Electrodeposition of Nickel Cobalt Oxide for the Application of Asymmetric Flexible Microsupercapacitor

A Thesis Submitted towards Partial Fulfilment of BS-MS Dual Degree Program

By

Kaustubh Tarmale

Reg. No. 20121068

Under the guidance of

Prof. Satishchandra B. Ogale

Department of Physics and Chair for Centre of Energy Science

IISER Pune, India

To

Department of Chemistry

Indian Institute of Science Education and Research (IISER) Pune

CERTIFICATE

This is to certify that this dissertation entitled **"Electrodeposition of nickel cobalt oxide for the application of asymmetric flexible micro-supercapacitor"** towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents the research carried out by **Kaustubh Tarmale** at IISER Pune under the supervision of **Prof. Satishchandra B. Ogale**, Department of Physics and Chair of Centre for Energy Science, IISER Pune, during the academic year **2016-2017**.

Tarmale

Kaustubh Tarmale

Reg Id: 20121068

Prof. Satishchandra B. Ogale

(Thesis Supervisor)

Date: 20th March 2017

Place: Pune

DECLARATION

I hereby declare that the matter embodied in the report entitled **"Electrodeposition of nickel cobalt oxide for the application of asymmetric flexible micro-supercapacitor"** are the results of the investigations carried out by me at the Department of Physics, IISER Pune, under the supervision of Prof. Satishchandra B. Ogale and the same has not been submitted elsewhere for any other degree.

Tarmale

Kaustubh Tarmale

Reg Id: 20121068

Prof. Satishchandra B. Ogale

(Thesis Supervisor)

Date: 20th March 2017

Place: Pune

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.
Kaustubh Tarmale

Dedicated to my beloved Family

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Abbreviations

SC	Supercapacitor
MSC	Micro-supercapacitor
DI	Distilled Water
XRD	X-ray Diffraction
FESEM	Field Emission Scanning Electron Microscopy
LIG	Laser Induced Graphene
NCO	Nickel Cobalt Oxide
CV	Cyclic Voltammetry
ESR	Electrochemical Series Resistance
EIS	Electrochemical Impedance Spectroscopy
EDAX	Energy Dispersive Analysis X-ray
PI	Polyimide

Abstract

Recently, flexible and wearable microelectronics has become one of the most exciting and trending fields of research. Various types of flexible and wearable devices have been introduced lately. In this work, we have demonstrated an easy and facile approach to fabricate all solid state asymmetric flexible micro-supercapacitor (MSCs) by using CO_2 laser scribing technique and electrodeposition. Ternary metal oxide (nickel cobalt oxide) was electrodeposited through electrodeposition at a particular value of I×t (current passed during deposition × time of deposition) and was used as electrode. PVA-H_3PO_4 is the gel electrolyte used for all the electrochemical measurements. Asymmetric nature of our fabricated device helped to widen the operating voltage range up to 1.4 V. The areal capacitance for the fabricated device was 2.02 mF cm^{-2} at 0.25 mA cm^{-2} current density. The fabricated micro-supercapacitor all solid state device also shows high flexibility (over 90% capacitance retention) at 120^o bending.

1. Introduction

Over past decade, there is an extensive boom in portable electronic devices which are compact in size and can be designed on flexible substrate along with the other components. Energy storage devices having bulk size are difficult to integrate in the miniaturized device arrays, hence to overcome the difficulties energy storage device are getting miniaturized as well as planer, which also allow increasing the device density[3]. In recent years, flexible micro-supercapacitors (MSCs) have become topic of interest among the different energy storage devices by various researchers due to its unique advantages such as long cyclic stability, flexibility, high power density, light weight and shape diversity [1]. One of the challenging factors of fabricating flexible MSCs is the electrode material having high electrochemical performance and good mechanical properties. Using functional materials like metal oxides/hydroxides, conducting polymers, carbonaceous materials in different flexible substrate as electrode material is one of the promising approach towards fabricating good flexible microelectronics devices [2]. Currently various fabrication techniques are being used to make micro patterned devices such as thermal evaporation, chemical vapour deposition, laser scribing technique, lithography etc.[3] All the available fabrication techniques except laser scribing technique consists multi step and time consuming approaches; hence laser scribing technique is most preferred due to its fast and single step processibility [4].

Solid state supercapacitors are alternatives to classical supercapacitors due to its high power density and convenient usage. Major components in solid state supercapacitors are solid state electrolyte (mainly gel based), flexible electrodes and packing material. Solid state electrolytes such as PVA-H_3PO_4 or PVA-H_2SO_4 are few examples of gel electrolyte which are commonly used in aqueous based flexible MSCs. Use of solid electrolyte has also solved one of the major problem of electrolyte leakage [5].

1.1 Supercapacitors

Supercapacitor which is also referred as supercap, Goldcap or ultracapacitor is one of the energy storage device which have higher capacitance value than conventional capacitor i.e. electrolytic capacitor. Supercapacitor (SC) is a high capacity capacitor and can store 100 times more charge compare to electrolytic capacitor. It has more cyclic stability than rechargeable batteries i.e. it can have more charge discharge cycles and can accept and release charge much rapidly than rechargeable batteries.

Types of Supercapacitors:

1. Electric Double layer capacitors(EDLC)
2. Pseudo capacitors
3. Hybrid capacitors

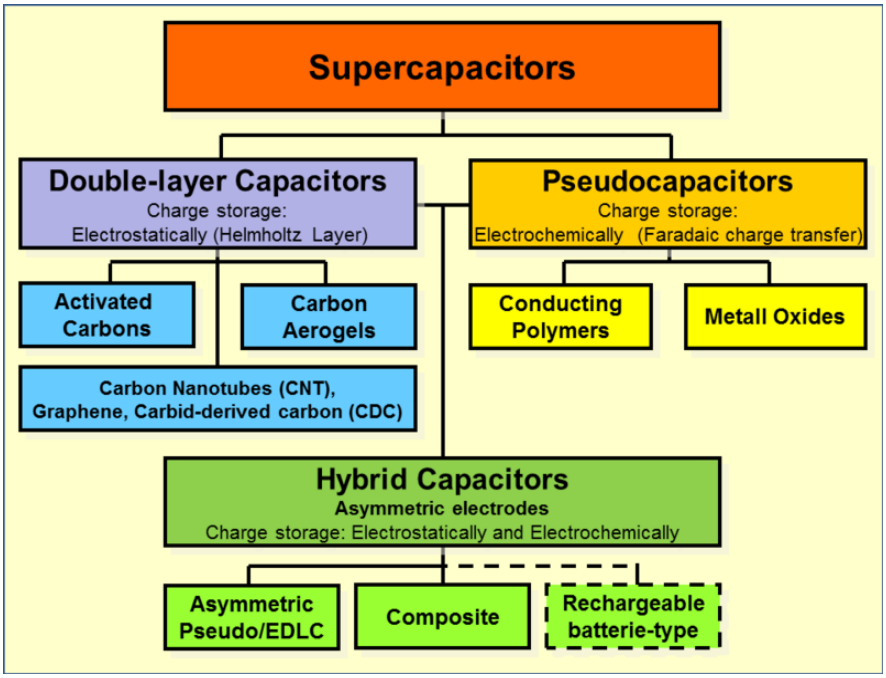


Figure 1. Classification of Supercapacitors. (adopted from https://en.wikipedia.org/wiki/Supercapacitor#/media/File:Supercaps-family.png)

Supercapacitors (SC) are classified on basis of their storage mechanism, which are double layer capacitor and pseudocapacitor. In double layer capacitor, electrostatic energy is stored by electrostatic storage due to charge separation in Helmholtz double layer whereas in pseudocapacitors, electrical energy is stored by electrochemical storage due to faradic redox reaction by charge transfer [6]. The third type of capacitor is Hybrid capacitor, where both electrostatic storage and electrochemical storage of electrical energy is done hence the respective electrodes exhibits different characteristics i.e. electrostatic capacitance and electrochemical capacitance respectively. The detailed description of different types of supercapacitors is given below.

1.1.1 Electrostatic Double Layer Capacitance

An assembly of electrochemical capacitor consists of two electrodes which are separated by a separator mechanically and connected by electrolyte ionically. Electrolyte comprises of both negative and positive ions dissolved in any solvent. Both the electrodes having metallic surface and large surface area gets in touch with liquid electrolyte in such a way that the two phases share a common boundary which are liquid electrolyte and the insoluble solid electrolyte leading to a phenomenon called double layer effect. Electric double layer is generated by applying a voltage to electrochemical capacitor. As name suggests ,the double layer comprises of two charge layers, one is inside the surface structure of electrode whereas other electronic layer having opposite polarity, comes from the electrolyte due to dissolved and solvated ions. A monolayer of solvent molecules separate the two layers which is called inner Helmholtz plane (IHP). Oppositely polarized ions are separated from each other due to physical adsorption of solvent molecules on surface of electrodes and can be called as molecular dielectric. The forces causing adhesion are physical forces (electrostatic force) and not chemical forces since there is no charge transfer occurring between the electrode and electrolyte. There are no chemical changes in the electrode even the adsorbed molecules get polarized, due to no transfer of charge between electrode and

electrolyte. Counter charges in outer Helmholtz plane (OHP) matches the magnitude of amount of charge in the electrodes, in this way electrical charges are stored in conventional capacitor via double layer phenomena. A electric field in molecular level of solvent is formed due to double layer charge in the IHP which is respect to the applied voltage [7].

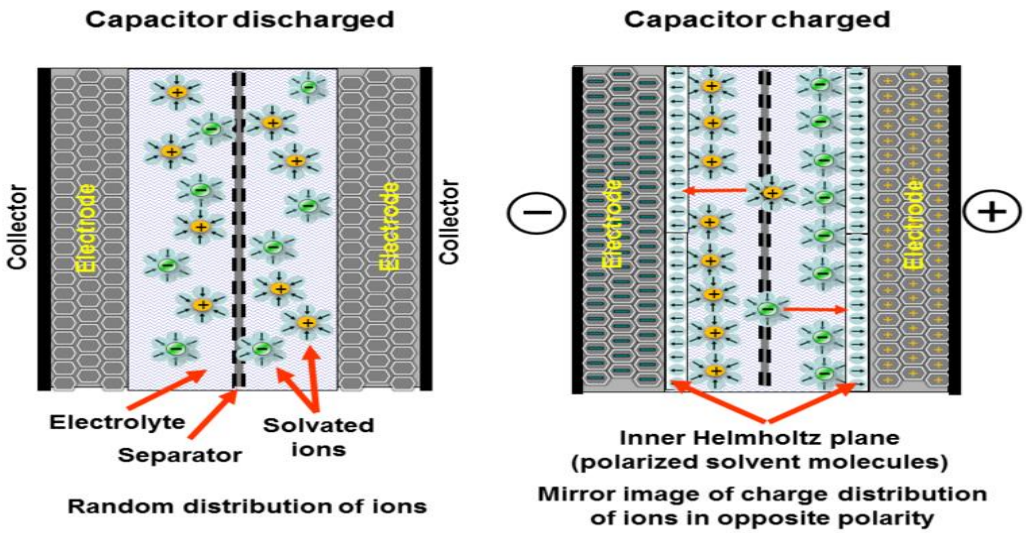


Figure 2. View of Ideal double layer capacitor. (Adopted from http://www.wikiwand.com/en/Double-layer_capacitance)

The general formula for calculating the capacitance of conventional plate capacitor is given by [8]:

$$C = \varepsilon \frac{A}{D}$$

Where: C= capacitance

ε= permittivity

A= area of the electrodes

d= distance between electrodes

Double layer capacitors exhibits higher capacitance value than the conventional capacitors due to high surface area of the electrodes and very thin double layer present. The amount of charge stored per unit voltage completely depends on the size of

electrodes. In case of conventional capacitors charge is transferred by electrons whereas in double layer capacitor capacitance depends on the speed of moving ions in electrolyte and also on resistive structure of electrodes. Technically since there is no chemical reactions involved, there should be unlimited charging discharging cycles for double layer capacitor, it can be decrease only due to evaporation of electrolyte [8].

1.1.2 Electrochemical Pseudocapacitance

The electrical energy is stored via faradaic redox reactions occurring on the surface of the electrodes in the electrochemical capacitor. Pseudocapacitance is observed due to electron charge transfer happening between electrode and electrolyte where one electron per charge unit takes part from de-solvated and adsorbed ion. The amount of pseudocapacitance we observed in electrochemical pseudocapacitor is through redox reaction mostly depends on the dimensions and structures of the electrodes and also on chemical affinity of electrode material to the ions adsorbed on electrode surface [9][10][11]. The oftenly used materials for electrodes in pseudocapacitors which exhibits redox behaviour are transition metal oxide such as MnO_2, RuO_2 etc. which are further embedded in the conductive electrode material like activated carbon and also conducting polymers like polyaniline (PANI) [12].

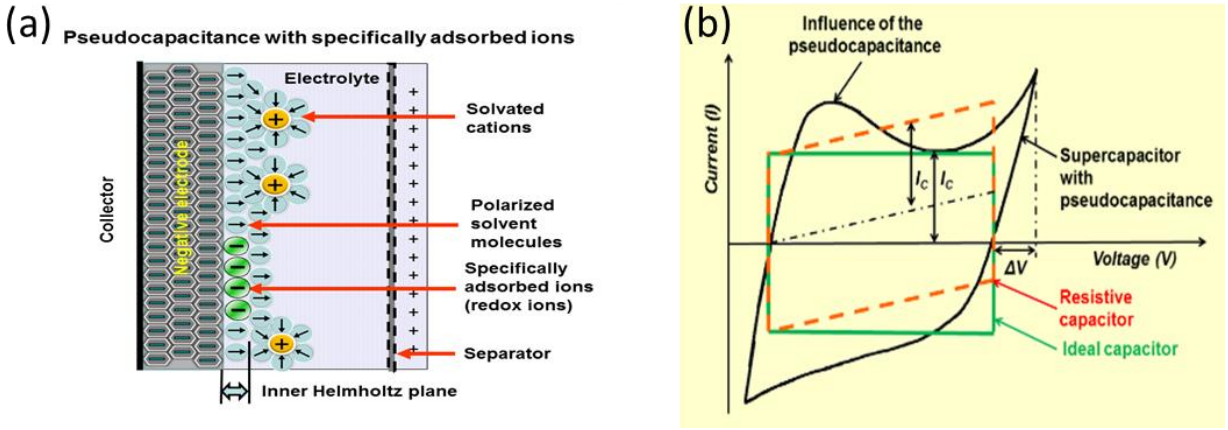


Figure 3. a) Simplified view of double layer. b) CV explaining difference between static capacitance and pseudocapacitance (adopted from

https://commons.wikimedia.org/wiki/File:EDLC-simplified-principle.png ,
https://en.wikipedia.org/wiki/Supercapacitor#/media/File:Voltagram-Engl.png)

1.1.3 Hybrid Supercapacitor

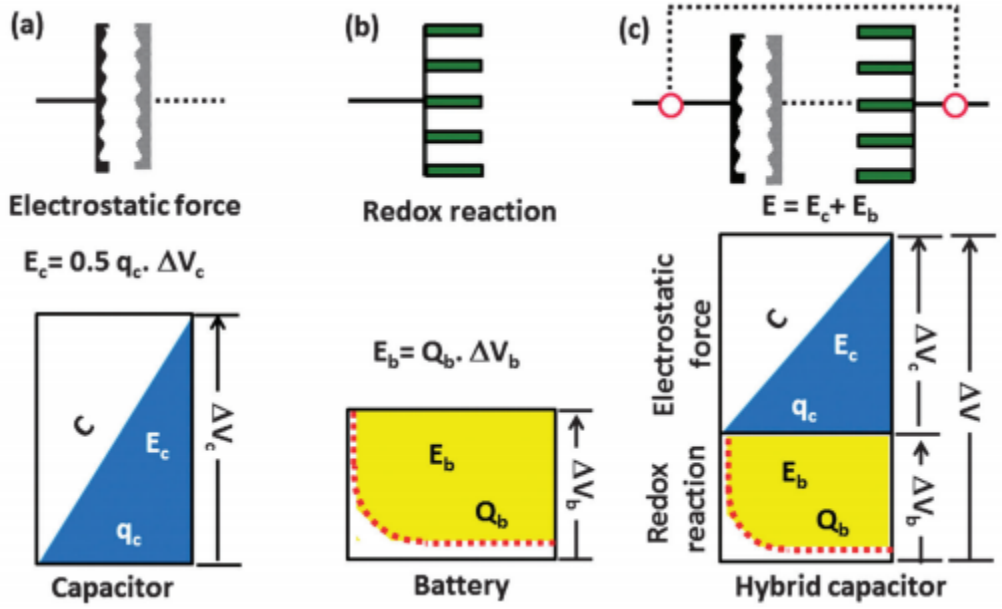


Figure 4. Schematic representations of hydrid capacitor system in terms of charge–potential profile (Ref. 13)

Hybrid capacitor is third type of supercapacitor where both electrostatic storage and electrochemical storage of electrical energy is done hence the respective electrodes exhibits different characteristics i.e. electrostatic capacitance and electrochemical capacitance respectively [6][13]. In case of hybrid supercapacitors, anode mostly consists of metal oxides or conducting polymers whereas cathode consists of mostly carbon based materials. The given supercapacitor is double layer capacitor or pseudocapacitor can be identified only by measuring their capacitance.

1.2 Graphene as EDLC electrode material

Graphene which is single layer of graphite, is also used as a prominent material for the electric double layer capacitor (EDLC). Graphene has a huge surface area around 2630

m^2 g^{-1}, which gives high capacitance value up to 550 F g^{-1}.Graphene also have high electrical conductivity than activated carbon [14][15]. The another main property of graphene which makes its use important as an electrode material is its 2D structure which increases charging discharging capability of the device. Since graphene has vertically oriented sheets which allows charge carriers migrate quickly in or out of the structures of the electrode [16].

1.3 Metal Oxides as Pseudocapacitor electrode material

Metal oxides are preferred as good electrode material for pseudocapacitors due to its important properties. Metal oxides have good electrical conductivity and can have multiple oxidation states. During reduction, free intercalation of protons into the oxide matrix occurs. Transition metal oxides generally have strong faradaic electron transferring reactions and low resistance. Pseudocapacitors having metal oxides as an electrode material exhibits high energy density as compare to conventional carbon based supercapacitors and exhibits high cyclic stability as compared to conducting polymer based pseudocapacitors. Iridium (IrO_2), ruthenium (RuO_2), Manganese (MnO_2) etc. are few examples of metal oxides used as an electrode material from which RuO_2 is most preferable due to its wide potential window, multiple oxidation states, low material resistance etc. RuO_2 shows capacitance up to 720 F g^{-1} whereas MnO_2 shows upto 1100 to 1300 F g^{-1} [17][18]. Currently research is being focussed on ternary metal oxide due to its good properties such as multiple oxidation states, high surface area and high electrical conductivity which leads to high performance.

1.3 Capacitance of Supercapacitor

Total capacitance can be calculated by the following formula where series circuit is formed by the both electrodes of individual capacitors C_1 and C_2 respectively.

$$\mathbf{C_{total}} = \frac{\mathbf{C_1} \times \mathbf{C_2}}{\mathbf{C_1} + \mathbf{C_2}}$$

Electrodes of supercapacitor mainly consist of two type: symmetric and asymmetric. Symmetric means both the electrodes having same capacitance hence the total capacitance is equal to half of the capacitance of single electrode ($C_{total}=0.5C_1$). Asymmetric means total capacitance will be equal to the capacitance of the electrode having lower value among them. (if $C_2>>>C_1$ then $C_{total}=C_1$) [8].

1.4 Energy Density , Power Density of Supercapacitor

Power density and energy density are one of the major components of any charge storage device which defines its effectiveness. The quantity of energy stored is given by energy density while the rate at which the energy is stored is given by power density [19].

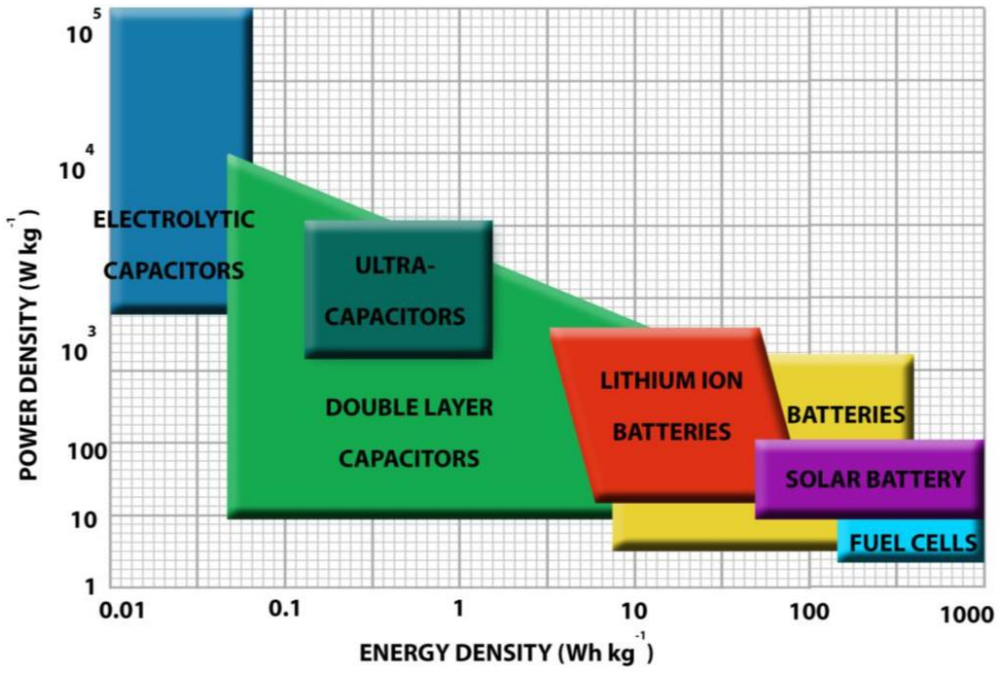


Figure 5. Ragone Plot for energy storage devices.
(adopted from https://www.researchgate.net/figure/263733888_fig1_Figure-1-Ragone-Plot-depicting-energy-vs-power-densities-of-common-power-devices)

Energy can be calculated by

$$\mathbf{E} = \frac{\mathbf{1}}{\mathbf{2} \times \mathbf{3600}} \mathbf{CV^2}$$

Where, E= energy stored in capacitor

C= capacitance

V= voltage applied between two electrodes

Power of the device can be calculated by

$$\mathbf{P} = \frac{\mathbf{E} \times \mathbf{3600}}{\mathbf{\Delta t}}$$

Where, P= Power of the capacitor

E= Energy density

Δt = discharge time

2. Experimental Section

2.1 Device Fabrication

Device Fabrication was carried out through following techniques: a) Laser Scribing technique through CO_2 laser b) Electrodeposition.

2.1.1 CO_2 Laser micro patterning - Laser writing.

Over the past decades, CO_2 laser which is basically a developed gas based laser have its wide application in various fields, for example, industrial cutting and welding, medical surgery, fabrication of micro fluidic device etc. CO_2 laser basically is continuous far infrared laser having low energy and highest power among the other available lasers. The basic setup of CO_2 laser consists of total reflector and output collector at both the respective ends and a gas discharge. The laser beam is moved by the mirrors which are connected to the X-Y moving stage. The Z-axis is used to move the laser stage of the system which helps to focus laser beam on the substrate.

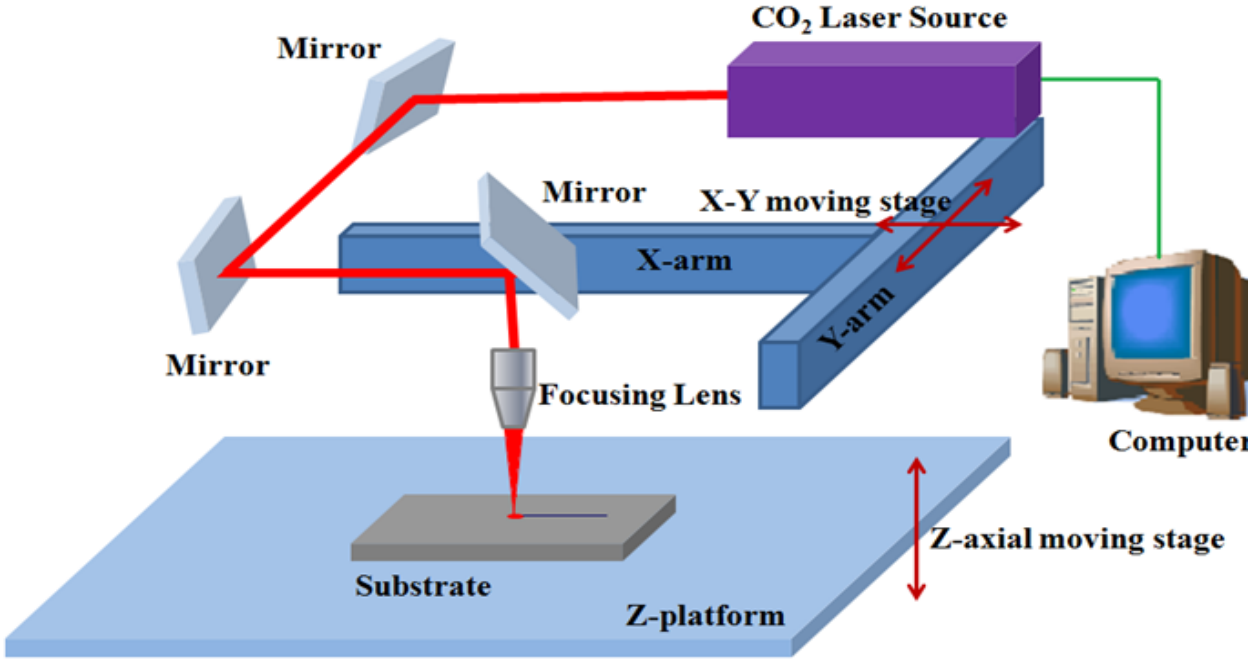


Figure 7: Basic setup of CO_2 laser system (adopted from https://www.linkedin.com/pulse/application-co2-laser-printed-circuit-board-pcb-apple-he)

Laser writing can be used for pyrolysing the organic molecules by creating high temperature of around 2000-2500^{o}C locally. The high temperature heating causes breaking of bonds in organic molecules such as C-O, C=O, C-N etc, which leads to the formation of 2D graphitic carbon. The produced porous graphitic carbon is known as Laser Induced Graphene (LIG) [20]. Tour.J; et.al. reported the synthesis of laser induced graphene on polyimide sheet i.e. Kapton which was further used for the application of supercapacitor. They reported easy single step of graphene synthesis where a polymer sheet gets directly converted into porous graphene sheets [21].

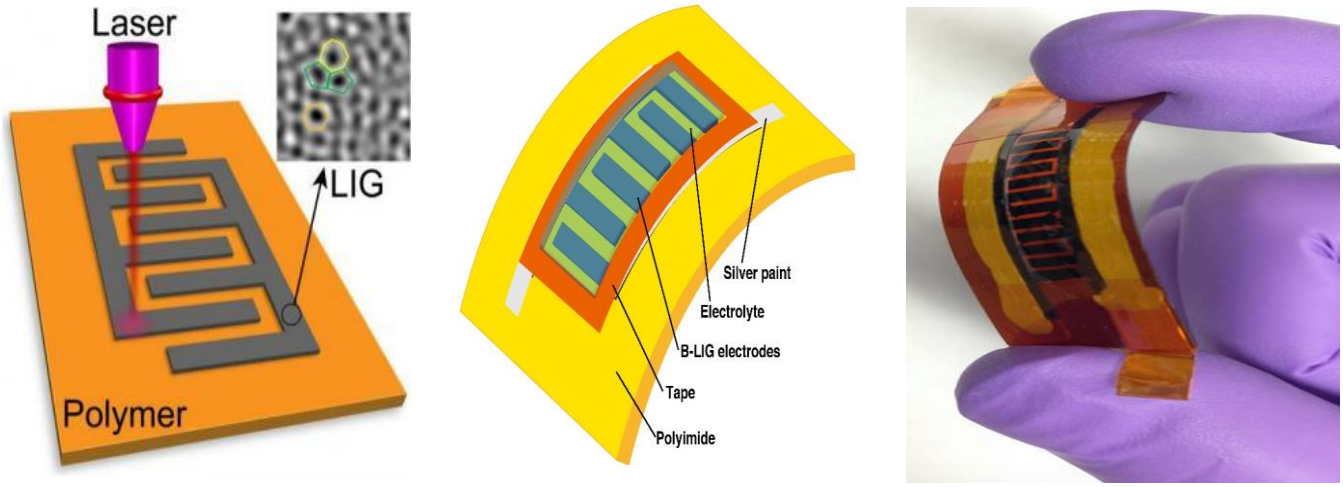


Figure 6. Laser scribing carried out on a polymer sheet and general structure of flexible interdigitated MSCs. (adopted from http://news.rice.edu/files/2014/12/1215-LIG-1-web.jpg)

In this work we have used similar technique where CO_2 infrared laser is being irradiated on a flexible polyimide sheet i.e. Kapton where interdigitated micro-sized electrodes where laser written in an alternative pattern in order to make an asymmetric flexible energy storage device. Laser was induced on Kapton leading the formation of micro-sized electrodes of dimension 0.015×0.5 cm. The distance between two electrodes was 300 micron.

2.1.2 Electrodeposition

Electrodeposition, also known as electrolytic deposition is the process where a thin layer of a metal is coated on the top of another metal to develop its surface properties. It is the process where cations are reduced of desired material through electrical current from electrolyte and are being coated on a conductive substrate surface as a thin film.

Let us explain this with an example of nickel chloride as an electrolyte solution where negatively charged chloride ions are anions and positively charged nickel ions are cations. When electric field applied through the solution, cations gets migrated towards cathode and gets discharged then deposites in the form of metallic nickel.

$$\mathbf{Ni^{2+} + 2e \rightleftarrows Ni\ (metal)}$$

Electrical neutrality gets maintained when nickel from anode dissolves into the solution.

$$\mathbf{Ni \rightleftarrows Ni^{+2} + 2e}$$

$$\mathbf{2H_2O \rightleftarrows 4H^{+} + O_2 + 4e}$$

Here platinum plate is anode where oxidation of water takes place. Concentration of Ni^{2+} gets decrease while that of concentration of H^{+} ions gets increase with the time where quantity of chloride ions remains unchanged during the electrolysis [22].

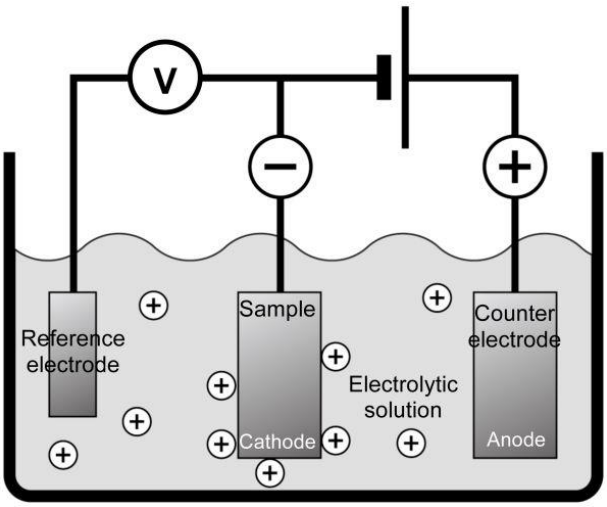


Figure 8. Simple Electrodeposition Setup (adopted from http://www.intechopen.com/source/html/8910/media/image13.jpg)

Due to applied potential, an electrical double layer is formed near electrode surface due to rearrangement of ions which is known as Helmholtz double layer.

2.2 Characterization Techniques for Material and device.

Cyclic voltametry (CV) studies were done with Auto Lab:model PGSTAT 30, eco-chemie. XRD was performed on Philips XPert PRO diffractometer with nickel filtered CuKα radiation ($\lambda = 1.5405\text{Å}$). Galvonostatic charge discharge, Impedance and Cyclic voltammetry were performed on Autolab potentiostat with Nova1.10. Scanning electron microscopy: SEM images were taken on NOVA NANOSEM 450. Laser scribing was performed on Universal Laser Systems Versa LASER VLS 2.30.

Figure 9. Autolab and Biologic potentiostats (lab instruments)

2.2.1 X-Ray Diffraction

It is one of the important technique used to obtain information regarding orientation of the crystal planes, average crystal size etc. of various materials. X-ray diffraction follows Bragg's diffraction law and is applicable for thin films as well as powder materials. In Bragg's law, the scattered x-ray beam undergoes destructive or constructive interference, only when the path difference between the two adjacent rays is integral multiple of nλ [23]. Where, λ= incident x-ray wavelength. Path difference between two adjacent x-ray beams can be calculated by 2dsinɵ where ɵ = scattering angle and d= inter planer distance

$$2d\sin\theta = n\lambda$$

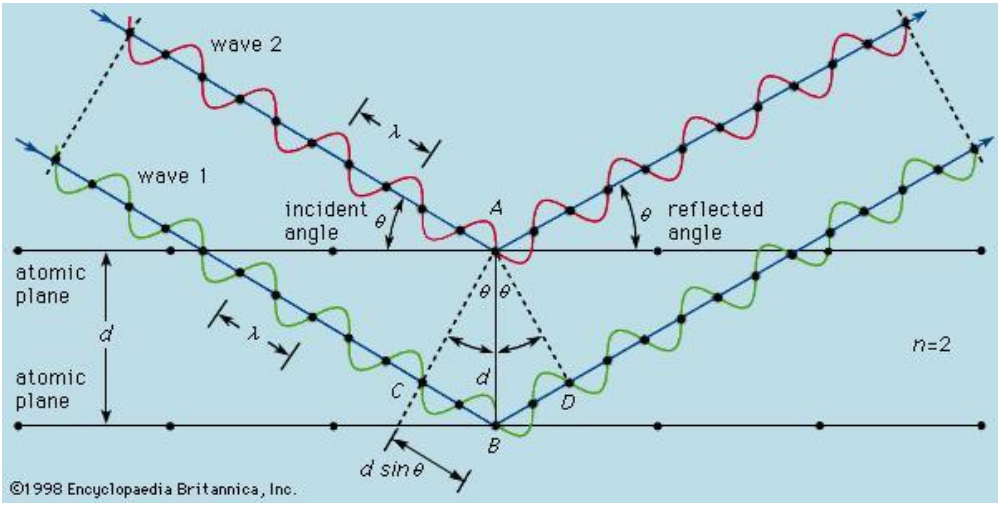


Figure 10. Schematic diagram of X-ray diffraction.(Adopted from https://www.britannica.com/science/Bragg-law)

2.2.2 Field emission scanning electron microscopy: FE-SEM

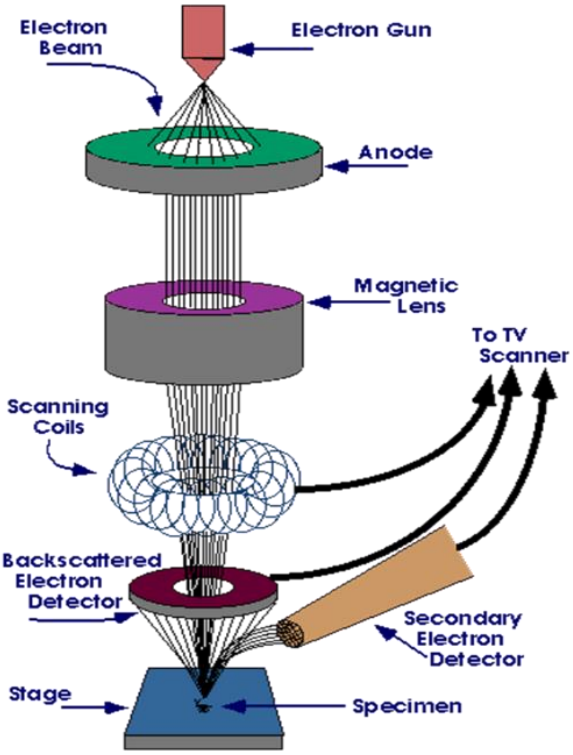


Figure 11. Schematic diagram of SEM working principle. (Adopted from https://www.purdue.edu/ehps/rem/rs/sem.htm)

Scanning electron microscopy is one of the useful technique which is used to study different materials at molecular level which includes composition and surface topography of the material. In this technique, field emission source emits focussed electron beams which scans over the surface. Here detection of emitted secondary electrons through atoms excited via electron beam is observed. An image is formed due to scanning of material through focussed electron beam where the secondary electrons are collected further with special detector [24]. A narrow beam of electrons is produced when emitted electrons are accelerated due to electric field gradient which is focused and deflected by magnetic lenses.

2.2.3 Cyclic Voltammetry

Cyclic voltammetry is one of the most useful and commonly used technique in electrochemistry for electrochemical studies to seek various information about complicated electrode reactions such as oxidation and reduction potential, reversibility of redox reactions etc. In CV, the applied electrode potential changes linearly with respect to time in cyclic phases. The change in rate of voltage with respect to time during the phase is termed as experimental scan rate. In cyclic voltammetry at a particular scan rate, current is measured between counter electrode and working electrode whereas, potential is measured between reference electrode and working electrode. The figure 12. shows the graph of current vs applied potential. Once the applied voltage between reference electrode and working electrode reaches to the maximum set potential (V_2) then it is reversed back to its initial set potential(V_1) [25][26]**.** Oxidation peak and reduction peak can be observed due to the redox couple, where the more reversible redox, the more symmetric peaks of oxidation and reduction can be seen with respect to each other.

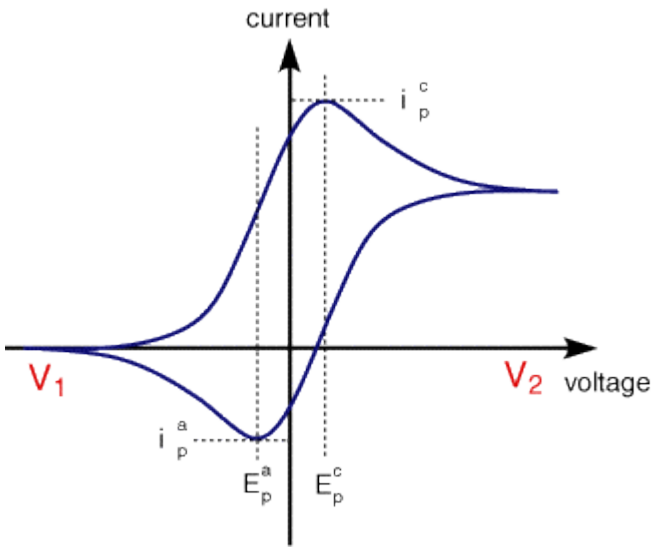


Figure 12. Cyclic Voltammogram plot (i_p^c and i_p^a denotes cathodic and anodic peak current respectively and E_p^c and E_p^a refers the corresponding potential) (adopted from http://www.ceb.cam.ac.uk/research/groups/rg-eme/teaching-notes/linear-sweep-and-cyclic-voltametry-the-principles)

2.2.4 Galvanostatic Charge Discharge

Charge discharge is another most commonly used technique for measuring the cyclic stability and charge discharge capacity of the device such as supercapacitors and batteries. Here constant current is applied between counter electrode and working electrode to measure variation in potential with respect to time. Figure 13.shows the voltage vs time graph of the supercapacitor.

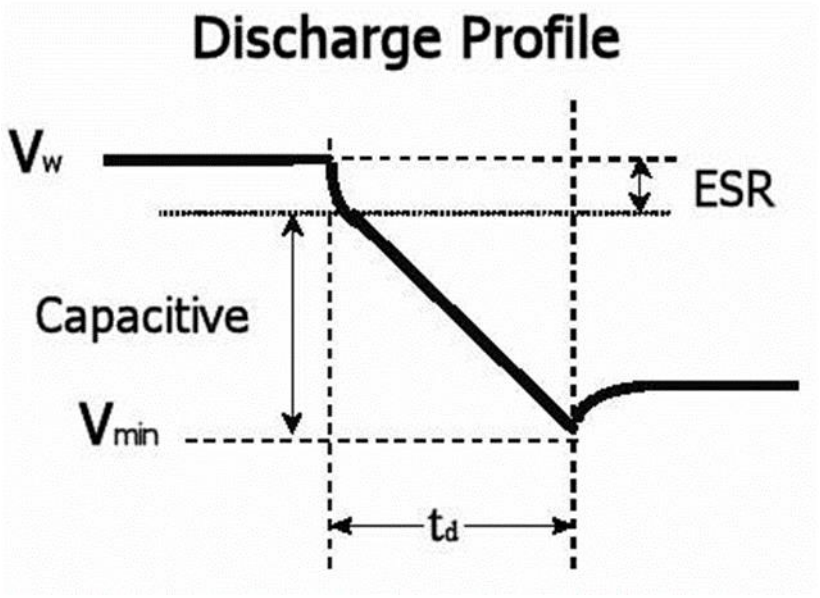


Figure 13. Typical Discharge curve of supercapacitor (adopted from https://www.tecategroup.com/ultracapacitors-supercapacitors/ultracapacitor)

Experimentally, charge discharge capacity can be calculated from the given graph in figure 13.which is calculated by [27]:

$$C = \frac{I \times \Delta t}{\Delta V}$$

Where, C= capacitance I= Current density

Δt= discharge time ΔV= applied voltage

2.2.5 Electrochemical Impedance Spectroscopy

Impedance spectroscopy is another important tool used for the electrochemical study of the energy storage device. In this technique when frequency is used for characterizing the voltage pulse, then the obtained impedance becomes frequency dependant [28]. The impedance which is also referred as generalised ac resistance of RLC circuit is given by:

$$Z = \frac{V}{I} = \frac{V^{\circ} e^{i\omega t}}{I}$$

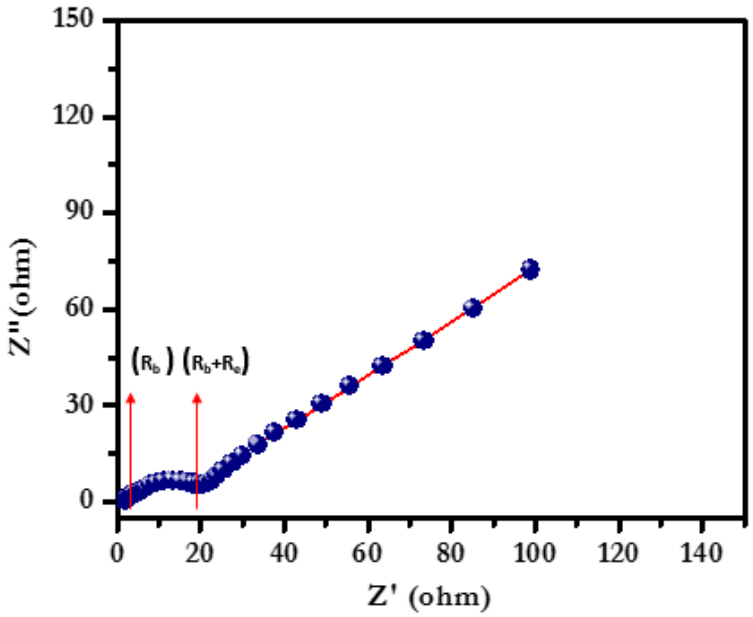


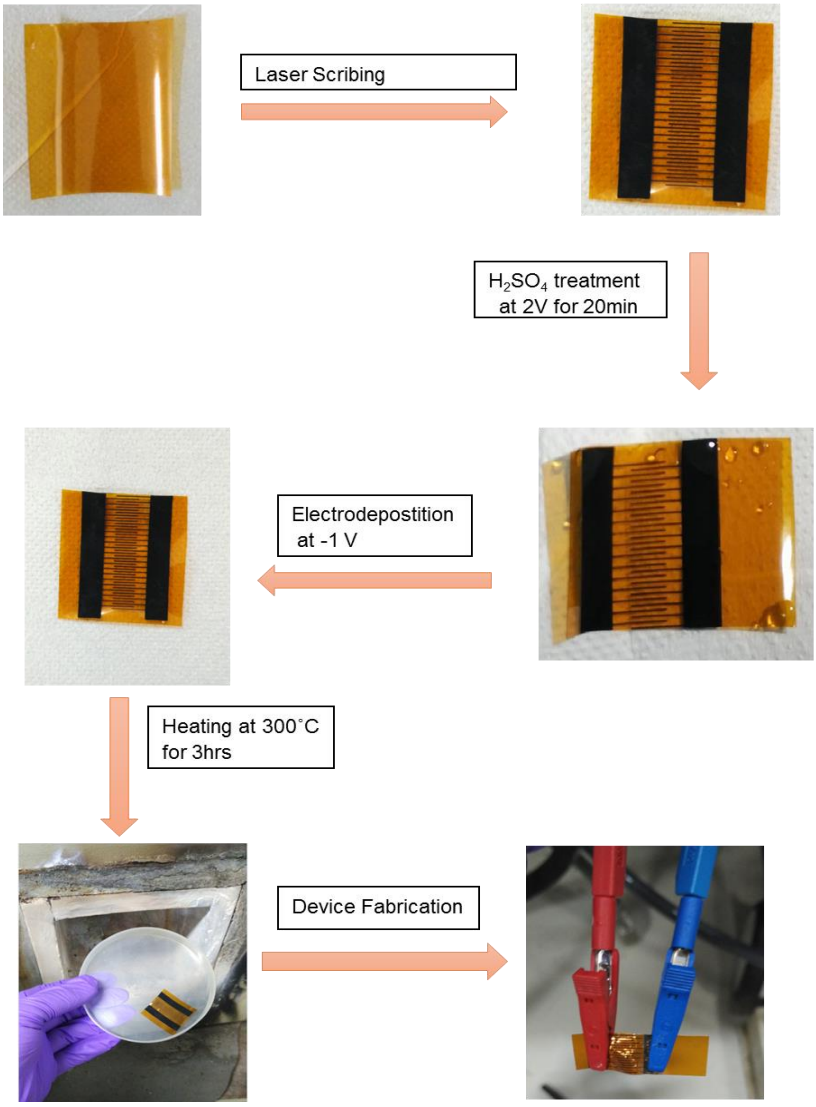
Figure 14. Nyquist Plot for supercapacitor

Electrochemist shows great interest in the frequency dependence of impedance since it is used for obtaining important information about various energy devices. Electrochemical series resistance (ESR), charge transfer resistance etc are few important parameters of EIS. Figure 14. shows the Nyquist plot of supercapacitor, where R_b denotes the series resistance of the system which also includes resistance of the electrode, electrolyte and current collector. Semicircle diameter (R_e) is used to calculate Charge transfer resistance at interfaces.

2.3 Synthesis of ternary metal oxide ($NiCo_2O_4$) electrode Material.

Micro-supercapacitor device was fabricated by two step process. Firstly, micro sized interdigitated carbon electrodes were laser written on Kapton substrate (flexible polymer sheet) followed by electrochemical etching in 1M H_2SO_4 solution to improve the hydrophilicity of the surface [8]. Three electrode system was used where Ag/AgCl was used as reference electrode. The substrate was electrochemically etched for 20min at constant voltage of 2V. Further gentle washing by DI water was given to remove excess acidic solution from electrode surface and then kept it for drying at room temperature. Then three electrode system was used for the further electrodeposition process where calomel electrode was the reference electrode, carbon paper was the counter electrode and the laser scribed Kapton sheet was the working electrode. Further a homogeneous solution of nickel nitrate [$Ni(NO_3)_2.6H_2O$] (0.09g) and cobalt nitrate [$Co(NO_3)_2.6H_2O$] (0.2g) in 100ml water was prepared by continuous magnetic stirring for 30min [29]. Then electrodeposition was carried out on one side of the carbon electrodes at a constant potential of -1V for I×t value 5 (I×t value = current passed during deposition × time of deposition). The electrodeposited electrodes then were kept for drying at 80^oC for 12hrs [30]. Further electrodes were annealed at 300°C for 3hr at rate of 5^oC/min. Annealing at 300^oC is done in order to convert the electrodeposited nickel cobalt hydroxide into nickel cobalt oxide since oxides have more capacitance than hydroxides.

2.3.1 Experimental Procedure



2.4 Characterization of Material and Device.

Material characterisation of electrodeposited nickel cobalt oxide was done through various techniques which include XRD, FE-SEM, EDAX to confirm its formation.

2.4.1 X-ray diffraction (XRD)

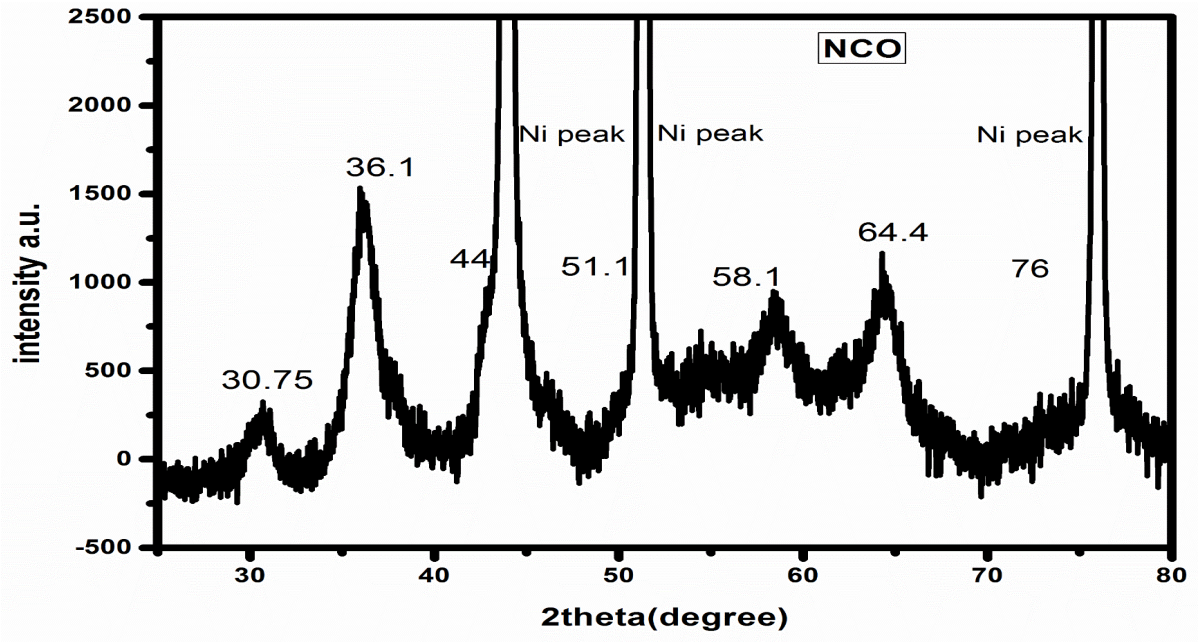


Figure 15. X ray diffraction pattern of $NiCo_2O_4$

XRD was studied of the material to confirm the formation of ternary metal oxide. Major peaks of nickel cobalt oxide were observed at 30.75, 36.1, 44, 51.1, 58.1 and 64.4 which confirms the structure of NCO. The visible diffraction peaks for the planes were at (200), (311), (400), (422), (333), (440).

2.4.2 Field Emission Scanning Electron Microscopy: FE-SEM

SEM images were studied for the fabricated MSC were a porous layer of laser induced graphene is clearly observed. Nanosheets of electrodeposited metal oxide (i.e nickel cobalt oxide) are seen on the surface of graphene in uniform manner which confirms the formation of NCO. It can be observed that the electrode have many ordered nanosheets interconnected to each other comprising to microporous structure.

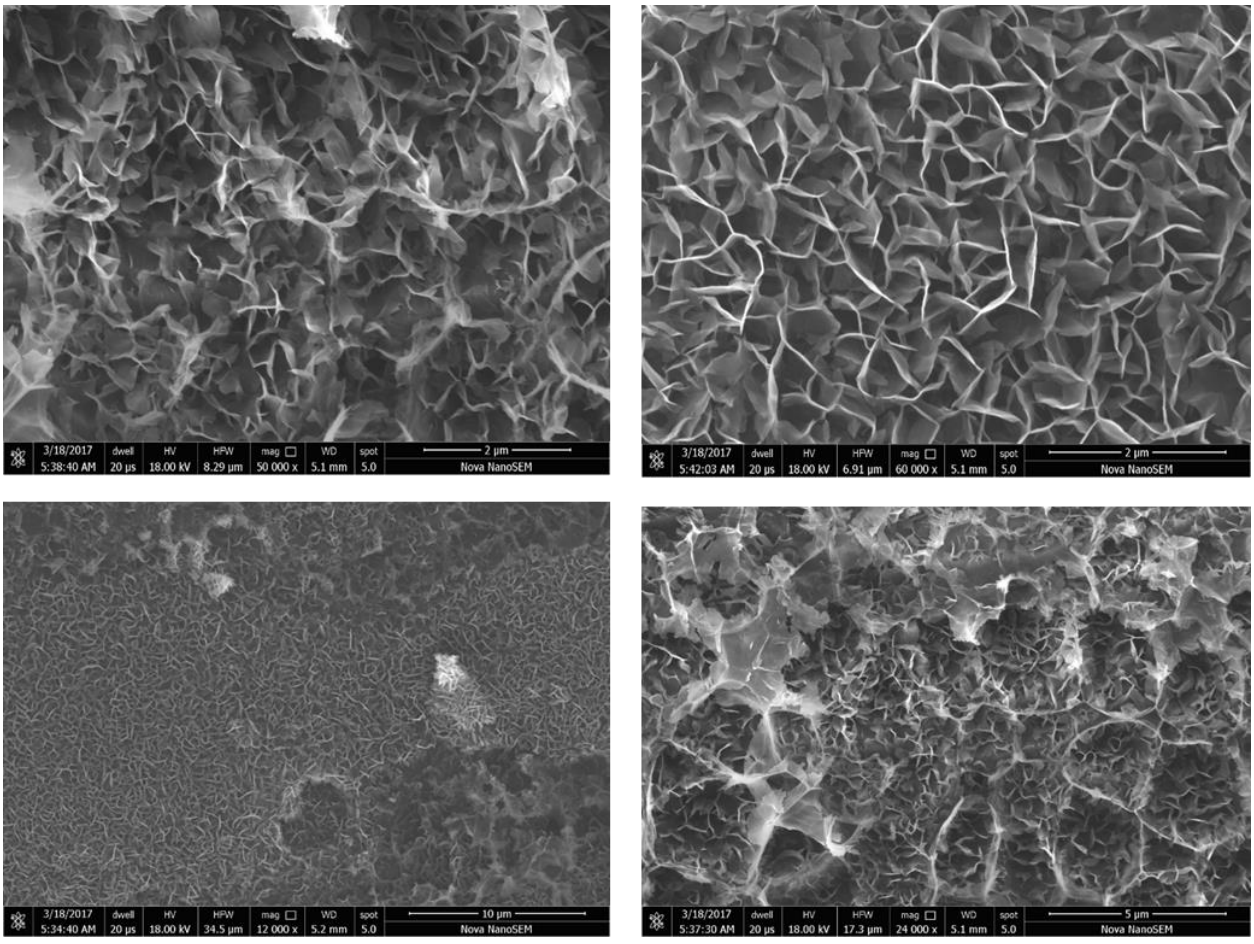


Figure 16. SEM images of electrodeposited nickel cobalt oxide nanosheets on laser written carbon electrodes of graphene.

2.4.3 Energy Dispersive Analysis X-ray (EDAX)

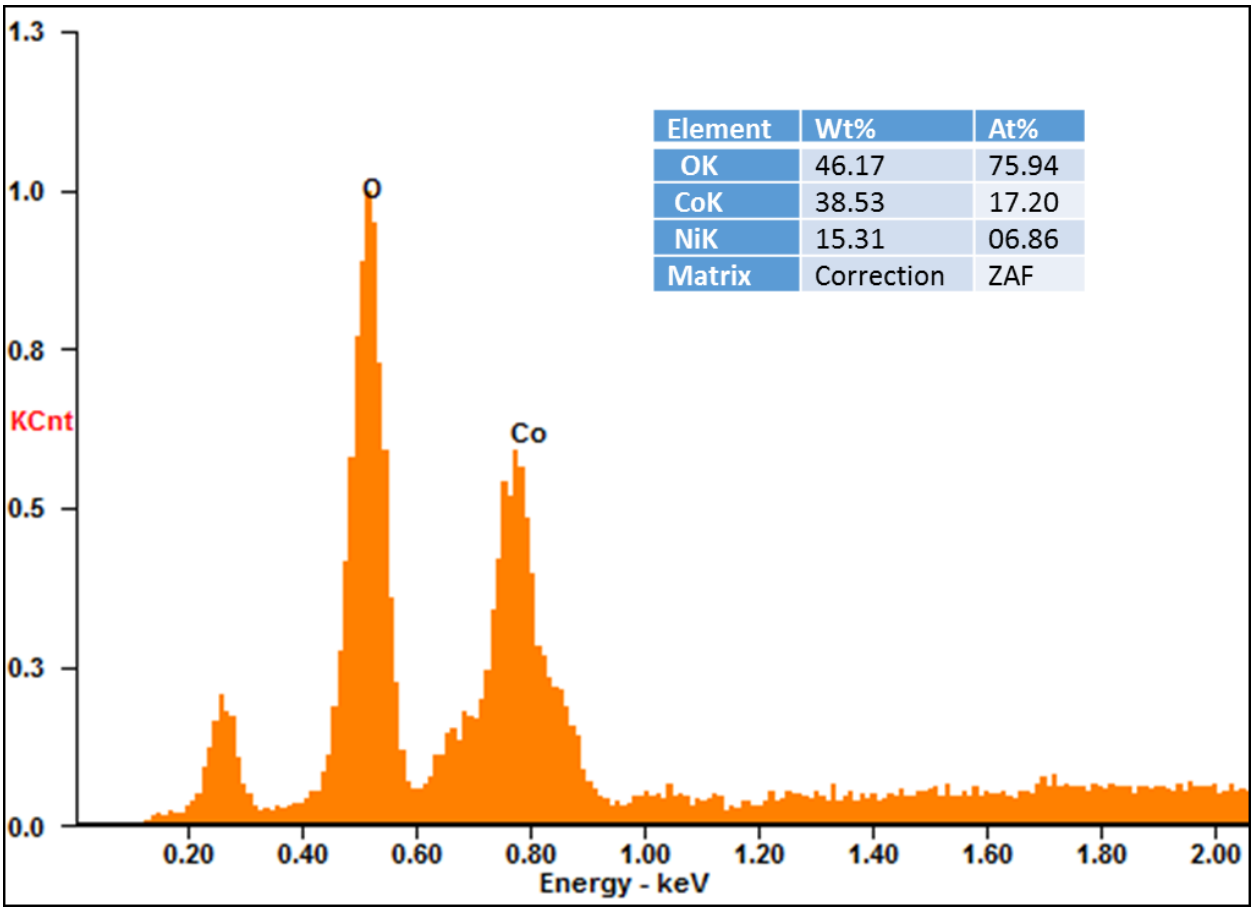


Figure 17. EDAX data of the electrode material ($NiCo_2O_4$).

EDAX for the synthesized electrode material was studied where ratio of Ni:Co in the material is approximately observed to be 1:2, which matches the stoichiometry of the metals present during the reaction. Peaks of nickel, oxygen and cobalt can be seen respectively in the image. From the above table we can see that amount of Cobalt present in the material is approximately double to that of Nickel present in it.

2.5 Synthesis of gel-electrolyte (PVA-H_3PO_4)

Gel electrolyte was used as a mode of charge carrier between the respective electrodes. PVA-H_3PO_4 was used as a gel electrolyte and was synthesised by following method: 2g of polyvinyl alcohol (PVA) was dissolved in 20ml DI water. An assembly was set up where PVA+DI water solution in round bottom flask was kept in an oil bath for constant stirring at 90^oC for 24 hrs. After obtaining the clear solution it was kept for cooling at room temperature and then 1.35 ml phosphoric acid was added in it. Again the mixture was kept for heating at 90^oC until the complete gel electrolyte was formed. Other than PVA-H_3PO_4, electrolytes such as PVA-H_2SO_4, PVA-KOH can also be used. But in this case since we have metal oxide on the electrode so using strong acid as electrolyte may cause various side reaction and may affect the stability and performance of the device. Sulphuric acid present in the electrolyte may for sulphates with the metal ions which are irreversible in nature. Hence mild acid such as phosphoric acid is used which does not allow any side reaction to occur and gives the actual capacitance value. Polyvinyl alcohol is used since it is easily soluble in water due the hydrogen bond formation among the OH^- molecule of PVA and H^+ molecule of water

3 Results and Discussion

3.1 Electrochemical Characterization

Electrochemical studies was performed such as cyclic voltammetry (CV), impedance spectroscopy, charge discharge, at room temperature. The measurements were done using Biologic potentiostats and Autolab

3.1.1 Cyclic Voltammetery

The Electrochemical characterization of $NiCo_2O_4$ microsupercapacitor was performed in two electrode system using 1M PVA-H_3PO_4 gel electrolyte. CV was performed on device over different voltage range of 0 V to 1 V and -0.4 V to 1 V at different scan rates 20 mV s^{-1}, 100 mV s^{-1}, 200mV s^{-1}, 500mV s^{-1}, 700mV s^{-1}, 1000mV s^{-1} .

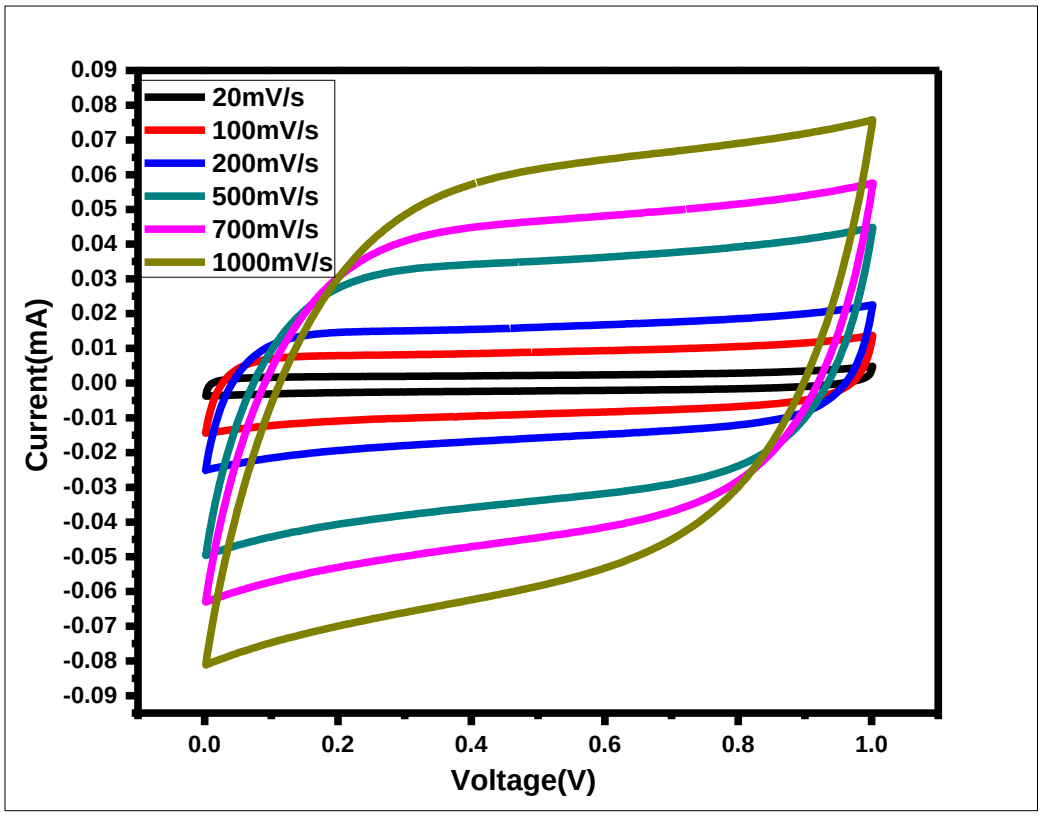


Figure 18. CV at different scan rates at voltage range of 0-1 V

The shape of the graph was nearly rectangular and gets deviated as the scan rate increases since as scan rate increases the electrolyte does not get enough time to percolate into the electrodes and also increase in impedance which limits the performance of device

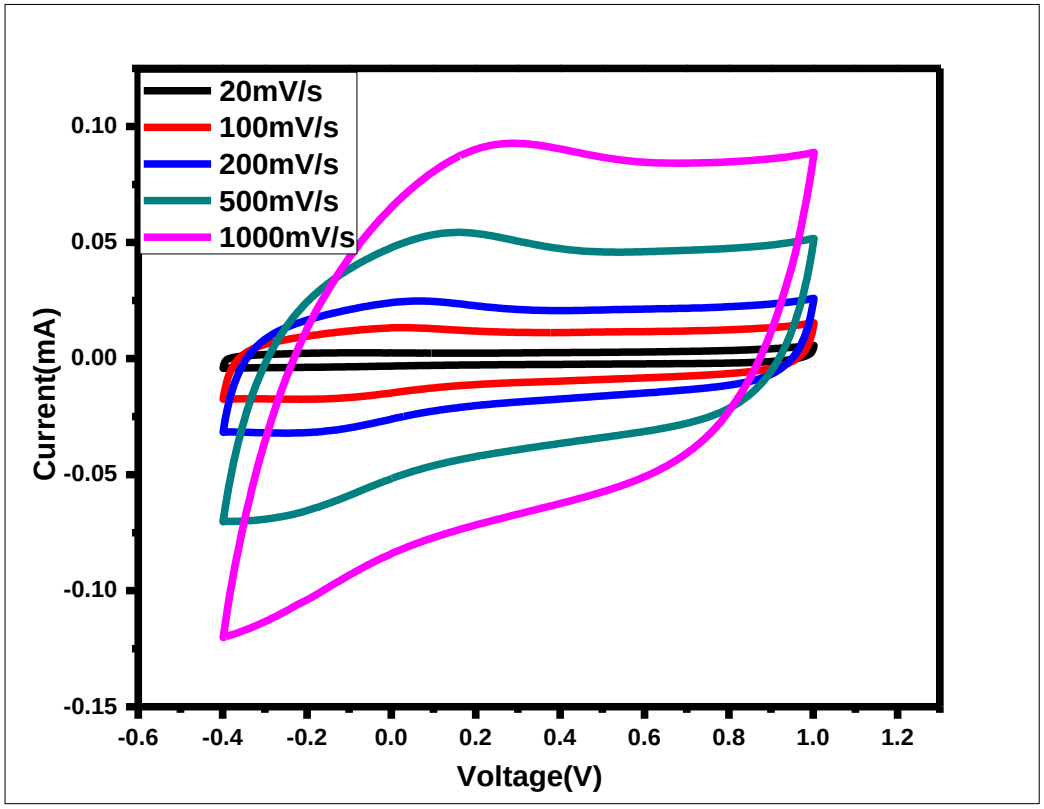


Figure 19. CV at different scan rates at voltage range of -0.4-1 V

In spite of having resistive behaviour of electrodes at high scan rate of 500 mV s^{-1}, the nature of cyclic voltammogram remains almost rectangular in shape and also shows a high rate performance.

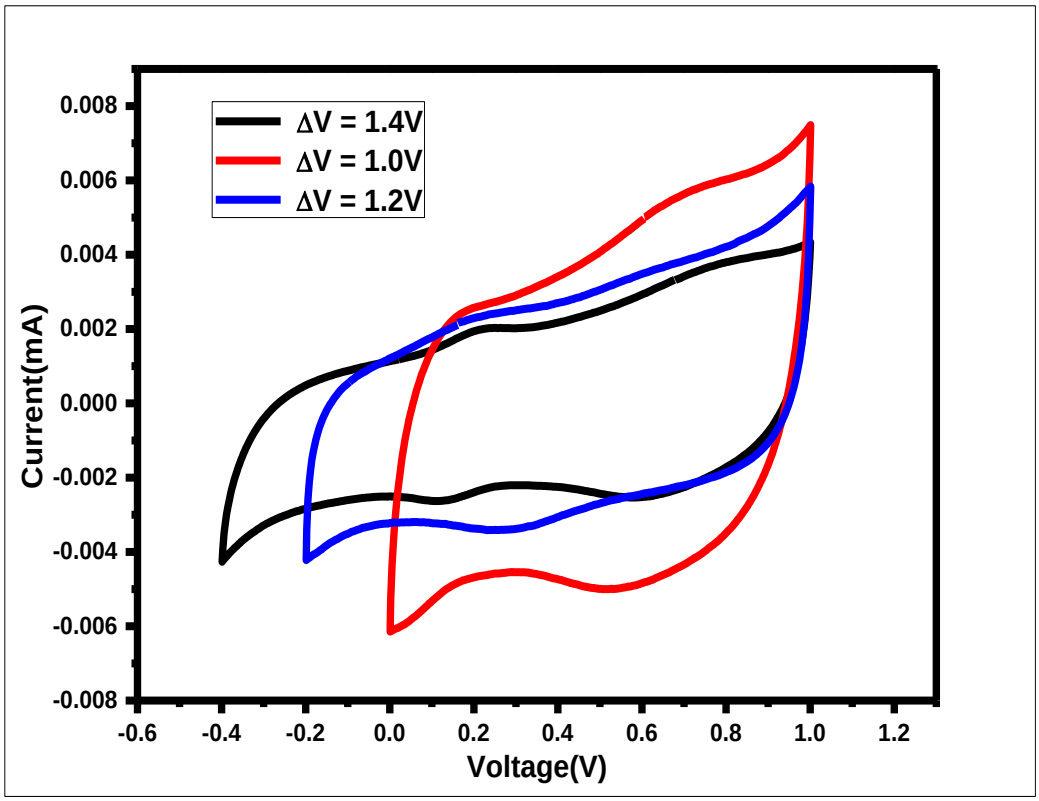


Figure 20. CV performed at different potential window ranging from -0.4 V to 1 V, -0.2 to 1 V and 0 to 1 V

CV was performed at different voltage window to show the wider voltage range accessibility of the fabricated asymmetric flexible microsupercapacitor. We can see that no water splitting has been observed at potential window of -0.2-1 V and -0.4-1 V respectively which shows the property of an asymmetric supercapacitor.

3.1.2 Flexibility

Flexibility was studied through cyclic voltammetry by bending the device at around 150^{o} and calculating the performance after retention of device. The CV was performed at the scan rate of 20 mV s^{-1} under relaxed and bend conditions. The micro supercapacitor exhibits around 98% of its performance value with respect to the normal relaxed device. Once the device is brought to its original state still it recovers its performance. The high flexibility of the device is due to strong carbon network existing inside the electrode.

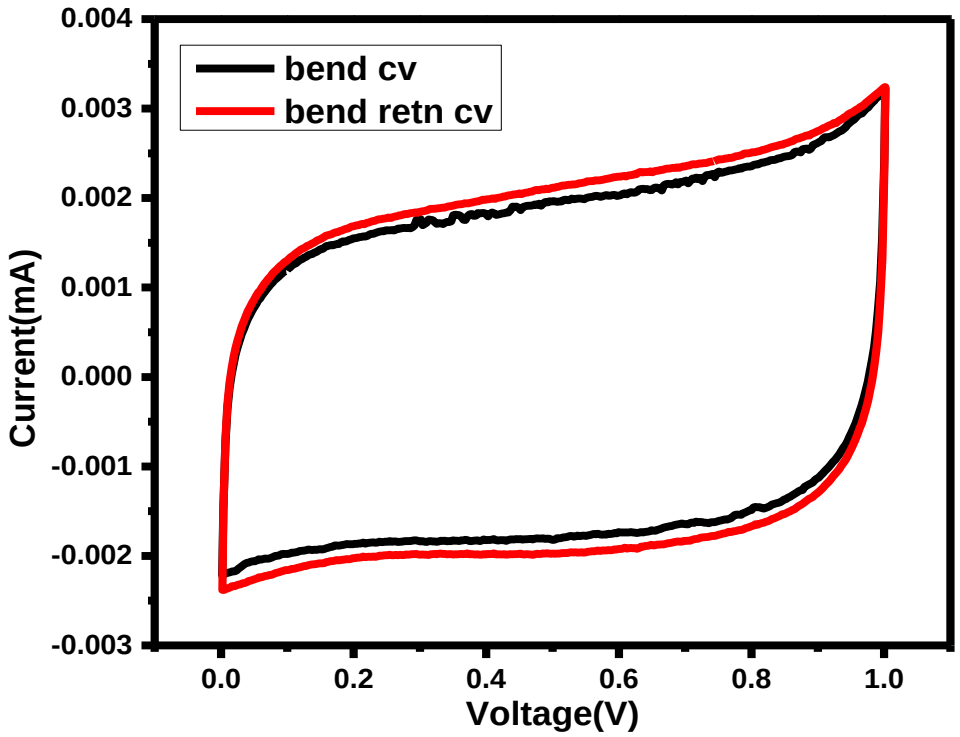


Figure 21. Comparison of cyclic voltammetry data for the device under bent and recovered condition at around 150^{o}

3.1.3 Charge-Discharge

Charge-discharge of the device was studied at different current densities ranging from 0.25 mA cm^{-2}, 0.5 mA cm^{-2}, 0.75 mA cm^{-2}, 1 mA cm^{-2}.The charge discharge curve is very non-linear and which clearly indicates the pseudocapacitive behaviour of $NiCo_2O_4$ electrodes.

Discharge capacitance value of the device was calculated by using the following formula:

$$C = I \times \Delta t \times \Delta v^{-1}$$

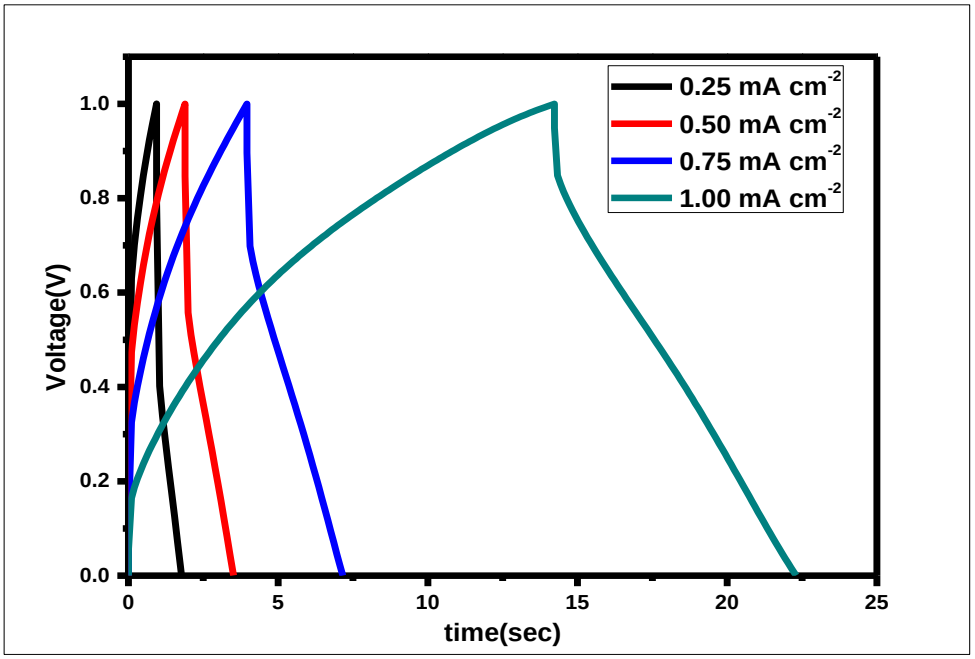


Figure 22. Charge discharge curve at different current densities 0.25 mA cm^{-2}, 0.5 mA cm^{-2}, 0.75 mA cm^{-2}, 1 mA cm^{-2}.

3.1.4 Electrochemical Impedance Spectroscopy : EIS

EIS study was carried out on the device to see its electrochemical behaviour as shown in the figure 23 .The impedance plot signifies two major things of the device. The small semicircle part at high frequency region is due to charge transfer resistance while the slope line in the lower frequency region describes mass transfer resistivity of electrolyte.

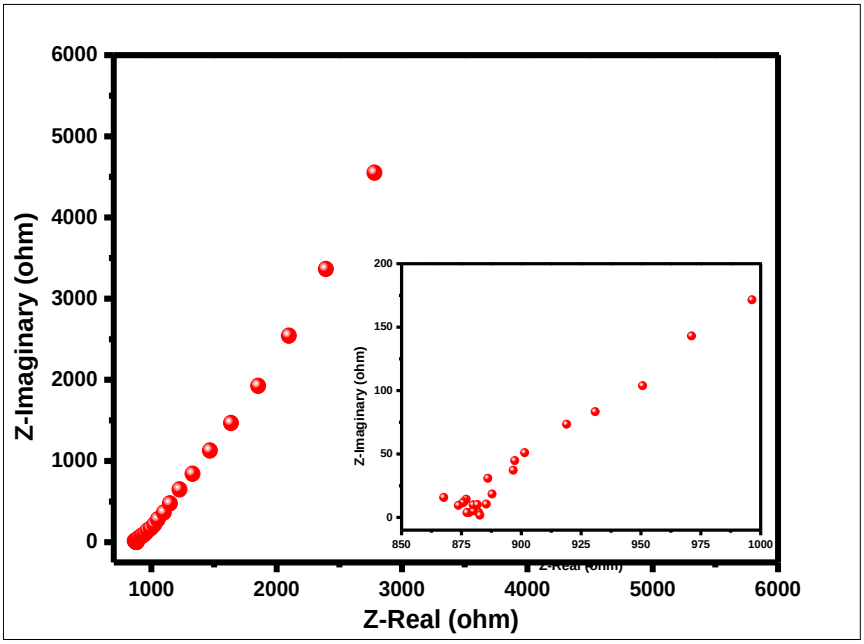


Figure 23. (Nyquist Plot) Impedance spectroscopy data for the solid state device

3.1.5 Ragone Plot

Energy density was calculated through given formula at different current densities and then power densities were calculated subsequently. The fabricated $NiCo_2O_4$ microsupercapacitor shows the energy density of 2.81×10^{-4} W h cm^{-2} at power density of 0.125 W cm^{-2}

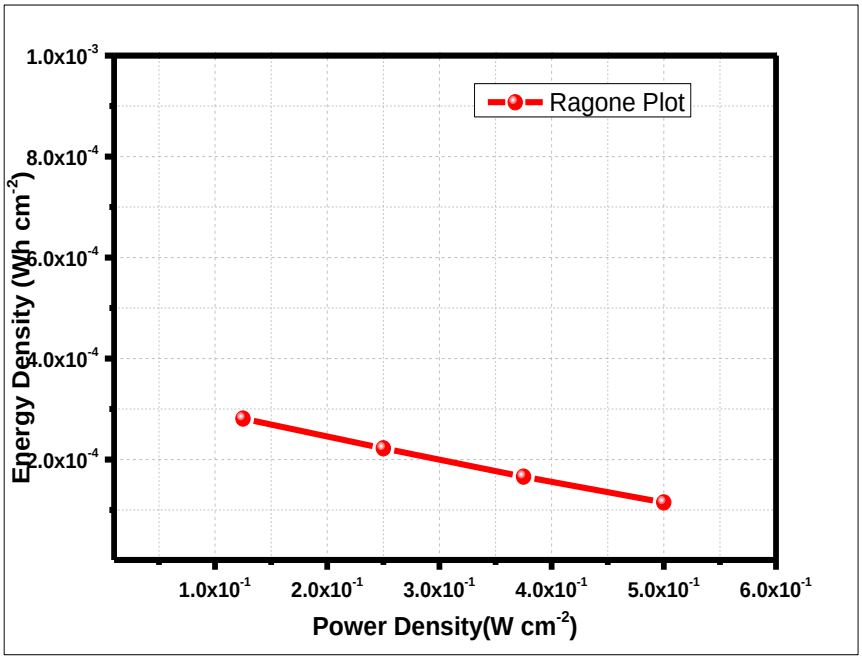


Figure 24. Ragone plot for the device (NCO microsupercapacitor)

3.1.6 IR drop vs. Current Density

IR drop vs Current Density was plotted for the device where a linear IR drop is observed with its respective current densities.

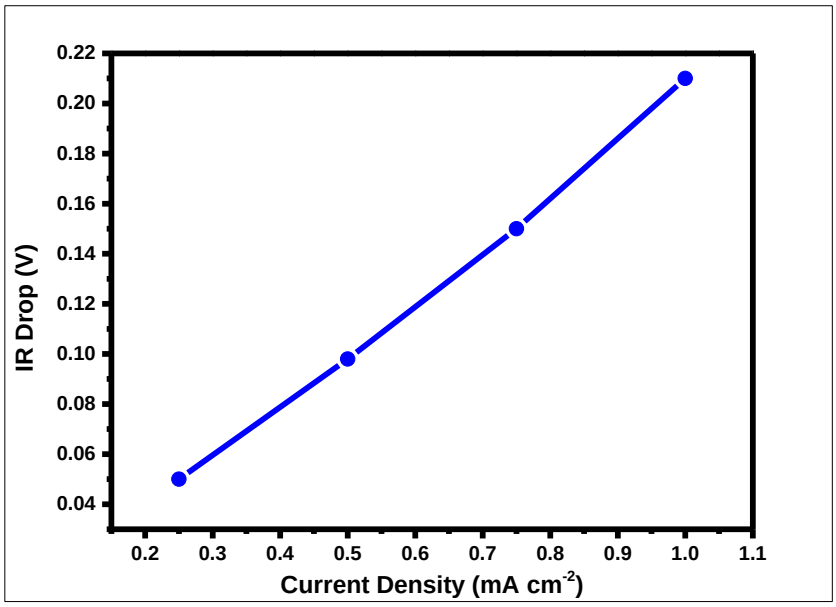


Figure 25. IR drop vs. current Density Plot of the device at different current densities.

3.1.7 Capacitance vs Current Density

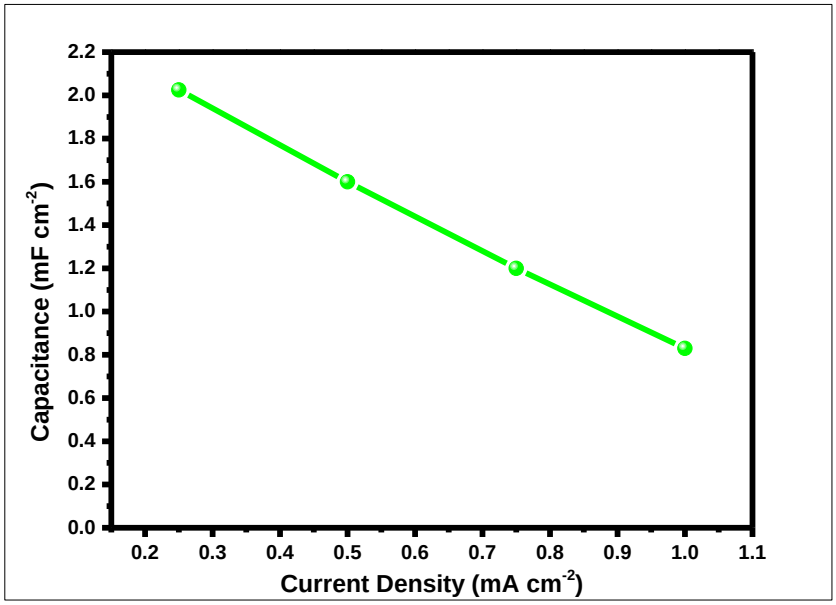


Figure 26. Capacitance retention with current density

Capacitance was plotted with respective current densities. Areal capacitance of the MSC was calculated at different current densities through charge discharge curves. Areal capacitance of 2.02 mF cm^{-2} was observed at the current density of 0.25 mA cm^{-2}

4 Conclusions

In summary, here we have successfully fabricated all solid state flexible asymmetric microsupercapacitor by using CO_2 laser writing on the PI film- Kapton and further electrodeposited films of nickel cobalt oxide nanosheets on the one set of laser written carbon electrodes. Laser induced graphene (LIG) having porous structure was one of the electrode exhibiting electric double layer nature while electrodeposited porous nanosheets of NCO on LIG was another electrode which exhibits pseuodocapacitance nature, ultimately leading to a good asymmetric flexible microsupercapacitor. PVA-H_3PO_4 was used as gel electrolyte for all electrochemical measurements. The device exhibited wide operational potential window up to 1.4 V along with an areal capacitance of 2.02 mF cm^{-2} at the current density of 0.25 mA cm^{-2} which is quite comparable with the previously reported high performance solid-state micro-supercapacitors. The fabricated device also shows high flexibility (over 90% capacitance retention) at 120^o bending.

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