced, which add to their environmentally friendly and low cost value [88-90]. For example, sodium carboxymethyl cellulose (CMC), styrene butadiene, polyacrylic acid, polyvinyl

alcohol (PVA), polyethylene glycol (PEG), and polyamide imide can be potentially processed using water instead of the non aqueous binders, therefore, greatly reducing the cost of production.

2.7 Electrolyte

The electrolyte, meaning the electrolyte salt + solvent, is one of the key components of supercapacitor, providing ionic conductivity and thus facilitating charge compensation on each electrode in the cell. The electrolyte within an supercapacitor not only plays a fundamental role in the EDL formation and the reversible redox process for the charge storage but also determines the supercapacitor performance. Currently, the majority of commercial ESs use organic electrolytes with a cell voltage of 2.5–2.8 V²⁵. Most organic electrolyte-based ESs use the acetonitrile (ACN) solvent while others employ the propylene carbonate (PC) solvent. The electrolyte nature, including: (a) the ion type and size; (b) the ion concentration and solvent; (c) the interaction between the ion and the solvent; (d) the interaction between the electrolyte and the electrode materials; and (e) the potential window, all have an influence on the EDL capacitance and pseudocapacitance, the energy and power densities as well as the supercapacitor cycle-life. For example, the electrochemical stable potential window of the electrolyte directly determines the supercapacitor's operational cell voltage, through which both the energy and power densities are affected. The ESR of an supercapacitor is directly related to the electrolyte's ion conductivity and can have a strong effect on the power density. Furthermore, the interactions between the ion and the solvent and between the electrolyte and the electrode material can affect the lifetime and self-discharge of supercapacitors.

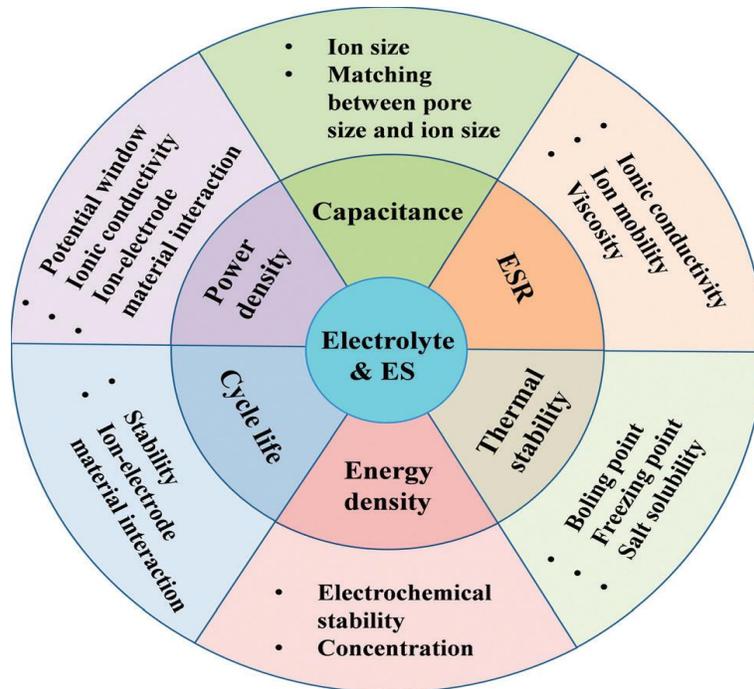


Figure 2.7: Effects of the electrolyte on the supercapacitor performance [91]

In general, various types of electrolytes have been developed and reported. As shown in Fig. 2.8, these electrolytes are mainly classified as liquid electrolytes and solid/ quasi-solid-state electrolytes.

In general, liquid electrolytes can be further grouped into aqueous electrolytes, organic electrolytes, and ionic liquids (ILs), while solid or quasi-solid-state electrolytes can be broadly divided into organic electrolytes and inorganic electrolytes. To date, there has been no perfect electrolyte developed, meeting all the requirements discussed previously. Each electrolyte has its own advantages and disadvantages. For example, supercapacitors using aqueous electrolytes possess both high conductivity and capacitance, but their working voltage is limited by the narrow decomposition voltage of aqueous electrolytes. Although organic electrolytes and ILs can operate at higher voltages, they normally suffer from much lower ionic conductivity. Solid-state electrolytes may avoid the potential leakage problem of the liquid electrolytes, but they also suffer from low conductivity. To overcome the drawbacks of targeted electrolytes, extensive efforts have been devoted to exploring new electrolyte materials to improve the overall supercapacitors performance. In this regard, several different approaches have been undertaken, including: (i) development of new and high-performing electrolytes to make a wider operating

potential window, higher ionic conductivity/viscosity, a wider working temperature range, and so on; (ii) exploration of the positive effects of given electrolytes on the supercapacitor properties such as capacitance, energy and power densities, thermal stability and the self-discharging process; and (iii) establishing a fundamental understanding of the effect of the electrolyte on the supercapacitor performance through advanced experimental, modelling and simulation methods [92].

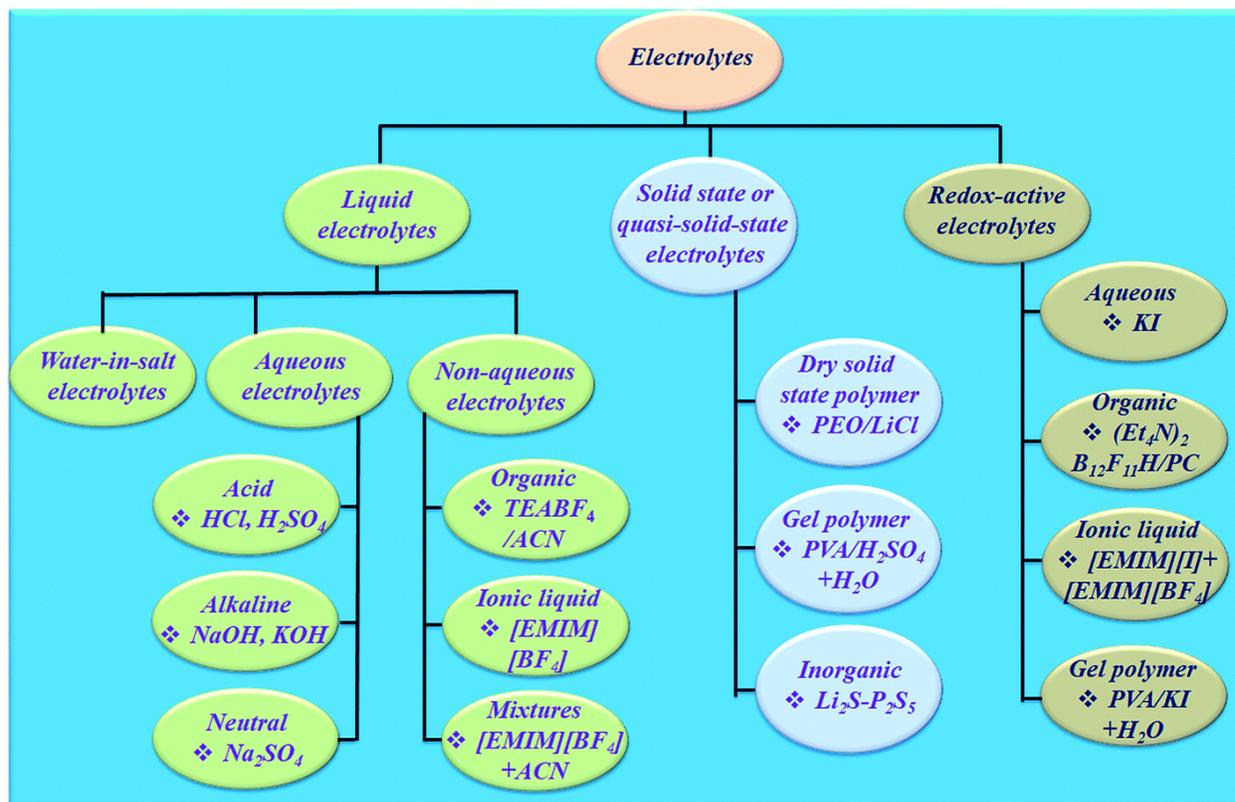


Figure 2.8: Classification of electrolytes for electrochemical supercapacitors

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CHAPTER THREE

EXPERIMENTAL PROCEDURE AND CHARACTERIZATION TECHNIQUES

3.1 Materials

Activated carbon (AC) powder (YP50-F, Kuraray Chemical) was used as the active material for the preparation of EDLC electrodes. Polyvinylpyrrolidone (PVP, Sigma Aldrich) of different molecular masses was used as dispersant/binder. The molecular mass of PVP was 89.000 g/mol as reported by the manufacturer.

3.2 Preparation of the electrode material

For the preparation of carbon slurry, initially, PVP was added to ethanol and kept on a stirrer for stirring for half an hour to make a homogeneous solution. After making the PVP solution, the carbon powder was mixed with the PVP solution and the slurry obtained is coated on an aluminium foil current collector with the thickness of 50-70 μm was obtained and placed in an oven at 80 degree Celsius for 30 minutes. The electrode was prepared by the following mixture, 0.2 g, 0.3 g and 0.4 g of PVP, each mixed with the constant mass of 0.1 g of activated carbon and 0.8 g of ethanol separately.

The electrode of 12mm diameter was punched out of prepared electrode sheets and use in symmetric two electrode cells using a paper separator 13mm diameter with the thickness of 260 μm . Table 3.1 shows the composition of each sample.

Table 3.1: The composition of sample

SAMPLE	MASS OF PVP(g)	MASS OF AC(g)	MASS OF ETHANOL(g)
1	0.2	0.1	0.8
2	0.3	0.1	0.8
4	0.4	0.1	0.8

3.3 Electrochemical Analysis

3.3.1 Cyclic Voltammetry (CV)

The CV measurement was carried out in a two-electrode configuration for each cell. The 2-electrode CV was conducted using the fabricated symmetrical devices, with a Gamry reference

600 workstation supplying the required potential. This test was carried out at scan rates of 5 mV s⁻¹ to 100 mV s⁻¹ at constant voltage of 1V; depending on the KOH electrolyte used to fabricate the device [1].

3.3.2 Galvanostatic Charge Discharge (GCD)

The galvanostatic charge/discharge was also carried out with same equipment for each of the samples with the current according to the mass of the samples.

The table 3.2 below shows the samples, masses, and current at which the GCD was carried out at 1.2V.

Table 3.2: The mass, the current at which galvanostatic charge discharge was carried out for various samples.

SAMPLES	WT. PVP	MASS (mg)	$i_1(mA)$	$i_2(mA)$	$i_3(mA)$	$i_4(mA)$	$i_5(mA)$	$i_6(mA)$
1	0.2g	10	2.5	5	10	15	20	30
2	0.3g	9.2	2.3	4.6	9.2	13.8	27.6	36.8
3	0.4g	10.6	2.65	5.3	10.6	21.2	26.5	30.85

The cyclic performance was evaluated for sample 1 at 15mA, for sample 2 at 27.6mA and sample 3 at 21.2mA all with 1.2 V potential difference [2, 3].

3.3.3 Electrochemical Impedance Spectroscopy (EIS)

The ion kinetics within the electrodes was probed using the electrochemical impedance spectroscopy (EIS) with amplitude of 10 mV at the frequency range of 10 MHz to 100 kHz [4]. A Bode plot which the relationship between the phase angle and the frequency was obtained alongside a Nyquist plot which showed the relationship between the imaginary and real part of the impedance of electrode material, equivalent series resistance of device and the charge transfer resistance [5]. The specific capacitance for the 2-electrode experiment was obtained by [3]:

$$C_{sp} = \frac{4I\Delta t}{mv} \dots\dots\dots 3.1$$

Where, C_{sp} is the Specific Capacitance (fg^{-1}), I represents current (mA), Δt represents the change in time (s), m is the Active Mass (g), and V represents the potential window (V). Also, the energy – density was obtained by [4]:

$$E_D = \frac{C_{sp}v^2}{28.8} \dots\dots\dots 3.2$$

Where; E_D is the Energy Density ($W\ hkg^{-1}$), C_{sp} represents the Specific Capacitance (fg^{-1}), and V represents the potential window (V). While power – density was obtained by [4]:

$$P_D = \frac{3.6E_{max}}{\Delta t} \dots\dots\dots 3.3$$

Where; P_D is the power density (Wkg^{-1}), E_{max} is the maximum energy density ($W\ hkg^{-1}$), and Δt is change in time (s).

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CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Electrochemical Analysis

4.1.1 Cyclic Voltammetry, Electrochemical Impedance Spectroscopy and Galvanostatic Charge Discharge

To understand the optimization of PVP as the potential and suitable binder for electrode materials of supercapacitor, we have separator with 6 M KOH as electrolyte between two symmetrical electrodes. The electrochemical performances of the fabricated device were tested by measuring cyclic voltammetry curves, electrochemical impedance spectroscopic and galvanostatic charge-discharge curves under various conditions. The CV curves of the device measured at various scan rates are shown in Fig. 4.1 (A), 4.3 (A) and 4.5 (A). The rectangular shape and symmetry of the CV curves indicate near ideal capacitive nature of the fabricated devices. As seen in the Fig. 4.1 (A), 4.3 (A) and 4.5 (A), the CV curves of devices are rectangular in shape without any significant redox waves, as the devices were constructed using two symmetrical electrode systems. The shape and symmetry of CV curves from the device is retained even at the high scan rates indicating high charge transfer stability of the device. It was also observed that the specific capacitance of the device decreases with increasing scan rate which could be due to insufficient time for electrochemical reactions at the electrode [1]. The charge storage capacity of the device was measured at different applied currents which are shown in Fig. 4.1 (B), 4.3 (B) and 4.5 (B) and Figure 4.1 (C), 4.3 (C) and 4.5 (C) shows the variation of specific capacitance with applied specific current. The decrease in the specific capacitance with increasing specific current could be due to increase of potential drop and insufficient faradic redox reaction at higher discharge.

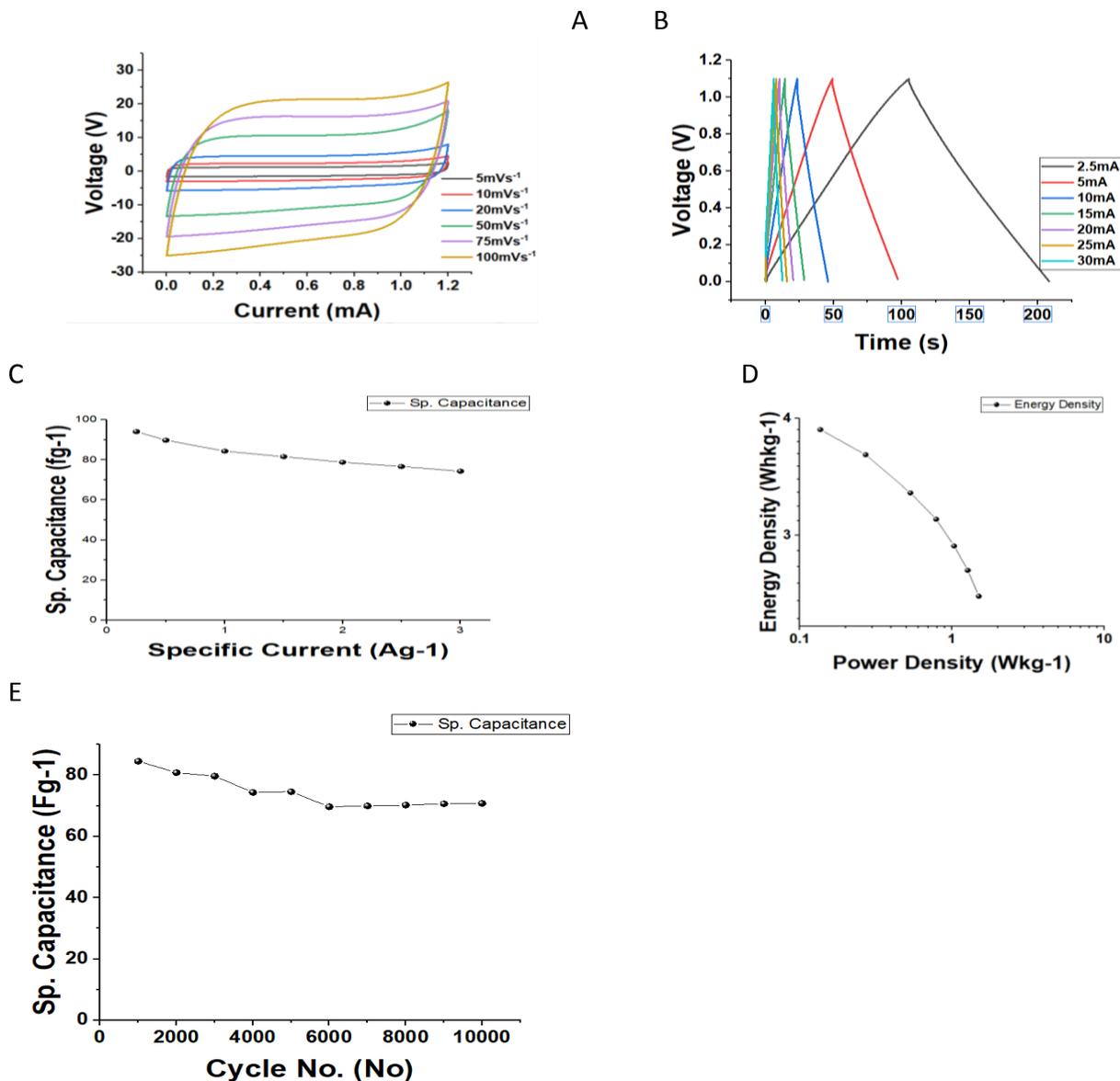
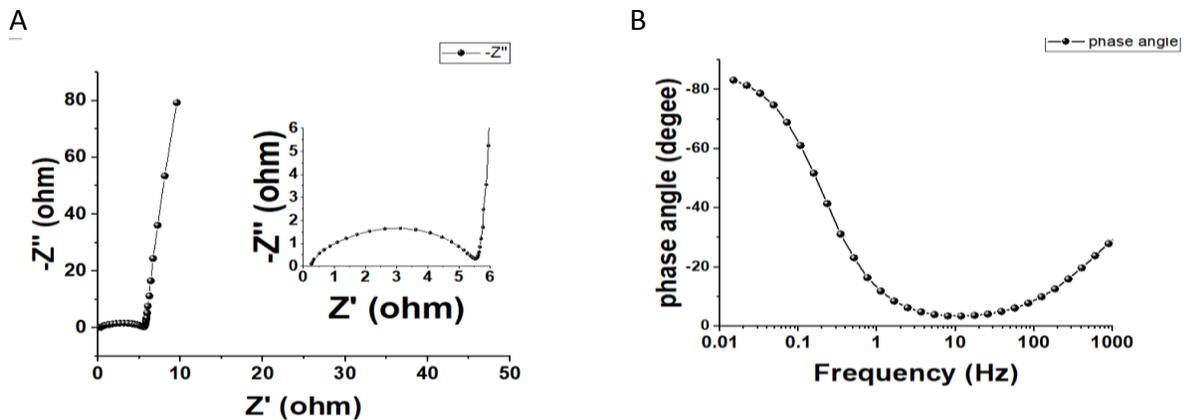


Figure 4.1: (A) CV curve, (B) Galvanostatic Charge/Discharge curve, (C) Specific current vs. specific capacitance graph, (D) Power density vs. Energy density graph, (E) Cyclic stability for sample 1

Figure 4.1 and 4.2 represent the electrochemical analysis of sample 1 which describes 0.2 g of PVP. Figure 4.2 (A) represents the CV of the supercapacitor device utilizing electrode sample 1 at a constant potential of 1.2 V and varying scan rate from 5 mV s^{-1} to 100 mVs^{-1} . Faster scan rates lead to a decrease in the size of the diffusion layer; consequently, higher currents are

observed [2]. The CV curves with a maximum potential window of 1.2 V of the EDLC at different scan rates showed quasi-rectangular shapes, indicating low charge transfer resistance and relatively ideal capacitance characteristics. As the scan rate increasing (up to 100 mV s⁻¹), there seems to be deviation from the quasi-rectangular shape into a leaf-like shape, showing that the charge transfer resistance became the dominant factor in the device [3]. This is because increasing the scan rate leads to a corresponding difficulty in the diffusion of electrolyte ions into the internal structure of electrodes and insufficient interaction between the electrolyte and materials of electrolyte thereby resulting in decrease of capacitance [3-5]. Figure 4.1 (B) represents the Galvanostatic charge/discharge curve at various current depending on the mass of the electrode. As the current increases, the charge/discharge time decreases, indicating the typical behaviour of supercapacitor. Cycling performance is one of the fundamental features of electrode material that determines its real-life application for supercapacitors. For this reason, cyclic stability evaluation of the electrode was carried out at a relatively high GCD constant current of 15 mA for 10000 cycles. As demonstrated in Figure 4.1 (E), *i.e.*, specific capacitance (F g⁻¹) as a function of number of cycles, it can be described that about 77.8% of the initial specific capacitance was retained even after 10000 cycles. Based on the stability of the cell under this extreme cycling condition, it is deduced that the material could be used effectively in supercapacitor applications. The capacitance 94.49, 89.52, 84.95, 81.55, 78.22, 76.62, and 73.51 fg⁻¹ was recorded.



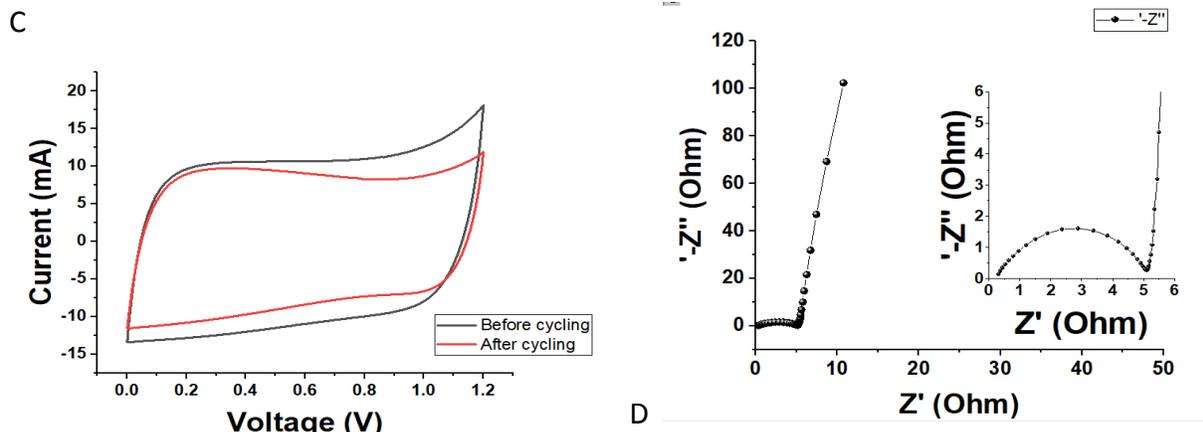


Figure 4.2: (A) Nyquist plot, (B) Bode plot (C) CV before and after stability (D) Nyquist plot after stability for sample 1

Figure 4.1 (C) and Figure 4.1(D) represent specific capacitance vs. specific current and energy density vs. power density graphs respectively. As the specific current increases the specific capacitance decreases in similar pattern as in figure 4.1(E) while the energy density decreases as the power density increases which is the typical behaviour of EDLC. The maximum energy density and its corresponding power density was recorded as 3.9 Whkg^{-1} and 0.14 Wkg^{-1} respectively. Figure 4.2(A) represents the Nyquist plot which is the frequency responses of the device, with the imaginary and the real impedances as a function of the frequency as shown in figure 4.2(A). The frequency range of 10 MHz to 100 kHz carried out on the EDLC using the as prepared electrode sample 1. A semicircle is observed at the high- frequency domain (inset) as seen by the diameter of the semicircle before stability and after stability as shown in figure 4.2 (D). Meanwhile, a semicircle was observed in the high frequency region Nyquist plot, which implies the slow charge transfer process of the redox reaction at the electrode/electrolyte interface [6]. Figure 4.2 (B) illustrates the PEIS bode plot of the device for a frequency range of 10 MHz to 100 kHz. The phase angle obtained is -85.2° which is somewhat close to -90° which is typical of ideal capacitors [7]. The faradaic reactions were revealed by the CVs carried out before and after stability as shown in the figure 4.2 (C). The figure mentioned show exponential peaks at high voltage which may be due to dissociation of the electrolyte with the surface of the electrode materials. There is also reduction of the shape size in the figure mentioned after stability which implies there is a loss of capacitance due to these mentioned factors.

Figure 4.3 and 4.4 represent the electrochemical analysis of sample 2 which describes 0.3 g of PVP.

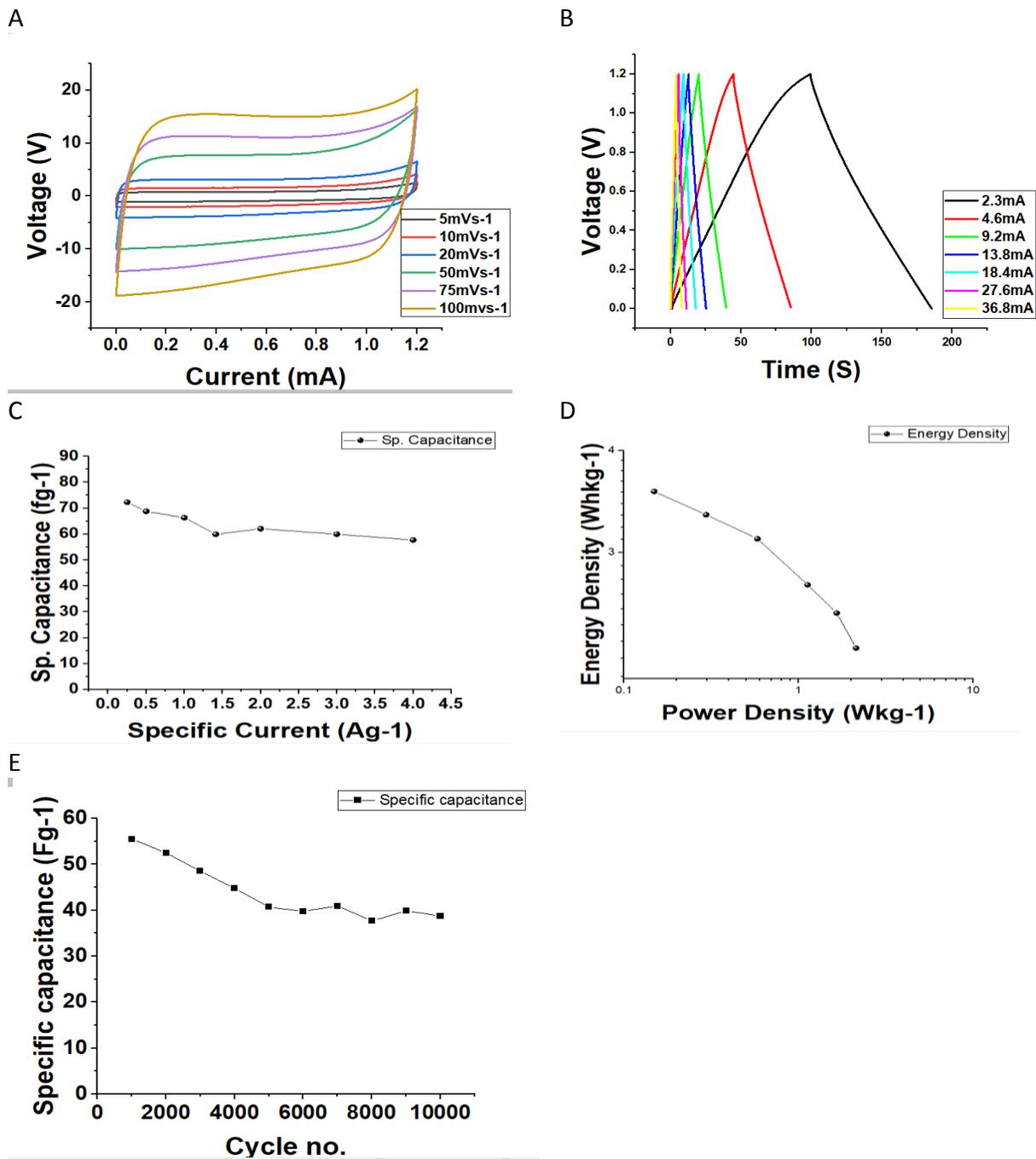


Figure 4.3: (A) CV curve, (B) Galvanostatic Charge/Discharge curve, (C) Specific current vs. specific capacitance graph, (D) Power density vs. Energy density graph, (E) Cyclic stability for sample 2

4.3(A) represents the CV curve of sample 2 that was carried out at a constant potential of 1.2V and varying scan rate from 5 mV s^{-1} to 100 mV s^{-1} similar to sample 1 CV curve, the CV curves with a maximum potential window of 1.2 V of the EDLC at different scan rates showed quasi-rectangular shapes, also indicating low charge transfer resistance and relatively ideal capacitance characteristics. There is also deviation of the CV curve from quasi-rectangular shape to a leaf-like shape as the scan rate increasing (up to 100 mV s^{-1}). Figure 4.3 (B) also represents the charge/discharge curve of sample 2 which also shows the behaviour of typical supercapacitor. The cyclic stability for the electrode was carried out at 21.2mA for 10000 cycles as shown in figure 4.3 (E). It can be described that about 79.8% of the initial specific capacitance was retained even after 10000 cycles. Based on the stability of the cell under this extreme cycling condition, it is also deduced that the material could be used effectively in supercapacitor applications. The capacitance, 72.30, 68.79, 66.31, 62.05, 59.91, 59.94, and 57.69 fg^{-1} were recorded. Figure 4.3 (C) describes the specific current vs specific capacitance graph and the power density vs energy density graph that exhibit the behaviour of supercapacitor but defer from sample 1 shown in figure 4.3 (D). The maximum energy density and its corresponding power density was recorded as 3.6 Whkg^{-1} and 0.15 Wkg^{-1} respectively.

Figure 4.4(A) represents the Nyquist plot which is the frequency responses of the device, with the imaginary and the real impedances as a function of the frequency as shown in figure 4.4(A). The frequency range of 10 MHz to 100 kHz carried out on the EDLC using the as prepared electrode sample 2. A semicircle is observed at the high- frequency domain (inset) as seen by the diameter of the semicircle before stability and after stability as shown in figure 4.4(D). Meanwhile, a semicircle was observed in the high frequency region Nyquist plot, which implies the slow charge transfer process of the redox reaction at the electrode/electrolyte interface [10] and the diameter of the semicircle for the electrode of the device is large as compare to sample 1. Figure 4.2(B) illustrates the bode plot of the device for a frequency range of 10 MHz to 100 kHz.

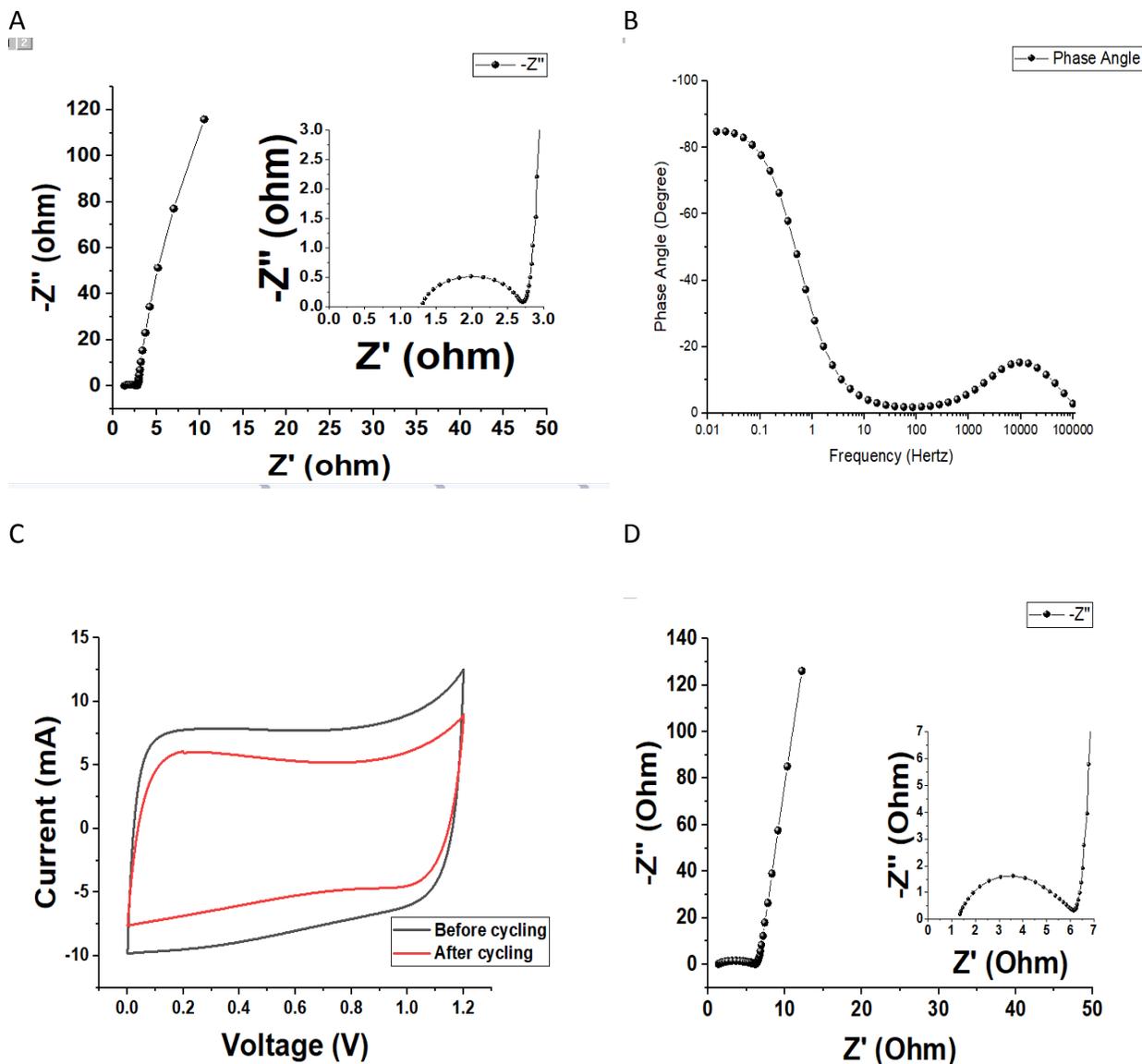
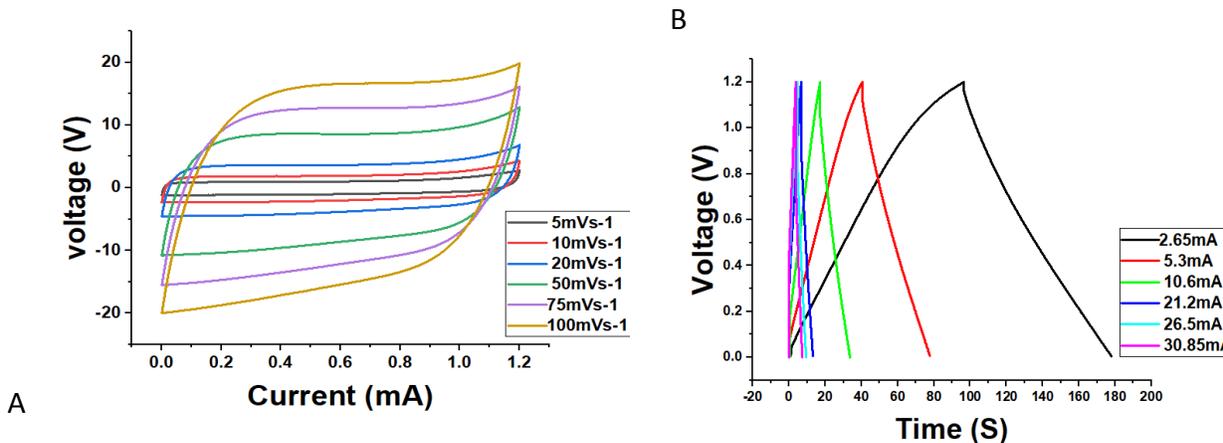


Figure 4.4: (A) Nyquist plot, (B) Bode plot (C) CV before and after stability (D) Nyquist plot after stability for sample 2

The phase angle obtained is -85.2° which is somewhat close to -90° which is also the same as in sample 1. The faradaic reactions were also revealed by the CVs carried out before and after stability as shown in the figure 4.4 (C).

Figure 4.5 and 4.6 represent the electrochemical analysis of sample 3 which describes 0.4g of PVP. 4.5(A) represents the CV curve of sample 3 that was carried out at a constant potential of 1.2V and varying scan rate from 5 mVs^{-1} to 100 mVs^{-1} similar to sample 1 and sample 2 CV curve, the CV curves with a maximum potential window of 1.2V of the EDLC at different scan rates showed

quasi-rectangular shapes, also indicating low charge transfer resistance and relatively ideal capacitance characteristics. There is also deviation of the CV curve from quasi-rectangular shape to a leaf-like shape as the scan rate increasing (up to 100 mV s⁻¹). Figure 4.5 (B) also represents the charge/discharge curve of sample 3 which also shows the behaviour of typical supercapacitor but a slight difference in shape maintenance as compare to sample 1 and 2. The cyclic stability for the electrode was carried out at 21.2 mA for 10000 cycles as shown in figure 4.5 (E). It can be described that about 58.7 % of the initial specific capacitance was retained even after 10000 cycles. Based on the stability of the cell under this extreme cycling condition, it is also deduced that the material could be used effectively in supercapacitor applications. The capacitance, 69.37, 64.13, 57.56, 48.27, 43.79, and 40.72 fg⁻¹ were recorded.



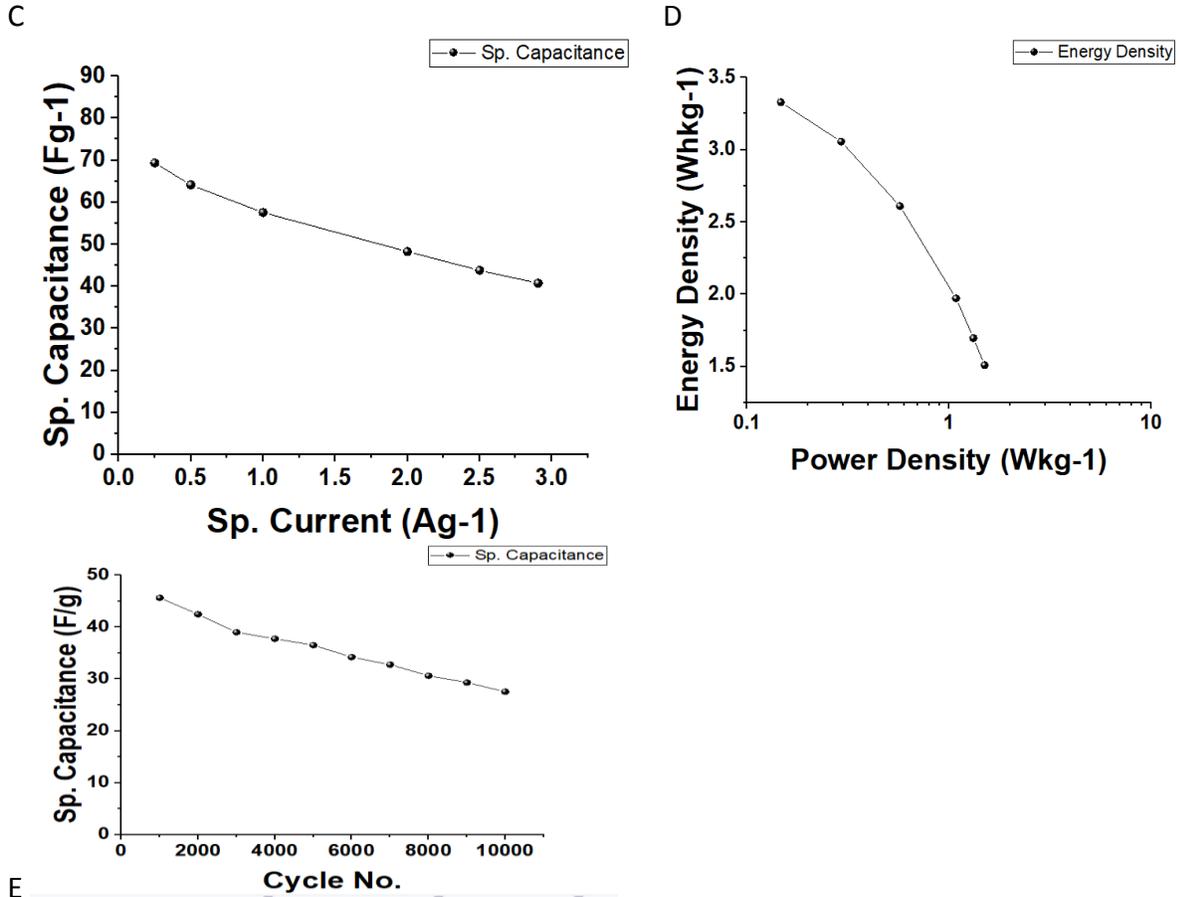


Figure 4.5: (A) CV curve, (B) Galvanostatic Charge/Discharge curve, (C) Specific current vs. specific capacitance graph, (D) Power density vs. Energy density graph, (E) Cyclic stability for sample 3

Figure 4.5 (C) describes the specific current vs. specific capacitance graph and the power density vs. energy density graph that exhibit the behaviour of supercapacitor but defer from sample 1 shown in figure 4.5 (D) The maximum energy density and its corresponding power density was recorded as 3.3 Whkg^{-1} and 0.15 Wkg^{-1} respectively. Figure 4.6(A) represents the Nyquist plot which is the frequency responses of the device, with the imaginary and the real impedances as a function of the frequency as shown in figure 4.6(A).

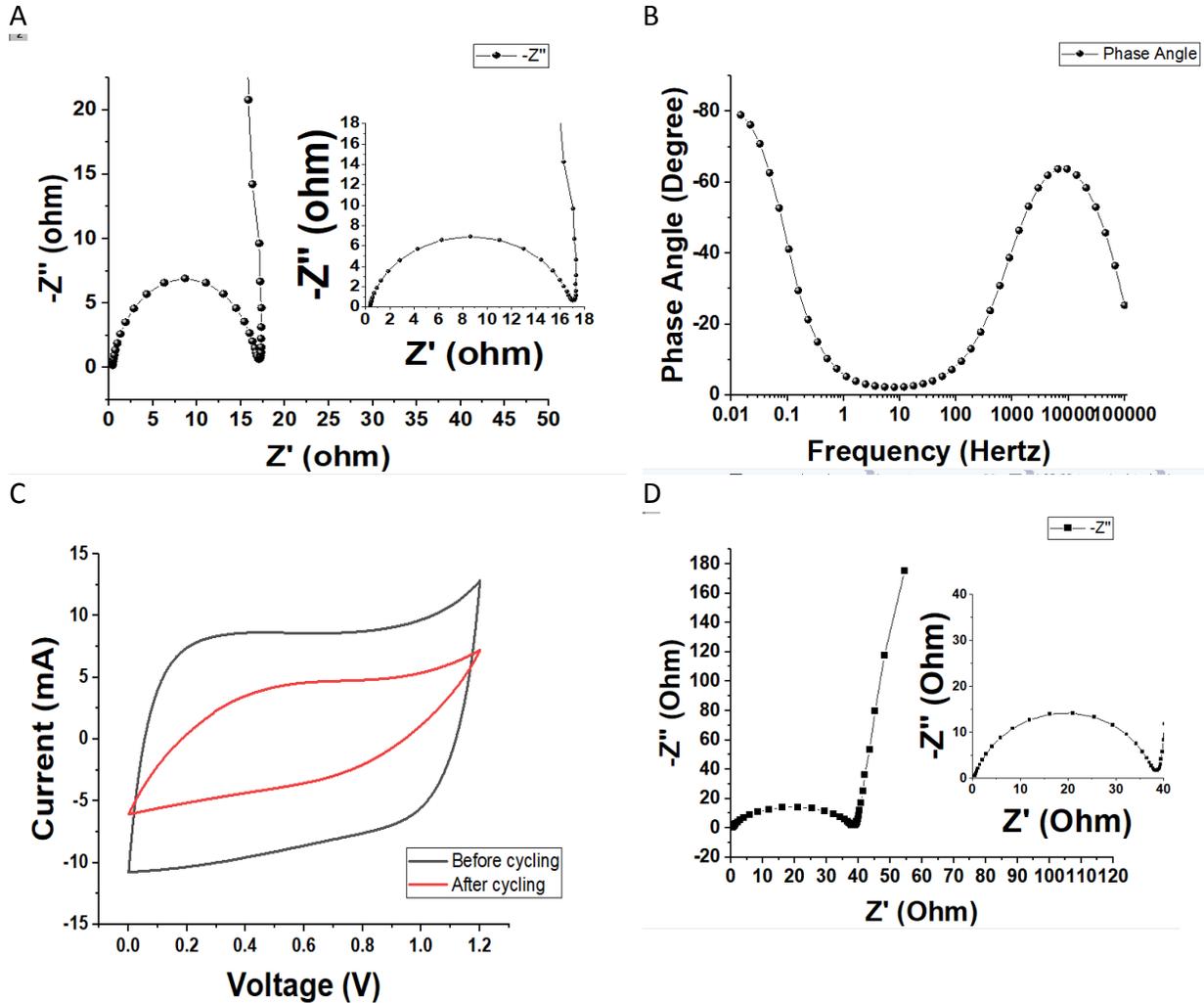


Figure 4.6: (A) Nyquist plot, (B) Bode plot (C) CV before and after stability (D) Nyquist plot after stability for sample 3

The frequency range of 10 MHz to 100 kHz carried out on the EDLC using the as prepared electrode sample 3. A semicircle is observed at the high- frequency domain (inset) as seen by the diameter of the semicircle largest than that of sample 1 and 2 before stability and after stability as shown in figure 4.6 (D).

Meanwhile, a semicircle was observed in the high frequency region Nyquist plot, which implies the slow charge transfer process of the redox reaction at the electrode/electrolyte interface and the for the electrode of the device is large as compare to sample 1 and 2. Figure 4.6 (B) illustrates the Bode plot of the device for a frequency range of 10 MHz to 100 kHz. The phase angle obtained is -80.5° which is somewhat far from to -90° as compare to the Bode plot in sample 1 and 2.

The faradaic reactions were also revealed by the CVs carried out before and after stability as shown in the figure 4.6 (C). The figure mentioned show exponential peaks at high voltage as mentioned in sample 1 and 2. There is also drastic reduction of the shape size and loss the quasi rectangular shape after stability. Table 4.1 exhibits the maximum specific capacitance, maximum energy density and the corresponding power density of the various samples in this project.

Table 4.1: The maximum Specific Capacitance, maximum Energy density and corresponding power Density of the three samples.

SAMPLE	MASS (g)	MAXIMUM SPECIFIC CAPACITANCE (fg^{-1})	ENERGY DENSITY ($Whkg^{-1}$)	POWER DENSITY (Wkg^{-1})
1	0.2	94.49	3.90	0.140
2	0.3	72.30	3.56	0.147
3	0.4	69.37	3.33	0.150

4.1.2 KOH Electrolyte

The performance of the device fabricated does not only depend on the electrode materials but also the KOH electrolyte. This electrolyte provides ionic conduction and also determines the electrochemical potential window which is 1.2V for this project. The 6M KOH was more suitable to enhance the electrochemical properties of the device due to the high ionic conductivity of KOH because of the high mobility of OH anion in water solution [8].

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CHAPTER FIVE

CONCLUSION AND RECOMMENDATION(S)

5.1 Conclusion

This project work has demonstrated a facile way to enhance the energy density of EDLC device, through the optimization of the amount of PVP binder in the electrode materials. The use of PVP as a binder in the electrode of supercapacitor gives rise to creating green environment because PVP is non-toxic. The electrode of three difference compositions were prepared, which are sample 1 0.2 g of PVP, 0.1 g of activated carbon, and 0.8 g of ethanol, sample 2, 0.3 g of PVP, 0.1 g of activated carbon and 0.8 g of ethanol, and sample 3, 0.4 g of PVP, 0.1 g of activated carbon and 0.8 g of ethanol. Supercapacitor device was fabricated by using the prepared electrode and 6 M KOH as the electrolyte. The device made from the composition in sample 1 exhibited outstanding electrochemical performance. The device made from sample 1 showed the peak specific capacitance of 94.49 fg^{-1} , the maximum power density of $3.93.3 \text{ Wkg}^{-1}$ and corresponding energy density of $0.143.3 \text{ Whkg}^{-1}$, at the operating voltage of 1.2 V. Furthermore, the phase angles for the device made with electrode sample 1 was -85.2° ; this value is close to the ideal supercapacitor phase angle value of -90° . Indeed, the electrode made out of PVP can conveniently serve as an alternative for the readily used binders for improved electrochemical capacitor applications and green environment.

5.2 Recommendation(s)

The scope of this work to explore the possibility of an optimum amount of PVP that can be used as binder in the electrode of EDLC devices. In the process of characterization the electrode with PVP binder, only electrochemical characterizations such as cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy were employed. Further characterization can be carried via techniques such as scanning electron microscopy (SEM) to understand the microstructure configuration of the electrode material, X-ray diffraction (XRD) to understand the structural composition and crystalline nature of the electrode material, differential scanning calorimetry (DSC) to ascertain the thermal stability of the electrode material and to determine the temperature range, Fourier transform infra-red spectroscopy to study the chemical bonding present and their vibrating behaviour between the electrode material and the

electrolyte. Furthermore, optimization should be carried out to expand the operating voltage window of the device. This can be achieved by varying the amount of ethanol to dissolve the best amount of PVP. The effect of this could create more room for increasing the specific capacitance and energy density value of the device. Further research and attempts could be carried out to reduce the ESR of the EDLC device to yield greater power density.