

SOLID-STATE ELECTROLYTE FOR SUPERCAPACITORS

by

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Abstract

Renewable energy has become a primary focus for scientific community since last decade. Great interesting investigations and creative works have been carried out to develop technology for powering our society, including disrupt technology for efficient energy storage and power manage. Supercapacitors (SP) also known as electrochemical double layer capacitors uses high surface area active electrode materials and various electrolytes to achieve capacitance of several order magnitude greater than the conventional capacitor, which allows energy density greater than that of conventional capacitors and power density greater than that of batteries. Electrolyte with suitable properties like high Conductivity, Thermal and Mechanical Stability, high charge Mobility, wide Electrochemical Stability Window (ESW) and compactible active electrodes are required for supercapacitors of high performance.

In this thesis work, our aim is to develop solid state electrolyte for high working voltage supercapacitors. First, gel polymer is prepared by using the poly vinylidene fluoride co-hexafluoropropylene (PVDF-HFP) with Acetonitrile and ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) and 1-ethyl-3-methylimidazolium dicyanamide (EMIM-DCA). Second, ion conducting promoters, such as, Zeolite and reduced Graphene oxide were added. The polymer electrolytes are characterized by a simple supercapacitor configuration, in which the active electrodes are prepared by mixing the Multiwalled Carbon Nanotube (MWCNT), PVDF-HFP and acetylene black/carbon black (CB), and Graphite sheet (GS) is used as current collector. The polymer electrolyte is sandwiched in the structure. The electrochemical working station is applied for the performance measurements. We obtained different characteristics of the supercapacitors, listed as, impedance spectroscopy, ion conductivity, ESW, and cyclic voltammetry (CV).

Preface

This thesis is submitted in partial fulfilment for the requirement in master degree from the Department of Micro and Nano System Technology in Faculty of Technology and Maritime Science at Høgskolen i Sørøst Norge.

This work has been conducted from September 2015 to December 2016 at the department of Micro and Nano System Technology at Høgskolen i Sørøst Norge.

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Acronyms

AB	Acetylene Black
CE	Counter electrode
CNTs	Carbon nanotubes
CV	Cyclic voltammetry
DSC	Differential Scanning Calorimetry
EDLC	Electrochemical double layer capacitor
EIS	Electrochemical Impedance Spectroscopy
EMIM-BF ₄	1 ethyl 3 methylimidazolium tetrafluoroborate
EMIM-DCA	1 ethyl 3 methylimidazolium dicyanamide
ESR	Equivalent series resistance
ESW	Electrochemical Stability Window
IL	Ionic Liquid
MWCNT	Multiwalled carbon nanotube
NE	Not Extractable
PVDF-HFP	Polyvinylidene fluoride-hexafluoropropylene
RE	Reference Electrode
rGO	reduced Graphene oxide

SE	Sense electrode
SEM	Scanning Electron Microscopy
SOHIO	Standard Oil of Ohio
SS	Stainless Steel
SWCNTs	Single-walled carbon nanotubes
WE	working electrode

Chapter 1 INTRODUCTION

1.1 Background

Limited amount of fossil fuel is one of the major concern for the world energy consumption. Renewable energy technology is only solution for sustainable development of our human being. One of challenge for using the renewable energy is the relocation and power management of the generated renewable energy. Portable electronics is increasing [1]. Energy storage by using electrochemical principles has been taken into serious consideration as long as which is the environment friendly technology. Electrochemical energy storage devices like batteries, fuel cells and electrochemical capacitors are widely used at moment. Electrochemical capacitors also known as electrochemical double layer capacitor (EDLC) or super capacitors. Comparing their characteristics, batteries have high energy density but low power density, fuel cells have high energy density but low power density, hybrid EDLCs have improved energy density and high power density.

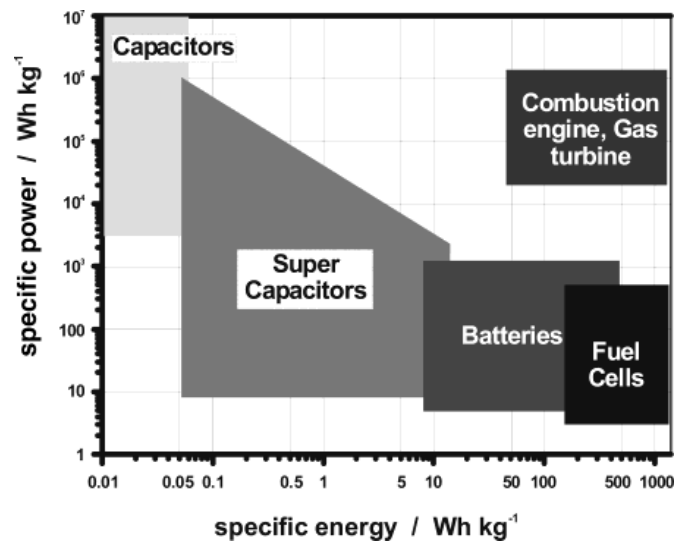


Figure 1: Ragone plot of various energy storage devices [2].

Solid-state Electrolyte for Supercapacitors

Fundamentally, high power density enables supercapacitor providing very short charging and discharging time with low equivalent series resistance. For the EDLCs, they own high working life cycle and great temperature performance. Thus supercapacitor fills the gap between conventional capacitor and batteries. Table 1 also shows that supercapacitors can work in extreme environmental condition better than conventional capacitor and batteries.

Table 1. Comparison of supercapacitor, capacitor and battery [3].

Parameter	Supercaps	Capacitors	Batteries
Energy Storage	W-sec of energy	W-sec of energy	W-Hr of energy
Charge Method	voltage across terminals	voltage across terminals	Constant current & constant voltage
Power Delivered	rapid discharge, linear or exponential voltage decay	rapid discharge, linear or exponential voltage decay	constant voltage over long time period
Charge/Discharge Time	msec to sec	psec to msec	1 to 10 hrs
Form Factor	small	small to large	small to large
Weight	1g to 2g	1g to 10kg	1g to >10kg
Energy Density	1 to 5Wh/kg	0.01 to 0.05Wh/kg	8 to 600Wh/kg
Operating Voltage	2.3V – 2.75V/cell	6V – 800V	1.2V - 4.2V/cell
Lifetime	>100k cycles	>100k cycles	150 to 1500 cycles
Operating Temp	–40 to +85°C	–20 to +100°C	–20 to +65°C

Solid-state Electrolyte for Supercapacitors

1.2 Supercapacitor History

From early 1950s, experimentation on porous carbon electrode began for the design of capacitors. By 1957, H. Becker developed the low voltage capacitor with porous carbon electrodes. Further in 1966 researchers at Standard Oil of Ohio (SOHIO) developed advanced version (capacitors) with higher energy density by using double layer capacitance of high area carbon material [4-6]. By 1978, the market expanded slowly and the product was used as successful device for supplying backup power application [7]. Panasonic began to manufacture the device naming “Goldcaps”. At the moment they were introduced to replace non reliable batteries. Panasonic used non – aqueous electrolyte and pasted electrode which give benefit of operating at higher potential [7].

Pseudo capacitors were developed in the period of 1975-1981. By 2006 various electronic system began to use ultra-capacitors Boost cap to provide emergency power backup purpose. Recently huge development on supercapacitors are done and still have possibility to explore more. Various electronics companies are investing more in the development of this supercapacitor field [8].

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1.3 Supercapacitor Classification

Supercapacitors are basically classified into two major categories i.e. Electric Double Layer Capacitors (EDLC) and Pseudocapacitors. Hybrid Capacitors are those which attempt to exploit the advantages and mitigate the relative disadvantages of EDLC and Pseudocapacitors. Hybrid Capacitors have achieved energy and power densities greater than EDLC's without sacrificing cyclic stability and affordability limiting the success of the Pseudocapacitors.

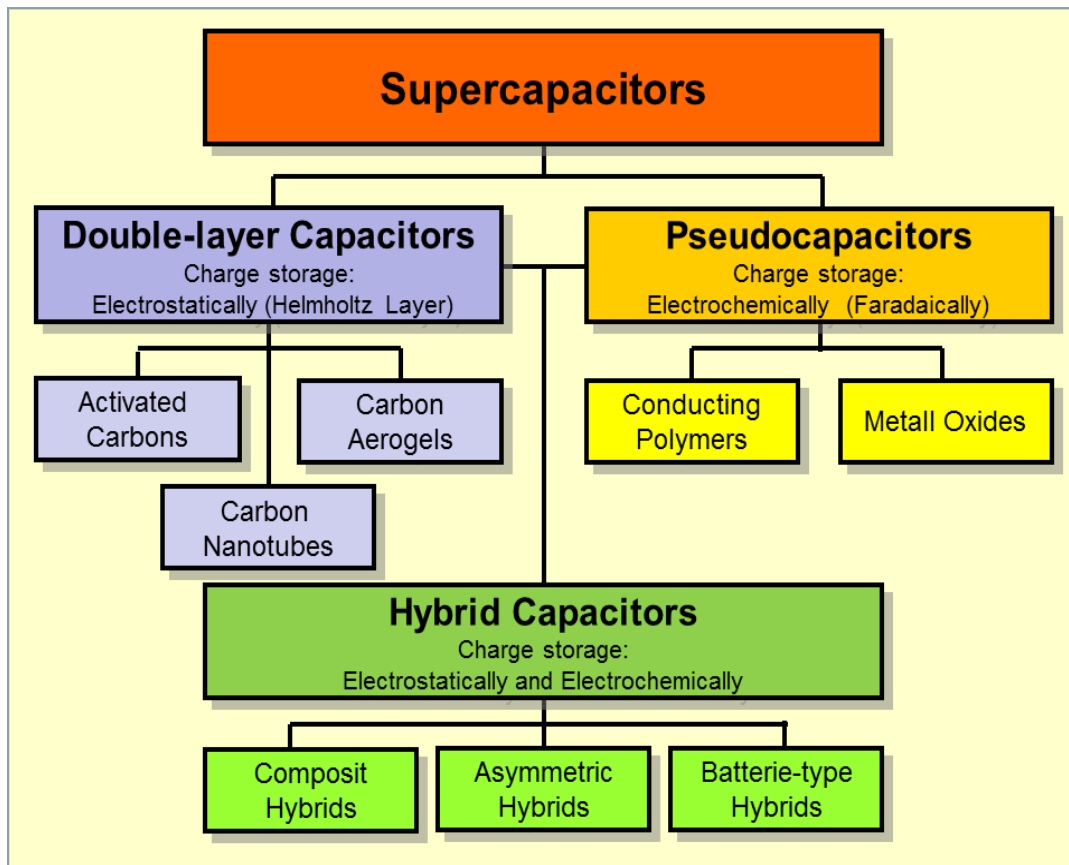


Figure 2: Supercapacitors classification [9].

Solid-state Electrolyte for Supercapacitors

Since late 1950s different types of Supercapacitors has been developed using different electrode and electrolyte material. Different form of carbon material like carbon aerogels, fibers, activated carbons and carbon nanotubes are being used because of their very convincing properties like high conductivity, high surface area, high temperature stability and other good properties [10]. EDLC does not contain any conventional dielectric. But an electrolyte (solid or liquid) is filled between the two electrodes. In EDLC electric double layer (also known as Helmholtz double layer) is formed between the electrodes and electrolyte which works as dielectric. Charging and discharging is caused by the process of ion absorption and desorption to the electric double layer.

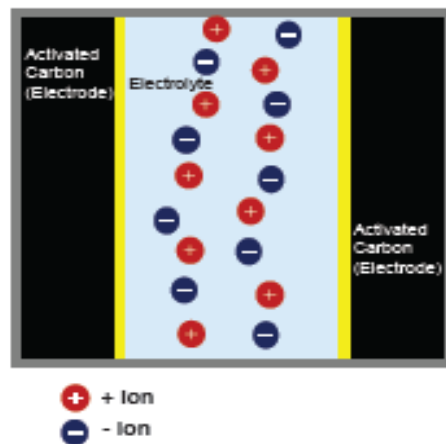


Figure 3: EDLC supercapacitor model [11].

While EDLC store charge electrostatically, Pseudocapacitors store charge Faradaically through the transfer of charge between electrode and electrolyte. This is accomplished by electro absorption, reduction-oxidation reaction and intercalation processes. Pseudo capacitor uses transition metal oxides (like RuO_2 , NiO , MnO_2 etc.) and polymers [12].

Solid-state Electrolyte for Supercapacitors

1.4 Solid-state Polymer Electrolyte in Brief

Polymer is derived from the Greek word “poly” and “meros” is a large molecules (or macromolecules) which basically means “many” and “parts” respectively. Polymer composed of repeating structural units connected by covalent chemical bonds. Polymers may be natural or synthetic both created by the process of polymerization of small monomers. They can be classified into different categories as

- Insulating polymers
- Semi-conducting polymers
- Ion conducting polymers or polymer electrolytes [13].

The choice of electrolyte in an EDLC is as important as the choice of electrode material. The capacitance of an EDLC is greatly influenced by the choice of electrolyte. Primarily there are two types of electrolyte in use in EDLCs: organic and aqueous. An electrolyte is a substance that is capable of producing conducting medium when dissolved in polar solvent. Conducting polymers are very good candidate for supercapacitor application because of their properties like good electrical conductivity, large pseudocapacitance and low cost. The attainable cell voltage of a supercapacitor will depend on the breakdown voltage of the electrolyte, and hence the possible energy density (which is dependent on voltage) will be limited by the electrolyte. Power density is dependent on the cell's ESR, which is strongly dependent on electrolyte conductivity [14].

The ability to store charge is dependent on the accessibility of the ions to the porous surface-area. So ion size and pore size must be optimal. The best pore size distribution in the electrode depends upon the size of the ions in the electrolyte, so both electrode and electrolyte must be chosen together.

Solid-state Electrolyte for Supercapacitors

Solid state capacitor is superior to liquid state capacitor because of the robustness and no need of encapsulation. Various polymers are used for supercapacitor but commonly used polymers are polyaniline (PANI), polypyrrole(PPY), poly[3,4-ethylene dioxythiophene](PEDOT) , polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) etc. Conducting polymers have large specific capacitance but poor mechanical stability due to interaction and depletion of ions during charging and discharging [15-16].

Solid-state Electrolyte for Supercapacitors

1.5 Thesis ambition

In this project, for solid polymer electrolyte for supercapacitor my tasks are

- Study for the solid state polymer electrolyte
- Design material system for making polymer based solid state electrolyte
- Experimental setup design, synthesis process development, fabrication of polymer electrolyte and characterization
- Optimization and improvising the performance of electrolyte
- Assembly and characterization of the device

Chapter 2 EQUIPMENT AND MATERIALS

2.1 Equipment and Materials

In this chapter, all the things that are preliminary requirement of the experimental process will be introduced. In order to perform the experimental process for the solid state polymer supercapacitor, we selected certain materials (or chemical materials) along with proper measurement devices as per the availability.

Chemicals like methanol, acetone and acetonitrile are used. Methanol or acetone is used to prepare electrode (slurry) while acetonitrile is used to synthesize the polymer film. Ionic liquid DMPIM-TFSI {1, 2 Dimethyl-3-propylimidazolium bis(trifluoromethyl sulfonyl)imide} has been used prior to the experiments and finally, comparison of the results between the ionic liquid EMIM-BF₄ (1 ethyl 3 methylimidazolium tetrafluoroborate) and EMIM-DCA (1 ethyl 3 methylimidazolium dicyanamide) was carried out.

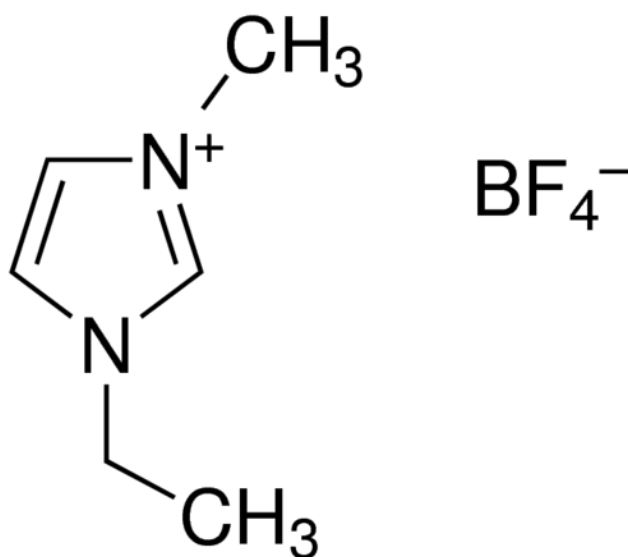


Figure 4(a): Structure of EMIM-BF₄ [17].

Solid-state Electrolyte for Supercapacitors

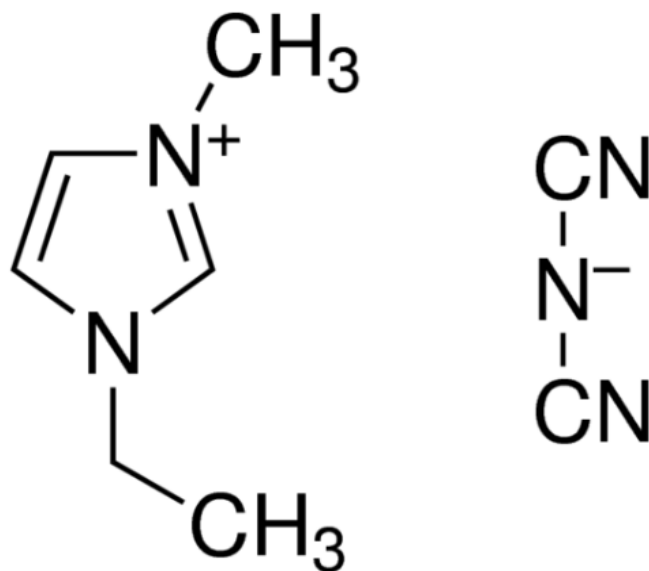


Figure 4(b): Structure of EMIM-DCA [18].

Materials like MWCNT (Multiwalled carbon nanotube), AB (Acetylene black), Graphite sheets and PVDF-HFP (Polyvinylidene fluoride-hexafluoropropylene) has been used to synthesize the electrolyte and electrode materials.

Mechanical clamping was used to hold the supercapacitor in between the two brass sheets to carry out the measurement on the impedance measurement unit (ZAHNER IM6, USA) which is supported by computer controlled Thales software. Leica optical microscope (Discovery.V12) was used to measure the thickness of the polymer films prepared for the supercapacitor application.

Solid-state Electrolyte for Supercapacitors

2.2 Properties of Materials

Chemicals like acetone and acetonitrile are used to prepare electrode and electrolyte material because of their friendly properties like volatility, which helps to dissolve the materials and afterwards will be removed from the mixture easily upon itself.

Some important properties of Ionic Liquid (IL) are listed below

- Low melting point
- Electric conductivity
- Interesting solvent properties
- High crystalline structure
- High electro elasticity
- High heat capacity
- Non-volatile
- Non-flammable
- Thermal stability
- Wide ESW (Electrochemical Stability Window) [19, 27].

Acetonitrile is a colorless liquid with sweet, ethereal odor. It is a hazardous chemical substance but with appropriate safety procedure no excessive danger from the chemical exists. Contact of this chemical with skin may cause irritation and short term consciousness or death if inhaled according to the concentration. Thus, use of this chemical was always used under the fume hood [20]. Acetonitrile (K43596703 250 EMSURE) was used for the experiment.

Carbon nanotubes (CNTs) are very attractive materials for electrode for capacitor. The most promising characteristics as electrode material for capacitor is not just their large surface area and storage spaces for electrolyte ions, but also their high electrical conductivity. Structurally MWCNTs consists of multiple layers of graphite superimposed

Solid-state Electrolyte for Supercapacitors

and rolled in themselves to form a tubular shape. Although single-walled carbon nanotubes (SWCNTs) have higher specific capacitance than MWCNTs due to larger effective surface area per unit mass but the high cost of SWCNT limits their feasibility for device applications. MWCNT have lower surface area than activated carbons, but their open pore structures allows faster charging and discharging. This leads to better power performance. Higher electrical conductivity of MWCNT facilitates further increase in power density as well [20, 21]. Carbon nanotube, multi-walled (724769-25G) >95% carbon content was used for the experiment.

Acetylene Black (AB) special type of carbon formed by an exothermic decomposition of acetylene. They are the purest form of carbon black. AB are highly absorptive and electrically and thermally conductive because of its unique three dimensional structure. It can absorb up to eight times its weight in liquid [23].

PVDF-HFP is one solid polymer electrolyte material which is used to synthesize the gel polymer electrolyte for the supercapacitor. Some Important properties of this polymer are listed below.

- High dielectric constant (8.4)
- Low crystallinity
- Help improve conductivity
- Low glass transition temperature
- Excellent chemical stability and plasticity [24, 25].

Zeolite are microporous aluminosilicate minerals commonly used as commercial adsorbent and catalysts. Zeolite have porous structure that can accommodate a wide variety of cations such as Na⁺, K⁺, Ca²⁺, Mg²⁺ and others. These ions are loosely bound and can easily be exchanged for others in contact [26]. Zeolites (96096-100G) particle with <45 µm size particles (powder form) was purchased from Sigma Aldrich, USA.

Solid-state Electrolyte for Supercapacitors

Graphene oxide is a by-product when oxidizing agents react with graphite, the interplanar spacing between the layers of graphite is increased. This completely oxidized compound can then be dispersed in a base solution such as water and graphene oxide is then produced. Graphene oxide and reduced Graphene oxide (rGO) has attracted research interest in recent years because of their exceptional properties [27, 28]. Graphene oxide (796034-1G, 4-10% reduced) with 1.8 gm/cm³ bulk density and 15-20 layer thickness powder was purchased from Sigma Aldrich, USA. Highly conductive rGO (600S/m) was unavailable at that moment.

Ionic liquid is basically a salt in liquid state. Some important properties of ionic liquids are low melting point, non-volatile, non-flammability, high thermal stability and wide electrochemical stability window. Both ionic liquids EMIM-DCA (00796-50G-F) and EMIM-BF₄ (711721-100G) $\geq 98\%$ purity were purchased from Sigma Aldrich, USA. PVDF-HFP (427160-100G, average molecular weight $M_w=400,000$) polymer was also purchased from Sigma Aldrich.

Flexible Graphite sheets with thickness of 0.5 mm, 99.8% purity was purchased from Goodfellow Cambridge limited, England for the experimental purpose.

Solid-state Electrolyte for Supercapacitors

2.3 Selection of Materials

Wide range of materials (or chemicals) are available in the market. Considering the requirement and theoretical research some materials were selected to perform the experiment.

Since this thesis is about the synthesis of the solid polymer electrolyte, one of the major task is to select the suitable polymer material. Various polymer materials has been used in the past but most commonly used are Polyniline (PANI), polypyrrole (PPY), poly[3,4-ethylene dioxythiophene] (PEDOT), polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) etc. But based upon the recent findings and experiments based on the ionic liquid incorporated polymer electrolytes based solid state electrical double layer capacitors (supercapacitors) some conclusion have been made. From the study, it is found out that PVDF-HFP based gel electrolytes perform better than PEO based and other electrolytes. The nonpolar nature of the PVDF-HFP gels provide structural integrity, and also allows the formation of high ionically conductive channels. Thus it offers their suitability as electrolytes in supercapacitor. Dielectric breakdown is a vital process parameter which needs to be addressed for using an insulating material under an external applied field which may result in mechanical damage and electrical conduction in the polymer material [25, 29- 30].

PVDF-HFP is not good considering the ion conducting properties but more behaves like resistive. Some ion conducting materials like ionic liquid are usually added with it to form a suitable polymer electrolyte having good conducting properties as well. Ionic liquids have high ionic conductivity along with wide chemical window and non-toxicity which makes them excellent electrolyte material. Mainly used ionic liquid for studying supercapacitors are imidazolium, pyrrolidinium and asymmetric aliphatic quaternary ammonium salts of anions such as tetrafluoroborate(BF_4), trifluoromethanesulfonate(Tf), bis(trifluoromethanesulfonyl)imide (TFSI/BTA), bis(fluoromethanesulfonyl)imide (FSI),

Solid-state Electrolyte for Supercapacitors

and hexafluorophosphate(PF_6) which have wider ESW than conventional organic electrolytes. Some ionic liquids are compared here based upon their viscosity, conductivity and ESW properties which are listed in the pictures below.

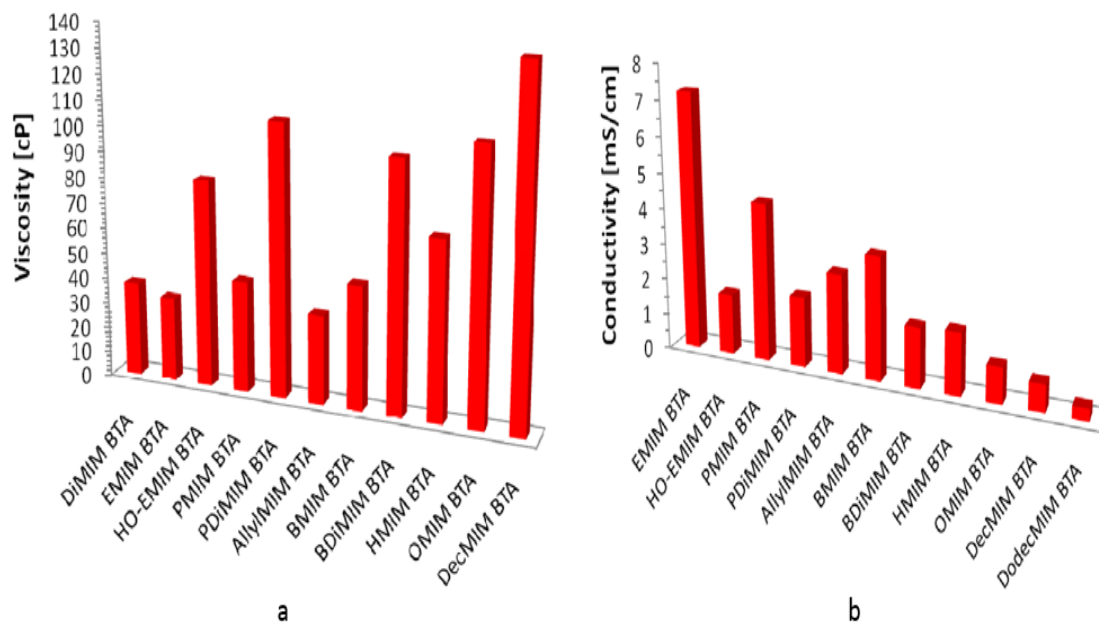


Figure 5: Viscosity and conductivity comparison of the BTA [31].

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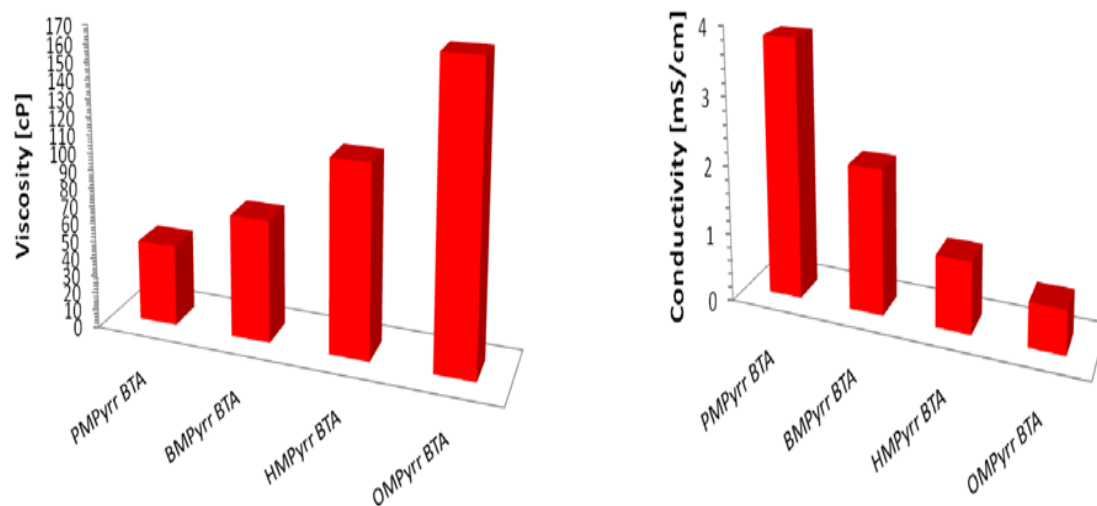


Figure 6: Viscosity and conductivity comparison of the Pyrrolidinium based BTA [31].

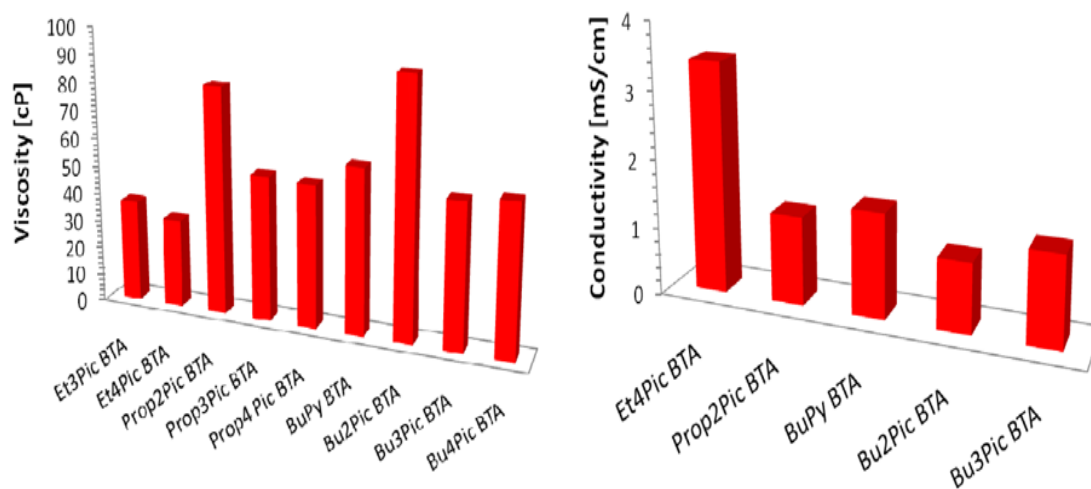


Figure 7: Viscosity and conductivity comparison of the Pyridinium based BTA [31].

Solid-state Electrolyte for Supercapacitors

From Figure 5, we can observe that despite little high viscosity EMIM-BTA have relatively higher conductivity. And from study it is also known that it has ESW of nearly 4.9V with electrode of silver/silver chloride. Figure 6 shows the comparison of the Pyrrolidinium based TFSI which have relatively higher viscosity and low conductivity compared to the EMIM-BTA. In Figure 7, we compared the pyridinium based BTA still they have lower conductivity despite comparable viscosity. From the Figures 5 to 7, we saw that EMIM-DCA has higher conductivity with lower viscosity. And EMIM-BF₄ which has relatively higher conductivity and comparable viscosity compared with the other ILs beside EMIM-DCA. These two ionic liquids were selected for the experiment and do further process to increase the conductivity of the film.

Table 2. Comparison of viscosity and conductivity of some ionic liquids [31].

Ionic liquids	Viscosity (cp)	Conductivity (mS/cm)
EMIM-DCA	19.4	25.3
EMIM-BF ₄	27	12
EMIM-BTA	33	6
EMIM-OTF	38.9	12

More comparison of conductivity and ESW of some ionic liquids based on EMIM, 1-butyl-3-methylimidazolium (BMIM), N-diethyl-N-methyl(2-methoxyethyl)ammonium (DEME), N-butyl-N-methyl-pyrrolidinium (PYR₁₄), N-methyl-N-propyl-pyrrolidinium (PYR₁₃), and N-methoxyethyl-N-methylpyrrolidinium cations with different anions at room temperature is shown in Figure 8 [32]. Based upon the all the review of the literatures

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and possibility EMIM-BF₄ and EMIM-DCA were selected to study and characterize the solid polymer electrolyte.

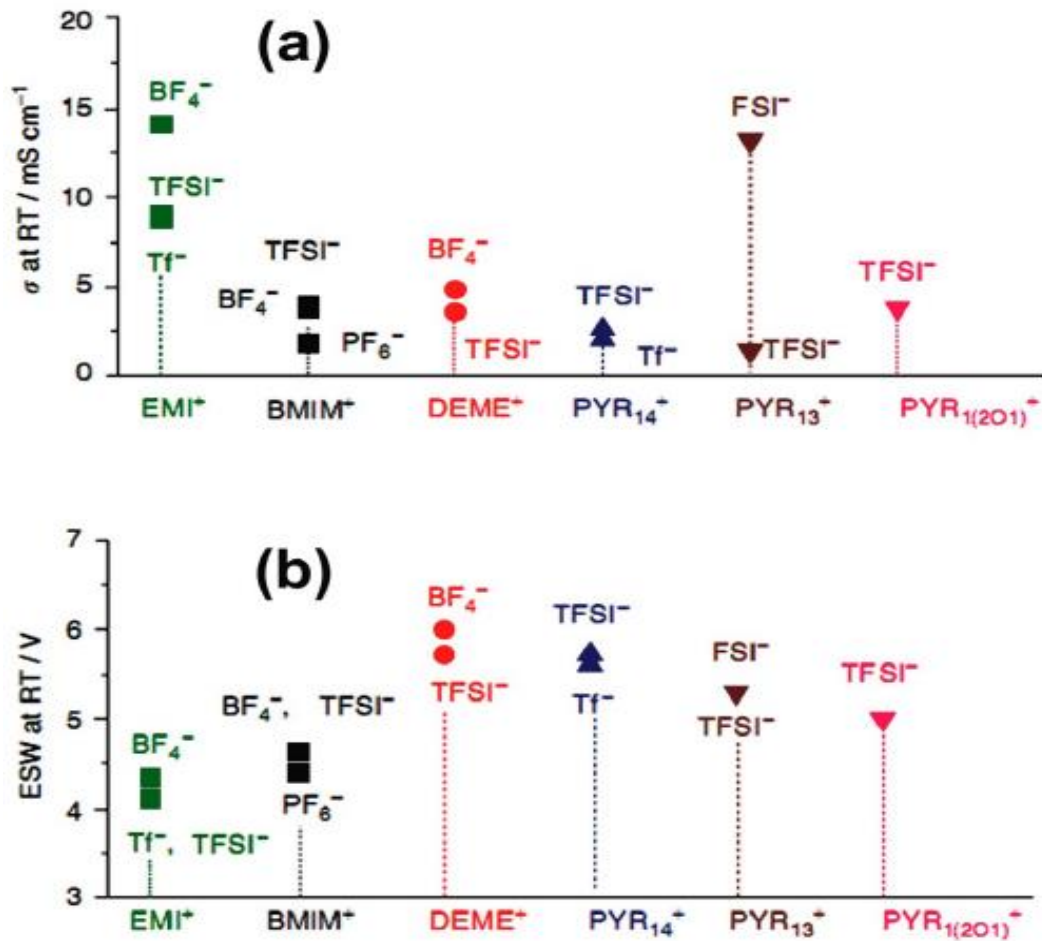


Figure 8: Conductivity and ESW comparison of different cations and anions [32].

Chapter 3 WORKING PRINCIPLE AND CHARACTERIZATION

3.1 Working principle

This project for the solid polymer electrolyte is carried out in two electrode setup. A two electrode configuration for the cell is used when precise control of the potential across the electrochemical interface is not critical (Figure 9). Given arrangement in Figure 9 is used to investigate electrolyte properties such as conductivity or to characterize the solid state system. The impedance is measured between the RE (Reference Electrode) and SE (Sense electrode) and CE refers to counter electrode and WE for working electrode [33].

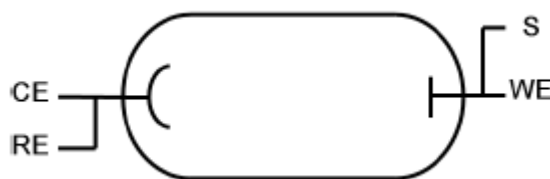


Figure 9: Schematic overview of two electrode setup [33].

Supercapacitors are similar to the conventional capacitors in the way they operate. It would thus be instructive to undertake a brief overview of electrostatic operation.

A conventional capacitor stores energy in the form of electrical charge and the device consists of two conducting materials separated by a dielectric. When an electric potential is applied across the conductors electrons begin to flow and charge accumulates on each conductor. Then potential is removed but conducting plates remain charged until they are brought into contact again, in which case the energy is discharged. The amount of charge that can be stored in relation to the strength of the applied potential is known as the

Solid-state Electrolyte for Supercapacitors

capacitance, and is a measure of a capacitor's energy storage capability. Given equations 1 and 2 does apply to an electrostatic capacitor.

$$C = \frac{Q}{V} = \epsilon \frac{A}{d} \quad (1)$$

$$U = \frac{1}{2} CV^2 = \frac{1}{2} QV \quad (2)$$

Where, C is capacitance in Farads, Q charge in Coulombs, V is electric potential in Volts, ϵ is the dielectric constant of the dielectric material, A is the surface area, d is the thickness and U is the potential energy.

EDLCs store electric charge in the similar manner as the conventional capacitor, but charge does not accumulate on two conductors separated by dielectric. Instead the charge accumulates at the interface between the surface of the conductor and electrolyte. The accumulated charge hence form an electric double-layer and an estimate of the capacitance can be found from the model proposed by Helmholtz (1853) where the double layer consists of two charged monolayers. One layer forms on the charged electrode and the other layer is comprised of ions in the electrolyte. The specific capacitance of such double layer can be calculated by using the following equation 3.

$$\frac{C}{A} = \frac{\epsilon}{4\pi\delta} \quad (3)$$

Electrochemical capacitors (supercapacitors) consists of two electrodes separated by a separator (electrolyte), where the electrolyte connects the electrodes electrically. Application of electric voltage across the capacitor form electric double layer at both the electrodes [32]. Given below is the schematic of the electrochemical double layer capacitor.

Solid-state Electrolyte for Supercapacitors

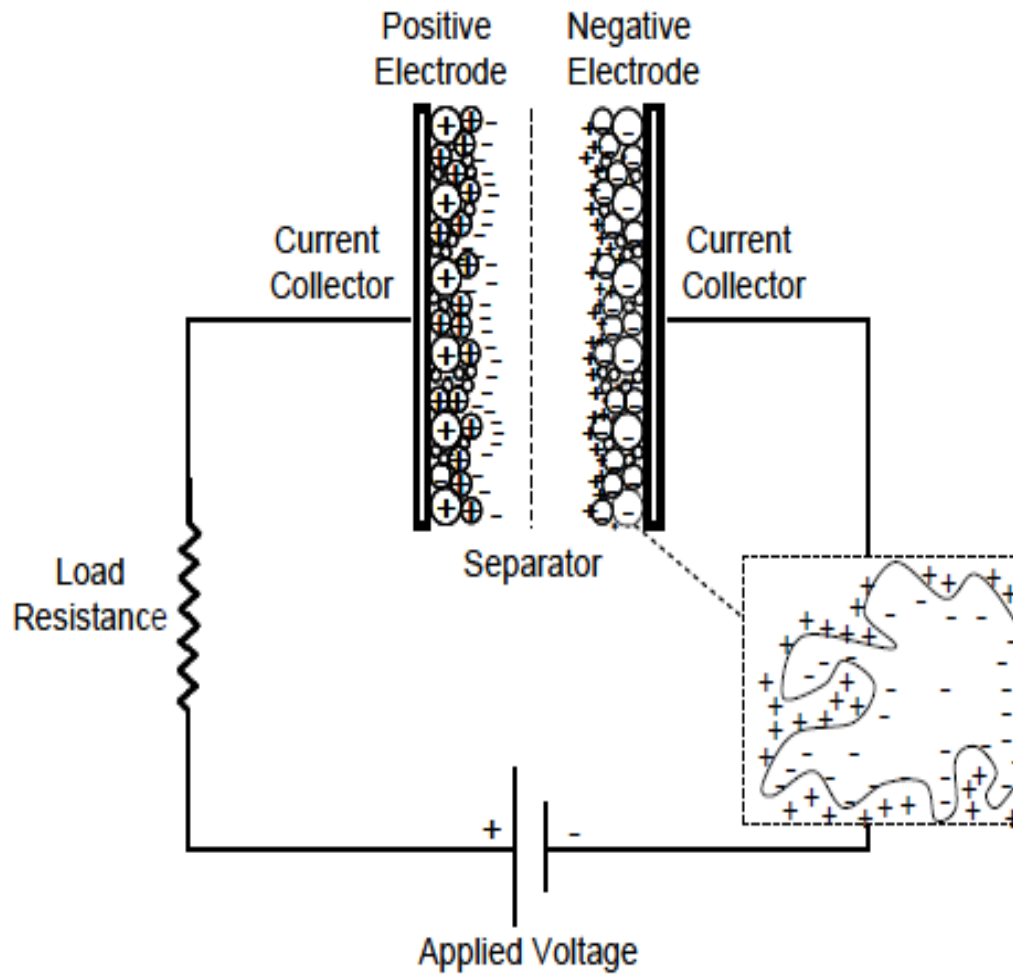


Figure 10: Schematic of electrochemical double layer capacitor [7].

Solid-state Electrolyte for Supercapacitors

3.2 Characterization

Electrochemical performance of the supercapacitor cells are tested by Electrochemical Impedance Spectroscopy (EIS), cyclic voltammetry (CV), and galvanometric charge-discharge methods. Structural characterization of the electrolyte were observed through Scanning Electron Microscope (SEM).

3.2.1 Cyclic voltammetry

Cyclic voltammetry (CV) provides a measure of a supercapacitor's charge-response with regard to a changing voltage, and is therefore a means of evaluating capacitance. The procedure for obtaining a voltammogram is simple and requires no specialized equipment.

To perform cyclic voltammetry tests a series of changing voltages at a constant sweep rate (dV/dt) is applied and the response current is recorded. The capacitance can then be calculated by Equation 4, where I is the current and s is the sweep rate in V/s [34]. Often the voltammetry will be graphed as capacitance vs. voltage instead of current vs. voltage.

$$C = \frac{I}{s} \quad (4)$$

An ideal capacitor with no resistance would display a rectangular shape, but most real EDLC voltammograms take the shape of a parallelogram with irregular peaks (Fig. 11). Prominent peaks that occur within narrow voltage windows are usually evidence of pseudo capacitive behavior. Faster sweep rates correspond to charging and discharging at higher power levels. Multiple plots obtained at increasing sweep rates are therefore often displayed on the same graph to demonstrate the impact of power levels on the charging characteristics (Fig. 12). From such plots it is evident that capacitance decreases at higher frequencies.

Solid-state Electrolyte for Supercapacitors

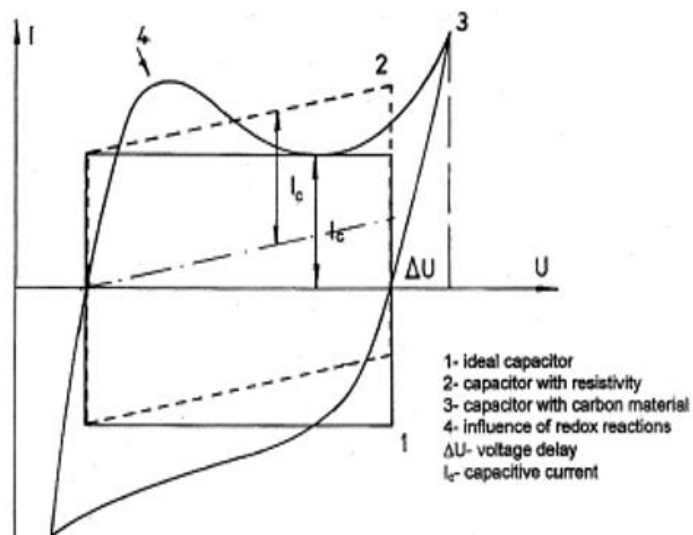


Figure 11: Comparison of real and ideal cyclic voltammograms [36].

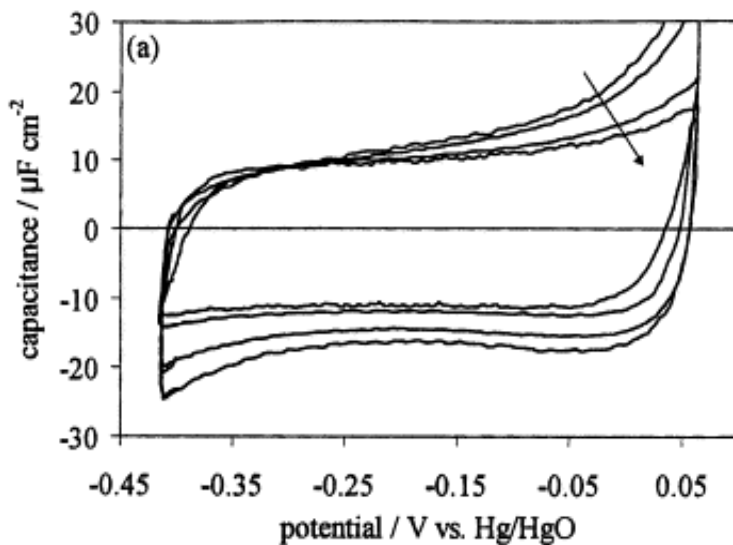


Figure 12: Cyclic voltammograms at increasing sweep rates
 (arrows in direction of increasing sweep rate) [35].

Solid-state Electrolyte for Supercapacitors

Voltammetry can also provide an indication of the degree of reversibility of an electrode reaction. A voltammogram that depicts a mirror-image represents a reversible reaction, but an irreversible process will have two separate charge and discharge profiles, the ends of which do not meet up. Reversibility is an important factor in search for new materials.

Solid-state Electrolyte for Supercapacitors

3.2.2 Impedance spectroscopy

Impedance spectroscopy is a powerful method of evaluating a component's performance in the frequency domain. Special equipment is required to apply a small AC voltage and measure the changes in magnitude and phase over a range of frequencies. The impedance can then be plotted on a Nyquist diagram (Fig 13). An ideal capacitor is represented by a vertical straight line shifted on the real axis by its ESR. At low frequencies a supercapacitor approaches a near vertical straight line shifted on the real axis by the equivalent series resistance (ESR) and an additional equivalent distributed resistance (EDR).

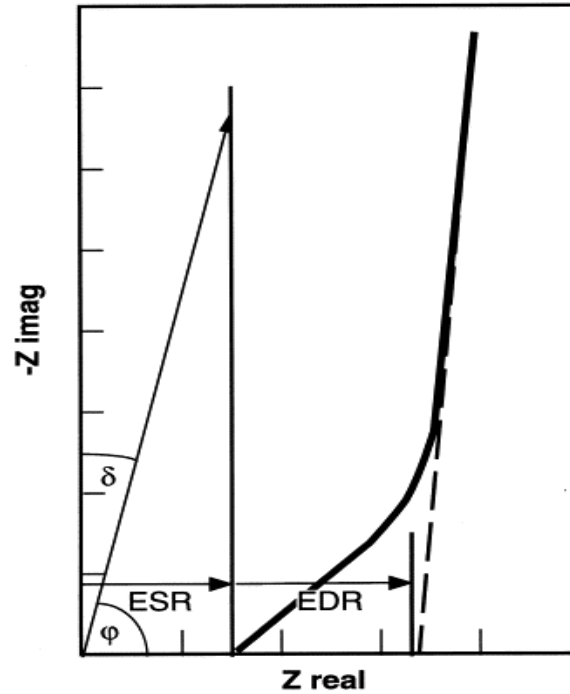


Figure 13: Nyquist impedance plot of an ideal capacitor and EDLC [36].

Solid-state Electrolyte for Supercapacitors

3.2.3 Conductivity and mobility

Ionic liquids have attracted great deal of attention as soon as they were found out because of their extreme qualities like low vapor pressure, non-flammability, good conductivity except most of them are in liquid state in room temperature. Thus to develop solid gel polymer electrolyte is to incorporate the ionic liquid with suitable polymer material which can give the best conductivity (ionic conductivity: σ) for the polymer gel. Conductivity and mobility is represented by the following equations.

$$\mu = \frac{q}{6\pi nr} \quad (5)$$

$$\sigma = nq\mu \quad (6)$$

Where μ , n , q represents mobility of ions, number of ionic charge carriers and columbic charge respectively. From the equations, we noticed that the mobility and conductivity of the ionic are directly proportional to each other and both of them are inversely proportional to the viscosity. Thus for selecting the ionic liquids we looked for the best one with higher conductivity and lower viscosity properties [37].

$$\sigma = \frac{t}{z'A} \quad (7)$$

Where t is the thickness of the film, z' is the bulk resistance of the film which is value of z' at z'' is zero. This data is evaluated at the higher frequency range. Using equation 7 conductivity of the polymer films were measured. The semicircle at the high frequency region in cole-cole (or Nyquist plot) plot disappears due to the increase in salt concentration and thus total conductivity is mainly the cause of the ionic conductivity [38-39].

Chapter 4 EXPERIMENTAL PROCEDURES

4.1 Preparation of Electrolyte

Preparation of Electrolyte is the initial step after identifying the suitable materials to be used. For preparing the solid electrolyte film we need some magnetic bead (for stirring) of suitable size according to the size of bottle used. Usually 0.6 mm to 2 mm diameter with length 1 cm to 2 cm long magnetic beads were used. Hot magnetic plate with controllable magnet spin and temperature is used to dissolve the polymer solution and mix them homogeneously. Following steps were used while performing this experiment.

- i. PVDF-HFP polymer is immersed into Acetonitrile for 24 hours in a bottle, so that this polymer soaks the chemical and easy to dissolve.
- ii. Magnetic bead of suitable size is immersed into the solution and placed into the hot plate at 50⁰C for 24 hours.
- iii. Ionic liquid is added and again dissolved in hot plate for 12 hours at same temperature (if the polymer film is ionic liquid blended).
- iv. Ionic conducting promoter (Zeolite or reduced Graphene oxide) is added to the solution and again dissolved for 12 hours at same temperature (if the polymer film incorporates the ionic conducting promoter).
- v. The mixed liquid solution is transferred to the petri dish and allowed to cool and blend into solid gel at room temperature from 48 hours (usually) to 96 hours.

Solid-state Electrolyte for Supercapacitors

To prepare the pure PVDF-HFP polymer film step iii and iv are skipped. Similarly, to prepare polymer film with ionic liquid only step iv is skipped [21, 32, 37, 38]. Polymer film dissolving process is presented in the Figure 14.

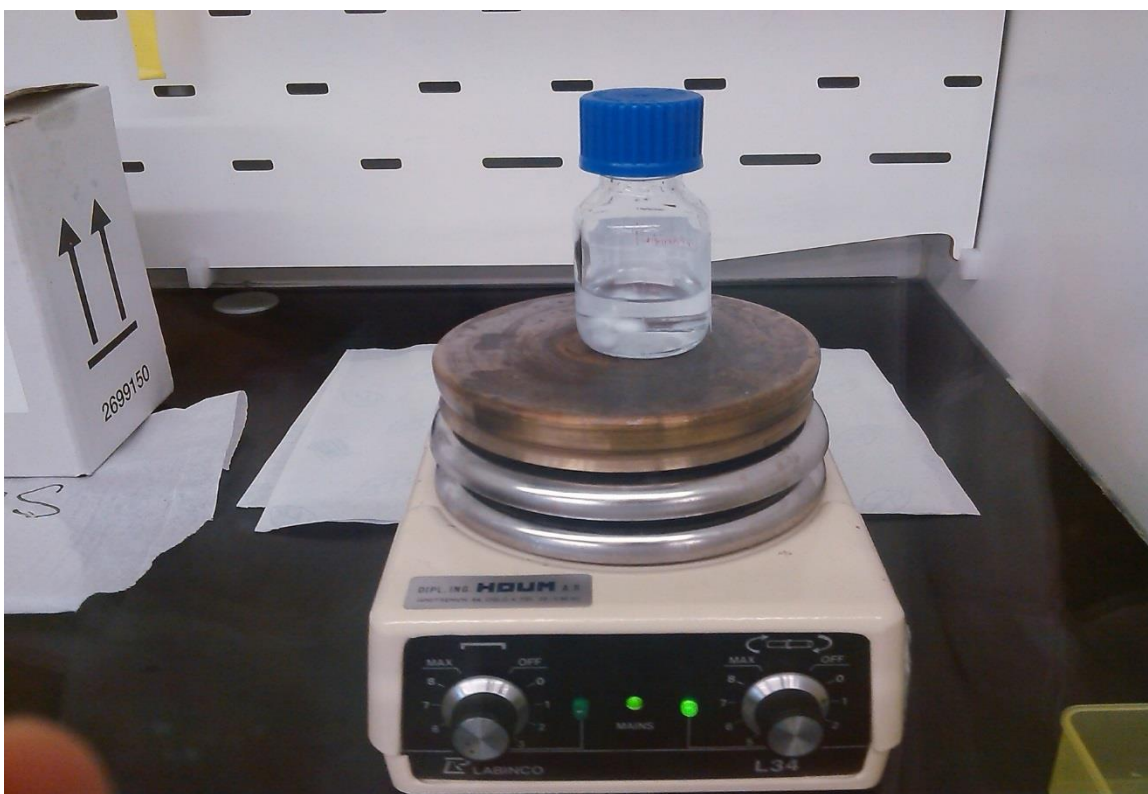


Figure 14: Dissolving the PVDF-HFP polymer and Acetonitrile in the hot magnetic plate under Bio-Fume hood.

Solid-state Electrolyte for Supercapacitors

4.2 Preparation of Electrode

After preparing the electrolyte, initial characterization were performed. But to perform the characterization of the full super capacitor we need to prepare the electrode from the suitable materials which can help us to characterize the device. The following process is opted for Electrode preparation.

- i. PVDF-HFP binder is crushed into smaller size (powder).
- ii. Multiwall Carbon nanotube (MWCNT), PVDF-HFP (powder) and Acetylene black is mixed in the ratio of 70: 20: 10 (w/w).
- iii. Acetone is added to the mixture slowly and made slurry with mortar and pestle for at least 30 minutes.
- iv. Slurry mixture (electrode) is then poured into a glass bottle and put into the ultrasonic bath with distilled water for 15 minutes to destruct the bigger particles into fine small particles.
- v. This prepared electrode (slurry mixture) is ready to use and can be stored and reused whenever required.

Thus, finally prepared electrode can be coated on the high density graphite sheets (current collector). Then we can use the electrolyte between the two similar graphite sheets coated with electrode material like sandwich structure and finally characterize the device [21, 32, 37, 38].

Solid-state Electrolyte for Supercapacitors

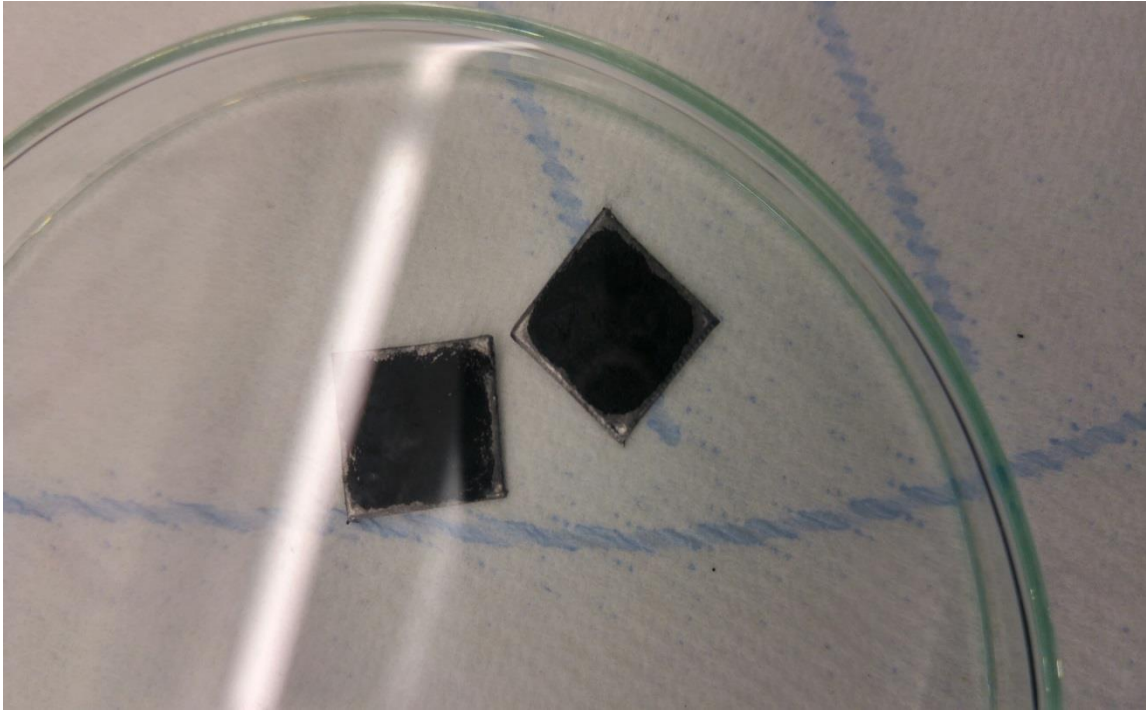


Figure 15: Electrode (MWCNTs slurry) coated over the current collector (Graphite sheets) for supercapacitor assembly.

Solid-state Electrolyte for Supercapacitors

4.3 Characterization experiment

After the preparation of the components of the supercapacitors, we need to characterize the device using suitable methods. Electrochemical Impedance Spectroscopy was used to measure the conductivity of the polymer film. Cyclic Voltammetry to calculate the capacitance and EIS for impedance plot and confirmation of capacitive behavior.

Conductivity determination of the each synthesized film is important part which later was used to find out the film with maximum conductivity and to perform the characterization of the assembled supercapacitor with the same film. To perform the conductivity measurement electrolyte film was placed between two Stainless Steel (SS) and the measurement was conducted by using computer controlled IMU measurement unit. For electrochemical characterization “Thales software” was used. Using EIS (electrochemical impedance spectroscopy) the conductivity was measured for each film. The bulk resistance of the film was calculated at z' value where z'' is zero. The following parameters we used to conduct this experiment.

- Current range -3mA to +3mA
- Frequency sweep 10mHz - 1MHz
- Amplitude 10mV

Cyclic Voltammetry was performed in little different way than conductivity measurement, since it requires electrode. Electrode material (slurry) prepared with MWCNTs is coated on to the each side of the two graphite sheets (or current collector). In this experiment, we basically coat the slurry with a small brush and try to coat it uniformly throughout the graphite sheet with uniform thickness (≈ 200 nm). The electrode coated current collector is sandwiched with the electrolyte separator (solid gel polymer) in between them. The capacitance measurement of the whole cell assembly is measured

Solid-state Electrolyte for Supercapacitors

afterwards with same IMU instrument using cyclic voltammetry. Figure 16 illustrates the assembly of the cell to perform the CV analysis.

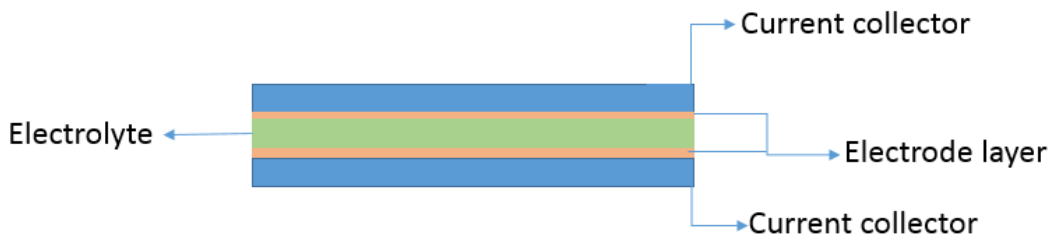


Figure 16: Sandwich structure of supercapacitor using electrolyte material in-between electrode material coated graphite sheet.

Following parameters were used while performing the CV analysis.

- Voltage sweep between -500m to +500m
- Slew rate of 5, 20 and 100 mV/s
- Current range -3mA to +3mA
- Frequency 100 KHz
- Amplitude 10mV

The electrochemical stability window (ESW) of the IL blended polymer film was calculated by using the cyclic voltammetry with stainless steel electrodes. The typical CV of PVDF-HFP + IL (or with addition of ionic conduction promoter) film is recorded at lower scan rate (5-20 mV/s). And ESW of the whole supercapacitor assembly is calculated by using the same CV method at lower scan rate until the cell reaches its dissociation potential and the potential values were noted.

Solid-state Electrolyte for Supercapacitors

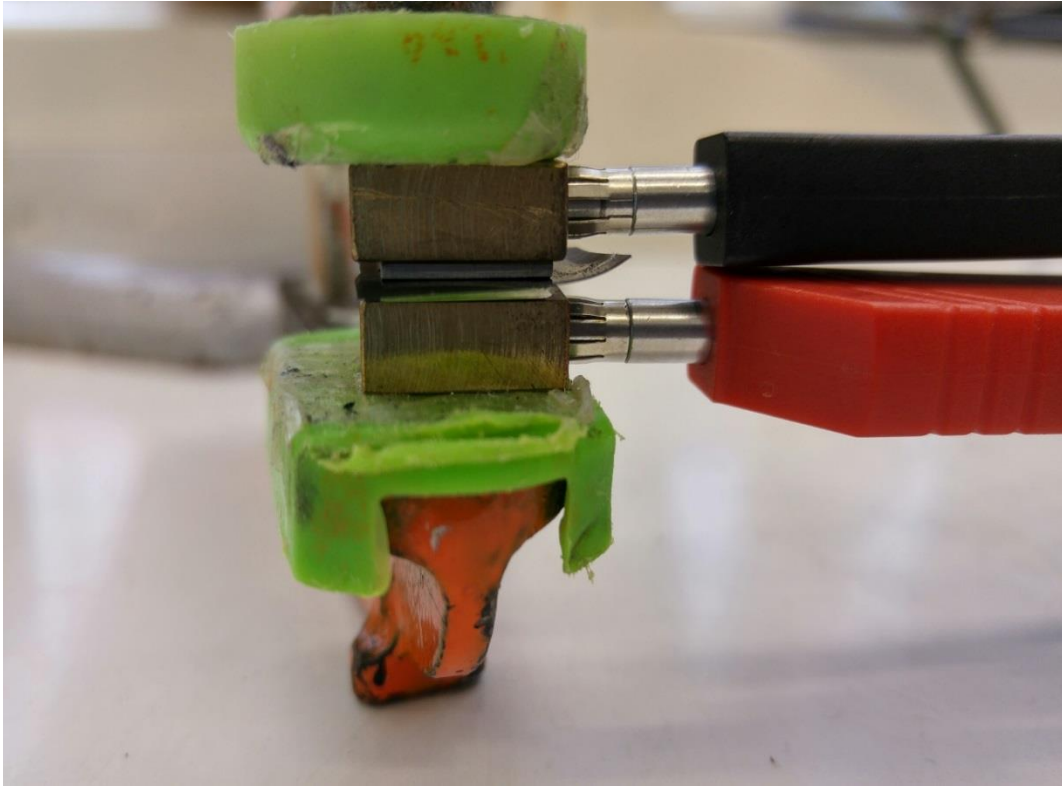


Figure 17: Sandwich structure of supercapacitor using electrolyte material in-between electrode material coated graphite sheet for measurement as illustrated in Figure 16.

Electrochemical impedance spectroscopy of the same cell as prepared for cyclic voltammetry is taken and the measurement can be processed with similar method on Thales software. But in this case we use EIS and certain parameters as listed below for the two electrode system.

- Frequency sweep range 10 (or 100) mHz to 100 KHz
- Current range -3mA to +3mA
- Amplitude 10 mV

Solid-state Electrolyte for Supercapacitors

In this system we can use different frequency sweep rate and starting frequency point to perform the measurement. One of the picture is shown below in Figure 18.

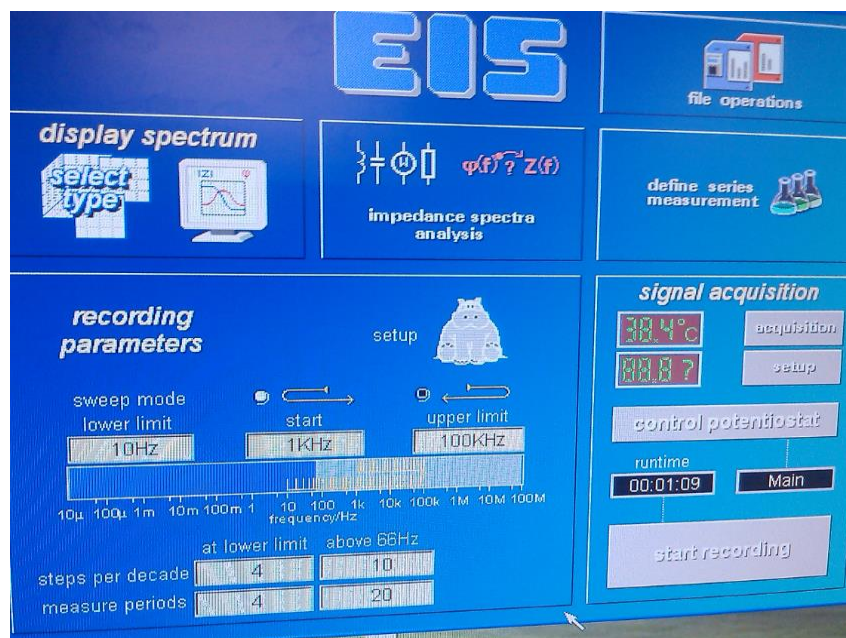


Figure 18: Parameters that can be controlled while performing EIS in Thales.

Chapter 5 RESULTS AND DISCUSSION

5.1 Pure PVDF-HFP film

The characterization of the device includes various steps including production or synthesis of the solid polymer electrolyte. First step of the synthesis is to prepare the pure PVDF-HFP film from the PVDF-HFP matrix. Polymer matrix of PVDF-HFP is dissolved into the Acetonitrile and this 100% pure PVDF-HFP film is subjected into various characterization techniques.

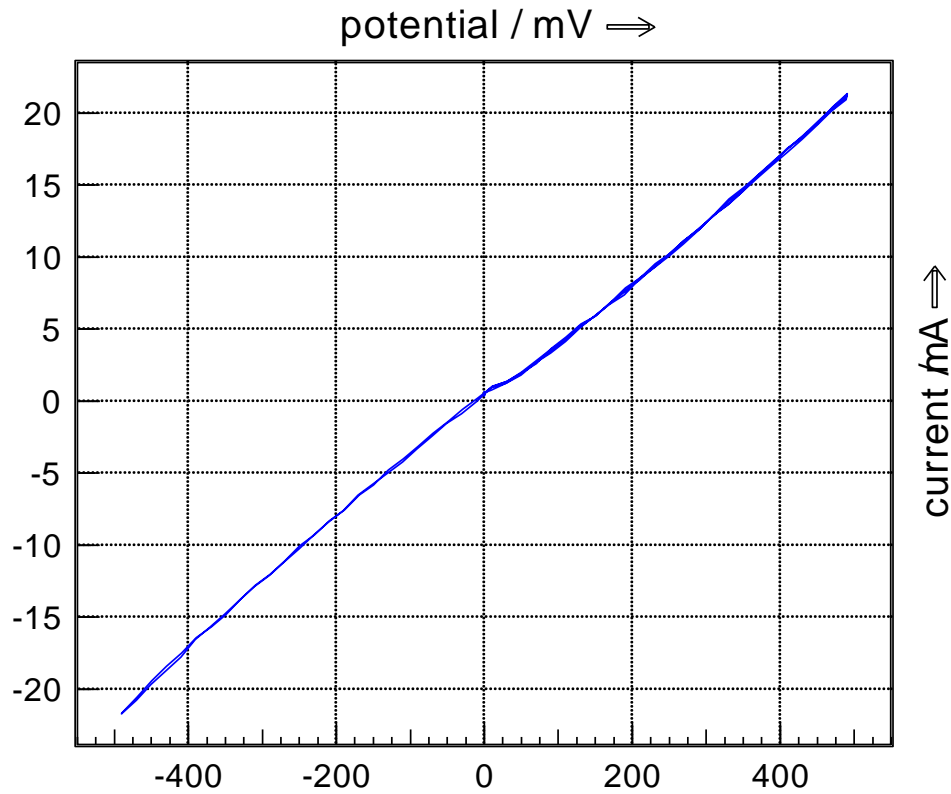


Figure 19: Cyclic Voltammetry of the pure PVDF-HFP film with MWCNT (electrode) and graphite current collector at 100mV/s.

Solid-state Electrolyte for Supercapacitors

This Figure 19 shows the CV analysis of the pure polymer film prepared from the polymer matrix. The current vs voltage curve is almost linear passing through origin and this type of behavior is represented by the resistive material. Thus it can be easily identified as this pure polymer film does not reflect the capacitive behavior. For CV analysis parameters like voltage sweep of $\pm 500\text{V}$, 100 KHz frequency, 10 mV amplitude signal and $\pm 3\text{ mA}$ current range were applied.

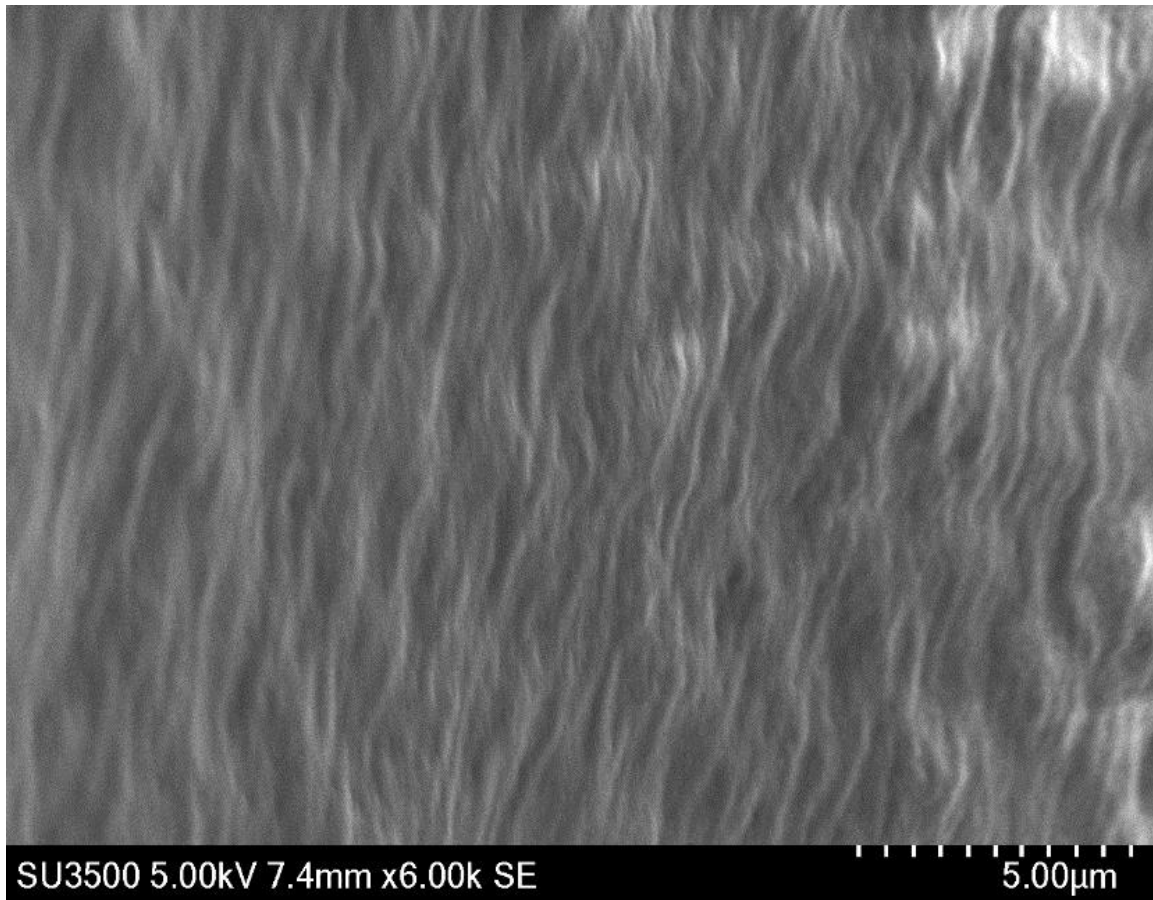


Figure 20: Scanning Electron Microscopy (SEM) image of the pure polymer electrolyte film.

Solid-state Electrolyte for Supercapacitors

Figure 20 represents the SEM image of the pure PVDF-HFP polymer film. This image shows some thread (or spaghetti) like structure which represents the presence or dominance of crystalline structure over the amorphous one. This optically transparent sample is imaged at the power of 5 K eV. Optical image of the pure PVDF-HFP polymer film is shown in the Figure 21.



Figure 21: Image of the pure PVDF-HFP (Transparent) polymer film.

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5.2 PVDF-HFP with EMIM-BF₄ (IL) in 1:2(w/w)

PVDF-HFP sample with EMIM-BF₄ ionic liquid is synthesized in different ratios and the maximum conductivity is found at the ratio of 1:2 (w/w). Optical image of the film is presented in Figure 22.

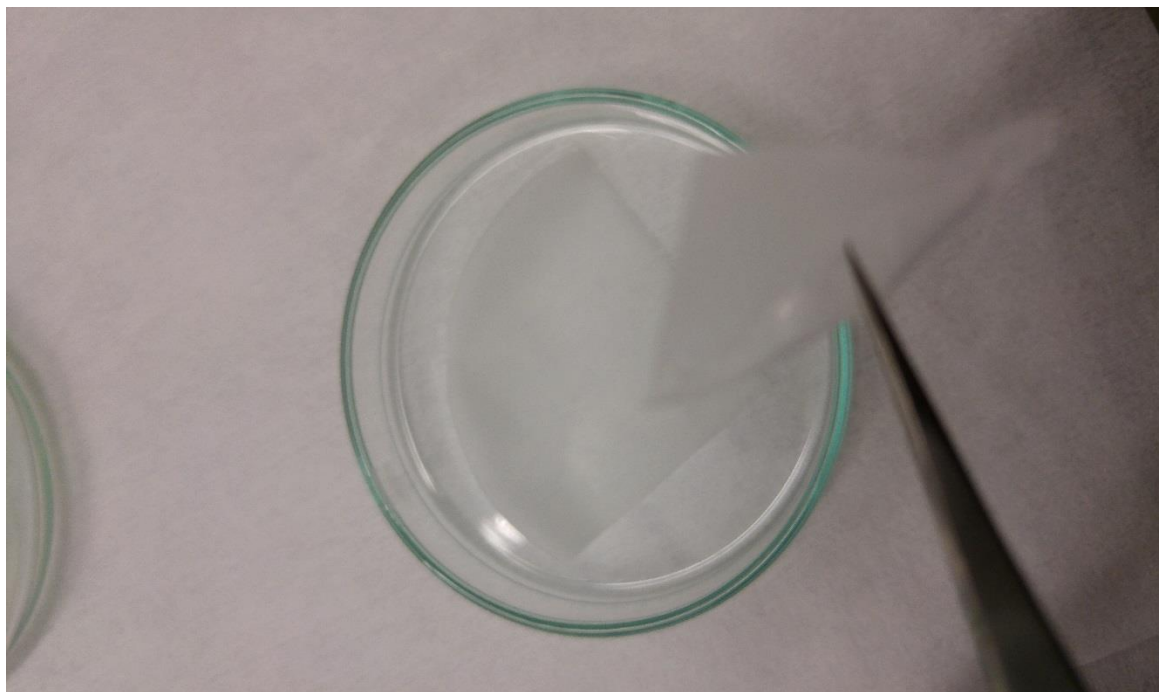


Figure 22: Image of the PVDF-HFP+EMIM-BF₄ (1:2 w/w) polymer film

The conductivity (electrical conductivity) experiment of the various samples (with different IL concentration) were measured and listed in the Table 3. Maximum conductivity of 1.87×10^{-3} S/cm is observed at 200% IL concentration and the films above that concentration were not extractable because they did not solidify properly and broke easily when attempted to take out from the petri-dish.

Solid-state Electrolyte for Supercapacitors

Table 3. Comparison of conductivity of PVDF-HFP with different EMIM-BF₄ (IL) concentration

IL-weight (%)	Conductivity (S/cm)
5	1.12×10^{-5}
50	4.02×10^{-4}
100	1.05×10^{-3}
200	1.87×10^{-3}
250	Not extractable
300	Not extractable

SEM image of the PVDF-HFP sample with IL (EMIM-BF₄) is shown into the Figure 23. From this image we can easily notice that the amorphous behavior of the PVDF-HFP is more enhanced by suppressing the crystalline behavior compared to the pure PVDF-HFP film. This obtained film is highly porous. This film doesn't have a particular shape (or pattern). The presence of little white structure is the bubble or may be water trapped inside the porous membrane. Thus the necessary procedure is opted like vacuum drying of the film before the further experiment.

Solid-state Electrolyte for Supercapacitors

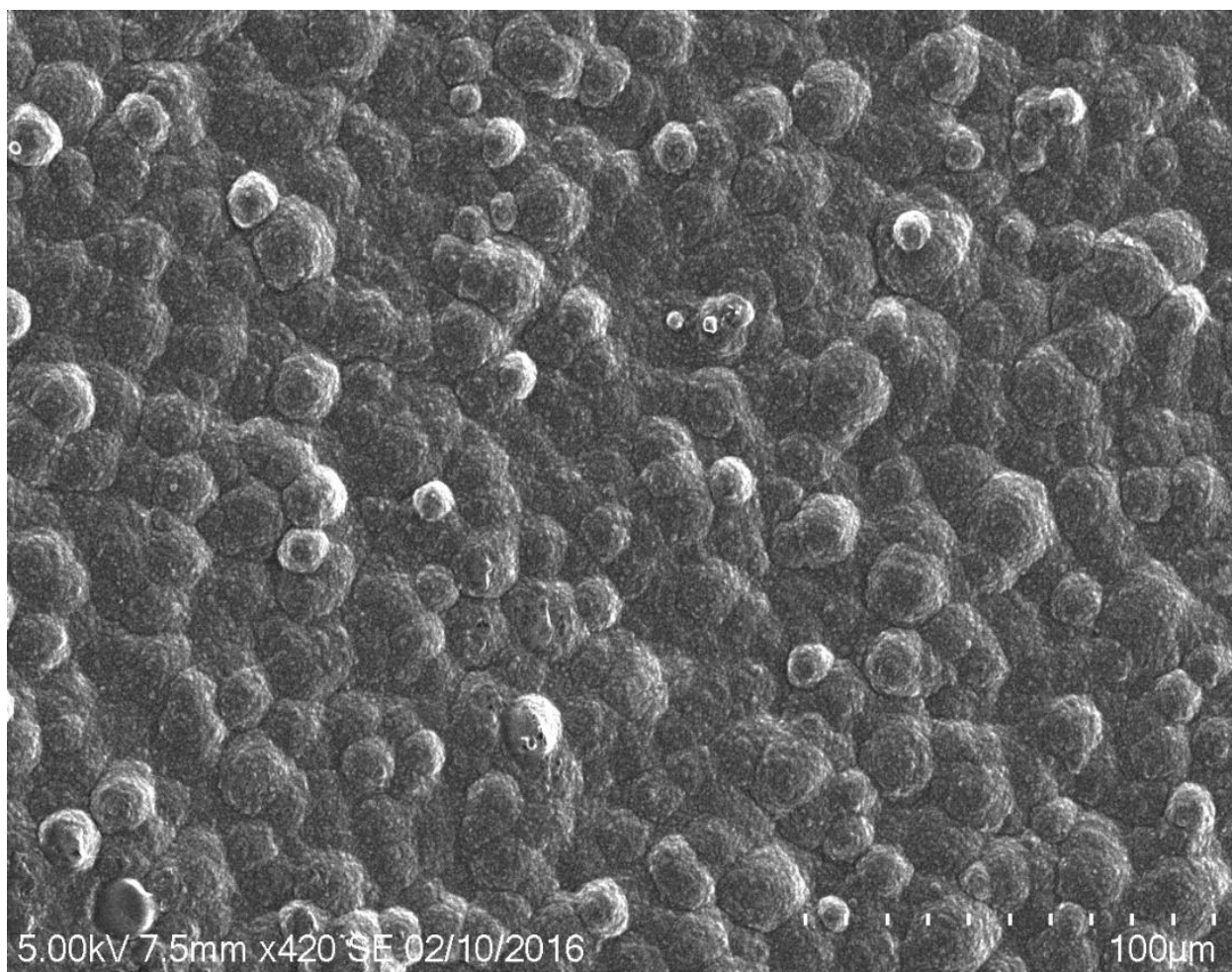


Figure 23: Scanning Electron Microscopy (SEM) image of the IL (BF₄) blended polymer electrolyte film

Solid-state Electrolyte for Supercapacitors

The Cyclic Voltammetry of this film is carried out with two current collectors (graphite sheets) coated with the MWCNT electrode (MWCNT slurry) and the solid polymer electrolyte film sandwich between them forming a complete supercapacitor cell.

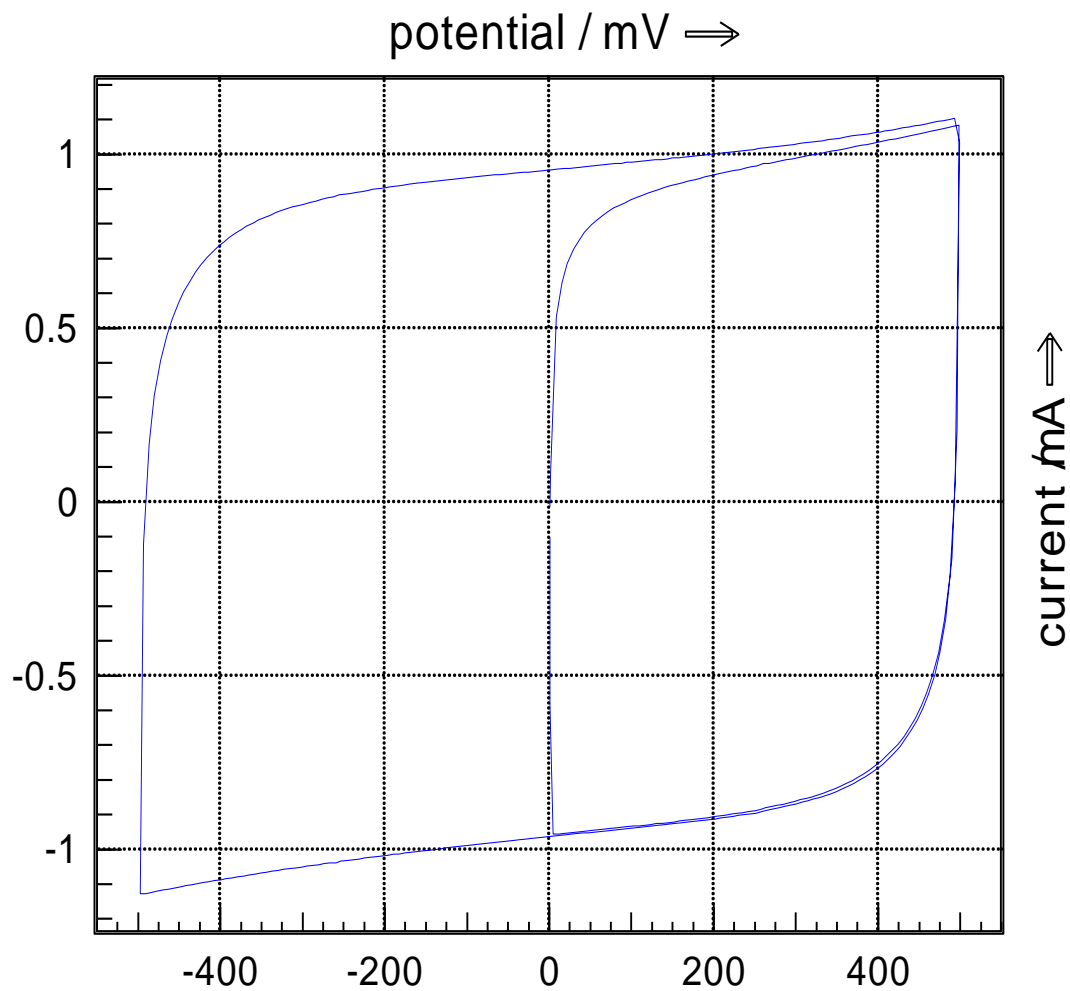


Figure 24: Cyclic Voltammetry of the PVDF-HFP+EMIM-BF₄ (1:2 w/w) supercapacitor assembly at 100mV/s.

Solid-state Electrolyte for Supercapacitors

The CV diagram of the Figure 24 for sample with maximum conductivity result shows the areal capacitance of the supercapacitor assembly to be nearly equal to $10\text{mF}/\text{cm}^2$.

For the next step, determination of the Electrochemical Stability Window (ESW) is an important properties to determine the safety window under which this polymer film can be used safely without damage or degradation. ESW was found to be 4V by using this polymer film in between the two stainless steel (SS) by CV. This curve in Figure 25 is not so smooth because of higher slew rate. Usually ESW is evaluated at lower slew rate.

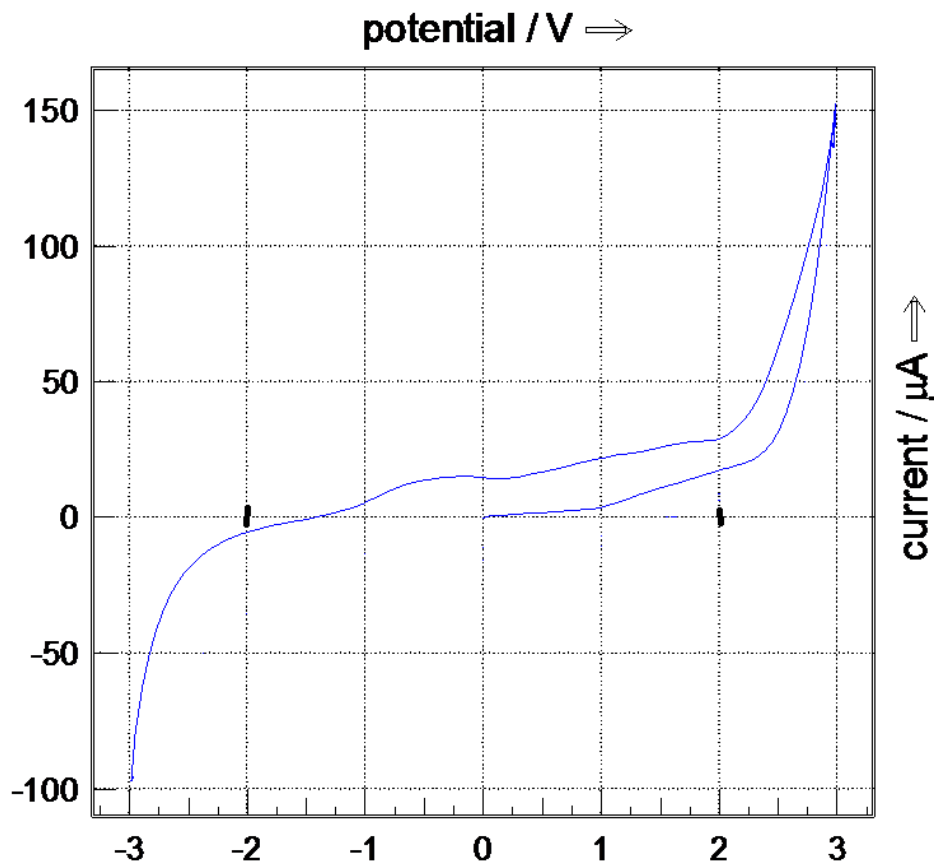


Figure 25: ESW of the PVDF-HFP+EMIM-BF4 (1:2 w/w)

Solid-state Electrolyte for Supercapacitors

Electrochemical Impedance Spectroscopy (EIS) measurement of this super capacitor configuration is another characterization technique to illustrate the capacitive behavior. Figure 26 shows the Nyquist plot of this supercapacitor cell. The step rising behavior of the complex impedance plot indicates the capacitive behavior of the supercapacitor cell. The experiment is performed in the frequency range between 10mHz (or 100mHz) to 100KHz.

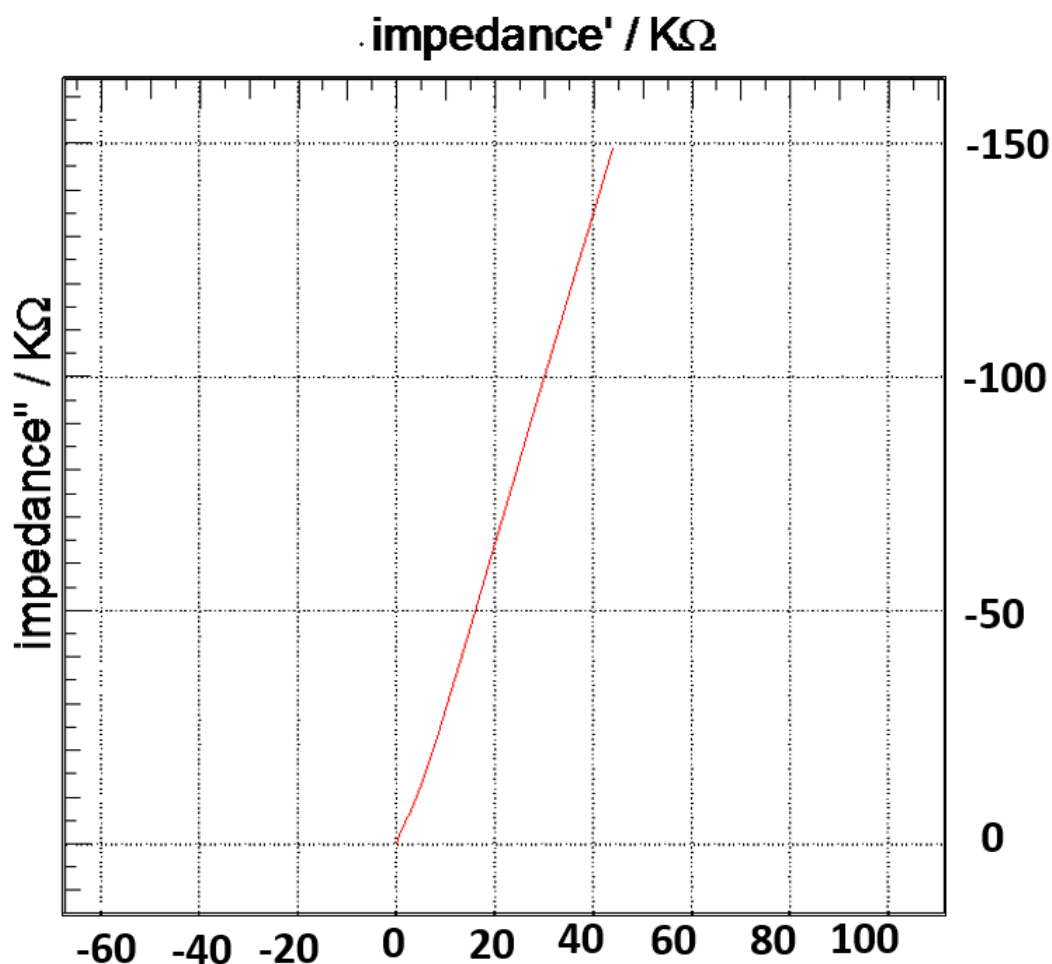


Figure 26: Nyquist plot of PVDF-HFP+EMIM-BF₄ (1:2 w/w) polymer film with supercapacitor assembly

Solid-state Electrolyte for Supercapacitors

5.3 PVDF-HFP with EMIM-DCA (IL) in 1:2.5(w/w)

PVDF-HFP sample with EMIM-DCA ionic liquid is synthesized in different ratios and the maximum conductivity is found at the ratio of 1:2.5 (w/w). Optical image of the film is presented in Figure 27.

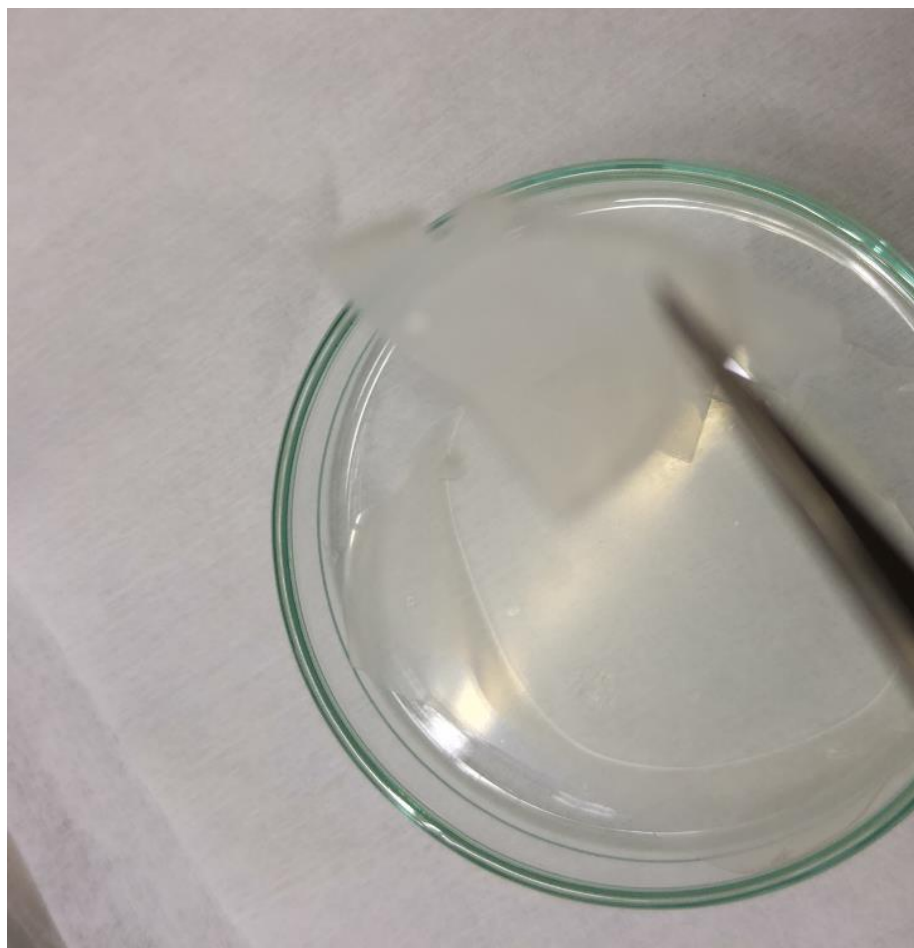


Figure 27: Image of the PVDF-HFP+EMIM-DCA (1:2.5 w/w) polymer film

The conductivity (electrical conductivity) experiment of the various samples (with different IL concentration) were measured and listed in the Table 4. Maximum conductivity

Solid-state Electrolyte for Supercapacitors

of 1.28×10^{-2} S/cm is observed at 250% IL concentration and the films above that concentration were Not Extractable (NE) because they did not solidify properly and broke easily when attempted to take out from the petri-dish.

Table 4. Comparison of conductivity of PVDF-HFP with various EMIM-DCA (IL) concentration

IL-weight (%)	Conductivity (S/cm)
5	2×10^{-5}
50	4.7×10^{-4}
100	5.45×10^{-3}
200	8.98×10^{-3}
250	1.28×10^{-2}
300	Not Extractable

The Cyclic Voltammetry of this film is carried out with two current collectors (graphite sheets) coated with the MWCNT electrode (MWCNT slurry) and the solid polymer electrolyte film sandwich between them forming a complete supercapacitor cell. The CV diagram of the Figure 28 for sample with maximum conductivity result shows the areal capacitance of the supercapacitor assembly to be nearly equal to 20 mF/cm^2 . And impedance plot of the supercapacitor cell is presented in Figure 29 where the frequency of the signal is varied between 10 mHz to 100 KHz. At lower scan rate of 5 mV/s the ESW of this polymer film is determined to be 3.5 V.

Solid-state Electrolyte for Supercapacitors

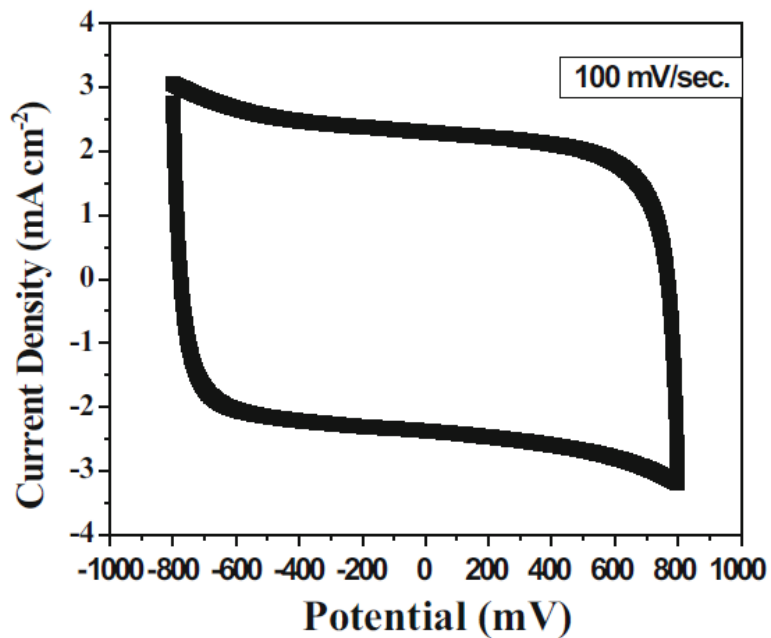


Figure 28: Cyclic Voltammetry of the PVDF-HFP+EMIM-DCA (1:2.5 w/w) [37]

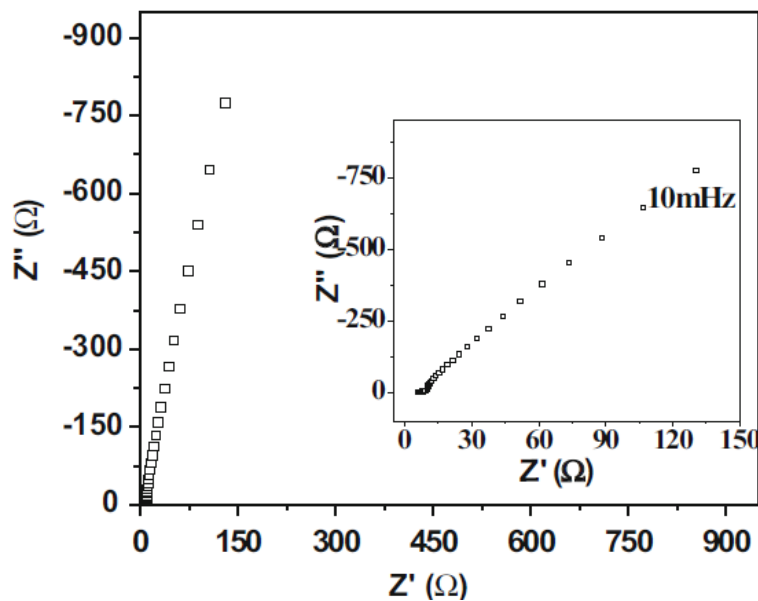


Figure 29: Nyquist plot of PVDF-HFP+EMIM-DCA polymer film in supercapacitor cell [37]

Solid-state Electrolyte for Supercapacitors

Until this part we managed to find the suitable polymer material (i.e. PVDF-HFP) which can be used to synthesize the solid polymer electrolyte by blending with two different ionic liquids (i.e. EMIM-DCA and EMIM-BF₄). These two polymer films with blended ionic liquids were tested for conductivities, SEM analysis and ESW. CV analysis and EIS analysis of the supercapacitor configuration were performed. The next step is to find suitable material (or mechanism) in order to enhance (or optimize) the properties of these films.

Since use of some ceramic particles is not a new concept which helps to improve the performance of the solid polymer electrolyte film. Nano particles are used in combination with ionic liquids which helps to improve the physical, electrochemical and mechanical properties of the film. Among several options we opted to choose two nano particles in combination with other two ionic liquid and prepare four different samples. We used Zeolite particle and reduced Graphene oxide (rGO) particles which has some interesting improvement in the performance of the solid polymer electrolyte film [26-28].



Figure 30: Preparation of different electrolyte films in magnetic hot plate.

Solid-state Electrolyte for Supercapacitors

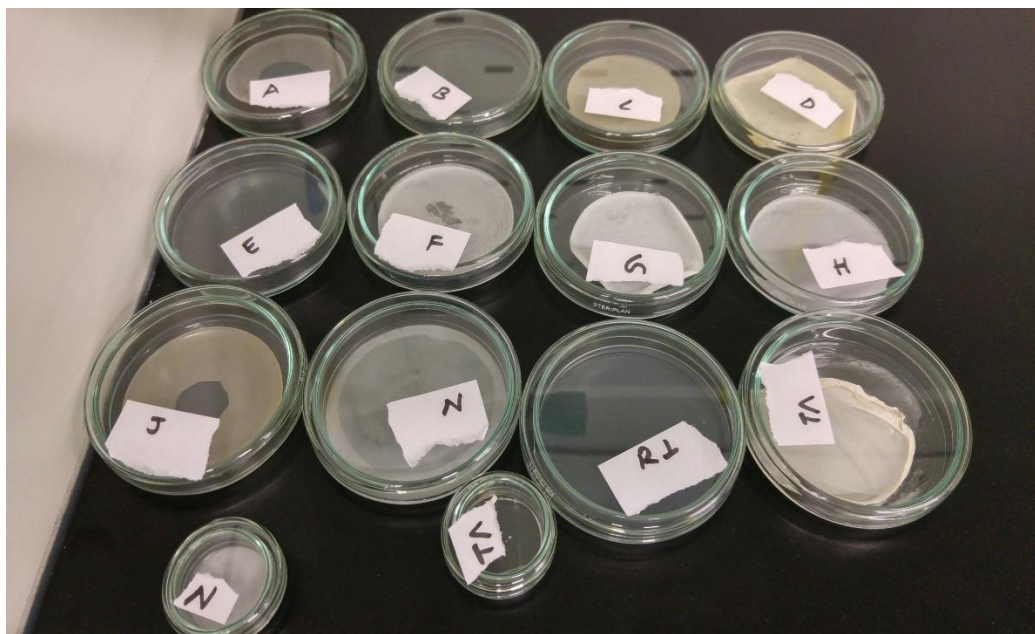


Figure 31: Pictures of different samples (polymer films) on petri-dish prepared using zeolite particles.

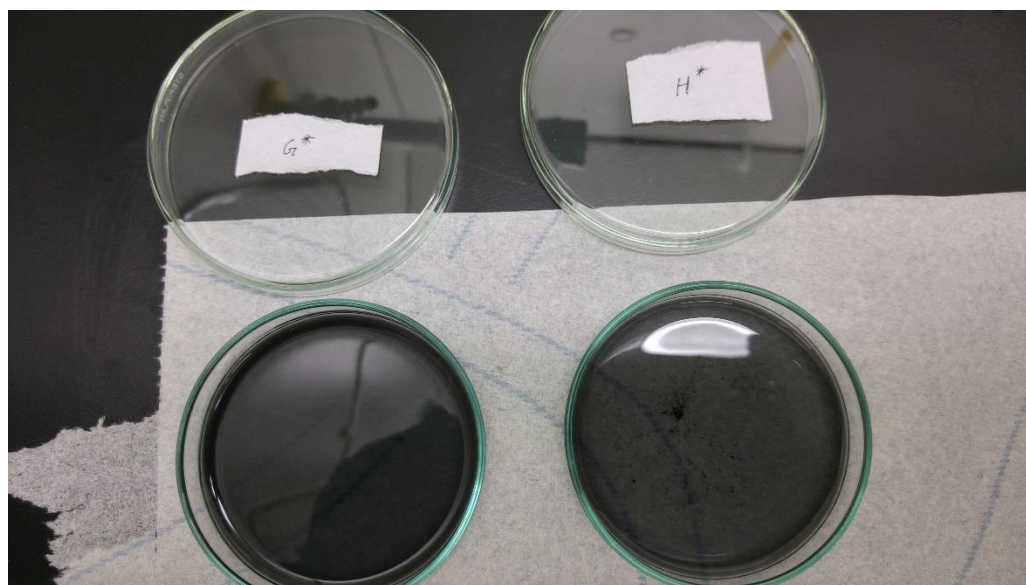


Figure 32: Some polymer sample (films) with rGO particles.

Solid-state Electrolyte for Supercapacitors

In the initial stage we prepared the electrolyte film with different ionic liquid samples concentration and different zeolite and reduced Graphene oxide particles as presented in Figure 31 and 32. Then each film were subjected to conductivity analysis procedure. These conductivity measurement were done at room temperature in the laboratory. The conductivity measurement data are presented in Table 5 and 6.

Table 5. Comparison of conductivity of PVDF-HFP with EMIM-DCA and EMIM-BF₄ (ILs) and Zeolite in various concentration

PVDF-HFP : EMIM-DCA (IL) : Zeolite	conductivity (s/cm)	PVDF-HFP : EMIM-BF ₄ (IL) : Zeolite	conductivity (s/cm)
1 : 2.5 : 0.01	7.92×10^{-3}	1 : 2 : 0.01	7.8×10^{-4}
1 : 2.5 : 0.1	2.3×10^{-3}	1 : 2 : 0.1	1.01×10^{-3}
1 : 2.5 : 0.3	5.6×10^{-4}	1 : 2 : 0.3	1.8×10^{-3}
1 : 2.5 : 0.5	1.23×10^{-4}	1 : 2 : 0.5	5.7×10^{-4}
1 : 3.5 : 0.01		1 : 3 : 0.01	
1 : 3.5 : 0.1	2.1×10^{-2}	1 : 3 : 0.1	4.1×10^{-3}
1 : 3.5 : 0.3		1 : 3 : 0.3	
1 : 3.5 : 0.5		1 : 3 : 0.5	
1 : 5 : 0.01	NE	1 : 5 : 0.01	NE
1 : 5 : 0.1		1 : 5 : 0.1	
1 : 5 : 0.3		1 : 5 : 0.3	
1 : 5 : 0.5		1 : 5 : 0.5	
1 : 2.5	1.28×10^{-2}	1 : 0 : 0.3	1.55×10^{-8}

Solid-state Electrolyte for Supercapacitors

Table 6. Comparison of conductivity of PVDF-HFP with EMIM-DCA and EMIM-BF₄ (ILs) and rGO in various concentration

PVDF-HFP : EMIM-DCA (IL) : rGO	conductivity (s/cm)	PVDF-HFP : EMIM-BF ₄ (IL) : rGO	conductivity (s/cm)
1 : 2.5 : 0.01	2.1*10 ⁻³	1 : 2 : 0.01	4.25*10 ⁻³
1 : 2.5 : 0.05	1.0*10 ⁻³	1 : 2 : 0.05	4.8*10 ⁻³
1 : 2.5 : 0.1	1.56*10 ⁻²	1 : 2 : 0.1	4.5*10 ⁻³
1 : 3.5 : 0.01	1.8*10 ⁻²	1 : 3 : 0.01	3.03*10 ⁻³
1 : 3.5 : 0.1		1 : 3.5 : 0.1	
1 : 5 : 0.01	NE	1 : 5 : 0.01	NE

These data represents various conductivities under same environmental condition inside the laboratory in room temperature. The data with marked bod is highlighted for having the highest conductivity for a particular polymer film with different concentration of ionic liquid and polymer enhancing particles (i.e. zeolite or rGO). From the above Tables 5 and 6 we obtained four samples with highest conductivity. For each of the four sample various electrochemical measurement like, Cyclic Voltammetry, Electrochemical Impedance Spectroscopy and Electro chemical Stability window was measured. Due to the limited amount of sample and time limit the experiment were performed upon the limited number of samples with various concentration of the each materials. The samples that does not solidify properly or broke easily when attempted to take out of the Petri dish is denoted in the tables as Not Extractable (NE).

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5.4 PVDF-HFP with EMIM-BF₄ (IL) and Zeolite in 1:3:0.1 (w/w)

The CV diagram for the sample with the concentration of PVDF-HFP, EMIM-BF₄ and Zeolite respectively in the ratio of 1:3:0.1 (w/w) with maximum conductivity result shows the areal capacitance of the supercapacitor assembly to be nearly equal to $15\text{mF}/\text{cm}^2$ which is shown in the Figure 33.

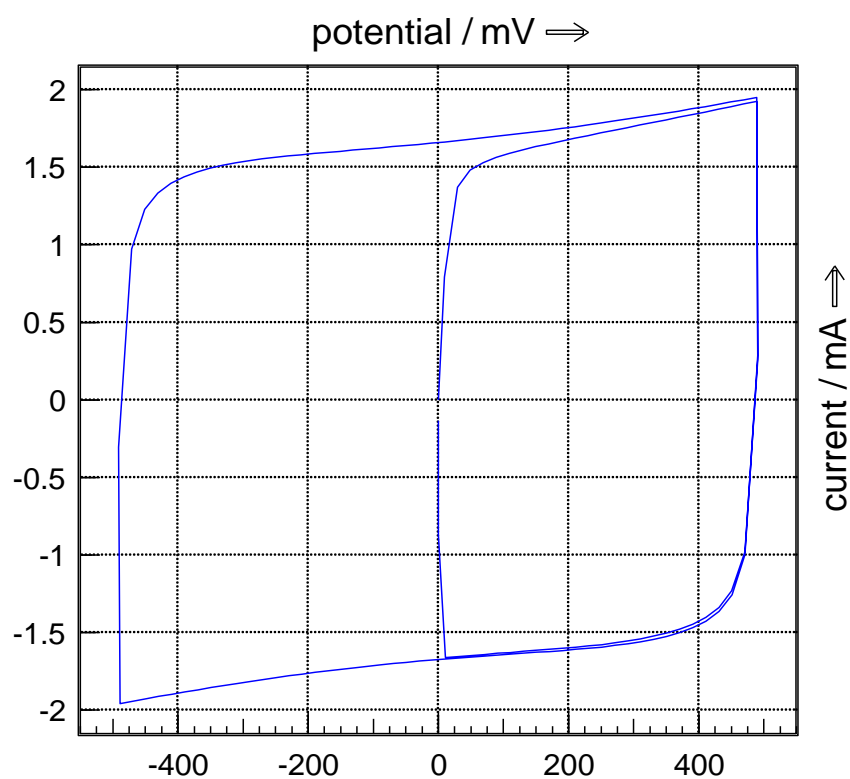


Figure 33: Cyclic Voltammetry of the PVDF-HFP+EMIM-BF₄+zeolite (1:3:0.1 w/w) polymer film with supercapacitor assembly at 100mV/s.

Figure 34 shows the Nyquist plot of this supercapacitor cell. The step rising behavior of the complex impedance plot indicates the capacitive behavior of the supercapacitor cell. The experiment is performed in the frequency range between 100mHz to 100KHz. The working potential of this cell is found to be nearly 3V.

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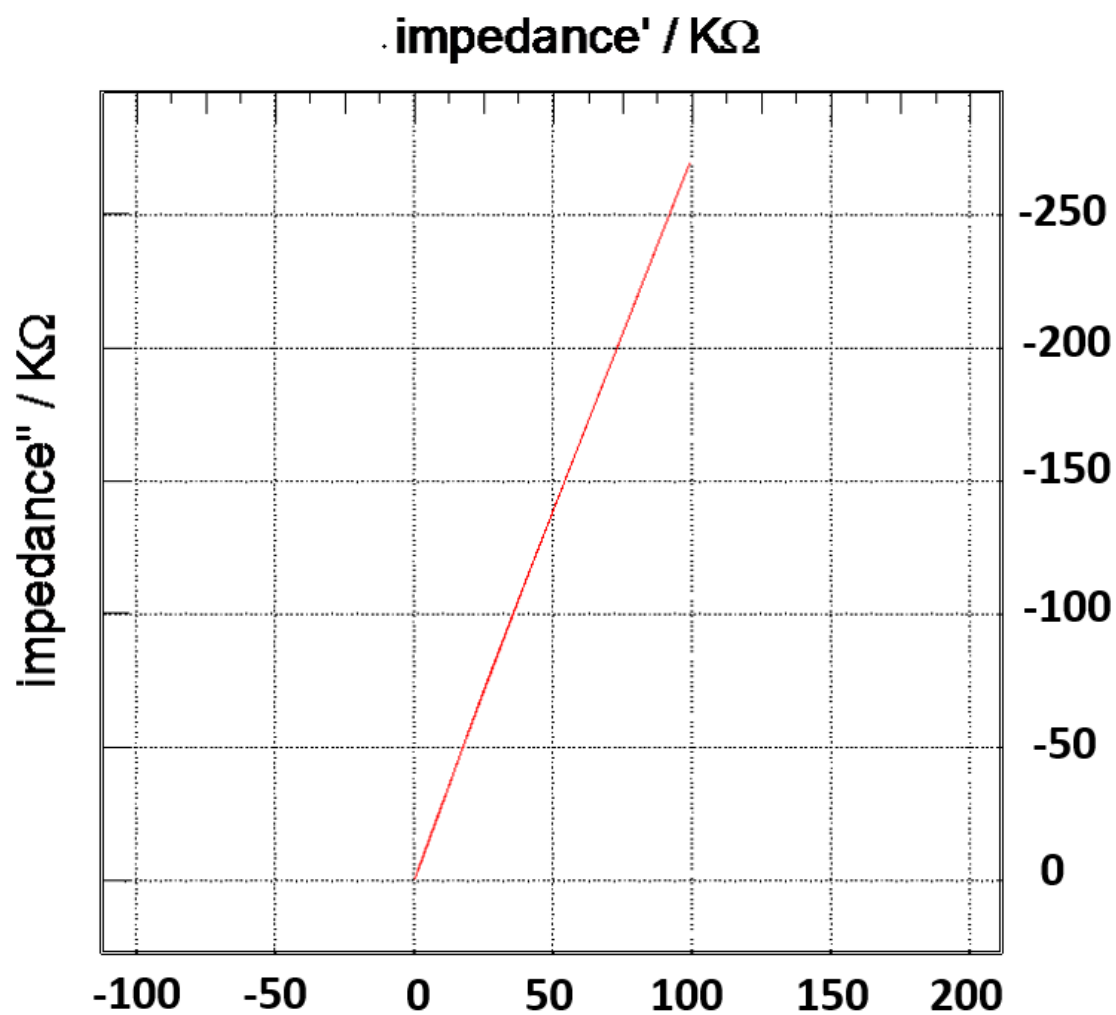


Figure 34: Nyquist plot of PVDF-HFP+EMIM-BF₄+zeolite (1:3:0.1 w/w) polymer film with supercapacitor assembly

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5.5 PVDF-HFP with EMIM-BF₄ (IL) and rGO in 1:2:0.05 (w/w)

The CV diagram for the sample with the concentration of PVDF-HFP, EMIM-BF₄ and rGO respectively in the ratio of 1:2:0.05 (w/w) with maximum conductivity result shows the areal capacitance of the supercapacitor assembly to be nearly equal to 15 to 20 mF/cm^2 which is shown in the Figure 35 and working potential to be around 3.5V.

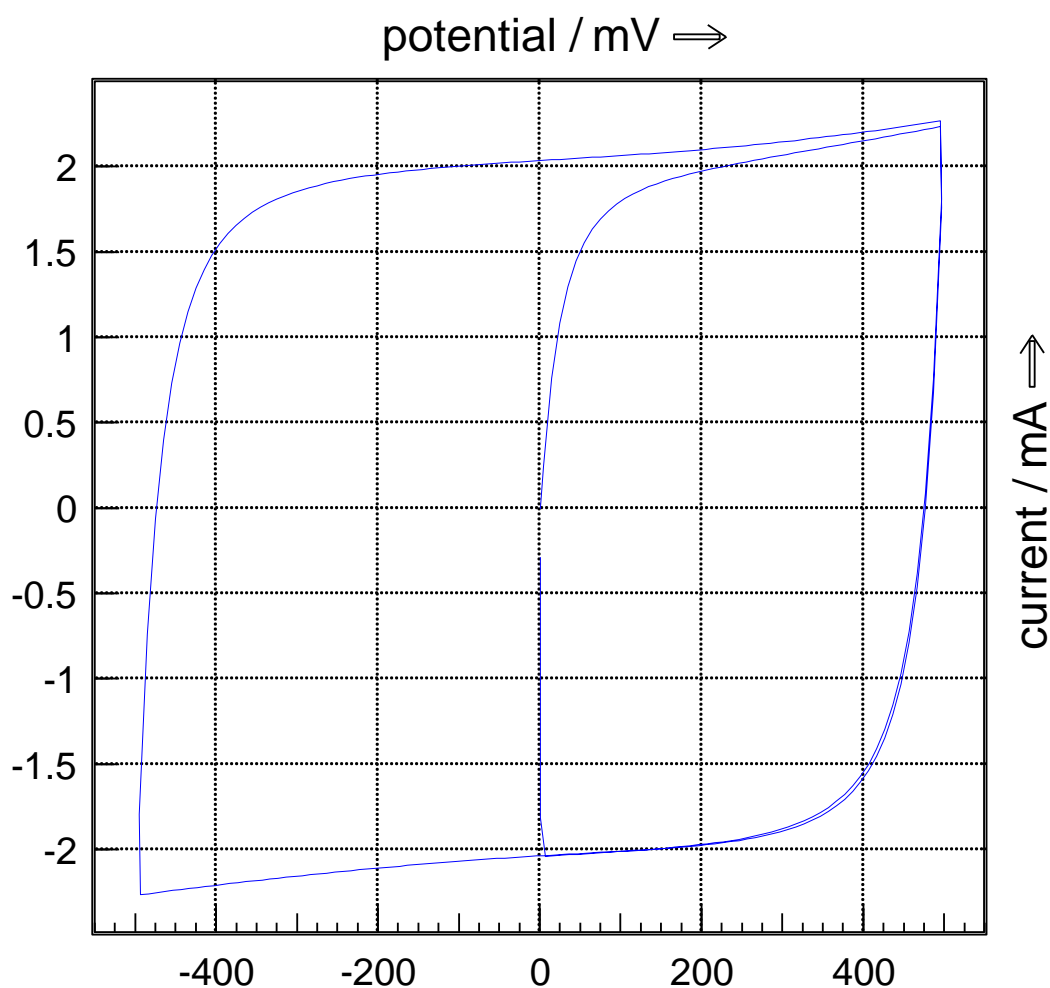


Figure 35: Cyclic Voltammetry of the PVDF-HFP+EMIM-BF₄+rGO (1:2:0.05 w/w) polymer film with supercapacitor assembly at 100mV/s.

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Nyquist plot of this supercapacitor cell is presented in Figure 36 below. The step rising behavior of the complex impedance plot indicates the capacitive behavior of the supercapacitor cell. The experiment is performed in the frequency range between 100mHz to 100KHz.

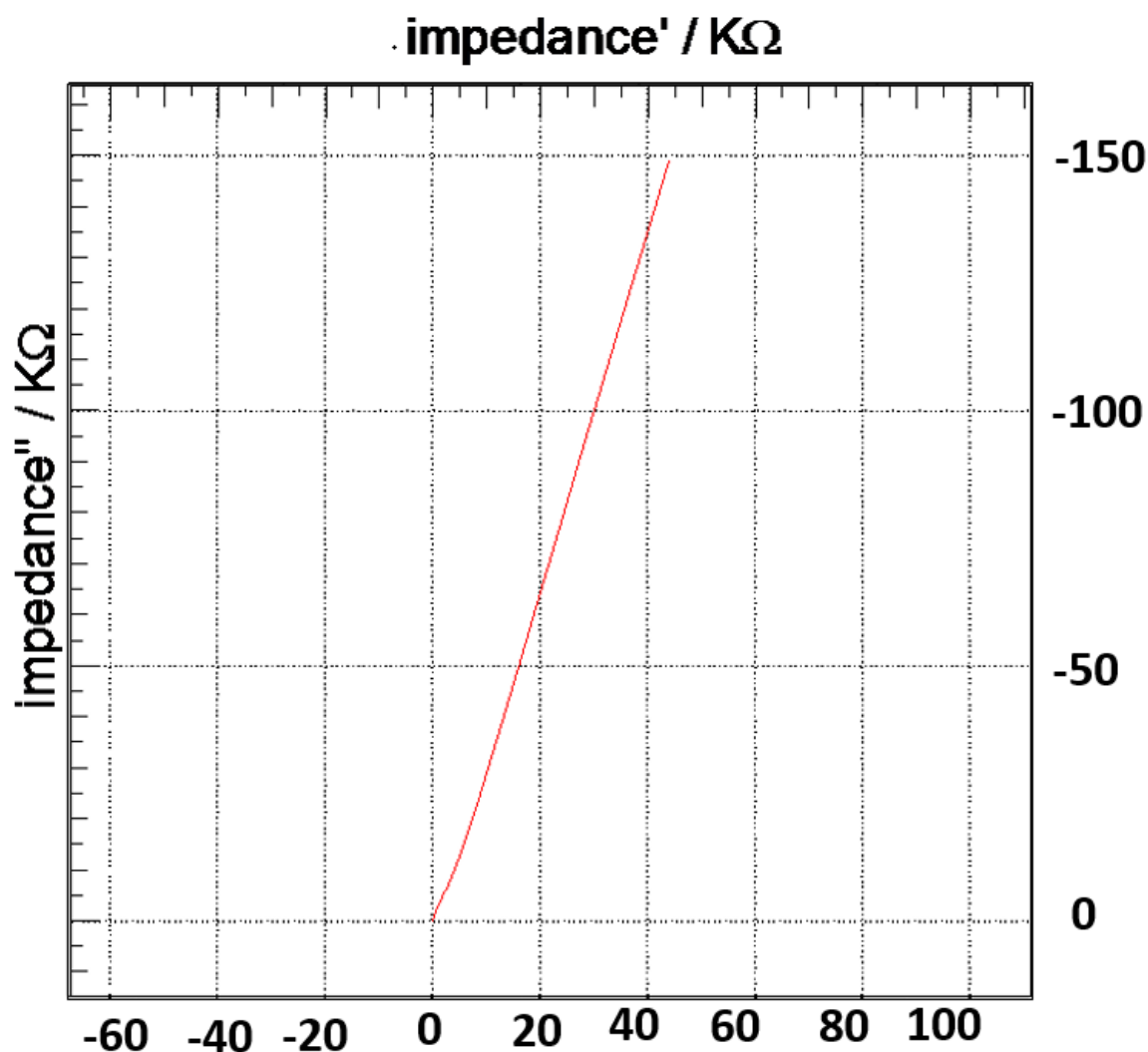


Figure 36: Nyquist plot of PVDF-HFP+EMIM-BF₄+rGO (1:2:0.05 w/w) polymer film with supercapacitor assembly

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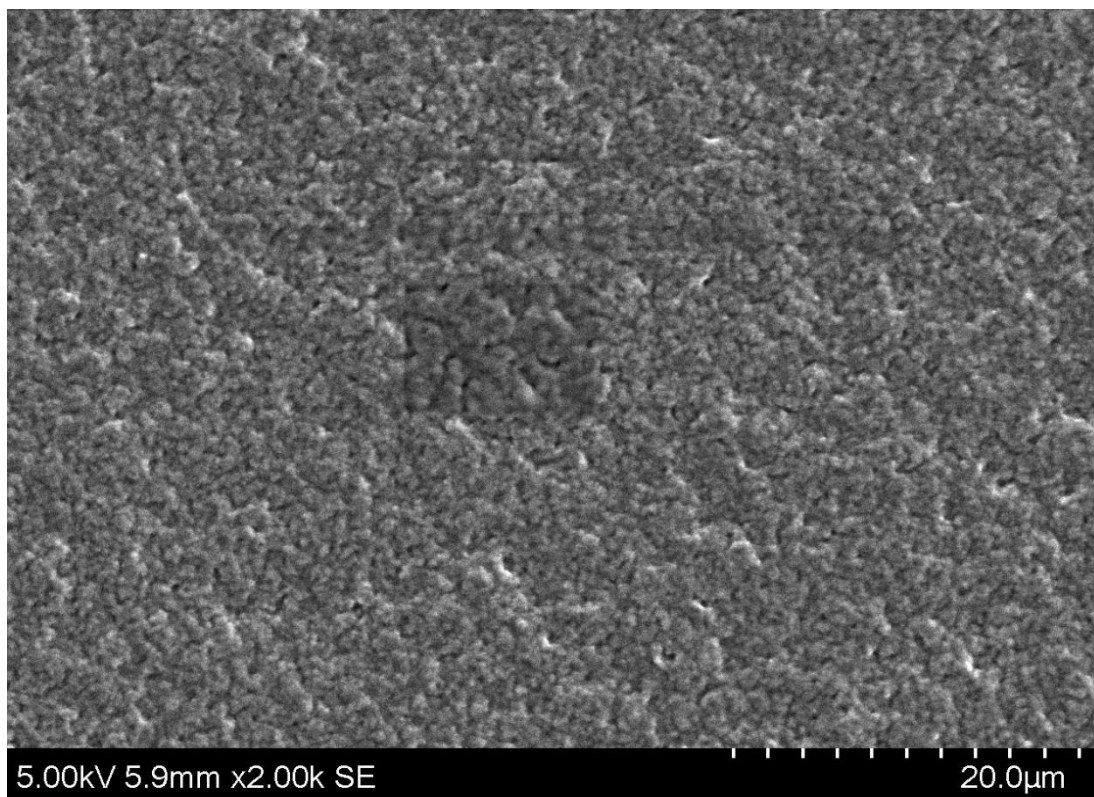


Figure 37: Scanning Electron Microscopy (SEM) image of PVDF-HFP+EMIM-BF₄+rGO (1:2:0.05 w/w) polymer film.

Figure 37 is the SEM image of the PVDF-HFP+EMIM-BF₄+rGO (1:2:0.05 w/w) polymer film. SEM is not much clear but we can clearly identify that with the addition of the reduced Graphene oxide particles the amorphous structure of the film is much improved suppressing the crystalline structure. This properties directs us to the conclusion that the polymer film with IL and rGO particles should have more conductive results than compared with the polymer with IL alone.

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5.6 PVDF-HFP with EMIM-DCA (IL) and Zeolite in 1:3.5:0.1 (w/w)

The CV diagram for the sample with the concentration of PVDF-HFP, EMIM-DCA and Zeolite respectively in the ratio of 1:3.5:0.1 (w/w) with maximum conductivity result shows the areal capacitance of the supercapacitor assembly to be nearly 20 to 25 mF/cm^2 which is shown in the Figure 38. Working potential of the cell assembly is nearly 3.2V.

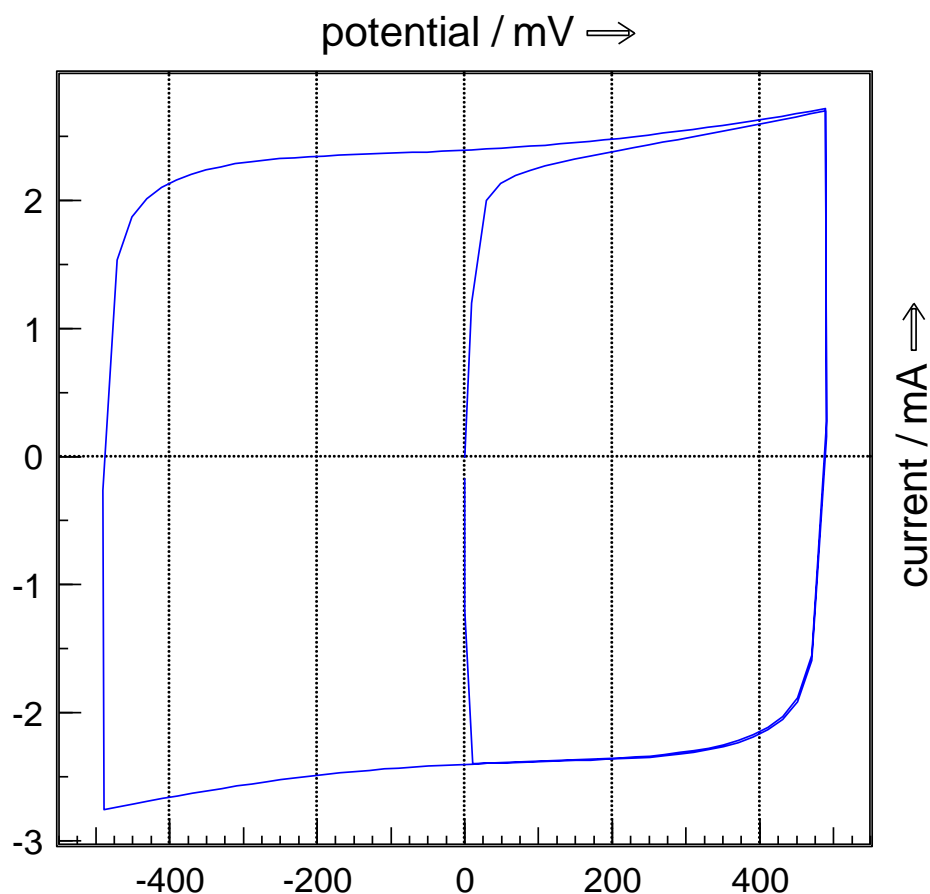


Figure 38: Cyclic Voltammetry of the PVDF-HFP+EMIM-DCA+Zeolite (1:3.5:0.1 w/w) polymer film with supercapacitor assembly at 100mV/s.

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Nyquist plot for this supercapacitor cell assembly is presented in Figure 39 below. The step rising behavior of the complex impedance plot indicates the capacitive behavior of the supercapacitor cell. The experiment is performed in the frequency range between 100mHz to 100KHz. In this Figure the impedance plot vary a little while going up into lower frequency and returning back. This may be due to the supercapacitor configuration is not so stable and contact between electrode and electrolyte variation.

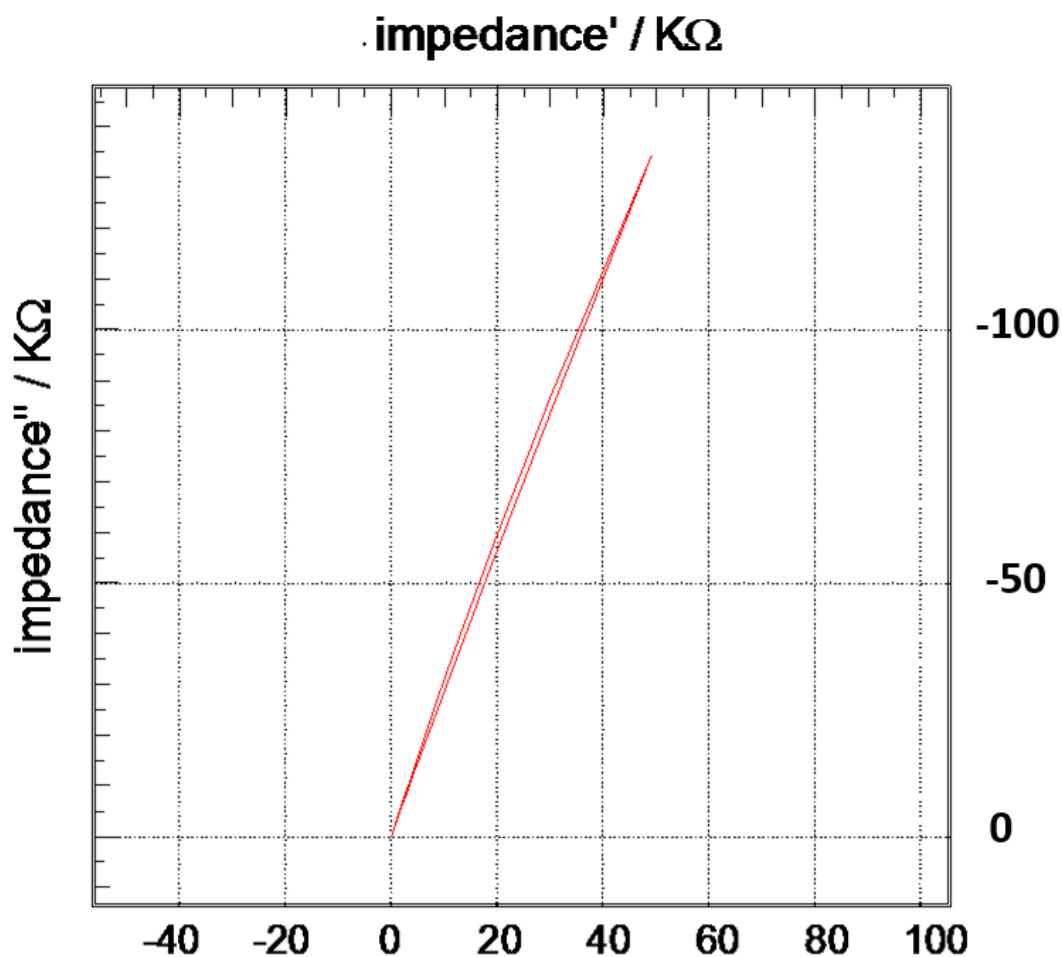


Figure 39: Nyquist plot of PVDF-HFP+EMIM-DCA+Zeolite (1:3.5:0.1 w/w) polymer film with supercapacitor assembly

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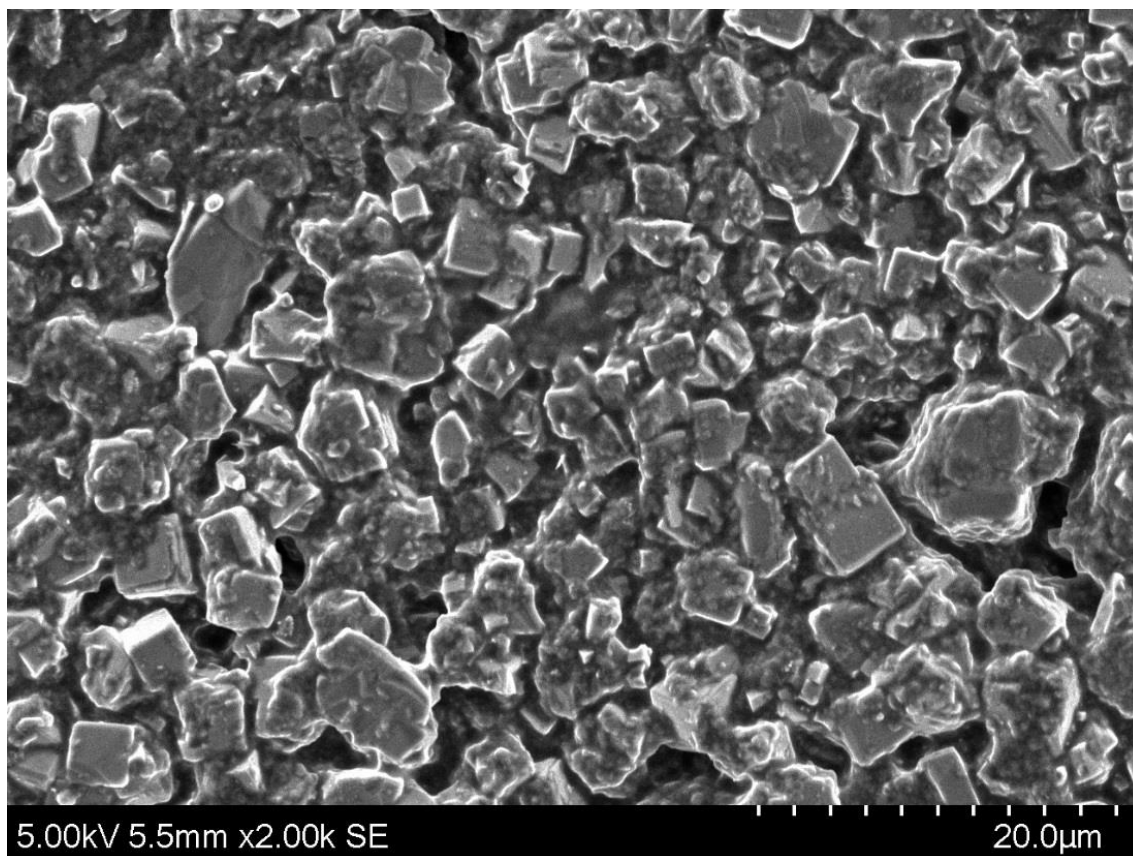


Figure 40: Scanning Electron Microscopy (SEM) image of PVDF-HFP+EMIM-DCA+Zeolite (1:3.5:0.1 w/w) polymer film.

SEM image of the PVDF-HFP+EMIM-DCA+Zeolite (1:3.5:0.1 w/w) polymer film is shown in Figure 40. Here the amorphous stage of the polymer film is much more improved than compared to both polymer film with IL and polymer film with IL and rGO particles. This clearly reflects in the results as well by showing the film with zeolite particles were more conductive than others.

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5.7 PVDF-HFP with EMIM-DCA (IL) and rGO in 1:3.5:0.01 (w/w)

The CV diagram for the sample with the concentration of PVDF-HFP, EMIM-DCA and rGO respectively in the ratio of 1:3.5:0.01 (w/w) with maximum conductivity result shows the areal capacitance of the supercapacitor assembly to be nearly 10 to 15 mF/cm^2 which is shown in the Figure 41. Working potential of the cell assembly is nearly 2.8V.

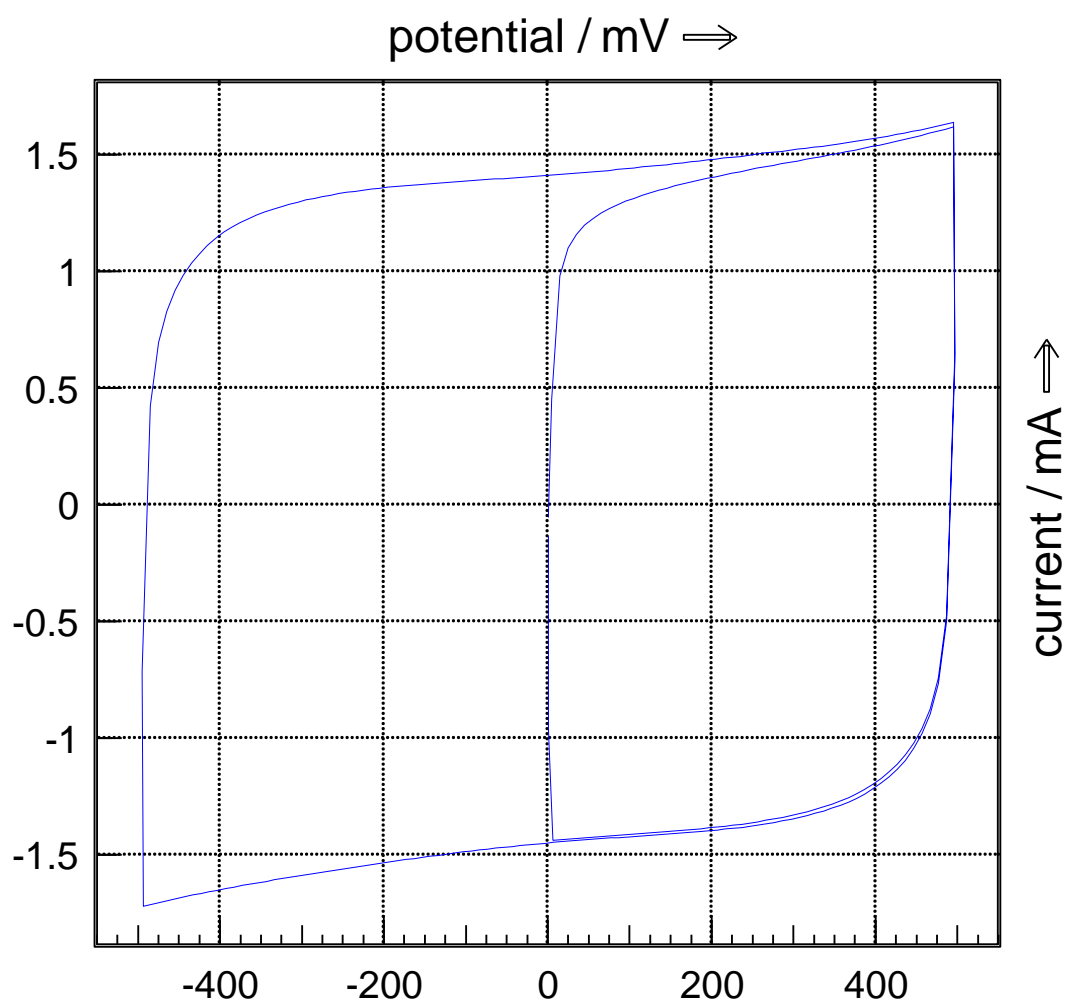


Figure 41: Cyclic Voltammetry of the PVDF-HFP+EMIM-DCA+rGO (1:3.5:0.01 w/w) polymer film with supercapacitor assembly at 100mV/s.

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Nyquist plot for this supercapacitor cell assembly is presented in Figure 42 below. The step rising behavior of the complex impedance plot indicates the capacitive behavior of the supercapacitor cell. The experiment is performed in the frequency range between 100mHz to 100KHz.

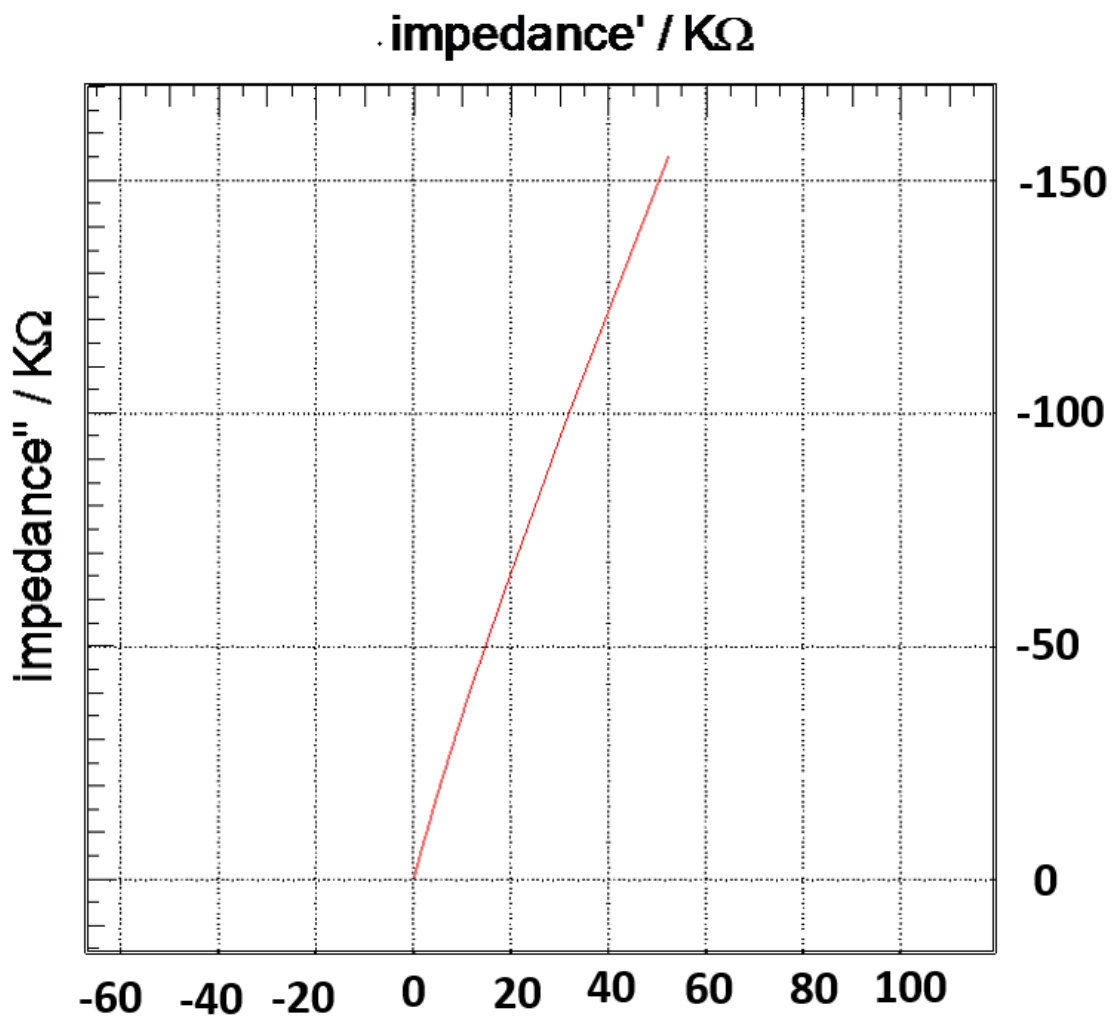


Figure 42: Nyquist plot of PVDF-HFP+EMIM-DCA+rGO (1:3.5:0.01 w/w) polymer film with supercapacitor assembly

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By performing various experiments of the different samples, we obtained different results and those results is presented in the Table 7 below.

Table 7. Summary of the results for conductivity of film with capacitance and working potential of the supercapacitor assembly

POLYMER FILMS	CONDUCTIVITY (S/cm)	CAPACITANCE (mF/cm ²)	WORKING POTENTIAL (V)
PVDF-HPF+EMIM-DCA (1:2.5)	$\sigma = 1.28 \times 10^{-2}$	20	3.5 V
PVDF-HPF+EMIM-DCA+zeolite (1:2.5)	$\sigma = 2.1 \times 10^{-2}$	20	3.2V
PVDF-HPF+EMIM-DCA+rGO (1:2.5)	$\sigma = 1.8 \times 10^{-3}$	15	2.8V
PVDF-HPF+EMIM-BF4 (1:2)	$\sigma = 1.87 \times 10^{-3}$	10	4 V
PVDF-HPF+EMIM-BF4+zeolite (1:2)	$\sigma = 4.8 \times 10^{-4}$	15	3 V
PVDF-HPF+EMIM-BF4+rGO (1:2)	$\sigma = 4.1 \times 10^{-4}$	20	3.5 V

The data presented in Table 7 shows different conductivity, ESW, and capacitance measurement results. PVDF-HPF+EMIM-DCA (1:2.5) polymer film has conductivity of 1.28×10^{-2} S/cm, 20 mF/cm^2 capacitance and ESW of 3.5 V. Adding zeolite (nano particles) improves the conductivity almost twice but cell capacitance doesn't change whereas addition of rGO particles improves the conductivity very little but cell capacitance get reduced to 15 mF/cm^2 . Similarly PVDF-HPF+EMIM-BF4 (1:2) polymer film has conductivity of 1.87×10^{-3} S/cm, 10 mF/cm^2 capacitance and ESW of 4 V. Addition of zeolite particle improves the conductivity almost by 2.5 times and capacitance to 15

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mF/cm^2 whereas on addition of rGO particles conductivity increases by almost 2 times and capacitance increases to $20mF/cm^2$. The addition of conductive Nano particles helps to improve conductivity of the solid polymer electrolyte but at the expense of the reduced working potential [40, 42-44].

Various papers has reported that there is decrease in the conductivity of the polymer film due to the increase in viscosity which degrades the mobility of the polymeric chains. Ion transport mechanism in electrolyte has been described by various models. Theory like Dynamic Bond Percolation Model, Angell's Decoupling Theory, Configurational Entropy model, Free Volume Theory etc. based on solvent –free solid polymer electrolyte models. Other models like gel polymer electrolyte model and model applicable to composite polymer electrolytes with different theories are present as well. Increase in ionic conductivity of the polymer electrolyte by increasing the flexibility and amorphous phase of the polymer which in turn increases the free volume within the electrolyte system and decreases the viscosity and making the mobility of ions easier according to the Free volume Theory. Application of heat increases the feed concentration and membrane becomes swelled and hydrophobicity of the swollen molecule decreases resulting the permeating molecule diffuse through the free volumes of the membrane. Thermal motion of the polymer chains in the amorphous region randomly produces the free volume breaking the crosslinked polymers. Increasing temperature increases the diffusion rate of permeating molecules which leads to higher permeating flux. Charge carriers like (EMIM⁺, BF₄⁻) interact with polymer structure reducing the intermolecular interaction between the polymer chain and thus increases the polymer chain segment mobility. Higher segmental mobility of the polymer chains means greater disorder in their arrangement which result in increased amorphous phase of the gel polymer electrolyte. Thus transport of ions in these system is greatly facilitated by rapid segmental motion typically found in rubbery, amorphous polymers [40-41].

Chapter 6 CONCLUSIONS AND FUTURE WORK

The main purpose of this thesis is to identify the suitable polymer film for supercapacitor application with good ionic conductivity. First step of this work was carried out by doing the initial research on good polymer material which has been used recently. PVDF-HFP is one of the best polymer film with good properties and used most recently. So opting this polymer this which has relatively poor conductivity but when used with blending the material with suitable ionic liquids showed good conductive performance.

Next step was to find out the suitable ionic liquids with good conductivity and low viscosity properties which can be blended into this PVDF-HFP polymer matrix. Considering these properties we choose two ionic liquids EMIM-DCA and EMIM-BF₄ and blended these with the same polymer matrix and studied the structural and electrochemical characteristics. These films gave certainly improved ionic conductivity. EMIM-DCA + PVDF-HFP polymer film has ionic conductivity in the range of 10^{-2} S/cm where as EMIM-BF₄ + PVDF-HFP polymer film has ionic conductivity in the range of 10^{-3} S/cm.

After preparing the solid polymer electrolyte film with suitable ionic liquids, the next task is to improve the conductivity of the polymer film. Use of nano size conducting material to improve the conductivity of the film has been reported in the past as well [42-44]. Several works has been done applying these nano size conducting particles upon the porous film. Out of many options we opted to select zeolite and graphene oxide (reduced) particles and tried to study their performance upon these polymer films. As per the result presented in Table 7, we can easily see that the application of these ion conducting promoter helps to improve the ionic conductivity as well as electrochemical performance of the supercapacitor assembly as well. But these came at the expense of reduced working potential by a little amount.

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These porous films depends upon relative humidity which should be considered with great emphasis. All the experiments were done in normal room temperature condition at the laboratory but for these types of electrochemical experiment special arrangement like the measurement in black-box should be used. Because the experiment was performed upon different humidity condition and other environmental factors could have affected the results as well (in small amount). The result vary a little bit for these types of films over time because of change in temperature and humidity of the environment across which the measurement was carried out.

Graphene oxide (reduced) used had relatively bigger size (15 layer thickness) than it could have been used (1 layer thickness). Use of this lower thickness particle will improve the conductivity of the sample with rGo particles probably by 5 to 10 times more. This rGO bigger particle is not properly reduced and did not have good electrical conductivity but despite this due to limited time and not availability of the smaller rGO (highly conductive) particles these were used. Thus it can be assumed that the use of rGO highly conductive particles these conductive results will increase drastically. The effect of ionic conductivity is highly dependent on the specific surface area and the surface characteristics of those additional materials. The role of small nano particles as illustrated from the SEM analysis shows that they help to improve the conductivity by changing the polymer film to more amorphous phase. Usually increase in conductivity is inferred by DSC studies. The formation of molecular complex between the nano fillers and the polymer compound is usually confirmed by infrared spectral analysis. These homogenously distributed nano fillers forms an ion highway to facilitate the ion transportation.

For increasing the performance of the supercapacitor cell, improved electrode like Graphene electrode could be used because the MWCNT electrode slurry used is not uniformly distributed when coated upon the current collector (Graphite).

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The stability of the supercapacitors were checked over repeated CV cycle. The instrument is capable of performing the CV cycle up to few hundreds only. By performing the CV cycling until 900 cycles the supercapacitor was very stable and show almost the same capacitance value (as in initial CV cycles) without any damage or deformation. As reported from the researches these kind of supercapacitors are very stable and can sustain nearly from few thousands up to 10,000 cycles with 80% capacitance retention [45, 46]. The capacitive performance of the supercapacitor was measured over different time (after weeks) but the result did not vary.

Wen Lu [47] has reported the conductivity of PVDF-HFP+EMIM-BF₄ (1:2.5 w/w) to be 3.7mS/cm which is twice than we obtained at our experiment. But both results are in the same order and some error factors like environmental condition (humidity, temperature) might have influenced the result. The writer also presented the conductivity of PVDF-HFP+EMIM-BF₄+Zeolite (1:2.5:0.06 w/w) to be 2.4mS/cm. We obtained higher result of conductivity as 4.1mS/cm but at different concentration (1:3:0.1 w/w), where more ionic liquid and zeolite particles were blended into the polymer film.

Xi Yang [48] has reported that the conductivity of PVDF-HFP+EMIM-BF₄+rGO (1:2:0.01 w/w) to be around 9mS/cm where as we got this conductivity to be 4.8mS/cm at (1:2:0.05 w/w) concentration. one of the main reason for variation in this result is mainly due to the use of different rGO materials as well. The writer has used nearly 99% reduced Graphene oxide (highly conductive) where as we used 10% reduced Graphene oxide (very low conductive).

P.K. Singh [37] has previously published the conductivity of PVDF-HFP+EMIM-DCA (1:2.5 w/w) to be 3.42mS/cm. But from this experiment we observed the conductivity of the same film was found to be 12.8mS/cm. This is relatively higher value and almost differ by an order difference. Thus, further work with the addition of zeolite and rGo particles on the films were performed and this gave improved conductive value for the

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electrolyte. With the addition of highly reduce graphene oxide particle it can be expected that the conductivity of the film will be more enhanced than the film with zeolite particles.

Thus for the future work, there is possibility of using more reduced and highly conductive materials (rGO or others) in the polymer film (for improving the electrolyte). There is possibility of using more conductive and uniformly distributed Graphene sheets (as electrodes) replacing the graphite sheets with MWCNT coated on it, which is not uniform (for improving the electrode and thus whole supercapacitor). This will increase the performance of the whole supercapacitor.

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