

**BIOACTIVE POLYMER AS AN ALTERNATIVE BINDER FOR
ELECTROCHEMICAL CAPACITORS**

A thesis presented to the Department of Materials Science and Engineering African
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In partial fulfillment of the requirements for the degree of

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By

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ELECTROCHEMICAL CAPACITORS**

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Certification

This is to certify that the thesis titled “*Bioactive Polymers as an Alternative Binder for Electrochemical Capacitors*” submitted to the Department of Materials Science and Engineering, 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 *Abu, Usman Onuminya*.

ABSTRACT

Binders are important components of electrodes of supercapacitors because of their ability to adhere active components and make the resultant slurry to adhere on current collectors. This work seeks to investigate the possibility of a bioactive polymer (chitosan) substituting the conventional fluoro-thermoplastic binders used in supercapacitors within the constraint of electrochemical characterizations. Chitosan based electrodes at 3% acetic acid concentration displayed the best electrochemical performance, also exceeding the limits of PVDF binder based electrodes. The supercapacitor devices fabricated based on chitosan binder displayed a capacitance of 113.56 F g^{-1} an energy density of 7.98 kWh g^{-1} in 6 M KOH and a capacitance of 88.42 F g^{-1} and an energy density of 18.04 kWh g^{-1} in 1 M Na_2SO_4 aqueous electrolytes,.

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DEDICATION

I dedicate this thesis to God, Who makes all things perfect in His Own time.

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CHAPTER 1

INTRODUCTION

1.1 Background

Generally, the entire globe looks at alternative sources of energy due to increasing human population which leads to increase in energy consumption and also; to the negative impact of over – dependence of fossil – fuels on our collective human existence. Alternative sources of energy such as solar, wind, tidal etc. are at a disadvantage by their weather dependency and thus, would require an energy storage component. In order to bridge this gap, development of energy storage systems and technologies have been one of the major focus for the past few decades. Some of the energy storage technologies are; batteries and electrochemical capacitors (supercapacitors). Batteries (rechargeable) store energy via a chemical reaction and are characterised by high energy densities due to bulk process, which enable them to be used for relatively long periods but take time to recharge. On the other hand, supercapacitors (SC) store energy using a surface phenomenon and are characterised by high power densities; meaning, they charge and discharge relatively faster but can be used for shorter periods compared to batteries. SCs use carbon material as a main electrode material, which can provide high power in a short time and have an excellent cycle life as a new energy storage device [1]. Therefore, SC is widely used in backup power, portable electronics and a variety of vehicles starting micro devices, which need high power density and long cycle life. In order to achieve the application of these devices, we need to give priority to the cost, environmental compatibility and the feasibility of industrial production.

There has been significant research effort in the area of SCs recently to improve their energy density so that they can come close to that of batteries and can be used in complimentary position to batteries as the need arise. The device architecture affect the electrochemical

performance of the fabricated devices and this is due to the various materials used in the fabrication of the devices. Electrodes are fabricated by brushing or pasting of slurry on a substrate such as nickel foam (NF). This paste or slurry is prepared by ultrasonically stirring a mixture of active materials, conductive agents and binders.

Binders are one of the main component that significantly affect the electrochemical performance and its main role is to bind active material and conductive agent together and also cohering with electrode material substrates, to avoid active materials falling off during the electrode formation and appropriates pore sizes. However, cohesive agents or binders inevitably cover some surface areas or pores of active materials. Thus, the properties of binders and their contents in the electrodes will directly influence electrochemical performances of SCs. The following properties might also affect the performance: appropriate cohesion between electrode components, strong adhesion of electrode coating to current collector, guarantee insolubility in electrolyte, satisfactory thermal, electrochemical and chemical stability while not retarding electron and ion transport, low cost, environmental compatibility and ease of processing [2]. Various binders exhibit different properties that lead to different electrochemical performance. Poly(tetrafluoroethylene), PTFE or Poly(vinylidenedifluoride), PVDF are the most commonly used binders typically between 5 and 10 mass percent [3][4][5]. PTFE prohibits direct casting unto metal current collectors. However, improved material integrity at the active material/ current collector interface may enhance the electrochemical performance for electrode systems directly attached to the current collector. PVDF is widely used for this purpose because of its chemical inertness and suitability of the rheological properties of the carbon slurry [6]. Furthermore, sufficient mechanical stability, high amounts of PVDF have to be added (~ 10 mass%) which increases the dead mass and potentially reduces the overall capacitance of the device by blocking access to the pore network [7]. Moreover, there are growing concerns regarding the use of PVDF because of the necessary addition (and

subsequent removal) of N-methyl-2- pyrrolidone (NMP) during electrode preparation which is a dipolar aprotic solvent classified as a reproductive toxicant [8]. In addition, the blending of the electrode material with binder impacts the electrochemical performance as binder may obstruct the access of ions to a significant portion of the total surface area and the defragmentation of carbon particles may cause an increase in electrical resistance [9]. Indeed, based on data of free-standing binder-free electrodes, it would be preferential to avoid the use of any binder [10][11][12]. However, this is not possible in most cases, as it would exclude the use of highly available and cost-attractive activated carbon powders. The selection of binder material has to balance a couple of partially diametrical properties. It is especially important to lower the amount of binder added 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. Furthermore, with environmental awareness driving the selection of SC components, interest has also increased in investigating “green” or “greener” materials [7]. The use of chitosan as binders for SC electrodes presents a green alternative to conventional binders and also makes sense from an economic and an environmental perspective; chitin from which chitosan is derived from is a by-product in the food industry and it is produced in large amounts [13]. Chitosan has a number of commercial and possible biomedical uses for in agriculture as a seed treatment and bio pesticide, helping plants to fight off fungal infections. Until now, there has been no systematic study using chitosan as a binder for EDLC electrodes that includes its effect on mechanical strength, the electrical conductivity of the electrodes, and the resulting electrochemical performance.

1.2 Motivation

Chitosan holds the potential as an alternative binder for SC fabrication because of its low cost and non – toxicity. Unlike PVDF, no toxic solvent is required for electrode fabrication. Hence, devices will be fabricated based on the chitosan binders and subjected to a number electrochemical characterisation in different electrolytes to ascertain the suitability of chitosan as an alternative to conventional binders.

1.3 Objective(s) of Research

The objectives of this research include:

- Fabrication of low-cost and environmental benign binder for SCs.
- Comprehensive evaluation of chitosan as a binder for EDLC electrodes for aqueous electrolytes.

1.4 Scope of Research

In this work, the main focus is not on the large scale design or applicability in a whole energy storage system but rather investigating techniques to improve the electrochemical properties of possible chitosan-based material composites for use as electrodes; i.e. optimizing the electrode material for intended laboratory scale applications and subsequently a larger scale in the near future. The electrochemical performance will be investigated with electrochemical techniques such as Electrochemical Impedance Spectroscopy (EIS) to Cyclic Voltammetry (CV) tests. Efforts to elucidate the reason for the observed enhancements by analysing the charge storage trend at varying specific current. The general objective of this thesis is to contribute to the collective knowledge database in the field of SC research. The results discussed are quite important in further understanding the internal processes within the composite electrode material as alternatives for future applications. With this, it provides an avenue for improvements where necessary. Thus, the key challenges to SC development leading to its full

commercialization remain dependent on the electrode stability and improvement of electrode operating voltage to increase the overall energy density to be comparable to much common high performance batteries presently in use. This thesis is divided into five chapters: Chapter 1 presents a general introduction to the global energy issue and a proposed solution with respect to modelling efficient, clean, reliable and environmentally friendly energy storage systems. Chapter 2 presents a literature review on ongoing research related to SCs and the way forward. Chapter 3 presents the detailed experimental procedure used in this study while Chapter 4 deals with the results obtained and detailed discussion of the results. A summary of each experimental result will be presented in Chapter 4. Chapter 5 contains general conclusions and details of future work. In particular, we have also demonstrated the use of Chitosan as an effective binder for SC electrode fabrication.

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CHAPTER TWO

LITERATURE SURVEY

2.1 World Energy Crisis

The adverse effects of global warming and the fast depleting reserves of fossil fuels have placed the world in a limbo regarding the possible sources of energy that would on one hand, meet the needs of heavy energy consumers and on the other hand, minimise the carbon footprint in the environment to a bearable minimum [14][15]. This concern has led to the increase in renewable energy production; however, the weather dependent nature of renewable energy sources call for the development of highly scalable and efficient energy storage devices such as supercapacitors with optimum energy densities and batteries with satisfactory power densities.

2.2 Electrochemical capacitors: Theory and Operation

A capacitor is a device with a large internal area comprising of two electrodes with a thin insulator in sandwiched between them; when voltage is applied, it amasses charges on one side until the internal voltage equals the applied voltage [16].

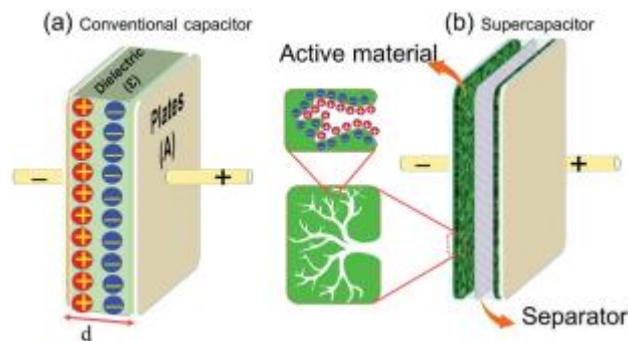


Figure 2.1: Conventional Capacitor and Supercapacitor [15]

Supercapacitors (SCs) are high-power devices that bridge the gap between electrolytic capacitors and rechargeable batteries. They have very thin internal insulation and very large electrode area allowing them to store large amounts of charge at low voltages which enable

them to accept and deliver charges much faster than a battery and are able to tolerate more charge and discharge cycles [16][17]. Figure 2.2 shows the plot of specific power against specific energy, otherwise known as the Ragone plot, where electrochemical capacitors are presently bridging the gap between batteries, conventional solid state and electrolytic capacitors; they are capable of storing charges up the magnitude of thousands more than the latter as a result of their large surface area [14].

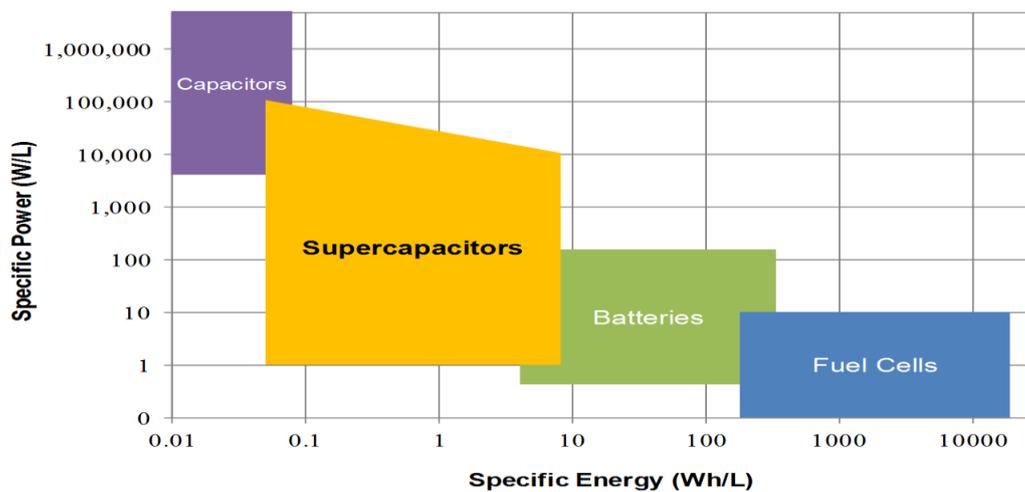


Figure 2.2: Ragone Plot [18]

2.2.1 Electrochemical Double-Layer Capacitors (EDLCs)

Simon & Gogotsi [14] reported that Becker filed the first patent describing electrochemical capacitors in 1957. Becker used a carbon with a high specific surface area coated on a metallic current collector in a sulphuric acid solution. Furthermore, they reported that a Japanese company, NEC, manufactured aqueous-electrolyte capacitors for use in power saving units in electronics, which signalled the commercial use of electrochemical capacitors. Noori *et al.* [15] described the mechanism in EDLCs to be based on the electrostatic adsorption of the electrolyte ions on the surface of the electrode active materials which is key to the high capacitance of EDLCs in using a very much accessible surface area and electronically conducting materials. Due to the requirements of high surface area, some of the electrode materials available for: graphene, activated carbon, carbon nanotubes, carbon nanohorns, carbon nanocoils, carbon

aerogels, carbide-derived carbons, zeolite-templated carbons, porous carbons etc. When EDLCs are charged, electrons are forced to go from the positive electrode to the negative electrode through an external circuit which causes cations within the electrolyte to concentrate in the negative electrode and anions in the positive electrode resulting in the formation of an electrochemical double layer (EDL) that compensates the external charge disparity [19]. However, during discharge, electrons travel from the negative electrode to the positive electrode through an external circuit and both kinds of pores become mixed again until the cell is discharged; the movement of ions into the pores is significantly influenced by pore size which affects double layer capacitance negatively if it is excessively small [19].

According to Simon & Gogotsi [14], charge separation occurs on polarization at the electrode-layer interface, resulting in what Helmholtz described as double layer capacitance, C:

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \text{ or } \frac{C}{A} = \frac{\epsilon_r \epsilon_0}{d} \quad (2.1)$$

where; ϵ_r is the electrolyte dielectric constant, ϵ_0 is the dielectric constant of vacuum, A is the electrode surface area, d is the effective thickness of double layer. However, if the electrode materials are mesoporous or microporous, their capacitance can be estimated using the following equations [19];

$$\frac{C}{A} = \frac{\epsilon_r \epsilon_0}{b \ln\left(\frac{b}{b-d}\right)} \quad (2.2)$$

Equation 2.2 estimates the capacitance for mesoporous electrode materials; where, b is the pore radius and d is the distance between the ion and carbon surface.

$$\frac{C}{A} = \frac{\epsilon_r \epsilon_0}{b \ln\left(\frac{b}{a_0}\right)} \quad (2.3)$$

Equation 2.3 estimates the capacitance for microporous electrode materials; where, a_0 is the effective size of the ion.

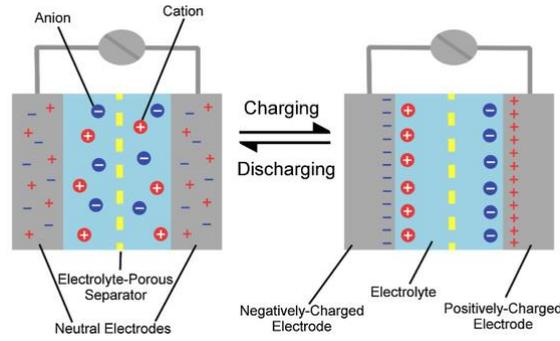


Figure 2.3: Schematic of an EDLC [20]

2.2.2 Pseudocapacitors

Pseudocapacitors (PCs) are those that use fast, reversible reactions at the surface of active materials [14]. Carbon-based materials have limited energy, thus, limiting EDLC-based SCs to applications requiring power delivery for few seconds in spite of their outstanding improvements in properties [15]. However, SCs with higher energy densities can be achieved using pseudocapacitive materials such as RuO_2 , Fe_3O_4 , MnO_2 and conducting polymers. However, Ruthenium oxide, RuO_2 , is widely studied because it is conductive and distinct oxidative states which are accessible within 1.2 V; the Pseudocapacitive behavior of RuO_2 can be described as fast, reversible electron-transfer together with an electro-adsorption of protons on the surface of RuO_2 according to equation 2.13 [14]:



where; $0 \leq x \leq 2$. This continuous change of x during proton insertion or de-insertion occurs over a window of about 1.2 V and leads to a capacitive behavior with ion absorption [14].

Dissimilar charge storage mechanisms can be distinguished in pseudocapacitive electrode: underpotential deposition, redox reactions of transition metal oxides, intercalation pseudocapacitance and reversible doping and de-doping in conducting polymers [19]. However, electrodes that demonstrate pseudocapacitance are susceptible to swelling and

shrinking on charge/discharge cycling which results in poor mechanical stability and low cycle life [19].

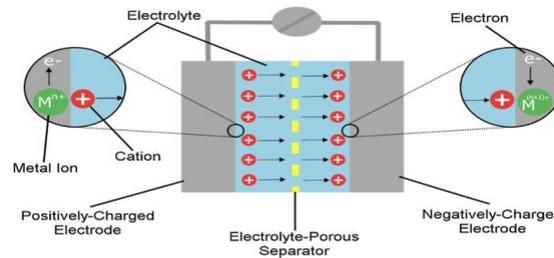


Figure 2.4: Schematic of a pseudocapacitor [20]

2.2.3 Hybrid Supercapacitors

Hybrid SCs presents an intriguing alternative to EDLCs by putting together battery-like electrodes with capacitor-like electrodes in the same cell; thereby making the device to exhibit both high energy and power densities [15] [14]. These devices seek to accomplish comparable performances to battery with respect to energy and also maintain the excellent power characteristic and good cycle life of SCs [15]. According to Simon & Gogotsi [14], two dissimilar approaches to hybrid systems have emerged: Pseudo-capacitive metal oxides with a capacitive carbon electrode and Lithium-insertion electrodes with a capacitive carbon electrode.

2.3 Electrochemical Testing of Cells

2.3.1 Electrochemical Testing of Electrode Material in a Three (3) and Two (2) - Electrode Configuration

There are basically three electrodes used in electrochemistry; namely: working electrode (WE), reference electrode (RE) and counter electrode (CE). The CE which is made from an inert material like Pt, graphite, Au or glassy carbon as a source or sink of electrons thereby acting to close to the electrochemical circuit without participating in the reaction [21]. The RE is an electrode which has a stable and well-known electrode potential that enables it to be used as

the point reference in an electrochemical set-up while the WE is the electrode of interest in which the electrochemical reaction is occurring.

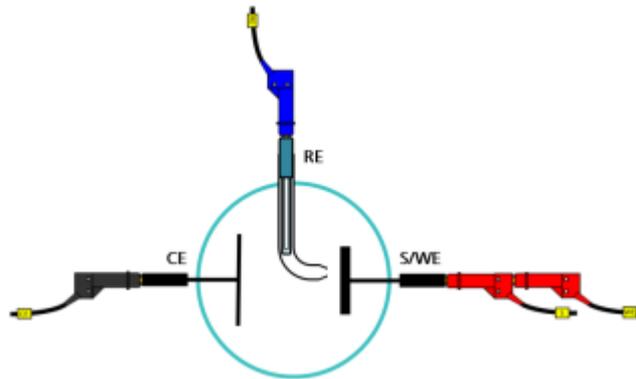


Figure 2.5: Schematic of a three – electrode setup [21]

The three – electrode is used to electrochemically characterise as – prepared electrodes. Current flows between the WE and the CE, and measured between the RE and the sense. The potential difference between the WE and RE is usually controlled so that it is equal to that supplied by the user [21].

The two – electrode setup comprise of a pair of closely spread out electrodes containing the electrode active materials and separated by an ion permeable and electrically insulating separator; the electrochemical performance of this set-up is influenced by the electrodes in a given insulator [15]. The CE and RE are shorted on one of the electrodes while the WE and the sense or shorted on the opposite electrode; the potential across the cell which include contributions from the CE/Electrolyte boundary and electrolyte itself is then measured [21].

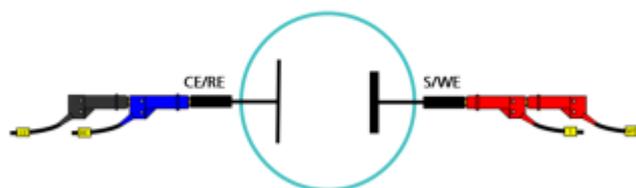


Figure 2.6: Schematic view of the two – electrode setup [21]

2.3.2 Fabrication of Electrodes for Testing

Qian *et al.* [22] prepared SC electrodes using PTFE as a binder. Activated carbon derived from human hair, carbon black and binder were in the ratio 80:10:10 wt. %, mixed and pressed to a thickness of 100 microns on a nickel foam and aluminium collectors for KOH and LiPF₆ in ethylene carbonate/dimethyl carbonate electrolytes respectively. The device was fabricated exhibited high charge capacity with specific capacitance of 340 F/g in 6 M KOH at a specific current of 1 A/g and good stability over 20 000 cycles. Karthikeyan *et al.* [23] produced electrodes for SCs using teflonized acetylene black as binders. Activated carbon obtained from pinecones, ketjen black and teflonized acetylene black in ethanol were mixed in the weight amounts of 5 mg, 1 mg and 1 mg respectively. The resulting slurry was coated on a stainless steel mesh and dried at 160 °C. A symmetric supercapacitor fabricated with two similar electrodes separated by a porous polypropylene separated and filled with 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate. The XRD patterns of the various ratios of activated carbon showed a highly disorganized nature of carbon derived from pinecones with discernible characteristics. These reflections indicate small domains of graphene sheets. The material with treatment ratio of 1:5 KOH to pine cone petals showed a maximum specific surface area of 3950 m²/g. Similarly, SCs fabricated with electrodes of same treatment ratio displayed enhanced supercapacitive behavior with the highest energy density of 61 Wh/Kg. An exceptional cycling ability with 90% of the initial specific capacitance after 20,000 cycles under harsh conditions was maintained.

Momodu *et al.* [24] developed the working electrode of a SC using PVDF binder. The electrode was created by mixing the different activated carbon synthesized from tree bark, with carbon black and polyvinylidene fluoride (PVdF) binder in the weight percentages 80:10:10 with 1-methyl-2-pyrrolidinone (NMP) in an agate mortar to form a viscous slurry. The morphology of the activated carbon obtained uncovered an exciting nexus of micro/mesoporous architecture

and a trend of increasing specific surface area as carbonization temperature increased. A maximum of specific surface area of 1018 m²/g alongside a high pore volume of 0.67 cm³/g. A specific capacitance of 191 F/g at a specific current of 1 A/g was obtained as the electrochemical properties of the electrode were characterized in 1 M Na₂SO₄ electrolyte. Furthermore, the symmetrical device fabricated showed a specific capacitance of 114 F/g at 0.3 A/g and an exceptional Coulombic efficiency of 100% after 5000 charge – discharge cycles at 5 A/g and a low capacitance floating time of 70 h. Similarly, Ahmed *et al.* [25] fabricated electrodes for SCs using PVDF-HFP binder. The working electrodes were prepared by mixing the carbon obtained from rotten carrot (85wt. %), acetylene black (10wt. %) and binder, PVDF-HFP (5wt. %) using acetone as dispersant. The activated carbon obtained from rotten carrot showed a maximum specific surface area of 1154.99 m²/g and a pore volume 0.9294 cm³/g. The observed pore distribution show the existence of micro- and mesopores. It further displayed a maximum specific capacitance value of 135.5 F/g at 10 mHz. The ionic liquid based electrolyte offered the highest specific energy (29.1 Wh/kg at 2.2 A/g) and specific power (142.5 kW/kg at 2.2 A/g).

Yang *et al.* [26] produced electrodes for supercapacitor using PTFE binder. The testing electrodes were prepared by mixing carbon prepared from corn leaf (80wt. %), acetylene black (10wt. %) and PTFE (10wt. %). The as-prepared hierarchical porous carbon derived from corn leaves displayed a maximum specific surface area of 2507 m²/g courtesy of 38.3% microporosity and 71.6% mesoporosity; while keeping channels of macroporosity. Furthermore, the porous carbon obtained exhibited electrochemical performance such as a specific capacitance of 20 F/g at the specific current of 0.1 A/g, impressive high-rate capability with retention of 91% from 0.1 to 5 A/g and good cycling stability of 99% capacitance retention after 10000 cycles. Ochai-Ejeh *et al.* [27] fabricated electrodes by combining activated carbon manufactured from lightweight cork, carbon black and polyvinylidene difluoride (PVDF) in the

weight ratios of 80:15:5 with the aid of an agate mortar. A viscous slurry of the mixture was then made by the drop-wise addition of 1-methyl-2-pyrrolidinone (NMP), the resulting slurry was then pressed on nickel foam current collectors. The morphology of the activated carbon derived from lightweight cork showed well-defined porosity with a surface area of 1081 m²/g and a high pore volume of 0.66 cm³/g. A specific capacitance of 166 F/g at 0.5 /g in 1 M Na₂SO₄ with energy and power densities of 18.6 and 449.4 W/kg respectively. The device exhibited a good cycling stability after floating test for 200 h at 1.8 V. The device further displayed 99.8% capacitance retention after cycling for 5000 cycles.

2.4 Evaluation of Electrode Material

2.4.1 Cyclic Voltammetry (CV)

The cyclic voltammetry (CV) is an electrochemical method for evaluating the capacitance of as – prepared electrode material in a chosen electrolyte by recording CV of the material from which the capacitance can be measured [28]. It involves the sweeping of potential linearly between two limits at a given scan rate while measuring current; the scan rate chosen can be varied from few microvolts per second to millions of volts per second [29]. In a Two – Electrode set – up the voltage is applied between the two electrodes while in Three – Electrode set – up it is applied between the potential is applied between the RE and the WE [15]. The capacitance can be calculated from the CV curve using [15]:

$$C_{sp} = \frac{\int_{v_i}^{v_f} i dV}{v \times \Delta V \times x} \quad (2.5)$$

Where; I is current (A), $\int i dV$ is the voltammetric charge (C) obtained by integrating the area of a cyclic voltammogram, ΔV is the capacitive potential window (V), v is the scan rate (mV s⁻¹), x could be the volume, mass or area of the electrode active material.

2.4.2 Electrochemical Impedance Spectroscopy (EIS)

The EIS testing measures the impedance of a system as a function of frequency; it can also be used to measure the capacitive behaviour of either a device or a single electrode [15]. The EIS measurement is carried out by collecting the impedance data at the open-circuit potential by applying a small amplitude of alternative disrupting potential over a wide range of frequency usually from 10 mHz to 100 kHz [28]. The output of the EIS test is represented as a Bode plot (magnitude and phase response vs frequency) or a Nyquist plot (imaginary vs real part of impedance) [15].

2.5 Electrode Materials

The process by which energy is stored in EDLCs is centred on electrostatic adsorption of the ions of the electrolyte on the surface of the electrode active materials; hence, using materials with very high surface area and also electronically conducting is the major way of achieving high capacitance [15]. In addition, the pore size of electrode materials determines the level of capacitance EDLCs can attain; increasing the pore and decreasing the pore sizes of electrodes drastically results in the a substantial increase or decrease in capacitance [28]. A number of materials are used in making electrodes for SCs because of their ability to be tuned to achieve the required properties expected of electrodes. Some of these materials include Conducting Polymers (CP), Transition Metal double hydroxide (t-MOH), Carbon materials, Composites, Biomass, etc.

2.5.1 Conducting polymers (CP)

Conducting polymers possess high conductivity in a doped state, high voltage window, high storage capacity and adjustable redox chemical modification, low cost and environmental compatibility [28]. These properties make them suitable as electrodes for SCs. Charging of conducting polymers take place through the bulk of the material and they enable faradaic reactions which lead to increased pseudocapacitance [20]. The configuration of CP-based

systems are as follows: Type I (symmetric) where a fully charged device has an electrode full – doped while the other is uncharged, Type II (asymmetric) where two different polymers are used and Type III where a device uses the same type of polymer that can be p- and n- doped at the same time [28]. Common examples of CP used are: Polyaniline (PANI), Poly(2-methyl thioaniline), Poly(3,4-ethylene-dioxythiophene) (PEDOT), Poly(3-methyl thiophene) (PMeT) etc.

2.5.2 Transition Metal Double Hydroxide (t-MOH)

Transition Metal double hydroxide (t-MOH) are a class two – dimensional anionic clays made up of positively-charged brucite-like host layers and exchangeable charge – balancing interlayer anions; they can be expressed as [30]:



Where; M^{2+} is divalent metal ion such as: Fe^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} or Zn^{2+} , M^{3+} is a trivalent metal ion such as: Cr^{3+} , Mn^{2+} or Fe^{3+} and x is the molar ratio of $\frac{M^{2+}}{M^{2+} + M^{3+}}$ which is usually between 0.2 and 0.4. According to Wang *et al.* (as cited in [30]), electrodes were manufactured from delaminated Layered Double Hydroxides (LDH) nanosheets of CoAl. Upon electrochemical investigation, they revealed a very good electrochemical performance that was due to its open framework and it has highly exposed electrochemical Co sites. SC electrodes from layered double hydroxides are considered promising for energy storage because of their high power density, low maintenance cost and longer cycle life; however, their cycle may be limited by low mechanical stability [30].

2.5.3 Carbon Materials

A large amount of SC electrodes being made are either carbonaceous or related materials; the most common being activated carbon (AC) [20]. The advantages of carbon materials as electrodes for SCs include: copiousness, low cost, ease of processing, non-toxicity, good

electronic conductivity, high chemical stability, high specific surface area and wide operating temperature range [28]. Nano-structured carbon materials have been with good electrical conductivity and high specific surface area have become the material of choice for SCs [15]. Some of these materials include graphene derivatives, carbon nanotubes, carbon nanocoils, carbon aerogels, zeolite templated carbons, carbon nanohorns etc. Sun *et al.* (as cited by [20]) reported high energy and power densities for SCs fabricated by using electrodes made by hydrothermally doping graphene with graphene oxide and urea.

2.5.4 Composites

These types of electrodes combine the carbonaceous materials with either metal oxides or conducting polymers in the same electrode resulting in enhanced electrochemical performance [31]. Mixing different materials to form electrode composites helps in minimizing particle sizes, enhancing specific surface area, inducing porosity, preventing particle agglomeration, facilitating electron and proton conduction, expanding active sites, extending the potential window, protecting active materials from mechanical degradation, improving cycling stability and providing extra pseudocapacitance [28]. Yan *et al.* (as cited in [31]) reports that a high specific surface area (SSA) carbon was synthesized by the carbonation of PANI and activated with KOH. The resulting electrode excellent specific capacitance; upon addition of graphene after 2000 cycles there was an increase in specific capacitance retention from 88.7% to 94.4%.

2.6 Binders

Binders are materials used in the fabrication of SC electrodes to ensure the adhesion of the active material and the conducting agent on the current collector and to avoid the falling off of active materials during operations [32]. Presser *et al.* [2] highlighted some of the requirements of the binders as follows: ability to ensure suitable cohesion between the active material particles and the additional electrode components. For example, the conductive agent, ability to guarantee strong adhesion of the electrode coating to the current collector, ease of electrode

processing upon sage, insolubility in electrolyte and low swelling of electrolytes, high thermal, chemical and electrochemical stability while not adversely affecting the movement of ions and electrons in the electrode, low cost and environmental compatibility. Zhu *et al.* [32] reported that binders unavoidably cover some surface areas of active materials; hence, properties of binders and their contents in the electrodes greatly influence the electrochemical performance of SCs, making very important to choose the right binder. Binders can be classified as follows according to Wang *et al.* [33]:

2.6.1 Non – Aqueous Binders

Examples of non – aqueous binders are; Polyvinylidene difluoride (PVDF), Polyacrylic acid (PAA), Polyvinylidene difluoride – hexafluoropropylene (PVDF - HFP) and Nafion. PVDF is a highly pure and inert thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride. It displays satisfactory electrochemical stability and bonding strength because of its excellent resistance to diverse solvents, acids, bases and thermal gradients. However, the processing of PVDF with other electrode materials requires an expensive and, in some cases, toxic solvent e.g., N-methyl-2-pyrrolidone (NMP). PAA is a linear polymer and superabsorbent polymer binder. It can dissolve in both water and NMP, and it is capable of forming strong hydrogen bonds with both active materials and current collectors. PAA facilitates the uniform distribution of electrolytes throughout the active layer owing to its electrolyte absorbing behaviors.

PVDF – HFP and Nafion in SCs based on polymer – gel electrolytes. This type of electrolytes find application in industries that require flexible energy storage devices. Sivachidambaram *et al.* [34] prepared SC electrodes using PVDF as a binder. The working electrodes were made of composite of activated carbon derived from *Borassus Flabellifer* flower, PVDF, and carbon black in the weight ratios 85:10:5, mixed in the organic solvent in n-methyl pyrrolidinone to form a slurry that was coated on a nickel foam (current collector). The AC coated electrode

was then oven-dried at 70 °C for 12 h to vaporize residual organic solvents residing in the micropores of electrodes. The mass of electrode material was 4 mg. The morphology of the activated carbon formed was akin to graphite and amorphous carbon. Activated carbons synthesized at 900 °C showed a specific surface area of 633.43 m²/g. It further showed a specific capacitance of 238.2 F/g at the specific current of 1 A/g while the conductivity at ambient temperature increased from 0.012 to 9.64 ohm⁻¹ cm⁻¹.

2.6.2 Water – Based Binders

Examples of water – based binders are; Polytetrafluoroethylene (PTFE), Sodium Carboxyl Methyl Cellulose (CMC) and Styrene – Butadiene Rubber (SBR). They have drawn interest in recent years because they permit the use of aqueous slurries in electrode processing. PTFE is a fluorinated thermoplastic that shows good resistance to different solvents, acids, bases and heat. Its electrochemical stability ensures its use with electrolytes commonly used for making SCs. In some cases, SBR and CMC can be in tandem to provide adequate adhesion. CMC being fluorine – free and easily formed into aqueous slurries presents it as an environment – friendly alternative. Li & Wu [35] fabricated SC electrodes using PTFE binder. The electrodes were prepared by combining the activated carbon derived from Water Bamboo, graphite powder and PTFE (binder) in the ratio 85:10:5 weight percentages. The active component of electrode weighed 1.2 mg. Carbon materials created at 2:1 weight ratio of KOH and pre-treated carbon exhibited excellent surface area, as high as, 2352 m²/g. In the same vein, they exhibited exceptional electrochemical performance with maximum specific capacitance of 268 F/g at a specific current of 1 A/g in 6 M KOH electrolyte and retained up to 222 F/g even at specific current of 10 A/g. In addition, the material also showed good capacity retention of 97.28% over 5000 cycles at a specific current of 10 A/g.

2.6.3 Chitosan

Rinaudo (as cited in [36]) defined chitosan as: “linear, semi-crystalline polysaccharide composed of (1→4)-2-acetamido-2-deoxy- β -D-glucan (N-acetyl D-glucosamine) and (1→4)-2-amino-2-deoxy- β -D-glucan (D-glucosamine) units”. The structure of Chitosan does not support its free occurrence but it can be extracted from the animal derived biomass, chitin.

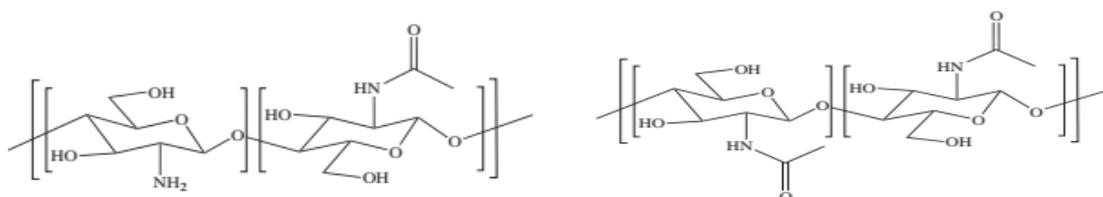


Figure 2.7 (a) Structure of Chitosan (left) (b) Structure of Chitin (right) [36]

Chitosan is touted as the most copious biopolymer after glucose [37]. It can be extracted from chitin via its partial deacetylation; in fact for the product to be considered as chitosan, the degree of deacetylation must be at least 60% [36]. Chitin obtained from the shells of crustaceans like crayfish, crabs, lobsters etc. Sivashankari & Prabakaran [38] described the extraction of chitosan from chitin in alkaline medium. According to these authors, a calculated amount of chitin is reacted with a corresponding amount of NaOH. The mixture is then stirred at intervals of half-an-hour with a magnetic stirrer upon reaching 100 °C. The idea behind the intermittent stirring during reaction is to ensure a variation of degree of deacetylation (DDA) in the product formed. Potivas & Laokuldilok (as cited by [38]) observed a linear relationship between reaction times and DDA. They synthesized chitosan with varying DDA in alkaline medium from 2 to 5 h and noticed DDA at 300 minutes was higher than that obtained at 120 minutes. Chai *et al.* [39] used chitosan as the electrode binder material for a spherical graphite anode in lithium-ion batteries. The reported enhanced electrochemical performance in terms of Coulombic efficiency, rate capability and cycling behavior compared to PVDF binder. In addition, after 200 charge – discharge cycles at 0.5 C, the capacity retention of the chitosan – based electrode was appreciably higher than that of the PVDF-based electrode.

2.7 Electrolytes

This is one of the vital components of SCs, supplying ionic conductivity and thus aiding charge compensation on each electrode in the cell [40]. The requirements for electrolytes in a SC are: wide voltage window, high electrochemical stability, high ionic concentration and low solvated ionic radius, low resistivity, low toxicity, low cost and availability at high purity [28]. In general, electrolytes are classified into aqueous electrolytes, organic electrolytes and organic liquids. Aqueous electrolytes generally provide low resistances and high ionic concentration; however, they are hampered by a low voltage window of around 1.2 – 2.0 V [40][28]. Examples are KOH, Na₂SO₄, NH₄Cl and H₂SO₄. Relative to aqueous electrolytes, organic electrolytes have voltage windows of around 3.5 V [28]. Examples of organic electrolytes are Acetonitrile, Propylene Carbonate etc. Ionic liquids are made when salts are melted to counterbalance their lattice energy. The unique properties they offer are: low vapour pressure, high thermal and chemical stability, low flammability and wide voltage window of about 4.5 V; however they have wider potential range with high conductivity in a wide temperature range [28]

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CHAPTER THREE

EXPERIMENTAL PROCEDURE AND CHARACTERISATION TECHNIQUES

3.1 Materials

Kuraray activated carbon (Model YP-50F was supplied by MTI Corporation from the USA.), chitosan (Aldrich), Acetic acid (Trust Chemical Laboratories), Polyvinylidene fluoride, Nickel foam, Acetylene black.

3.2 Preparation of the Electrode Paste

Acetic acid solution was prepared in different concentrations of 0.5, 0.75, 1, 2, 3, 4 and 5 wt. % of acetic acid in water inside a 50 ml beaker. The mixture was allowed to stir for 10 minutes at 300 rpm. The homogeneously stirred solutions were used for the preparation of the chitosan-based binders of wt. concentrations 1 and 1.2 % respectively. This was allowed to stir until all chitosan dissolved giving a homogeneous and clear viscous solution. The as-prepared chitosan binders were then used to prepare the electrode pastes in the weight percent ratio of 85:10:5 in terms of activated carbon, binder and conducting carbon; in a beaker and then allowed to stir to homogeneity [23]. Similarly, for comparison purpose electrode paste was also made from PVDF dissolved in NMP with the same ratio; in an agate mortar and then allowed to stir for homogeneity.

The prepared pastes were then neatly coated on a 1 cm² surface area of nickel foam substrates which have been previously weighed. The coated substrates were then oven-dried for 12 h at 40 °C to ensure that the electrodes were completely dried. For the full device fabrication pairs of 16 mm of coated nickel foam substrates with equal masses were then used to fabricate a coin cell device using 6 M KOH and 1 M Na₂SO₄ electrolytes respectively at an approximate mass loading of 30 mg [27]. Filter papers were used as separators for the device. The flow chart below summarises the fabrication procedure and test analysis techniques used.

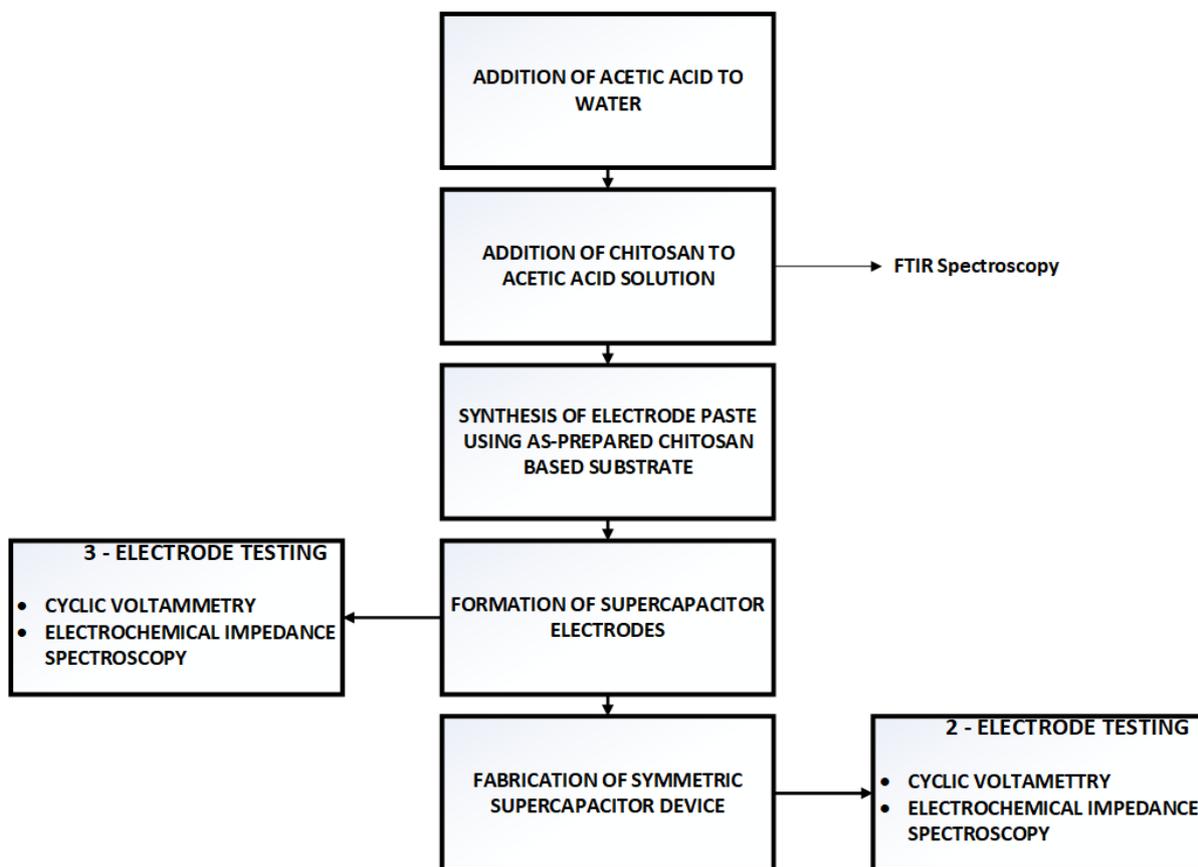


Figure 3.1: Experimental Procedure

3.3 Fourier Transform Infra-red Resonance (FTIR) Spectroscopy of Chitosan Binder

Fourier transform infra-red spectroscopy was carried out the binder prepared using a Thermo-Scientific Nicolet iS5 spectrometer within a wavenumber range of 500 – 4000 cm^{-1} [24].

3.4 Electrochemical Analysis

3.4.1 Cyclic Voltammetry (CV)

The CV measurement were carried out in three and two electrode configuration. For the 3-electrode CV was conducted using an Ag/AgCl reference electrode, graphite counter electrode and the s electrode served as the working electrode. These electrodes were immersed in 2 M KOH electrode while a Gamry reference 600 electrochemical workstation was used to supply potential across the set-up. The CV was carried out at a constant scan-rate of 30 mV s^{-1} and

potentials of -0.6 V, -0.7 V, -0.8 V and -1.0 V respectively. The specific capacitance for the 3-electrode experiment was obtained by [15]:

$$C_{SP} = \frac{Charge}{m V} \quad (3.1)$$

where; C_E = Specific Capacitance ($F g^{-1}$), Charge = Area of Voltagramm (C), m = Active Mass (g), V = Potential Window (V).

The 2-electrode CV was measured using the fabricated symmetrical devices, with a Gamry reference 600 workstation supplying the required potential. This test was carried out at scan rates of $10 mV s^{-1}$ to $100 mV s^{-1}$ and voltage varied from 0.6 V to 1.9 V; depending on the electrolyte used to fabricate the device. The specific capacitance for the 2-electrode experiment was obtained by [15]:

$$C_{sp} = \frac{4It}{m V} \quad (3.2)$$

where; C_E = Specific Capacitance ($F g^{-1}$), I is the current, t is the time, m = Active Mass (g), V = Potential Window (V). Also, the energy – density was obtained by [41]:

$$E_D = \frac{0.5 Charge V^2}{3.6 m} \quad (3.3)$$

where; E_D = Energy Density ($kWh g^{-1}$), Charge = Area of Voltagramm (C), m = Active Mass (g), V = Potential Window (V), While power – density was obtained by [41]:

$$P_D = \frac{4 V^2}{m R} \quad (3.4)$$

where; P_D = Power Density ($kW g^{-1}$), V = Potential Window (V), m = Active Mass (g), R = Equivalent Series Resistance

3.4.2 Electrochemical Impedance Spectroscopy (EIS)

The ion kinetics within the electrodes was probed using the electrochemical impedance spectroscopy (EIS) with an amplitude of 10 mV at the frequency range of 10 mHz to 100 kHz [41]. A Bode plot which the relationship between the phase angle and the frequency was obtained alongside a Nyquist which shows the relationship between the imaginary and real part of the impedance of electrode material, equivalent series resistance of device and the charge transfer resistance [28].

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CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Fourier Transform Infrared (FTIR) Spectroscopy

Figure 4.1 is the result of the FTIR spectrum conducted on the chitosan-based binder synthesised. The bands observed between $3600 - 3400 \text{ cm}^{-1}$ confirm the presence of hydroxyl and amino groups which are both present in chitosan, while acetic acid contains only a hydroxyl group [42]. The presence carbon-carbon and carbon-oxygen bands were also confirmed at wavenumbers of 1094 cm^{-1} and 1636 cm^{-1} respectively [42][24]

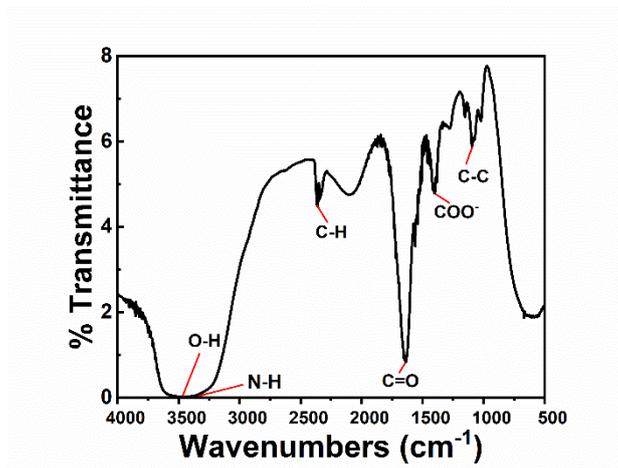


Figure 4.1: FTIR Spectra of Chitosan-Based Binder

4.2 Electrochemical analysis

4.2.1 Three (3) – Electrode Testing

The electrochemical performance of as-prepared electrodes were probed within a potential range of 0.1 V to -1.0 V at a scan rate of 30 mV s^{-1} and it was observed that chitosan-based binder at 3 wt.% Acetic Acid concentration stored the most charge. This is due to the enhancement of electrochemical energy storage with minimal pseudocapacitance contribution by this electrode [43]. Figure 4.2 shows the CVs at different potential with all CVs showing a quasi rectangular shape indicating that the produced electrodes exhibit the typical EDLCs behavior. Similar the CV were compared with the conventional PVDF that is often used for the

fabrication of electrodes and the chitosan based electrodes exhibited good electrochemical performance showing that they can be a potential replacement for PVDF. The enhancement in performance may due to the presence of the acetic acid, which might improve the conductivity of the prepared electrodes materials.

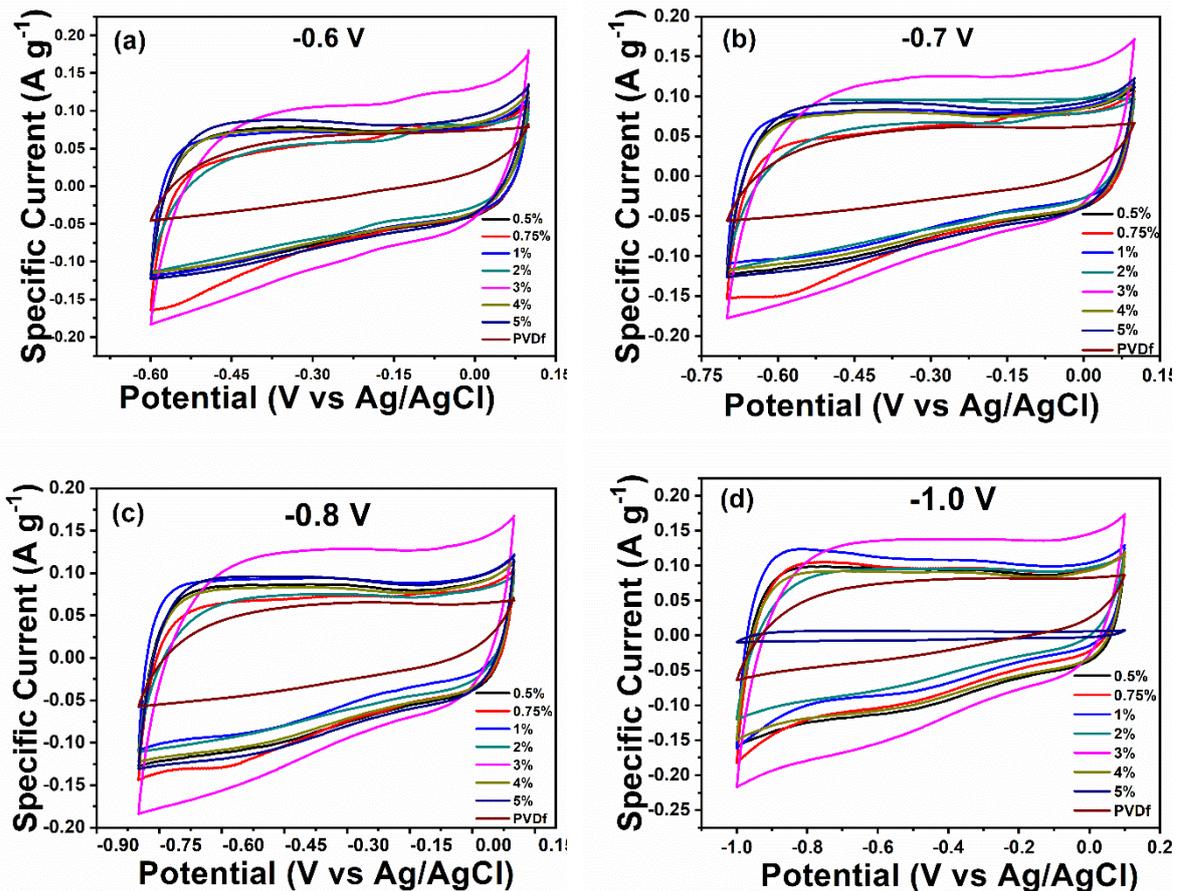


Figure 4.2: CVs of electrodes at different concentration of the chitosan binders at fixed potentials

Figure 4.3a and 4.3b shows all the concentrations as a function of the varying potential of the fabricated electrodes. All CVs obtained describe the rectangular shape for the EDLCs as the concentration was varied from 0.5 wt.% to 5 wt.%. Electrodes made with PVDF binder showed the least current and capacitance due to their tendency to leach into the electrolyte as time passes. It can be observed that as Acetic acid concentration increased from 0.5 to 1 wt. %, the

current range of the electrode increased as well, this is due to increased conductivity of the solution. Furthermore, the current response of the electrodes formed chitosan binders increased to a maximum at 3 wt.% Acetic acid concentration decrease as concentration of acid decrease.

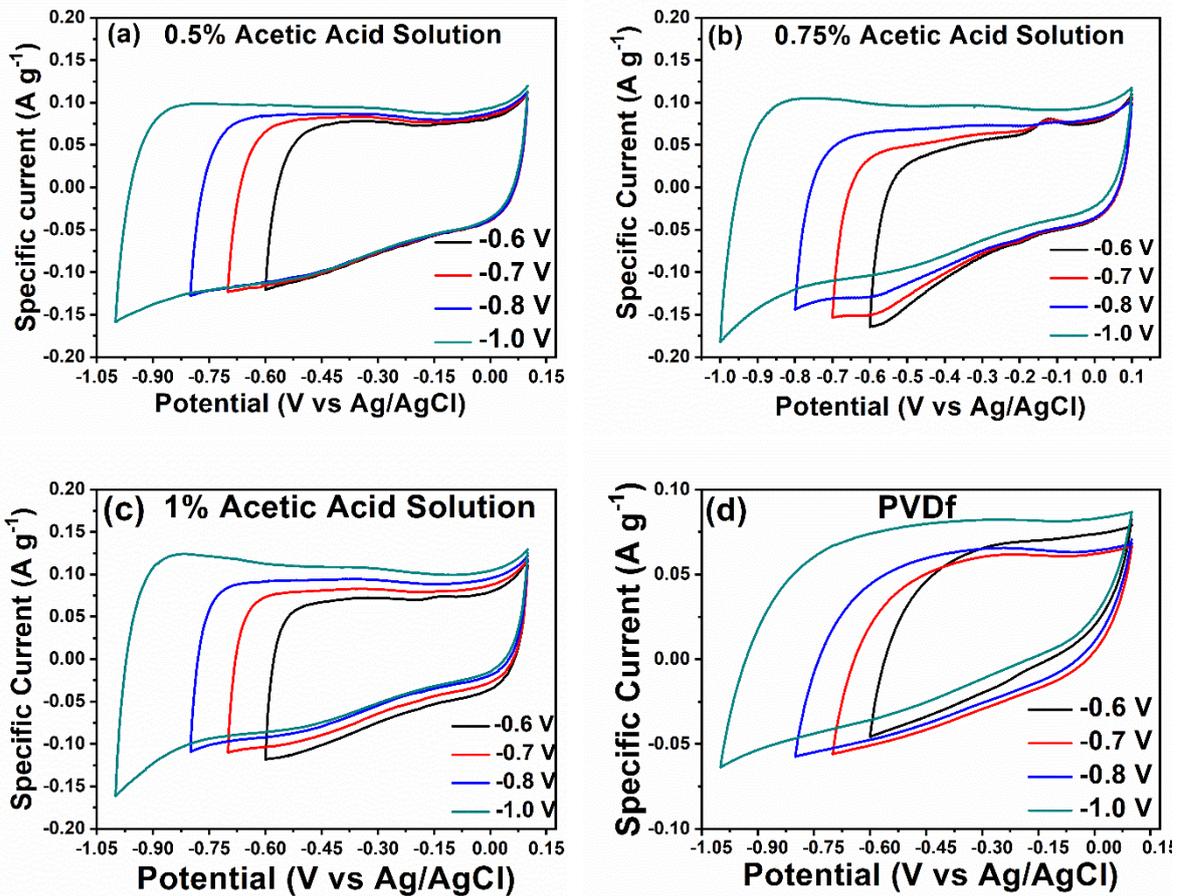
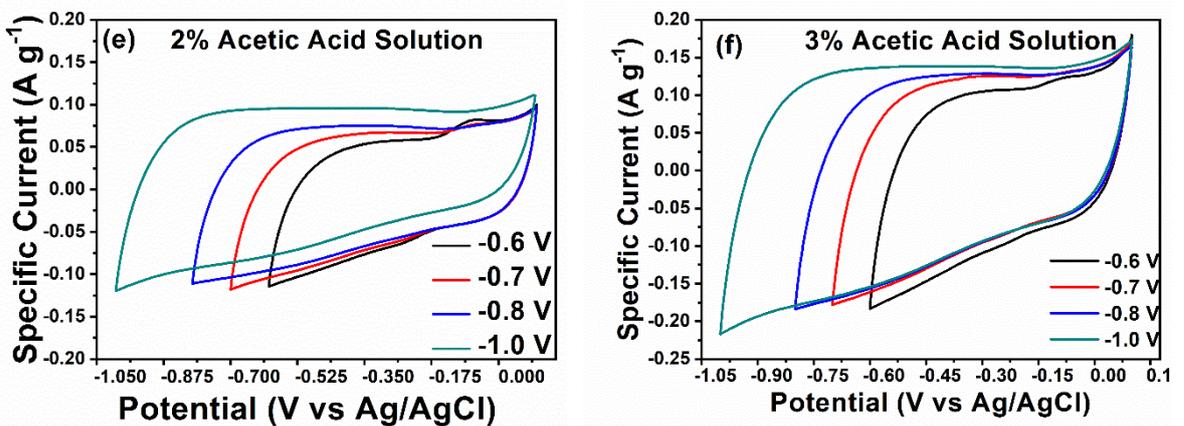


Figure 4.3a: CVs of as-prepared electrodes at different potentials



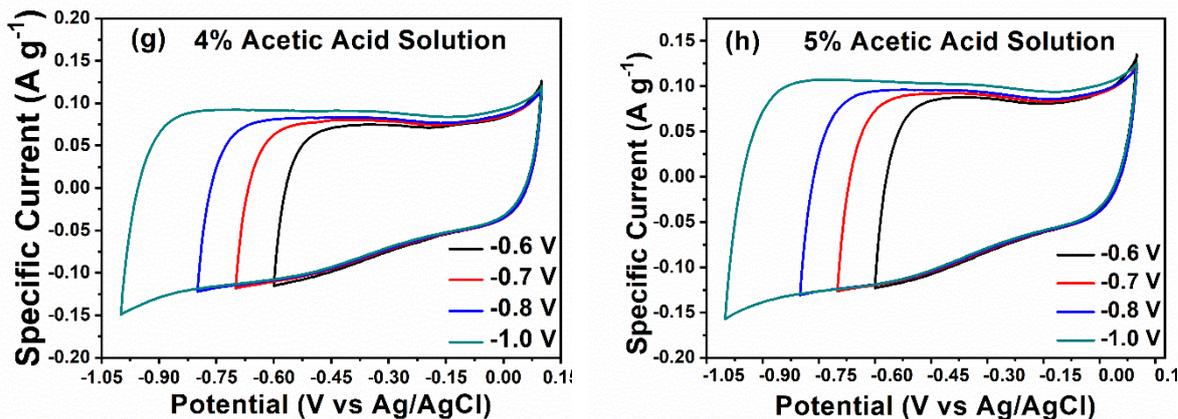


Figure 4.3b: CVs of as-Prepared electrodes at different potentials

The specific capacitances of the electrodes fabricated with Chitosan binders were all higher than that formed with PVDF binder as shown in figure 4.3c, this is because of the propensity of PVDF binders to leach into the electrolyte over time. The peak capacitance obtained was 11.32 F g^{-1} at 3% Acetic acid concentration.

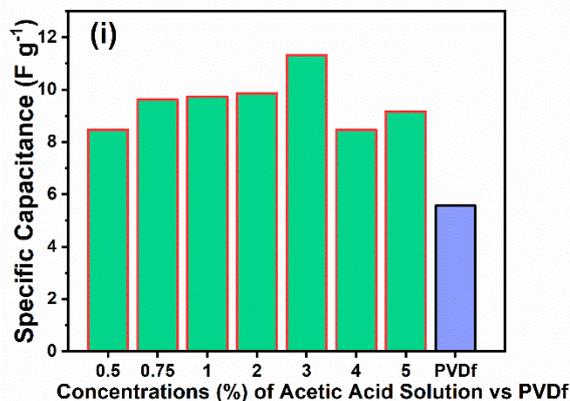


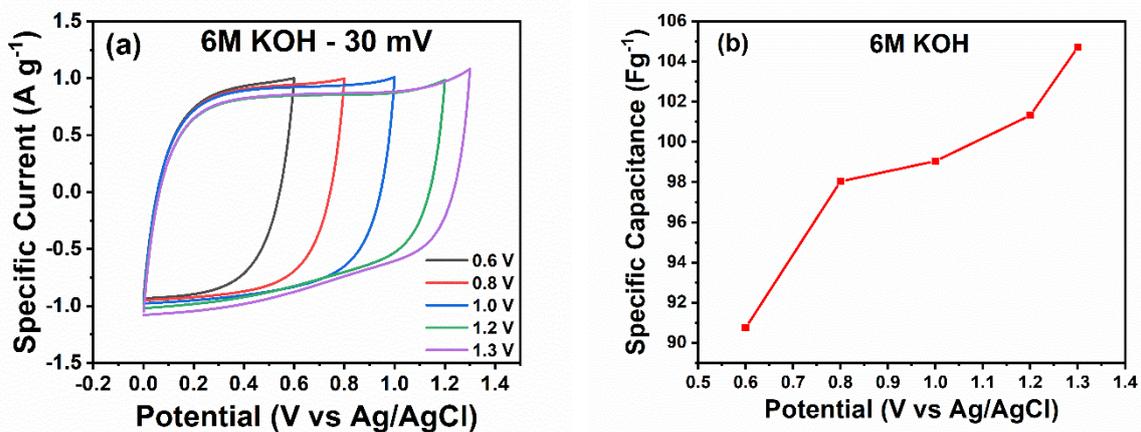
Figure 4.3c: Capacitance as a function of varying concentration and PVDF

4.2.2 Two Electrode Measurements

4.2.2.1 Device Measurement in 1 M KOH Electrolyte

Figure 4.4 (a) shows the CVs of the devices fabricated using KOH electrolyte a rectangular shape up to a voltage of 1.3 V was observed indicating a good capacitive behaviour and an

electric double-layer storage mechanism, with rapid ion/charge transport [27][24]. Figure 4.4 (b) depicts the inverse relationship between specific capacitance of the device with KOH electrolyte and the scan rates it was subjected to during the cyclic voltammetry test. The specific capacitance decreased from 113.56 F g^{-1} to 94 F g^{-1} as the scan rate increased from 10 to 100 mV s^{-1} indicating a capacitance retention of 82.7 % as the scan rate increases. This is because increasing 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 [44]. Figure 4.4 (c) displays the Nyquist plot of the EIS for a frequency range of 10 mHz to 100 kHz carried out on the device. The equivalent series resistance was found to be 0.72Ω and the charge transfer resistance for the device was approximately 1Ω . The semi-circle observed is due to the porous nature of the electrodes and resistance at the boundary between electrode and electrolyte [28]. The device displays a vertical line along the y-axis which resonates with the required capacitive behaviour with minimal resistance at the electrode/electrolyte interface [43]. Figure 4.4 (d) illustrates the Bode plot of the EIS for a frequency range of 10 mHz to 100 kHz performed on the device. The phase angle obtained is -80.76° which is close to -90° typical of ideal capacitors [27].



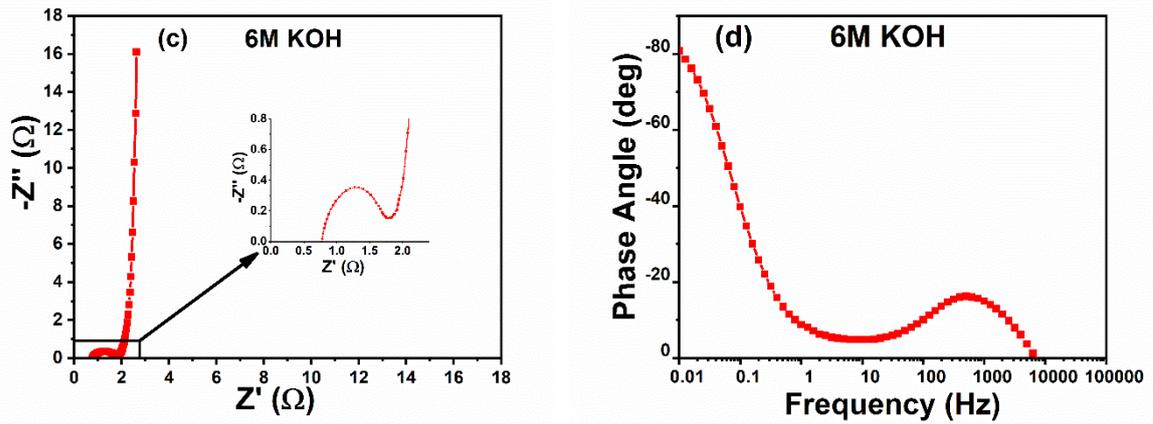


Figure 4.4: Results for Chitosan-based Supercapacitor formed with 6 M KOH Electrolyte

Figure 4.5 (a) shows the effect scan rate and fixed potential on capacitance. As the scan rate increased, the deviation from the rectangular shape of the CVs increased. This is because at higher scan rates, the charge transport became slower as a result of building equivalent series resistance [27]. Figure 4.5 (b) depicts the direct relationship between specific capacitance and potential. The charge of the device increased up to 1.3 V, which is within the potential window of KOH electrolyte.

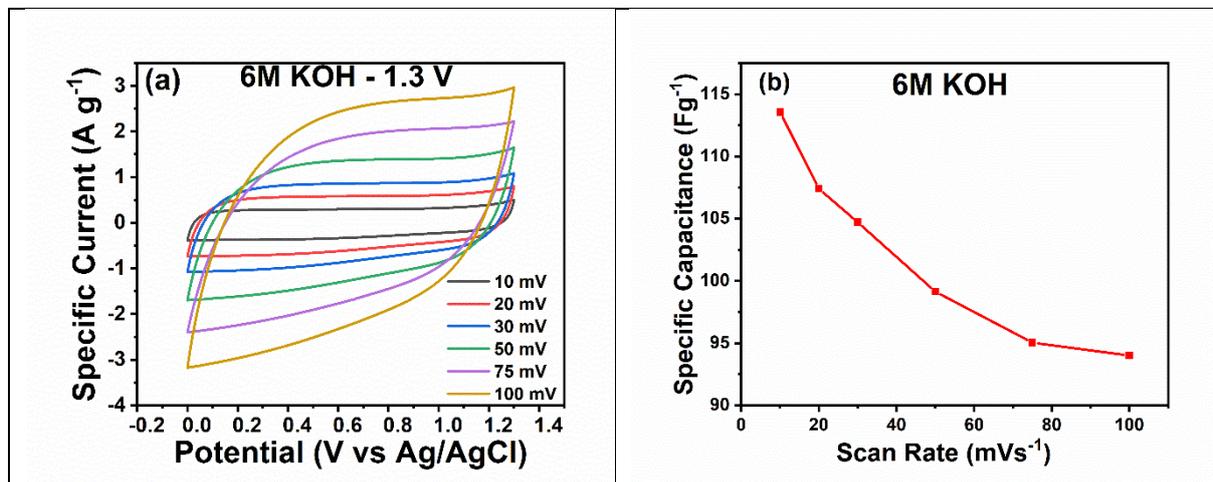
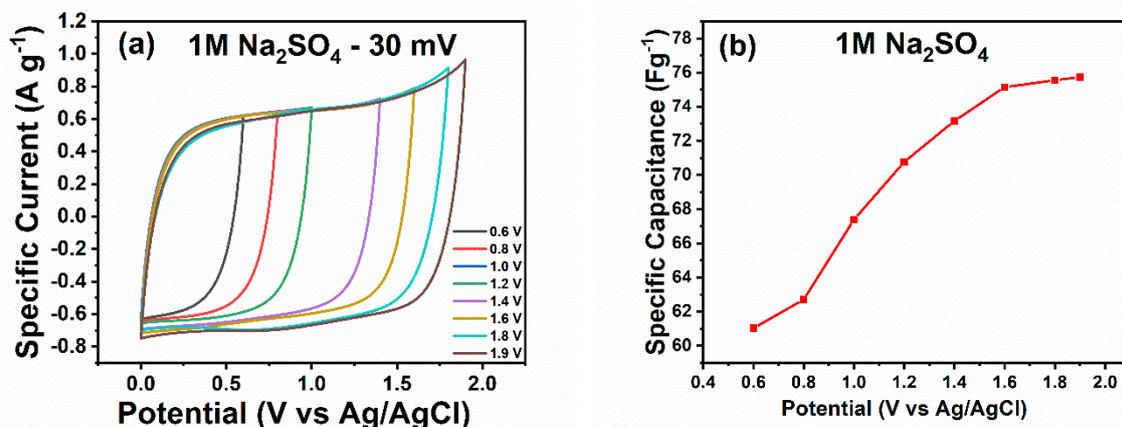


Figure 4.5: Results for Chitosan-based Supercapacitor formed with 6 M KOH Electrolyte

4.2.2.2 Devices Measurement in 1 M Na₂SO₄ Electrolyte

Figure 4.6 (a) shows the CV of the device fabricated with Na₂SO₄ displaying a rectangular shape up to a voltage of 1.9 V which indicates a good capacitive behaviour and an electric

double-layer storage mechanism, indicating rapid ion/charge transport [27][24]. Figure 4.6 (b) depicts the inverse relationship between specific capacitance of the device formed with Na₂SO₄ electrolyte and the scan rates it was subjected to during the CV test. The specific capacitance decreased from 88.42 F g⁻¹ to 65.80 F g⁻¹ as the scan rate increased from 10 to 100 mV s⁻¹ indicating a 74.4% retention. This is because increasing scan rate leads to a corresponding difficulty in the diffusion of electrolyte ions into the internal structure of electrodes. Also, the insufficient interaction between the electrolyte and materials of electrolyte results in decrease of capacitance [44]. Figure 4.6 (c) displays the Nyquist plot of the EIS for a frequency range of 10 mHz to 100 kHz carried out on the device. The equivalent series resistance was 1.72 Ω and the charge transfer resistance for the device was approximately 0.9 Ω. Which is slightly above that obtained in the KOH electrolyte this is also because of the ionic conductivity. The semi-circle observed is due to the porous nature of the electrodes and resistance at the boundary between electrode and electrolyte [28]. The device displays a vertical line along the y-axis which resonates with the required capacitive behaviour with minimal resistance at the electrode/electrolyte interface [43]. Figure 4.6 (d) illustrates the Bode plot of the EIS for a frequency range of 10 mHz to 100 kHz performed on the device. The phase angle obtained is -76.48° which is close to -90° typical of ideal capacitors [27].



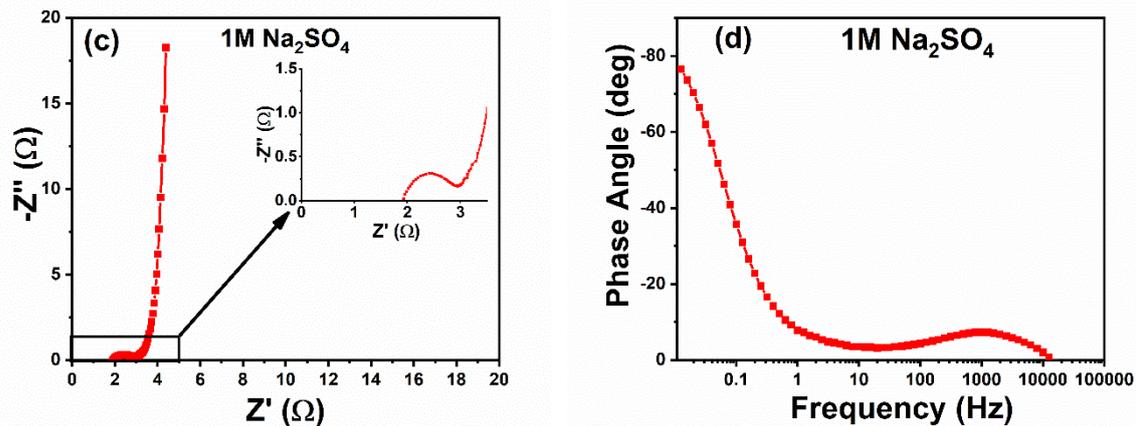


Figure 4.6: Results for Chitosan-based Supercapacitor formed with 1 M Na₂SO₄ Electrolyte

Figure 4.7 (a) shows the relationship between scan rate and fixed potential on capacitance. As the scan rate increased, the deviation from the rectangular shape of the CVs increased. This is because at higher scan rates, capacitance become hampered by insufficient diffusion due to the effect of polarisation [23]. Figure 4.7 (b) depicts the direct relationship between specific capacitance and potential. The charge of the device increased up to 1.9 V, which is within the potential window of Na₂SO₄ electrolyte.

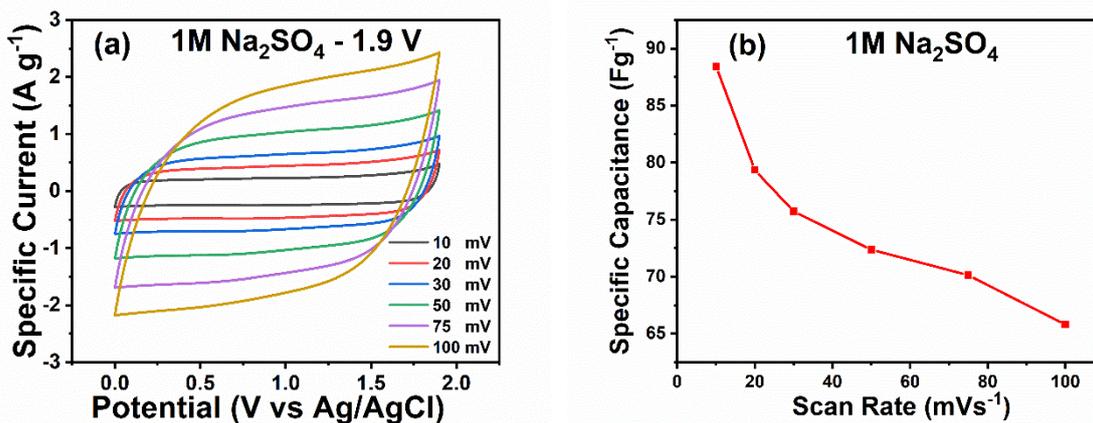


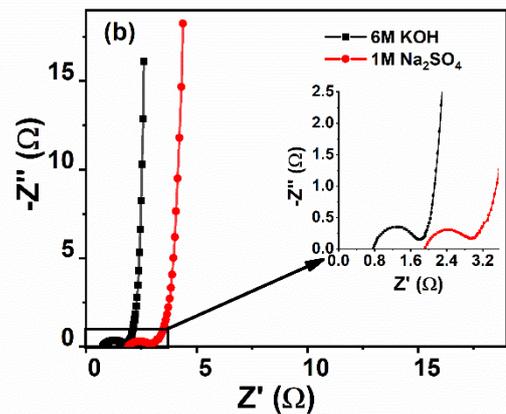
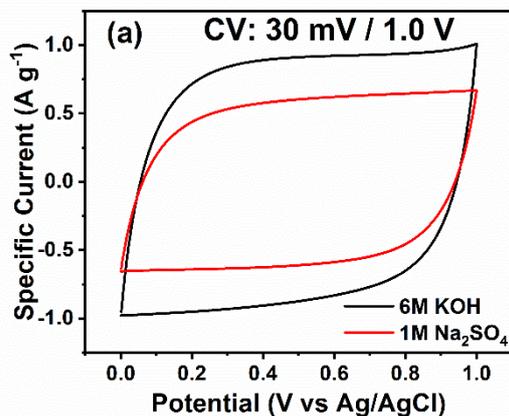
Figure 4.7: Results for Chitosan-based Supercapacitor formed with 1 M Na₂SO₄ Electrolyte

4.2.3 Comparison between KOH and Na₂SO₄ Electrolytes

Figure 4.8 (a) compares the CV of devices made with KOH and Na₂SO₄ electrolytes at a voltage of 1.0 V. The device made with KOH electrolyte showed higher specific capacitance

because of the higher ionic conductivities of alkaline electrolytes and compare to that made with Na_2SO_4 showed an operating voltage window of 1.9 V due to its increased stability [40].

Figure 4.8 (b) relates Nyquist plots from the EIS of the devices formed. While the device made with 6 M KOH electrolyte showed a lower equivalent series resistance of 0.72Ω , the one made with 1 M Na_2SO_4 displayed a lower charge transfer resistance of 0.9Ω . The higher equivalence series resistance observed with Na_2SO_4 electrolyte can ascribed to the increased polarisation of the electrodes in the electrolyte [39]. Figure 4.8 (c) displays Bode plots from the EIS of the devices formed. Devices formed with KOH and Na_2SO_4 electrolytes displayed satisfactory phase angles of -80.76° and -76.48° respectively, which is, close the -90° phase angle of ideal capacitors. Figure 4.8 (d) gives the Ragone plot of the devices fabricated. The device formed with Na_2SO_4 electrolyte gives a maximum energy density of 18.04 kWh/g while that fabricated with KOH yielded a peak energy density of 7.98 kWh/g . The higher energy density displayed by Na_2SO_4 is a result of its large operating voltage of 1.9 V.



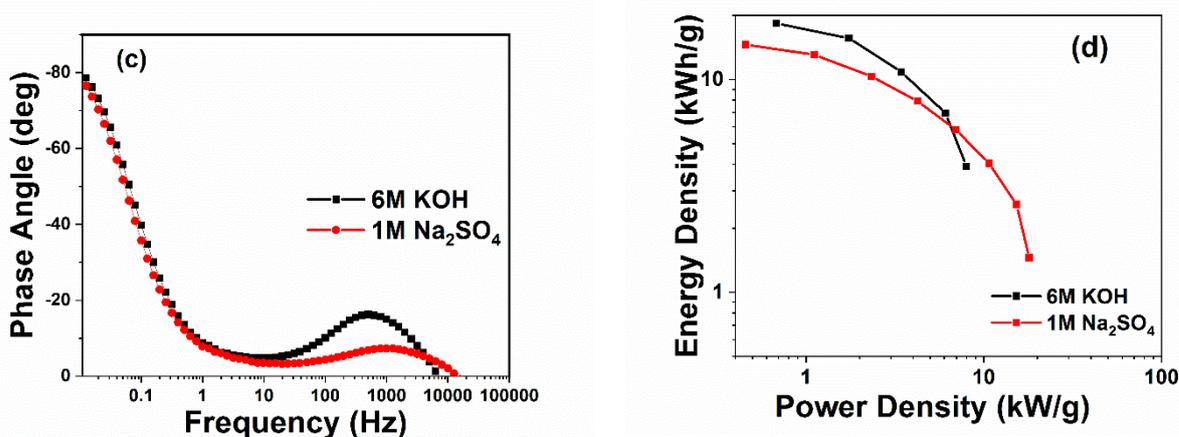


Figure 4.8: Results for Chitosan-based Supercapacitor formed with 6 M KOH and 1 M Na₂SO₄ Electrolytes

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CHAPTER FIVE

CONCLUSION AND RECOMMENDATION(S)

5.1 Conclusion

Electrochemical capacitor electrodes were fabricated with PVDF, and Chitosan binders at varying acetic acid concentrations. A 3 wt. % concentration acetic acid and the Chitosan binder exhibited the highest specific capacitance. Electrochemical devices fabricated in aqueous electrolytes exhibited a specific capacitance of 113.56 F g^{-1} with energy density of 7.98 kWh g^{-1} in 6 M KOH. While a specific capacitance of 88.42 F g^{-1} and energy density of 18.04 kWh g^{-1} in 1 M Na_2SO_4 . The phase angles were measured to be -80.76° and -76.48° in both electrolytes, which are close -90° for ideal capacitive system. Bioactive polymers such as Chitosan, can conveniently serve as an alternative to the Fluoro-thermoplastic that are conventionally used.

5.2 Recommendation(s)

This work was constrained to probing the suitability of a bioactive polymer, Chitosan, as an alternative binder in electrochemical capacitors. Investigating the compatibility of chitosan-based activated carbons and binder electrochemical capacitors. This would greatly help towards achieving a totally green device and the environmental benefits that accrues to that. Furthermore, the cycle life and stability of devices form should be probed in a galvanostatic charge/discharge (GCD) test to have an idea of their suitability in real time.