

**T.C.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL**

SCREEN PRINTED GRAPHENE SUPERCAPACITORS



KÜBRA TİÇ

**A THESIS OF MASTER OF SCIENCE
DEPARTMENT OF INTERDISCIPLINARY
NANOSCIENCE AND NANOENGINEERING
NANOSCIENCE AND NANOENGINEERING PROGRAM**

ADVISOR: ASSOC. PROF. DR. NIHAN AYDEMİR

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**T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ**

**SERİGRAFİ BASKILI GRAFEN
SÜPERKAPASİTÖRLER**

KÜBRA TIĞ

**YÜKSEK LİSANS TEZİ
DİSİPLİNLERARASI NANOBİLİM VE
NANOMÜHENDİSLİK ANA BİLİM DALI
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ABSTRACT

This study aims to investigate the impact of adding LIG-derived graphene powder on the structural, morphological, and electrochemical properties of supercapacitor electrodes produced via screen printing techniques. Energy storage, one of the most important applications of supercapacitors, offers many significant advantages, such as high power density and long cycle life. However, their performance largely depends on the microstructure of the electrodes and the continuity of the conductive network. Graphene stands out among other potential electrode materials for supercapacitors due to its high surface area and excellent electrical conductivity.

In this study, graphene was produced in LIG form using a CO₂ laser on a polyimide substrate, mechanically pulverized, and obtained as graphene powder. Conductive inks created using different ratios of graphene/ethyl cellulose were formed into electrodes using the screen printing method. The structural and chemical properties of the electrodes were investigated using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) analyses. Their electrochemical performance was investigated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) methods. It was shown in the study that the ratio of graphene to ethyl cellulose has an influence on both the microstructure of the electrode as well as the transport of ions and electrons. The use of printing techniques to produce LIG-derived graphene-based electrodes provides an affordable and scalable method for producing supercapacitors; therefore, it may be a suitable alternative.

Keywords: Laser-Induced Graphene (LIG), Screen Printing Electrodes, Graphene-Based Inks, Electrochemical Energy Storage

ÖZET

Bu çalışma, lazerle üretilmiş grafen (LIG) türevi grafen tozunun, serigrafi yöntemi ile üretilen süperkapasitör elektrotlarının yapısal, morfolojik ve elektrokimyasal performansı üzerindeki etkisini araştırmayı amaçlamaktadır. Süperkapasitörler, yüksek güç yoğunluğu ve uzun çevrim ömrü gibi avantajları nedeniyle enerji depolama uygulamalarında önemlidir; ancak performansları büyük ölçüde elektrotların mikro yapısına ve iletken ağıın sürekliliğine bağlıdır. Bu bağlamda, grafen, yüksek özgül yüzey alanı ve üstün iletkenlik özellikleri nedeniyle umut vaat eden bir elektrot malzemesi olarak öne çıkmaktadır.

Bu bağlamda, grafen poliimid bir altlık üzerinde CO₂ lazer ile LIG biçiminde üretilmiş, mekanik kazıma işlemiyle toz haline getirilmiş ve farklı grafen/etil selüloz oranları kullanarak iletken mürekkepler oluşturulmuştur. Elde edilen mürekkepler, screen printing yöntemi kullanılarak elektrot formuna dönüştürülmüştür. Elektrotların yapısal ve kimyasal özellikleri, tarayıcı elektron mikroskobu (SEM), enerji dağınımı spektrometrisi (EDS), Raman spektral analizi, X-ışını fotoelektron spektroskopisi (XPS) ve X-ışını difraksiyonu (XRD) analizleri kullanılarak incelenmiştir. Elektrokimyasal performansları, cyclic voltammetry (CV), galvanostatik şarj-deşarj (GCD) ve elektrokimyasal empedans spektroskopisi (EIS) yöntemleriyle incelenmiştir. Sonuçlar, grafen ile etil selüloz arasındaki oranların elektrotun mikroyapısını ve iyon-elektron taşınımını önemli ölçüde etkilediğini göstermektedir. Ayrıca, LIG-türevi grafen bazlı elektrotların baskı yöntemleriyle üretilmesinin süperkapasitör uygulamaları için düşük maliyetli ve ölçeklenebilir bir çözüm sunduğu vurgulanmaktadır. Bu durum, umut verici bir alternatif sunduğunu göstermektedir.

Anahtar Kelimeler: Lazerle Üretilen Grafen (LIG), Serigrafi Elektrotları, Grafen Bazlı Mürekkepler, Elektrokimyasal Enerji Depolama

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LIST OF SYMBOLS AND ABBREVIATIONS

AC	: Activated Carbon
C	: Capacitance
Cdl	: Double Layer Capacitance
CNT	: Carbon Nanotube
CV	: Cyclic Voltammetry
EDS	: Energy Dispersive Spectroscopy
EDLC	: Electrochemical Double-Layer Capacitor(s)
EIS	: Electrochemical Impedance Spectroscopy
ESS	: Energy Storage System(s)
GCD	: Galvanostatic Charge-Discharge
Gr-EC	: Graphene- Ethyl Cellulose
GO	: Graphene Oxide
ITO/PET	: Indium Tin Oxide / Polyethylene Terephthalate
LIG	: Laser-Induced Graphene
PC	: Pseudocapacitor
PI	: Polyimide
PVD	: Physical Vapour Deposition
R _{ct}	: Charge Transfer Resistance
rGO	: Reduced Graphene Oxide
R _s	: Equivalent Series Resistance
SEM	: Scanning Electron Microscope
SWCNT	: Single-Walled Carbon Nanotube
σ	: Electrical Conductivity
W	: Warburg Diffusion Element
XPS	: X-ray Photoelectron Spectroscopy
XRD	: X-ray Diffraction
Z	: Impedance
MSC	: Microsupercapacitor

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1. INTRODUCTION

Energy is an essential component in supporting a modern way of life. To provide all the necessary components of a modern way of life, numerous activities are dependent upon a constant supply of this energy source (i.e., manufacturing, heating, communication, transportation, and healthcare services) **(Chu et al., 2016)**.

There has been an exponential rise in technological advancements, which has ultimately ensured that electronic devices are an integral part of everyday life. The increased use of these devices has led to an exponential rise in overall energy consumption. In response to the growing demand for energy, there is an ever-increasing need for energy supply, and the expectation that existing systems will continue to become increasingly efficient. In addition, as the need for energy continues to grow, it is equally important for energy storage and production methods to be more affordable, easier to implement, and produce better performance.

Conventionally, the bulk of energy needs has been supplied by a centralised generation of energy using various methods of generation, such as the use of large-scale generation facilities located in one place (i.e., thermal power station, hydroelectric power station, nuclear power station) and the energy being transmitted from these generation sites to the end user via distribution networks **(Sayed et al., 2023)**. Although they have been able to satisfy our growing demand for energy due to their low costs, the inability of current power generation systems to meet increased energy demand levels, as well as to direct energy from production to consumption as quickly as it is generated, limits them. Renewable energy-based energy production systems generate electricity at times that vary with seasonal and environmental factors, and for this reason, the management of energy will become increasingly complicated by the same or additional reasons. Thus, energy storage for a reasonable time has become a necessary step to optimize the performance of current systems, as well as ensure the equilibrium between the supply and demand for energy.

The use of Energy Storage Systems enables surplus electricity produced at times of low consumption to be saved and reused for increased consumption demands. Therefore, these energy storage systems have an important function in the field of

energy management, as they both help to provide equilibrium between generation and consumption, as well as contribute to an improvement in the quality of electric supply through voltage regulation. In addition to the functions previously mentioned, the continued development and proliferation of electronic devices, the increasing need for portable systems, and the variability in renewable energy production necessitate the development of multiple energy storage methods to improve energy safety and efficiency (Elalfy et al., 2024).

Energy Storage Systems (ESS) can be categorized depending on the application and the need for a large amount of energy over a longer duration, or in accordance with the nature of the energy being stored.

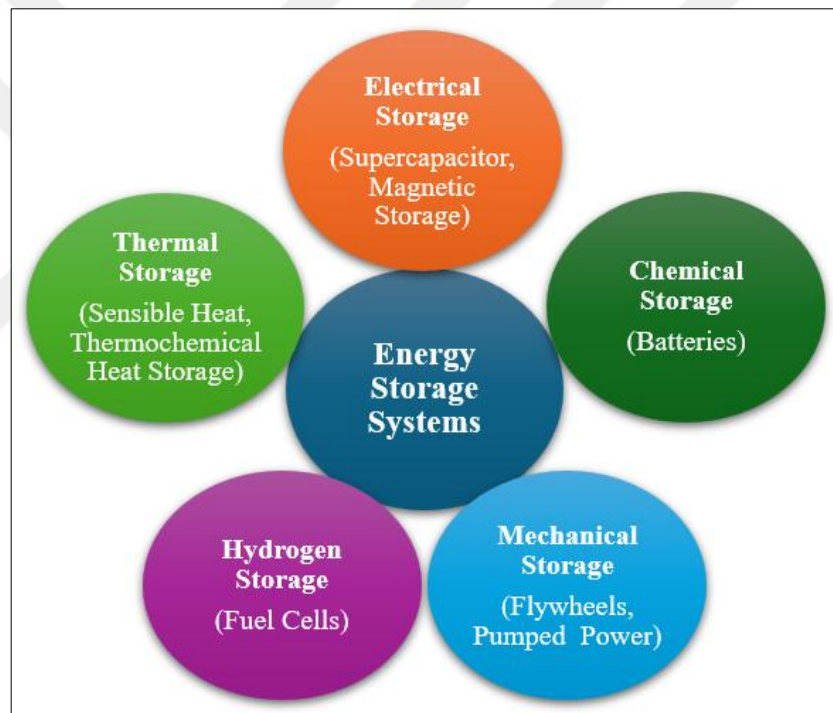


Figure 1.1: Energy storage systems.

Mechanical Energy Storage Systems, for example, store potential energy from water held at different elevations and kinetic energy from compressed air or rotating disks. Chemical Energy Storage Systems use the conversion of electrical energy to chemical energy using redox reactions between electrodes. The storage capacity of chemical systems depends on the electrode surface area, the properties of the electrolyte to allow ion transport, and the efficiency of the redox reaction (Mitali et al., 2022).

Supercapacitors also store electrostatic energy, but with faster response time and higher power densities than conventional capacitors; however, conventional capacitors have limited energy storage capability. Therefore, researchers have implemented multiple alternatives for creating new capacitor designs. Supercapacitors, which are structurally similar to conventional supercapacitor designs, have been created with high surface area electrodes and electrolytes to enhance the ions' ability to move, resulting in the ability to store larger amounts of energy. Due to the supercapacitor's rapid charge/discharge cycle rates, long lifespan, and widespread applicability, they have become a critical part of current and future energy storage technology designs (Gopi et al., 2025).



2. AIM OF THE STUDY

The main objective of this study is to create conductive inks in various formulations using graphene powder obtained from a laser-induced graphene (LIG) layer produced on a polyimide (PI) surface using a CO₂ laser. Additionally, it aims to produce supercapacitor electrodes using screen printing techniques with inks made from this graphene. The effects of the graphene/ethyl cellulose (Gr: EC) ratio on microstructure and electrochemical performance are being thoroughly investigated. In the literature, LIG is generally used as an electrode structure produced directly by a laser. However, there are only a limited number of studies on converting graphene obtained from LIG into powdered ink and using this ink in screen-printed supercapacitor electrodes. Therefore, this study investigates the effects of increasing the graphene content in different formulations while keeping the total solid content constant on print quality, film integrity, surface chemistry, and capacitive performance.

With this objective, graphene powder was obtained from the LIG layer produced using optimized laser parameters by mechanical scraping. The obtained graphene powder was dispersed in ethanol, and four different conductive ink formulas were prepared with the specified binders and additives. The inks were applied onto the ITO/PET substrate using the doctor blade method, and electrodes with a homogeneous surface morphology were obtained through controlled drying stages. The morphology of the obtained electrodes was examined using scanning electron microscope (SEM) images. Energy-Dispersive Spectroscopy (EDS) was used for the determination of the elemental compositions of the electrodes as well as for the distribution of elements on the surfaces of the electrodes. The structural order and defects present in the graphene were identified by Raman Spectroscopy. Crystal structures and phase properties of the electrodes were identified by X-ray Diffraction (XRD) Analysis. Finally, the surface chemistry, including the oxidation states of atoms, bonding type(s), and degree of oxidation, was identified by X-ray Photoelectron Spectroscopy (XPS) Analysis.

The electrodes developed at this last stage, when paired with a PVA/KOH-based semi-solid gel electrolyte, produced flexible, sandwich-type symmetric supercapacitors. The electrochemical properties of these devices were analyzed using cyclic voltammetry (CV), galvanostatic charge and discharge (GCD), and electrochemical impedance spectroscopy (EIS) methods via a two-electrode system. The results from

these analyses can be compared to demonstrate how the increase in graphene concentration affects the electrical conductivity, capacitance, inner resistance, and ion mobility. Additionally, a detailed evaluation was performed to establish the optimal Gr-EC ratio. Finally, this study proposes an original approach to provide a solution to a significant problem in the literature concerning the design of cost-effective, printable, and flexible supercapacitor technology.



3. SUPERCAPACITORS

Super-capacitors are developing at a rapid pace as they can provide a lot of energy when compared to their weight and have a long life-cycle, and will help meet the increasing demand for energy while also providing a way to develop green technologies for storing energy (Conway et al., 2013). Figure 3.1 shows the Ragone chart, which is a graphical representation of the relationship between the specific power and the specific energy of several types of storage devices. The specific energy of a device is defined as the total amount of energy stored by the device per unit of its mass, while the specific power is the rate of energy transfer from the device per unit of time. Fuel cells are unique in that they contain a large amount of energy (specific energy Wh/kg) in addition to providing a high energy density, allowing them to supply energy for long durations. Super-capacitors can provide a large amount of energy in a very short period of time due to their high specific power (W/kg) densities, which is a measurement of the energy consumed per unit of time. Battery technologies fall somewhere in the middle of the spectrum of energy and power, and conventional dielectric capacitors have both low energy storage capabilities and high power densities (Gopi et al., 2025).

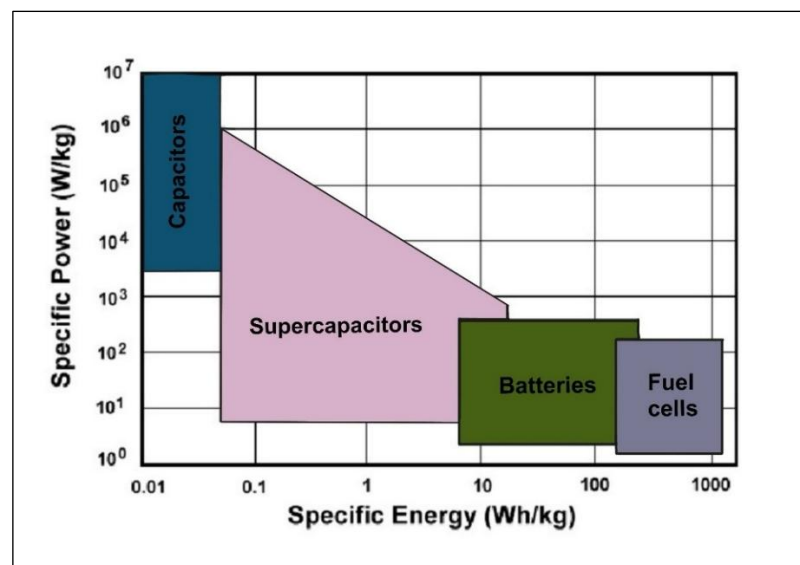


Figure 3.1: Ragone plot; specific energy and power capacities. (Pandolfo and Hollenkamp 2006).

Compared to other capacitors of the same weight or size, supercapacitors have an enormous amount of electrical energy stored within them. In other words, even with a small size or weight, they can store 20 to 200 times more electrical charge than classic capacitors. Therefore, supercapacitors fill the gap between traditional capacitors and batteries. Compared to batteries, supercapacitors have high reversibility, shorter charge-discharge times, higher cycle power, and longer lifespans. Thus, supercapacitors represent an additional form of energy storage technology relative to batteries and fuel cells.

The Ragone chart is very effective at providing information about the trade-off between the power density and the energy density of an energy storage system; however, due to the omission of many important factors, including, but not limited to, the cost, the number of charge/discharge cycles, the operational temperature range, and manufacturing feasibility, the Ragone chart does not provide sufficient information regarding how well the performance of an energy storage device will be realized by itself (**Pandolfo et al., 2006; Tiwari et al., 2020**).

Table 3.1 provides an overview of different types of energy storage units, e.g., standard capacitors, supercapacitors, batteries, and fuel cells, with respect to their specific energy, number of cycles per unit of time for charging/discharging, and their storage mechanisms.

Due to their ability to store electricity for extended periods of time while providing a large amount of power when required, the supercapacitor is positioned uniquely compared to the battery and capacitor. Conventional capacitors offer high power but have low energy storage capacities (**Raza et al., 2018**).

Likewise, the high energy density of a battery is offset by its slow charge-discharge times and low cycle life. The supercapacitor, therefore, represents an intermediate point in terms of energy and power capabilities. Furthermore, the fact that the maximum operating voltage of an electrochemical capacitor depends on several factors, including the electrodes and the electrolyte, also shows that the chosen material will affect the performance of a supercapacitor (**Pandolfo et al., 2006**).

Table 3.1: Performance metrics of electrochemical ESSs. (Raza et al., 2018).

Characteristics	Capacitors	Supercapacitors	Battery
Specific Energy (Wh/kg)	<0.1	Up to 1091	Up to 1606
Specific power (W/kg)	>10,000	Up to 19,6000	< 1000
Discharge time	10^{-6} – 10^{-3} S	s to min	0.03 – 3 h
Charge time	10^{-6} – 10^{-3} S	s to min	1 -5 h
Coulombic efficiency (%)	About 100	Up to 99	70 – 85
Cycle life	Almost infinite	>500,000	About 1000
Charge storage determinants	Electrode area and dielectric	Microstructure of electrode and electrolyte	Thermodynamics and active mass

4. ENERGY STORAGE MECHANISM

Capacitor energy storage mechanisms can be divided into two main classes, as shown in **Figure 4.1**: i) conventional capacitors, and ii) supercapacitors. Electrical charge is stored by supercapacitor types as either electrostatically at an electrode-electrolyte interface, known as electrochemical double-layer capacitors (EDLCs), or through reversible surface redox reactions, also known as pseudocapacitors (PCs). Hybrid capacitors use both electrostatically accumulated charge from the EDLCs and the reversible surface redox reaction of PCs to store electrical energy (**Raza et al., 2018**).

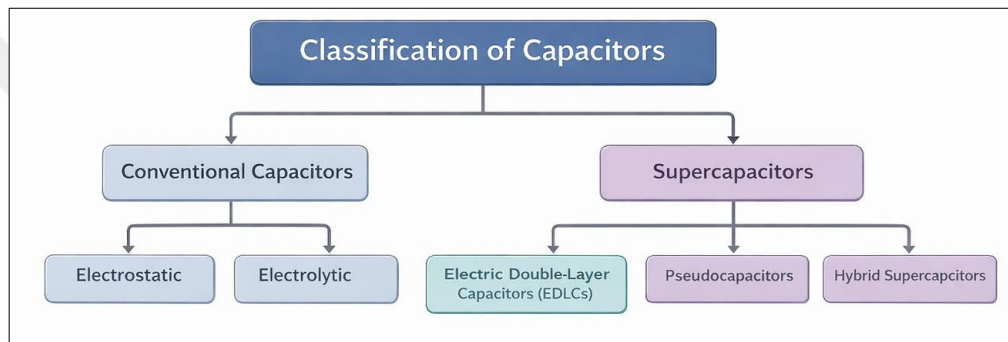


Figure 4.1: Capacitor categories and mechanisms of energy storage.

4.1. Electric Double Layer Capacitor (EDLC)

Double-layer supercapacitors (EDLC) are the most basic class of supercapacitors. This system is a physical energy storage mechanism based on the ionic charge separation that occurs at the electrode-electrolyte interface. The purpose here is to optimize this physical interaction by utilizing the separation created by the orderly arrangement of ions on the electrode surface. Since the charge storage process in this mechanism does not depend on any chemical transformation and occurs through fast and reversible electrochemical interactions, close to the surface, the system can respond extremely quickly. The charge-discharge time is on the order of seconds, and performance loss remains minimal over thousands of cycles. Therefore, they are preferred in situations that require very fast energy transfer rather than long-term energy storage. Compared

to traditional batteries, EDLCs offer higher cycle stability and require less maintenance (Banerjee et al., 2025).

An EDLC cell consists of two electrodes and an electrolyte in contact with these electrodes. In such a structure, each electrode and electrolyte surface represents a capacitor. Thus, these two double layers can be thought of as two capacitors connected in series electrically.

Therefore, the total capacitance equation for a symmetric cell is equation (4.1) as follows:

$$C_{cell} = \left(\frac{1}{c_1} + \frac{1}{c_2} \right)^{-1} \quad (4.1)$$

Here, it refers to the double-layer capacitance formed at the C1 and C2 electrodes.

This approach was first suggested in the 19th century by Hermann von Helmholtz in his work explaining the relationship between the arrangement of surrounding ions on charged surfaces. Helmholtz proposed that this structure, formed by the arrangement of oppositely charged ions in a tight layer at the atomic level on the electrode surface, was similar in structure to traditional parallel-plate capacitors (Zhang et al., 2012). This model (Figure 4.2) presents the double-layer structure as a simple compact capacitor, which is the most fundamental explanation of the EDLC.

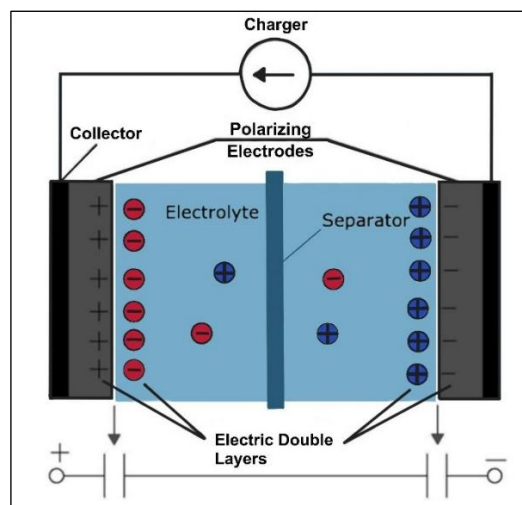


Figure 4.2: Typical configuration of an EDLC cell (Jayalakshmi et al., 2008).

However, Helmholtz's solid layer approach has proven insufficient over time. Gouy and Chapman expanded this approach by also considering the diffusion behavior of ions in solution. According to the Gouy-Chapman model, ions with opposite charges spread out over a certain thickness. The ion concentration is defined by a Boltzmann distribution that increases as it approaches the surface. While this model is accurate for lower charge densities, it is insufficient to represent high charge density systems, as it underestimates the actual thickness of the double layer.

Stern developed the Stern model, which forms the basis of modern EDLC structures, by combining both approaches to address all these shortcomings. This model describes the double layer as consisting of two layers: the compact or Stern layer (first), and the diffusion layer (second).

This region, which we call the "compact" layer, refers to the area near the surface of the electrode that includes hydrated ions adsorbed onto the surface of the electrode in either a specific manner or in a non-specific manner. The diffusion layer, as opposed to the compact layer, is the zone in which the electrode's electrostatic field balances the random movement of ions within the solution due to thermal energy; therefore, the thickness of the diffusion layer is dependent upon the temperature and type of electrolyte. Stern's model gives the most accurate representation of present-day EDLC behavior by considering both ion adsorption and the diffusion layer (**Yan et al., 2014; Raza et al., 2018**).

The amount of charge that is stored in an EDLC is directly related to the electrodes developing a double layer; therefore, as indicated in **Figure 4.3**, the parameters affecting the magnitude of capacitance are.

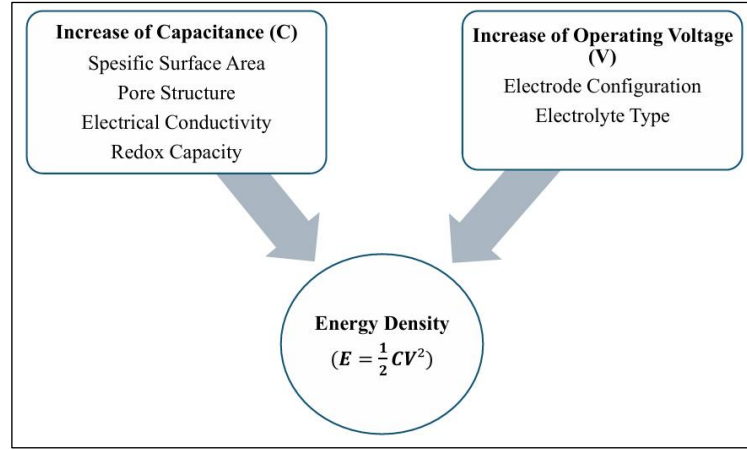


Figure 4.3: Key parameters that affect energy density (Yan et al., 2014).

To improve energy density, we have to consider the capacitance as well as the operating potential of materials.

In general, the energy (E) and power (P) of EDLCs are determined by the following equations:

$$E = \frac{1}{2} CV^2 \quad (4.2)$$

$$P = \frac{V^2}{4R_s} \quad (4.3)$$

In these equations:

E: Energy density

P: Power density

R_s : Equivalent series resistance (ESR).

As per the above equations, energy is a function of capacitance and operating voltage, while lower power means higher ESR values, which implies that the EDLC can be charged/discharged rapidly; therefore, they are better suited for applications that require high power over high energy storage as opposed to battery systems (Alabadi et al., 2016).

Also, the physical mechanism of EDLCs has some restrictions. The interaction between electrode materials with large surface areas and liquid or gel electrolytes that conduct ions is the source of EDLCs' energy storage capacity. In contrast to traditional capacitor technology, where the storage of electrical energy occurs at the dielectric located between the metal plates, the charge separation in EDLCs is accomplished by arranging ions on the electrode's surface. Because the charge separation is limited to a double-layer region of less than several nanometers and because the amount of electric field (voltage) at which the electrolyte can no longer support itself represents an upper limit on the voltage level that can be applied to the cell, the energy density of these types of cells will always be lower than that of batteries.

The physical characteristics of the electrodes, such as electrode geometry, the extent of ion access to the surfaces of the electrodes, and the pore structure of the electrodes, all have a direct influence upon the behavior of this type of cell. Therefore, modern research focuses on overcoming these limitations with carbon-based structures (graphene, carbon nanotubes, activated carbon derivatives) that have a high surface area and electrolyte designs that facilitate ion conduction **(Raza et al., 2018)**.

4.2. Pseudocapacitor (PC)

Pseudocapacitors (PC) are based on a mechanism involving Faradaic charge transfer at the electrode-electrolyte interface. This process essentially enables charge accumulation through electron transfer via rapid oxidation-reduction reactions. In some materials, this Faradaic process produces irreversible products as a result of the reaction, while in other cases, it is completely reversible, and no new chemical species are formed during the reaction **(Schötz et al., 2022)**.

This is similar to the electrostatic behavior seen in EDLCs. However, compared to EDLCs, the charge storage that occurs in pseudocapacitive materials results from rapid redox reactions occurring on or near the surface. Therefore, this mechanism provides much higher specific capacitance and energy density. However, the advantage of the nature redox-based mechanism results in lower power density compared to EDLCs and a more limited cycle life **(Pandey et al., 2024)**.

Common electrode materials used in pseudocapacitors are transition metal oxides and conductive polymers, which enable fast and reversible electron exchange. The pseudocapacitive behavior of metal oxides is based on the principle of redox reactions occurring in regions close to the surface, with protons or alkali metal cations rapidly entering and exiting the structure. Metal oxide structures such as RuO_2 , MnO_x , Fe_3O_4 , and NiO are frequently preferred because they can produce high capacitance due to the redox pairs on their surfaces. Other oxides in this class, such as Co_3O_4 , SnO_2 , and NiO_2 , stand out because of their low cost and ease of synthesis. However, their poor conductivity and limited cycle life limit the use of these structures (**Viswanathan et al., 2024; Kumar, Thangappan, et al., 2022**).

Conducting polymers, which include polyaniline, polypyrrole, PEDOT, and a variety of derivatives of polythiophene, are also being looked at for use as redox electrode materials due to their electrical conductivity, good processability, and relatively low cost. The ability of charge to be stored using the doping-dedoping mechanism is made possible by the π -electron system within the backbone structure of each polymer. However, material degradation occurs due to volume changes that occur with repeated electrochemical cycles; therefore, cycle stability is generally poor for conducting polymers (**Singh et al., 2023**).

Research in recent years has centered on developing new carbon-based composite systems with a focus on increasing both the thermal stability and electrochemical stability of metal oxides and conductive polymers, due to their inherent instability when used as electrodes. As such, researchers are focusing their efforts on the use of graphene as the support material, as it possesses a large surface area, significant mechanical strength, and is electrically conductive, enabling enhanced charge transport characteristics and the structural integrity of the electrode, thereby enhancing the overall performance of a supercapacitor through maintaining the beneficial aspects of the redox-active constituents (**Kumar N., et al., 2022**).

4.3. Hybrid Supercapacitor

Hybrid supercapacitors allow for the development of EDLCs (advantages: long cycle-life; high power-density; stable) and Pseudocapacitance (advantages: higher capacitance; higher energy-densities due to redox), which is being researched currently

because neither mechanism has sufficient characteristics individually. The major limitation with EDLCs is that they lack sufficient energy density. Similarly, pseudocapacitive behavior lacks sufficient stability.

Bridging Technology (hybrid-supercapacitors) has been researched for the purpose of an increased energy density through the improvement of the capacitance of the supercapacitor cell, and also the enhancement of the cell voltage. The most common type of active material for the positive electrode in hybrid structures includes metal oxide pseudo-capacitance or conductive polymers. The most common type of negative electrode materials includes carbon-based electrochemical double-layer capacitor (EDLC) materials, which are required to have a large surface area. Therefore, the total cell voltage will be increased by the potential difference created between the two electrodes. Battery-type hybrids combine the high energy storage capability of batteries with the fast charge/discharge capabilities of supercapacitors, but they do this from a single architectural platform. On the other hand, composite hybrid structures are designed as multi-phase structures that allow both capacitive and faradic components to work together in each electrode. These composite hybrid systems consist of carbon-core structures with high surface area, coated with pseudocapacitive phases that form the active regions of the electrode **(Sun et al., 2022)**.

The combination of energy-power and other characteristics, such as charge/discharge rate, number of charge/discharge cycles, and the operating voltage window, along with capacitance in Hybrid Supercapacitors, makes it possible to optimize each of them simultaneously. One of the most significant advantages of Hybrid Supercapacitors that has led to the increased focus on their development in recent years is that they are able to combine the power density of standard supercapacitor designs with the high energy storage capacity of lithium-ion battery systems. Therefore, Hybrid Supercapacitors represent the basis for developing future generations of electrical energy storage systems that can be rapidly charged and will provide reliable power for an extended period of time; Hybrid Supercapacitors would be particularly useful for electric vehicle systems, portable electronic systems, and systems that store power and utilize large current levels **(Rudra et al., 2024)**.

5. ELECTROLYTE

In addition to electrode performance and cell configuration, the supercapacitor's electrochemical behavior is also dependent upon the type of electrolyte that is used. The nature of an electrolyte impacts the energy and power density of a supercapacitor structure, since it determines two critical characteristics - the cell operating voltage and the ion transport. Ideally, an electrolyte should have the fundamental properties, including high ionic conductivity, good chemical stability, sufficient ion concentrations, low cost, and safe and reliable operation. Supercapacitor electrolytes are typically classified into three major categories: (1) aqueous electrolytes, (2) organic electrolytes, and (3) ionic liquids (Yan et al., 2014).

The aqueous electrolyte is attractive due to its low cost and lack of potential for flame spread. Electrolytes such as H_2SO_4 , Na_2SO_4 , and KOH are also well known because they can be easily prepared on an industrial or laboratory scale and have dissolved ions that are of a small enough size so that diffusion is quick (Mendhe et al., 2023). However, aqueous systems are insufficient on their own for applications requiring high voltage due to the electrolysis reactions of aqueous solutions starting at around 1.23 V and the working voltage being limited to ~ 1 V (Zhang et al., 2012).

Organic electrolytes consist of large cation/anion pairs, such as tetraethylammonium, dissolved in organic solvents. These electrolytes offer wider voltage ranges, such as 2.5-3 V, which can increase energy density. However, the use of these organic electrolytes has been limited due to safety concerns such as low ionic conductivity, high viscosity, sensitivity to moisture, and flammability. In addition, the most basic disadvantage limiting the large-scale use of these electrolytes is their high production costs and sensitivity to H_2O .

Ionic liquids are electrolytes composed entirely of ionic species that can exist in a liquid state at room temperature. Their ability to operate over a wide electrochemical window of approximately 4 V makes them a viable option due to their good thermal and chemical stability. However, their potential has been limited due to their high viscosities, low conductivities at low temperatures, and their high costs (Yan et al., 2014).

In addition to the three main types of materials described above, a new type of material has recently become widely used in flexible and safe supercapacitor designs, which are referred to as gel polymer electrodes or gel aqueous electrolytes. The structure is obtained when an aqueous electrolyte is incorporated into a polymeric network. Gel polymer electrolytes provide a number of important characteristics, including leakage resistance and mechanical flexibility, as well as structural integrity that maintains the electrical conductivity of the solution. Even though this type of electrolyte belongs to the aqueous electrolyte class, it exists as a hydrogel. By creating continuous paths for the transport of ions through a porous matrix of polymer chains that hold ions, hydrogels can be advantageous because they exhibit both high conductivity and mechanical strength in flexible device configurations **(Lan et al., 2025)**.



6. MATERIALS OF SUPERCAPACITORS

The quality of electrodes in supercapacitors is one of the most important factors affecting the total energy storage capacity of the supercapacitor. The capacity of a supercapacitor is largely dependent on the electrochemically accessible surface area of the electrode material and the extent to which ions can effectively reach this surface. For this reason, many researchers have recently been working on developing electrode materials with suitable pore structures, fast ion movement, and high electrical conductivity for future supercapacitors (**Zhou et al., 2022**).

The electrochemically active surface area is affected by several factors, including the total surface area of the material as well as whether or not the ions from the electrolyte can physically contact (access) the surface. The pore size and distribution on the electrode will directly impact the extent to which ions from the electrolyte can come into physical contact with the surface of the electrode. By creating pores in the electrode such that the pore size corresponds to the size of the ions in the electrolyte, a significant increase in the capacitance of the system can be achieved. The pores need to be smaller than the size of the ion to prevent ion migration; the larger pores create less interaction with the surface as a result of the increased distance between the surface and the electrolyte ions, thus resulting in decreased capacitance (**Largeot et al., 2008**).

As with all supercapacitor electrodes, the appropriate size of micro-mesopores will significantly affect how well ions can travel across the material and form the double layer that is so critical for charge storage. As a result of these characteristics, carbon materials may be the most suitable choice for use in supercapacitor electrodes because they are inexpensive, have high surface areas, and are chemically stable (**Forouzandeh et al., 2020; Lu et al., 2015**).

Electrode materials that are commonly used in supercapacitors can be divided into four categories: namely, carbon-based materials, conductive polymers, and metal oxide-based materials.

6.1. Metal Oxide-Based Electrode Material

Transition metal oxides have numerous advantages as an ideal candidate material for PC electrode materials due to their special crystal structure, large theoretical capacitance, and their ability to undergo fast redox reactions. A major advantage of metal oxides over carbon-based EDLC electrodes is that, in addition to storing charges between the electrode and the electrolyte through reversible redox reaction, they can store charge very rapidly. As a result, it is possible to achieve greater specific capacitance and energy density compared to that achievable with carbon-based EDLCs.

The electrochemical behavior of transition metal oxides will depend upon the chemical properties of multivalent metal ions, which facilitate fast electron transfer (**Liang et al., 2021**). The electrochemical characteristics of the above-mentioned material are also greatly influenced by factors other than the crystal structure and the space for ion movement in the solid state. This is why many researchers have been studying oxides like MnO_2 , NiO , Co_3O_4 , V_2O_5 , Fe_2O_3 , and Fe_3O_4 as they have highly adjustable structural properties and are very accessible. Controlling the pore architecture and nano-structures in the metal oxides allows the ions to travel to active zones at higher speeds, allowing for a greater amount of capacitance (**Yadav et al., 2020**).

While Ru_2O has the best performance for a pseudo-capacitor within scientific literature, it has very little application potential due to both its cost and environmental impact. Consequently, research into developing alternative, cost-effective, and environmentally-friendly options has focused on low-cost metals that offer good performance, such as Iron, Manganese, Nickel, and Cobalt Oxides (**Islam et al., 2022**).

Iron oxides have the advantages of being environmentally benign and having structural stability over a wide range of potentials; however, their inherently low intrinsic conductivity has limited their use in practical applications. Generally speaking, approaches for improving the performance of a metal oxide include creating nanostructured or composite forms that can be used to increase the surface area where ions diffuse through the structure. One-dimensional nanorods, two-dimensional thin structures, and three-dimensional porous lattice structures allow for the optimal use of the material to expand the surface area from which ions diffuse. Also, using metal

oxides in a hybrid combination with carbon nanotubes, graphene, or another metal oxide is used to increase the electrical conductivity of the hybrids and make the hybrids more cycle-stable.

Hybrid electrode material combinations such as MnO_2 /graphene or $\text{NiO}/\text{V}_2\text{O}_5/\text{MnO}_2$ show increased capacitance values and longer cycle lives than do electrodes created with only a single type of metal oxide (Islam et al., 2022; Cuihua An et al., 2019).

6.2. Conductive Polymer-Based Electrode Material

Conductive Polymers are useful for use as an electrode material in a Supercapacitor due to the potential of conductive polymers to exhibit electrical conductivity due to their conjugated bonds, which exist throughout their molecular structure.

The presence of a conjugated π -electron system within the molecular structure of these polymers will allow charge transporters to move freely along the polymer backbone; thus, like other polymer structures, they may display semiconductor or metal-like behavior when it comes to electrical properties. The characteristics mentioned above make these conductive polymers very appealing as electrode materials in supercapacitor applications, since they are lightweight, easily synthesized, chemically modifiable, inexpensive, and responsive to rapid electrochemical reaction changes (Suriyakumar et al., 2021).

The first instance of a conductive polymer was noted when it became apparent that the conductivity of polyacetylene had substantially increased with the addition of a chemical dopant, prompting research into other polymers in this class. The dopant facilitates the formation of polaron/bipolaron through the reduction of the polymer chains by providing electrons (doping) or by creating holes through electron removal (de-doping). thus, the polymer's structural configuration can transition from its neutral state to highly conducting states. The primary chemistry of the polymer chain remains intact during the doping process. The doping process is reversible; therefore, conductivity can be adjusted as required. the electrostatic equilibrium of the charged polymer chain and oppositely charged ions directly influences the electrical, optical, and magnetic characteristics of these materials.

Flexible energy storage products can be appealing for a variety of reasons. For example, they are often very lightweight and therefore do not require large amounts of materials to produce them. They also provide mechanical flexibility to the electrode they support. Additionally, conductive polymers such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh) have been used in supercapacitors because of their ability to show pseudocapacitive activity and provide high specific capacitance by redox reaction on the surface of the material.

Conductive polymers provide energy densities that are greater than those provided by carbon materials, which is another advantage when using conductive polymer electrodes in supercapacitor technology (Sumdani et al., 2022; Guimard et al., 2007).

Nano-scale designs for conductive polymers that incorporate nano-rods, nano-sheets, nano-plates, or three-dimensional networks with porosity can increase the surface area available for activity; they also allow for quicker access to the electrolyte ions in the polymer. These types of morphologies are advantageous because they provide benefits, including enhanced electrochemical performance through fast charge transfer within the polymer chain, large capacitance, and low resistivity.

The advantages of conductive polymer structures are many; however, there are also some major disadvantages of conductive polymer structures. One of those major disadvantages is the volumetric changes in the structure along with the mechanical degradation resulting from repeated charge/discharge cycles. The repeated oxidation/reduction of polymer chains during an electrode potential cycle can produce cracking, volumetric expansion/contraction, and loss of capacitance on the material surface. Recent research has focused on overcoming these deficiencies through the production of composite structures utilizing materials such as carbon nanotubes, graphene, and metal oxides. These materials have shown great electrical conductivity and mechanical stability. In addition to providing a balance between the excellent redox properties of polymers, composite structures provide superior mechanical stability compared to pure polymer structures (Tadesse et al., 2024).

Synthesis Methods of Conductive Polymers. In addition to the other parameters that affect the performance of conductive polymers, there is yet another factor that will contribute to the performance of conductive polymers: synthesis methods. As well as

being an easy method to apply to materials, chemical polymerization is typically used for its ability to create conductive polymers due to its providing a simpler means of creating conductive polymers. Electrochemical polymerization, on the other hand, will provide increased performance to coatings through increased thickness, degree of crystallization, and control.

The reason why conductive polymers are preferred as supercapacitor electrode materials is primarily due to the properties that they exhibit, including: a large amount of faradaic charge storage within a short time frame, flexibility in design, lower costs compared to other electrode materials, and a high level of specific capacitance. However, the limitations of conductive polymers include: low cycle stability of the material and the material's inability to be mechanically stable. Due to this, conductive polymer composites with suitable architectural designs are an area of study that is currently being researched. Through the use of nano-structure-based materials and a variety of composite-based materials, it is anticipated that the performance of supercapacitors can be enhanced to greater levels by utilizing conductive polymers (Suriyakumar et al., 2021).

6.3. Carbon-Based Electrode Material

The most popular type of material for a supercapacitor electrode is the carbon-based material; the reason for this preference stems from its properties as well as those of the materials themselves. These carbon-based materials provide a structure for the electric charge storage mechanism in electric double-layer capacitors (EDLC) because they have an abundance of surface area, are inexpensive, and conduct electricity. The surface area and porosity of these materials allow ions to easily access the electrical interface; however, the surface area, the pore size, pore distribution, and the surface functionality, conductivity, and the characteristics of electron transport will determine how an EDLC will behave. As a result, research into carbon materials used for the electrodes of supercapacitors has resulted in the development of structures with high conductivity at the nanoscale, including activated carbons, carbon nanotubes, and graphene (Dhilip Kumar et al., 2022).

As a result of their high surface area, relatively low costs, and high conductivity, Carbon materials have been one of the most common options for use as electrodes in

supercapacitors. Unlike other alternatives, these carbon-based materials are designed with a form that is suitable for charge-storing mechanisms of electric-double-layer-capacitor (EDLC) technology. The increased porosity allows for an increase in the specific capacitance values as it enables ions to reach the electrochemical interfaces. However, in addition to the surface area of a material, the pore size, pore-size distribution, surface functional characteristics, conductivity, and electron transport characteristics can influence the performance of an EDLC. As a result, the carbon materials being utilized in supercapacitors are evolving to include nano-scale conductive architectures such as activated carbon, carbon nanotubes, and graphene (Wang et al., 2020).

6.3.1. Activated Carbon (AC)

Activated carbon (AC) is carbon based materials that has a high surface area and enhanced porosity derived from both organic and inorganic precursors; its preparation is primarily through pyrolysis (carbonization) of precursor material within an inert atmosphere to produce activated carbon and subsequent chemical and physical activation to develop the pore architecture (Kierzek et al., 2004). The surface areas of ACs may be specifically developed depending on the chemical and physical activation techniques used, ranging from 500 m²/g to 3000 m²/g. Due to these properties, these materials can be classified as fundamental electrode materials for EDLC structures.

The most critical properties of AC structures are their ability to provide a hierarchical porous architecture at the micro (50 nm) scale. Micro-pores with a large surface area and load storage capacity, along with meso- and macro-porous structures that enable rapid transport of electrolyte ions through the pore channels, reduce load transfer resistance. This allows for good performance even at high current densities. Literature studies in this field have shown that activated carbon materials, which can be obtained from lignocellulosic structures, natural waste materials, and fruit peels, can exhibit a surface area of over 2000 m²/g and high specific capacitance. These results, combined with the achievement of an optimal pore architecture, demonstrate that AC materials possess power density and cycle stability comparable to other commercial systems (Frackowiak et al., 2013).

As with other types of materials, a large surface area alone is not sufficient for AC materials. The electrolyte ion diameter must also be compatible with the pore size. This is because incompatibility between these dimensions results in poor surface functions and electrolyte interaction, or excessive activation, leading to a decrease in carbon density. This, in turn, causes a decrease in the specific capacitance value. However, certain functional groups carry the risk of degradation in organic electrolyte environments. This also affects electrolyte stability. Thus, developing a pore structure that can be optimized is crucial to these materials as well (**Luo et al., 2022; Bizuneh et al., 2023**).

6.3.2. Carbon Nanotubes (CNT)

Since their introduction to the world in 1990, Carbon nanotubes (CNTs), which represent a type of nanostructure made of cylindrical structures of carbon atoms that have a similar arrangement to graphite and are sp^2 hybridized, have emerged as an extremely popular choice for use as supercapacitor electrodes. CNTs may be categorized into two types: Single-Walled (SWCNT) and Multi-Walled (MWCNT). The material characteristics of CNTs include the ability to conduct electricity, a low density or lightness, and incredible mechanical strength. CNTs also provide a very polarizable electrode surface when storing charge.

Although CNTs have less pore volume than activated carbons as a material for supercapacitors, the space between individual tubes in a CNT produces mesoporosity that is capable of accelerating the transport of ions through the material; thus, decreasing performance loss with increased current density (**Pour et al., 2023**). In addition to increasing the rate of ion transport, the mesoporosity also provides the shortest possible distance for electrons to be transported and increases the rate of mobility of the electrons, decreasing the internal resistance of the device.

Surface-functionalized, chemically-activated, and networked with a variety of other conductive media, including carbon fiber and graphene, composite electrodes made from modified CNTs are used as electrode materials to improve the electrochemical performance of CNTs. The composite electrode material combines the flexible structure of nanotubes, the large surface area and electrical conductivity of graphene, and the porous nature of AC's structural features to enhance the composite electrode's

performance characteristics for use as an electrode material. Studies of the literature have demonstrated superior electrochemical properties of composite electrode materials composed of CNTs than those constructed solely of CNTs, such as greater specific capacitance values, excellent mechanical durability, and superior cycling performance **(Reddy et al., 2023)**.

6.3.3. Graphene

It was believed before the discovery of two-dimensional materials that a two-dimensional material would be inherently unstable from a thermodynamic point of view and therefore could never stand alone as a structure. However, this view changed in 2004 when Geim and Novoselov experimentally isolated graphene. This carbon layer, which is only one atom thick, is not only an intermediate state of the graphite structure but also a functional material with a stable structure on its own. Graphene has set a framework that guides the field in terms of both energy storage technologies and condensed matter physics technologies.

Graphene is formed by rearranging sp^2 hybridized carbon atoms into a two-dimensional structure that forms a honeycomb-like lattice. Each carbon atom in the structure forms strong sigma (σ) bonds with its three remaining bonds while also forming delocalized π bonds perpendicular to the plane. This enables it to exhibit metal-like high conductivity and good optical properties. Single-layer graphene structures have become an excellent option as supercapacitor electrode materials due to their high specific surface area, high thermal conductivity, and superior mechanical properties **(Geim et al., 2007; Sahoo et al., 2023)**.

Compared to other carbon-based materials, graphene is similar to activated carbon materials in terms of its high surface area, but it can exhibit superior properties to many graphitic structures in terms of electrical conductivity and ion transport **(Reddy et al., 2023)**. When compared to carbon nanotubes, graphene exhibits high conductivity and mechanical strength. However, due to its one-dimensional nature, the active surface area accessible to ions is lower, resulting in carbon nanotubes performing less effectively than graphene. Due to its two-dimensional structure, graphene can provide an open surface to the electrolyte even when not stacked properly, giving it a direct advantage in terms of charge storage in EDLCs **(Le Fevre et al., 2019)**.

When considering supercapacitor structures, graphene electrode materials are considered through two fundamental mechanisms:

- i) EDLC behavior, the electric double layer formed between the graphene surface and electrolyte ions
- ii) In pseudocapacitive contribution, redox processes are observed in reduced structures of graphene, particularly those containing oxygen functional groups, or in composite systems formed with graphene.

It has been observed that pure graphene structures with high crystallinity mostly exhibit EDLC performance, but the presence of defects, functionalized structures, or composite components activates Faradaic processes on the surface, thereby increasing the specific capacitance **(R. Kumar et al., 2022)**.

In addition to all these advantages, the use of graphene in supercapacitors also presents certain structural challenges. Single-layer graphene structures tend to stack and aggregate. Furthermore, the π - π interactions formed between the layers cause narrowing of ion diffusion pathways in electrode structures and a reduction in accessible surface area. Current studies aimed at overcoming this limitation by designing graphene structures in three-dimensional porous structures, foam-like aerogel structures, or as thin film layers grown on conductive substrates **(Worsley et al., 2022)**. Various additives, such as conductive polymers, metal oxides, and MXene, are incorporated into graphene structures to increase capacitance and ensure mechanical stability and a good cycle life. The specific capacitance values obtained in graphene-based supercapacitor structures depend on the type of electrolyte used, the pore architecture, the number of layers, and the defect density parameters. In fact, so much so that they provide an alternative device architecture with respect to traditional carbon electrode architectures and lithium-ion battery architectures, which can bridge the performance gap.

Therefore, the practical application of graphene's superior characteristics into actual devices depends on graphene's morphology, production process, layer number, defect structure, and functional group density. Hence, the next segment will detail all graphene production processes to assist in understanding the performance of the graphene-based supercapacitor **(Sahoo et al., 2023)**.

7. GRAPHENE–FABRICATION METHODS

Graphene can be produced using two methods of graphene manufacturing: Top-Down and Bottom-Up. The Top-Down method uses a bulk, solid graphite structure as a starting point for the formation of single-layer graphene. The layers of graphene are peeled to produce single-layer graphene. In the Bottom-Up approach, graphene is obtained based on the principle of starting from atoms or molecules and building a large structure from small units (**Rudrapati et al., 2020**).

7.1. Mechanical Exfoliation

This was one of the first simple methods discovered and was developed by Geim and Novoselov. It is also known as the ‘Scotch tape method’ in the literature. This method allows highly oriented pyrolytic graphite to be produced at low cost by physically peeling it off the surface dozens of times with the help of tape. As a result, a single-layer thin graphene sample is obtained by peeling 1 μm graphite flakes.

The main disadvantage of this technique is that the mobility of the graphene sample is limited as a result of the contamination of the electric charge carrier (electrons and vacancies) with the adhesive residues from the tape. In order to remove these residues, the sample placed on the substrate has to be heat-treated by heating it up to about 500 °C under vacuum pressure. This process sequence is limited to smaller-scale productions due to the non-uniformity and labor-intensive nature of graphene films (**Novoselov et al., 2004**).

7.2. Chemical Exfoliation

This method involves first obtaining a single or multilayer graphene oxide (GO) structure by using chemical methods and then reducing this structure to reduce graphene oxide (rGO). Since the rGO structure obtained by this method may contain structural defects (missing bonds) during oxidation and reduction, it is produced with lower quality (**Parvez et al., 2015**).

7.3. Chemical Vapor Deposition (CVD)

Chemical Vapour Deposition (CVD) is the most suitable method for producing single or multiple layers of graphene on large scales. Somani et al. first used this method in 2006 to synthesize a graphene film with very few layers on a Ni substrate using camphor as a precursor. Later, great progress was made by controlling the thickness of graphene layers deposited on different metal substrates.

Thus, by using this method, the need for complex chemical and mechanical processing will be reduced, resulting in the production of high-quality graphene layers (**Liu et al., 2022**).

When the Cu (copper) substrate is exposed to a vacuum and directly interacts with the flow of hydrogen (H_2) and methane (CH_4) gases, catalytic decomposition occurs on the Cu surface. Thus, C_xH_y species are formed at a certain temperature. The saturation of these species formed on the surface is highly dependent on temperature and partial hydrogen-methane flux.

Then, after the structure is supersaturated with C_xH_y species on the Cu substrate surface, it cools, and the formation of nuclei will occur. These nuclei grow and start to form graphene regions on the substrate surface. After a while, the surface is completely covered with graphene, and the process is completed (**Li et al., 2016**).

7.4. Physical Vapor Deposition (PVD)

This method is based on the principle of obtaining a graphene layer by deposition on the surface of carbon atoms produced by evaporating a solid carbon source (e.g., graphite), but the crystal arrangement of graphene obtained by this method is less developed than that obtained by chemical vapor deposition (CVD) (**Zhang, Rui et al., 2025**).

7.5. Laser-Induced Graphene (LIG)

The research approach is based on an in situ carbon rich conversion of carbon-rich polymer surfaces through direct exposure to CO_2 IR-laser beams into a conductive and porous sp^2 -carbon structure. Referred to as LIG, or Laser-Induced Graphitization, was

first introduced in 2014 for the creation of carbon-rich polymer precursors, including both natural and synthetic polymers, as well as small molecules, and also porous three-dimensional graphene structures created from the same source of laser beam in one step and with scalable patterning (Moon et al., 2024).

There are several benefits to this method, namely, high porosity and the ability to produce low-cost patterned masks in an atmospheric environment, without the use of a gas vacuum or catalytic reaction. Due to the versatility and benefits of this method, it has attracted a significant amount of attention from various disciplines such as electronics, catalysis, and bioapplications (Liu J. et al., 2022).

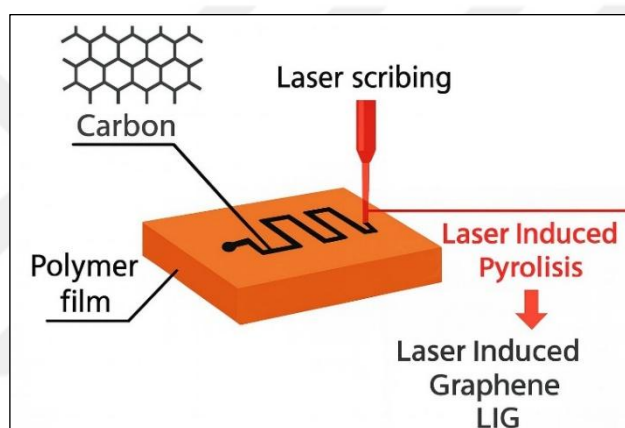


Figure 7.1: Schematic of laser-induced graphene (LIG).

The laser beam creates rapid photothermal heating on the polymer surface, breaking C=O, C O, and N-C bonds in the polymer, and oxygen, nitrogen-containing groups, and volatile compounds are removed as CO, CO₂, H₂O, and NH₃. After this removal, with the increasing carbon density in the polymer chain, the sp³-bonded skeleton structure transforms into a sp² rich structure by gradual carbonization. Thus, the structure is transformed from an amorphous polymeric to a sp² hybrid conductive and ordered graphitic structure (Liu et al., 2022).

The resulting structure creates multiscale porosity and a foamy three-dimensional graphene skeleton on the surface; this structure with micro/mesoporous morphology increases the electrochemically active area due to its specific surface area and provides open channels for ion diffusion. These graphene structures obtained by the LIG

method offer a continuous carbon structure and a well-networked electron conduction pathway **(Zhu et al., 2021)**.

The laser parameters used have a great influence on the chemical and physical properties of the produced graphene. It has been observed that increasing the laser power increases the conductivity, while the thickness of the formed film can increase the conductivity to the same extent.

Depending on the application rate of the laser, it was observed that the carbon structures in the produced graphene were found in pentagonal-heptagonal hybrid lattice structures instead of the traditional hexagonal lattice. This has been termed 'kinetic graphene' due to the fact that the lattice structure does not have time to reach equilibrium due to rapid cooling after laser irradiation **(Vivaldi et al., 2021)**.

The graphene character is confirmed by the presence of prominent D, G, and 2D peaks in the Raman spectrum characterization of graphene produced by this method; the D/G ratio gives clues about the defect/edge density, which can also be tuned by laser parameters. The LIG method has a wide range of applications, including wearable sensors, gas/water purification membranes, energy storage, and electrocatalysis. Direct patterning and substrate integrity, especially in flexible electronic human-computer interaction systems, allow antennas and interconnectors to be quickly **(Sartanavičius et al., 2023)**.

8. ELECTROCHEMICAL CHARACTERIZATION OF SUPERCAPACITORS

The electrochemical performance of supercapacitor structures depends on parameters such as specific capacitance, power density, equivalent series resistance (ESR), operating voltage, and cycle stability. These parameters are determined by the physical properties of electrode materials, by the rate of ion transport across the electrode-electrolyte interface, and by the mechanism of charging/discharging of the supercapacitor. Literature reviews have used three main techniques to evaluate the electrochemical structure of a supercapacitor: cyclic voltammograms (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) (Pholaupyphon et al., 2024).

8.1. Cyclic Voltammetry (CV)

The Cyclic Voltammetry (CV) is one of the most common measurement techniques for studying the electrochemical characteristics of a Supercapacitor cell. The CV works in accordance with the concept of lineal voltage application to the working electrode in a defined potential window, measuring the generated current as a result of the applied voltage; this allows the separation of the capacitive and Faradic process according to the amount of charge accumulated at the electrode's surface (Pholaupyphon et al., 2024).

CV plots offer some information on the charge storage capacity of an electrode through its characteristics. CV curves provide evidence of oxidation/reduction reaction by peak shapes when observing the structure in PC materials, whereas, in the case of EDLC materials, CV plots are generally rectangularly shaped. Additionally, CV plots collected with varying scan rates allow researchers to study both diffusion-controlled processes and changes in cycle stability (Perdana et al., 2024).

8.2. Galvanostatic Charge-Discharge (GCD)

This method uses a constant current source and the change in voltage with respect to time to find the various characteristics of a super-capacitor system (cycle life, energy density, theoretical capacitance). The parameter of specific capacitance can be determined through the calculation of the dV/dt ratio, which is determined from the slope of the discharge curve, and additionally, any break points found in the discharge curves or ohmic drops due to the internal resistance may help determine the ESR (**Kim et al., 2015**).

Additionally, the symmetry of the discharge curves obtained by this method can provide information about the transport rate of ions and the reversibility of the electrode material. A flat discharge curve indicates EDLC structures, while a curved discharge curve indicates reaction and diffusion limitations in PC structures. Long-term charge/discharge tests allow for the evaluation of the stability of the electrode material (**Pholauyphon et al., 2024**).

8.3. Electrochemical Impedance Spectroscopy (EIS)

This method uses a different approach to measure ion mobility in the porous material, as well as the characteristics of interest of the pores (pore size distribution, charge transfer impedance, etc.) by applying an alternating low-amplitude signal over a wide frequency spectrum.

The high frequency parts of the EIS plot produced by this testing procedure have an arc shape that is a result of the charge transfer kinetics, and the semicircle is representative of the diffusion of the electrolyte in the pores of the electrode material and the ion transport through the porous structure.

Using the EIS testing method gives insight into how well the electrolyte diffuses, how efficiently the pores in the electrode are filled with electrolyte, and how efficiently ions are transported within a supercapacitor system (**Sharma et al., 2023**).

9. EXPERIMENTAL

9.1. Materials

Ethanol (absolute, $\geq 99.8\%$, Supelco, Germany) was used as the solvent and ethyl cellulose (viscosity 100 cP, Sigma-Aldrich, USA) as the binding agent in the experiments. When necessary, sorbitol ($\geq 98\%$, Sigma-Aldrich) was added as a plasticizer, and isopropyl alcohol (IPA, $\geq 99.5\%$, Merck, Germany) was added as a cosolvent.

Polyvinyl alcohol (PVA, molecular weight = 44,500 g mol⁻¹, Kimyacıınız, Turkey) was used in the preparation of the gel electrolyte.

9.2. Fabrication of Laser-Induced Graphene Powder

A polyimide (PI) film substrate was used as a carbon-rich source to produce graphene powder via the laser-induced graphene (LIG) method. This process was carried out with a K40 type CO₂ laser system. The laser parameters used were optimized to 18.5 W of laser power and a scanning speed of 400 mm/s⁻¹.

After the laser beam is applied to the polyimide surface, graphene layers are formed. These layers were carefully scraped off the surface and converted into powder form. The powdered graphene was stored sealed in a dry environment for use in conductive ink synthesis.



Figure 9.1: Fabrication of laser-induced graphene using a K40 CO₂ laser system.

9.3. Preparation of Graphene-Based Conductive Ink

Graphene-based conductive ink was prepared by homogeneously dispersing graphene powder obtained using the laser-induced graphene (LIG) method in ethanol and then adding ethyl cellulose binder. In the basic formulation, 100 mg graphene powder was dissolved in 0.5 mL ethanol and sonicated with an ultrasonic probe sonicator at 40% power for a total of 15 minutes with 3 s on/off cycles. With this process, a homogeneous decomposition of the graphene layers was achieved.

To the homogenized graphene-ethanol dispersion, 0,1 mg of ethyl cellulose (EC) powder was added as a binder, and the mixture was stirred in a magnetic stirrer at 45 °C for about 1 hour. During this step, a viscous and homogeneous ink structure was obtained by controlled evaporation of ethanol from the mixture.

The process steps for obtaining graphene powder using the LIG method, preparing the conductive ink, and printing it in electrode form are presented schematically in **Figure 9.1**.

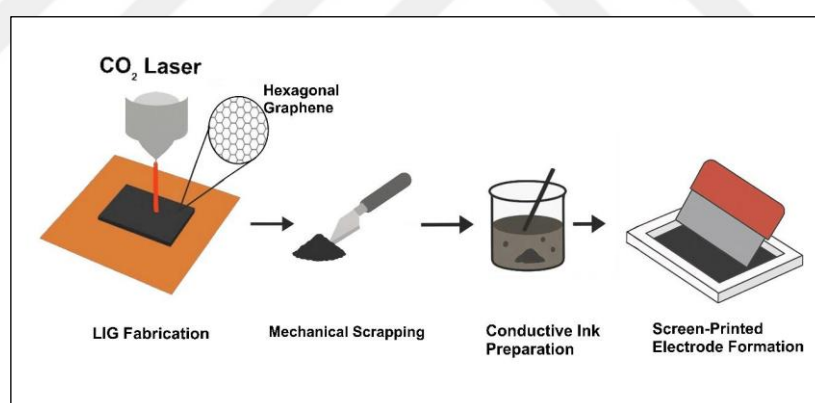


Figure 9.2: Schematic of LIG-derived graphene and screen-printed supercapacitor electrodes.

In formulations with higher graphene content, such as 2:1, 3:1, and 4:1, sorbitol was added at 20% of the ethyl cellulose used as a binder to increase film integrity and elasticity in the electrodes prepared using the ink. To increase the solubility of sorbitol and stabilize the evaporation of the solvent, 1 mL of isopropyl alcohol (IPA) was added to the mixture. With this optimization, a more uniform and compact film morphology was obtained by preventing the formation of curling or cracking on the surface after drying.

Table 9.1: Graphene- Ethyl cellulose (Gr-EC) conductive ink formulation ratios.

Gr-EC	Graphene (mg)	Ethyl Cellulose (mg)	Total (mg)
1:1	100	100	200
2:1	133	67	200
3:1	150	50	200
4:1	160	40	200

Different conductive ink formulations prepared at ratios of 1:1, 2:1, 3:1, and 4:1 (Graphene: EC) according to increasing amounts of graphene, while keeping the total solid content constant, are presented in **Table 9.1**.

9.4. Preparation of Electrodes

The doctor-blade coating method was used for the coating process of the prepared graphene-based conductive ink on the substrate. In order to define the coating area on the substrate, double-sided adhesive tape (acrylic-based, 0.1 mm thickness) was used as a mask. This tape, which will be used as a mask, was cut in the desired geometries using the cutting system of the K40 type CO₂ laser device.

The cut and prepared masks were carefully glued to the surface of ITO-coated PET substrates used as a conductive base. The mask was designed to have a square opening in the center. The outer dimension of this square was optimized to be 30 x 30 mm, and the inner opening to be 20 x 20 mm. In this configuration, the footprint is limited so that the edge thickness of the mask is approximately 10 mm.

On the masked ITO/PET substrate, the pre-prepared graphene-based ink was coated at constant speed, in one direction, and with uniform thickness using the doctor-blade method. This coating process was carried out under room conditions. The prepared samples were dried in air to remove the solvent in the ink completely. During the drying period, the samples were kept in a dust-free, horizontal position.

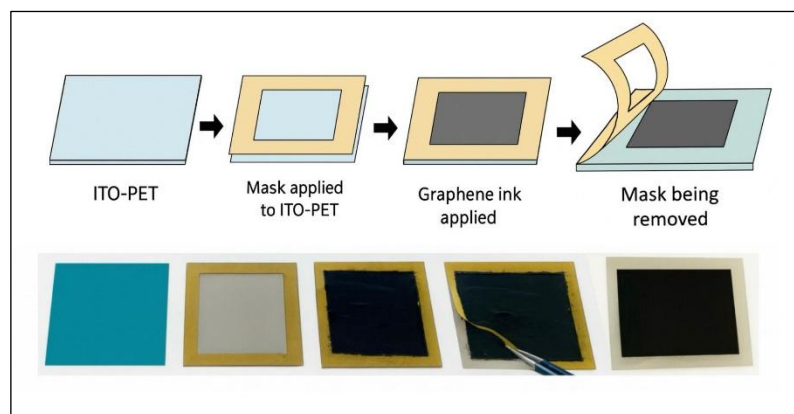


Figure 9.3: Schematic and photographic representation of the planar electrode preparation.

With this method, it was possible to control the ink thickness of the prepared samples reproducibly and to obtain graphene films with homogeneous surface morphology.

A schematic representation of the processes of applying a mask onto the ITO/PET substrate, coating it with the prepared conductive ink using the doctor blade method, and removing the mask to obtain planar electrode structures is shown in **Figure 9.3**.

9.5. Preparation of PVA/KOH Gel Electrolyte

The gel electrolyte was prepared based on polyvinyl alcohol (PVA, molecular weight = 44,500 g mol⁻¹) and potassium hydroxide (KOH, M = 56.11 g mol⁻¹). The formulation was based on dissolving 6 g PVA and 3 g KOH in 60 mL of deionized water (DI water).

Polyvinyl alcohol (PVA) was gradually added to deionized water heated to 90 °C on a temperature-controlled magnetic stirrer, and the mixture was stirred continuously at 350 rpm for 30-60 minutes. Following the vigorous stirring process to create the PVA solution, a uniform, transparent, and viscous liquid was obtained.

A KOH pellet was then dissolved in de-ionised water in a separate container at room temperature using vigorous stirring as well. The dissolution was slightly exothermic, and the mixture was colorless and clear upon completion.

To preserve the polymer chain structure and prevent deterioration of the ionic conductivity and mechanical strength of the prepared gel, a KOH solution was added

after the previously homogeneously dissolved PVA solution was cooled to approximately 45 °C. Thus, KOH remains stable at this temperature, and ionic conductivity is ensured.

The KOH solution was added to the PVA solution without interrupting the stirring process, then stirring was continued for another 10-15 minutes. After this mixing process, a whitish, translucent, and slightly viscous gel form was obtained.

This viscous gel was poured into molds and kept in room conditions to complete the gelation process. As a result of these processes, the prepared gel became a semi-solid, flexible, hydrogel electrolyte with good mechanical properties.

9.6. Device Assembly and Electrochemical Measurement

Graphene-based conductive ink coated onto ITO/PET (planar electrode) was integrated with the semi-solid PVA/KOH hydrogel electrolyte as an active material to create a sandwich-type flexible supercapacitor structure. The gel electrolyte was placed as a thin homogeneous layer between the two electrodes, and the film surface formed with the prepared ink was brought into contact. The two electrode active surfaces are oriented directly toward one another and positioned on top of each other in order to create an electrical connection that is symmetrical in both directions within the supercapacitor (this is referred to as a "symmetric" or "planar" configuration).

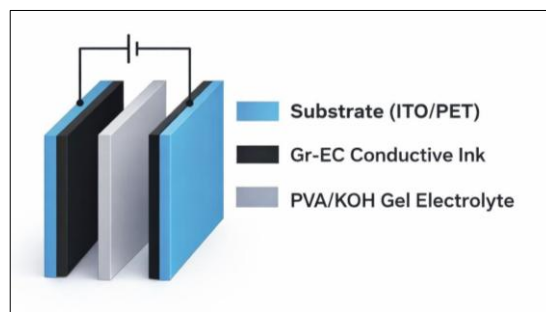


Figure 9.4: Schematic of the assembled symmetric flexible supercapacitor.

After the supercapacitor had been set up in the above-described manner, the supercapacitor was allowed to sit at room temperature for several hours, during which time the gel electrolyte penetrated the space between the electrode surfaces and

solidified, thereby giving structural integrity to the supercapacitor. Thus, the supercapacitor became a flexible film.

All electrochemical testing was performed at room temperature. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were performed directly in a two-electrode supercapacitor configuration, rather than a three-electrode system.



10. RESULT AND DISCUSSION

10.1. Physicochemical Characterizations

The physico-chemical characterization techniques are used to analyze the properties of materials (morphology, crystalline structure, chemical elements, surface chemistry) that can be associated with the synthesis route of materials intended to have specific characteristics for their use in different fields (energy storage, sensors, etc.). A variety of analytical techniques were employed for a detailed characterization of the electrode material prepared with varying mass ratios by examining the relationship among the structural, chemical, and electroactive characteristics of the developed material through the application of all of the above analytical techniques. The relationships among the electroactive, structural and chemical properties of the developed materials were obtained from the results of a combination of analytical techniques such as **SEM (scanning electron microscopy)** which is utilized for morphological analysis of the electrode material, **EDS (energy-dispersive spectroscopy)** for elemental analysis, **Raman Spectroscopy** for examination of crystalline phases in carbon based materials, **XPS (X-ray photoelectron spectroscopy)** for chemical group analysis, and **XRD (X-ray diffraction)** for crystallographic phase identification.

10.1.1 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

SEM images of the electrode sample with a Gr–EC (1:1) ratio were analyzed to show the surface morphology in detail at different magnification scales (**Figure 10.1**). In **Figures 10.1A-B**, images show that the electrode surface generally exhibits a homogeneous coating feature, with no film breaks or significant phase separations at the macro level. This indicates that the graphene and ethyl cellulose components are homogeneously distributed in the ink formulation and form a continuous film structure. After screen-printing, graphene flake stacking is shown to be irregular and non-planar in **Figure 10.1C**, forming a three-dimensional porous structure through which ions can move through the material, providing a potential pathway for ion migration and advantageous structural properties for supercapacitors.

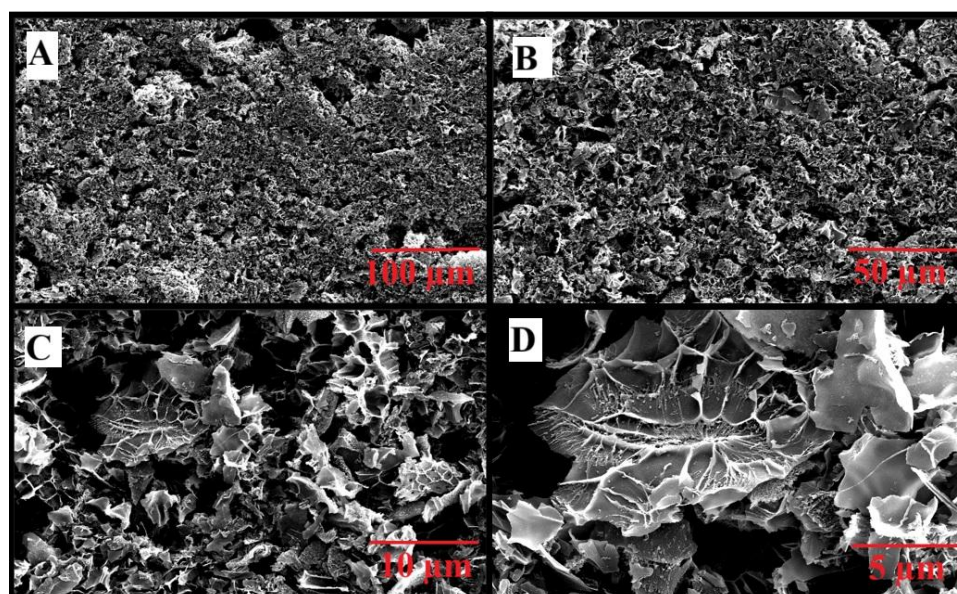


Fig.10.1: SEM surface images of Gr-EC (1:1) electrode sample at different magnifications.

In addition to providing a clear view of the edge areas of the flake and lamellae structures of the flakes in **Figure 10.1D**, it can be seen that there are porous areas of micro- and mesopore size between the flakes. The ethyl cellulose binder phase provides mechanical support for the graphene flake agglomeration; however, it does not provide a complete surface coverage of the graphene flake surfaces, thereby allowing the continuous formation of an electrical percolation path. This structure has a balanced composition in terms of mechanical strength and conductivity, which is important for flexible supercapacitor electrodes.

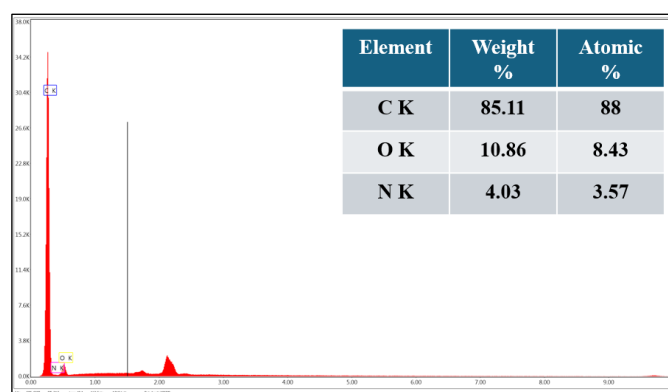


Figure 10.2: EDS analysis of Gr-EC (1:1).

The elemental composition of the Gr-EC (1:1) electrode sample was determined by EDS analysis, and the findings are shown in Figure 10.2. This high carbon percentage indicates that the graphene-based conductive structure has been successfully formed and that the electrical conductivity of the electrode is largely provided by the carbon grid. The oxygen ratio stems from the oxygen-containing functional groups on the graphene surface and the polymer structure of ethyl cellulose. The presence of oxygen groups facilitates better contact between the electrode surface and the electrolyte, making it easier for ions to reach the active surfaces. The nitrogen content determined in the EDS analysis can be considered to be related to nitrogen-containing compounds in the structure of LIG-derived graphene. This low ratio can be said to reveal that graphene essentially consists largely of sp^2 hybridized carbon atoms.

Overall, when SEM and EDS results are considered together, it is observed that the ink with a Gr-EC (1:1) ratio forms a homogeneous, porous, and carbon-rich electrode structure.

For Gr-EC (2:1), **Figure 10.3A-B** shows that the electrode surface generally maintains its continuity but exhibits more pronounced surface roughness compared to the 1:1 ratio sample. Due to the increase in graphene content, the surface topography has become more irregular and textured. This situation reveals a morphology that has the potential to increase the effective surface area of the electrode.

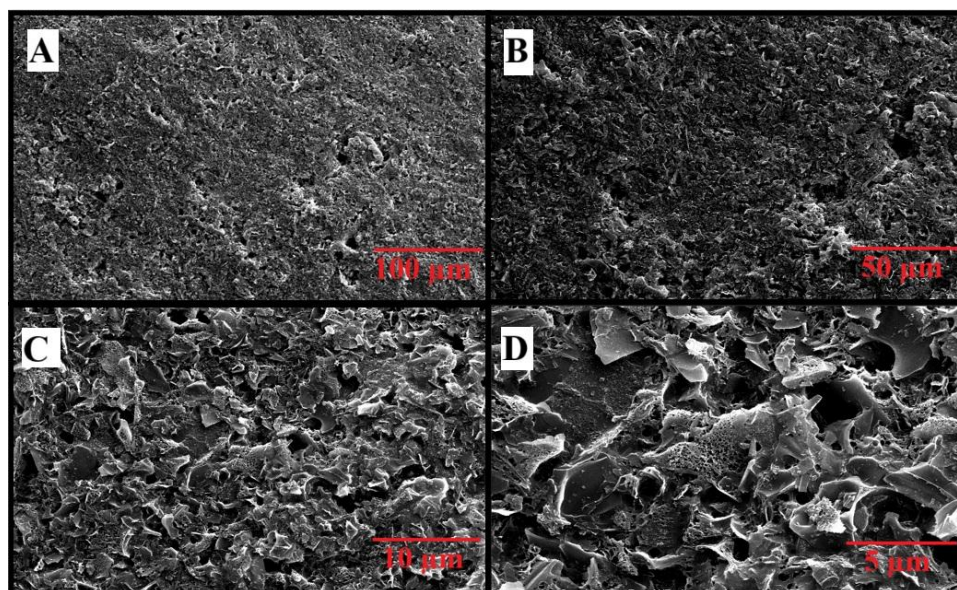


Fig.10.3: SEM surface images of Gr-EC (2:1) electrode sample at different magnifications.

Figure 10.3C shows that graphene flakes are more densely packed within the film and form a network structure in contact with each other. In other words, this is evidence that an increase in the quantity of graphene forms more conductive paths for the electrons to travel through, as well as a better arrangement for electron transfer within the electrodes. As shown in **Figure 10.3D**, it is evident that the layers of graphene have a curled and layered structure, and local agglomerations exist in certain sections. The local agglomerations could also be directly attributed to an insufficiency in the stabilization of the graphene flakes from the small percentage of binder phase; however, they do not disrupt the overall continuity of the electrode and continue to form conductive pathways throughout the entire layer of graphene.

Figure 10.4 shows that the high carbon content is prominent in the electrode structure of the graphene-based conductive frame. Compared to the 1:1 sample, the decrease in binder amount indicates a significant change in the carbon/oxygen ratio. However, the decrease in binder amount may lead to the formation of some local agglomerations. This structure creates a balance that focuses on increasing conductivity by providing mechanical strength and electrical conductivity. This can be considered an important intermediate formulation for enhancing the efficiency of supercapacitor electrodes.

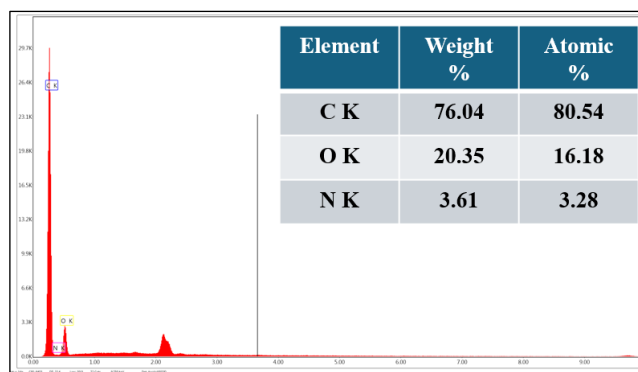


Figure 10.4: EDS analysis of Gr-EC (2:1).

Although **Figure 10.5A-B** displays an electrode surface with a relatively uniform and consistent coating layer (compared to the 2:1 ratio sample) and shows fewer irregularities on a larger scale than were seen in the previous sample, this suggests that the binder phase maintains the integrity of the electrode even as the amount of graphene is increased.

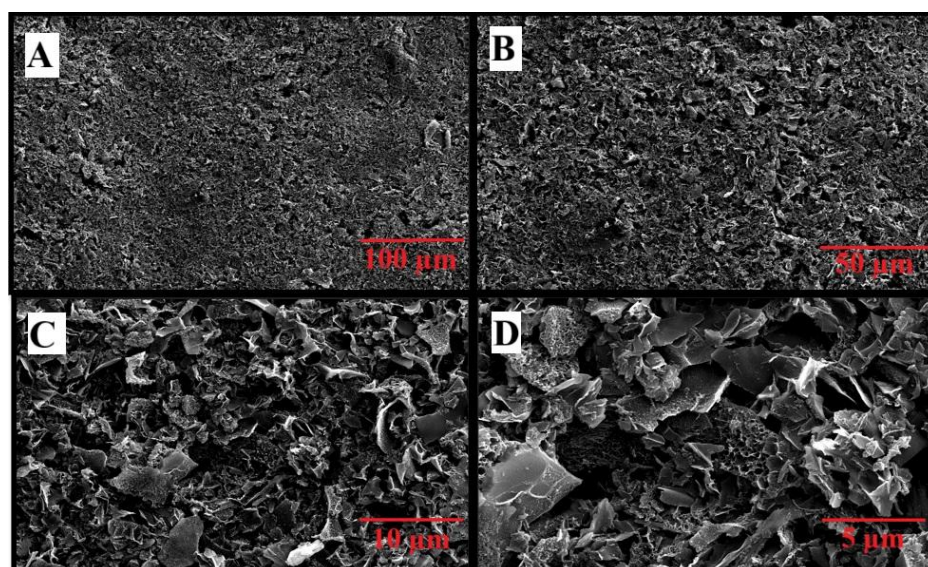


Fig.10.5: SEM surface images of Gr-EC (3:1) electrode sample at different magnifications.

As shown in **Figure 10.5C-D**, due to their high density and three-dimensional network structure where graphene particles touch one another, it is possible for continuous electrical pathways to be formed by electrons through the electrode. The morphology also facilitates good conduction of electrons. Compared to the local agglomeration that was evident in previous ratios (1:1, 2:1), the graphene flakes appear to have a relatively more uniform distribution in this ratio.

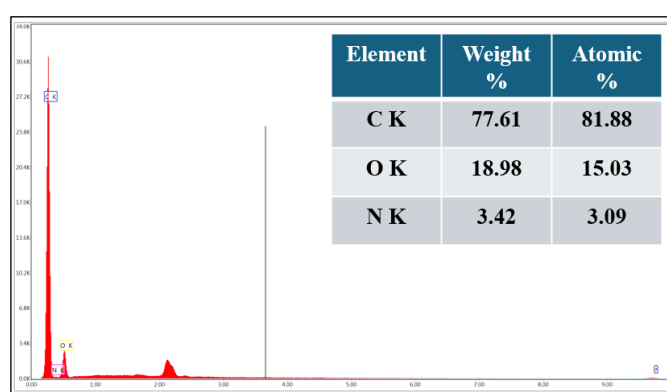


Figure 10.6: EDS analysis of Gr-EC (3:1).

The Gr-EC (3:1) electrode structure reveals that carbon has a significant weight and that the distribution of elements shows a consistent trend with previous ratios (Figure

10.6). This indicates that the increase in the ratio of graphene in the composite structure does not affect the expected elemental balances.

As shown by SEM imaging, the Gr-EC (4:1) sample shows the most pronounced tendency for agglomeration of graphene within the microstructure of the electrodes (shown in **Figure 10.7**). While the surface quality at lower magnification seems continuous, it can be seen at higher magnifications that large aggregates are formed from the graphene particles, and the binder phase is unable to uniformly stabilize these structures. The very large degree of aggregation of the graphene particles results in limited utilization of the effective surface area of the material and severely limits ion transport through the electrode.

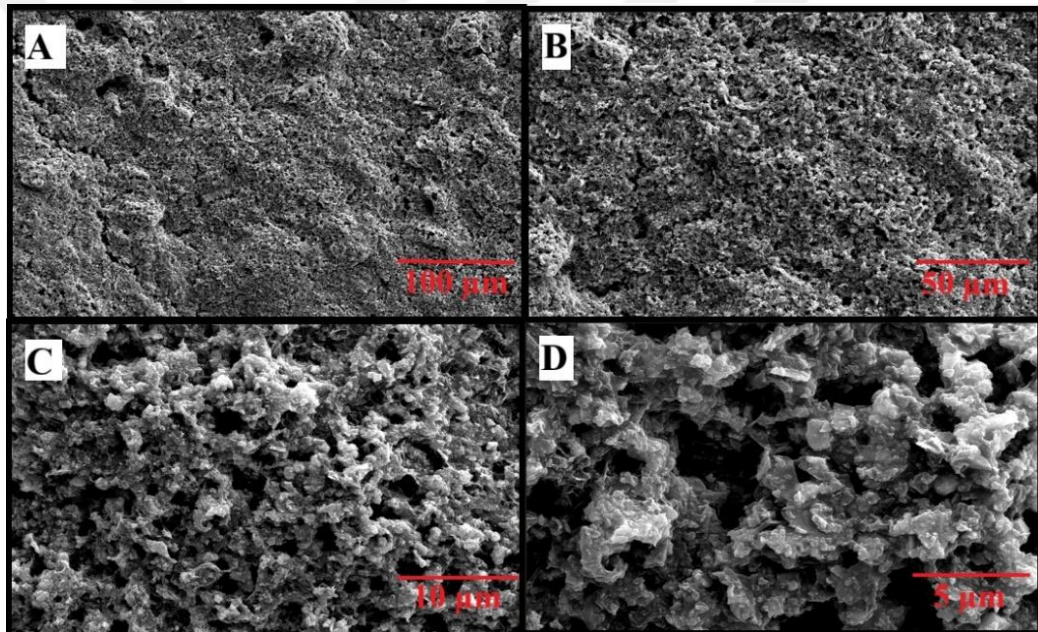


Fig.10.7: SEM surface images of Gr-EC (4:1) electrode sample at different magnifications.

Figure 10.8 shows that increasing the graphene content does not allow for the formation of a uniform percolating network. The Gr-EC (4:1) composition ratio is therefore regarded as being detrimental to both structural integrity and effective conductivity due to excessive agglomeration caused by insufficient binder. Increasing the ratio of graphene and ethyl cellulose has caused significant changes in the microstructure of the electrode.

At a 1:1 ratio, a smoother and mechanically robust film structure was obtained, while at a 2:1 ratio, the graphene network became denser, and surface roughness increased.

The 3:1 ratio achieved the most balanced microstructure by maintaining the continuity and porous structure of the conductive phase.

On the other hand, excessive agglomeration caused by weak bonding at a 4:1 ratio negatively affected both structural integrity and effective conductivity. For this reason, the Gr-EC mixture at a 3:1 ratio was determined to be the most suitable electrode composition in the study.

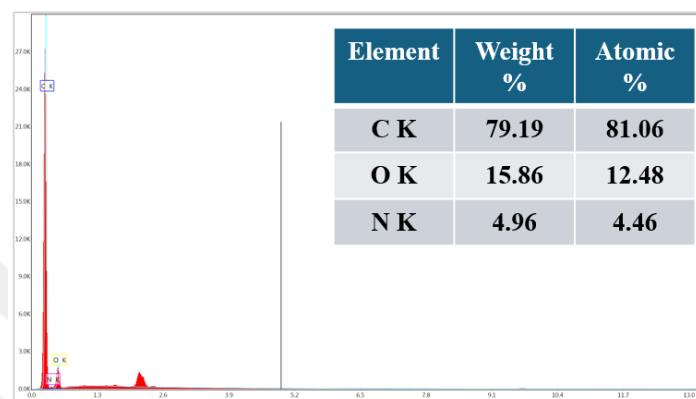


Figure 10.8: EDS analysis of Gr-EC (4:1).

10.1.2. Raman Spectroscopy

Raman Spectroscopy analysis was conducted in order to assess how the graphene-to-ethyl cellulose (Gr-EC) ratio impacts the structural composition and graphitic attributes of Laser Induced Graphene Composite Electrodes. A primary reason for choosing Raman Spectroscopy analysis is that it directly offers information concerning the condition of the sp^2 carbon structure, density of defects, and the degree of interaction between layers.

In all Gr-EC formulations presented in **Figure 10.9 (A–D)**, the D ($\sim 1350\text{ cm}^{-1}$), G ($\sim 1580\text{ cm}^{-1}$), and 2D ($\sim 2700\text{ cm}^{-1}$) bands characteristic of the graphitic carbon structure were detected. In comparison to the G band, which arises from the vibrations of sp^2 hybridized carbon atoms in the same plane, the D band is generally ascribed to structural imperfections or irregularities. The 2D band is a significant band for understanding the layer-to-layer stacking of graphene layers and their electronic structures. The fact that this Raman band occurs at the same location within each sample implies that, despite different compositions, the fundamental graphitic framework remains intact.

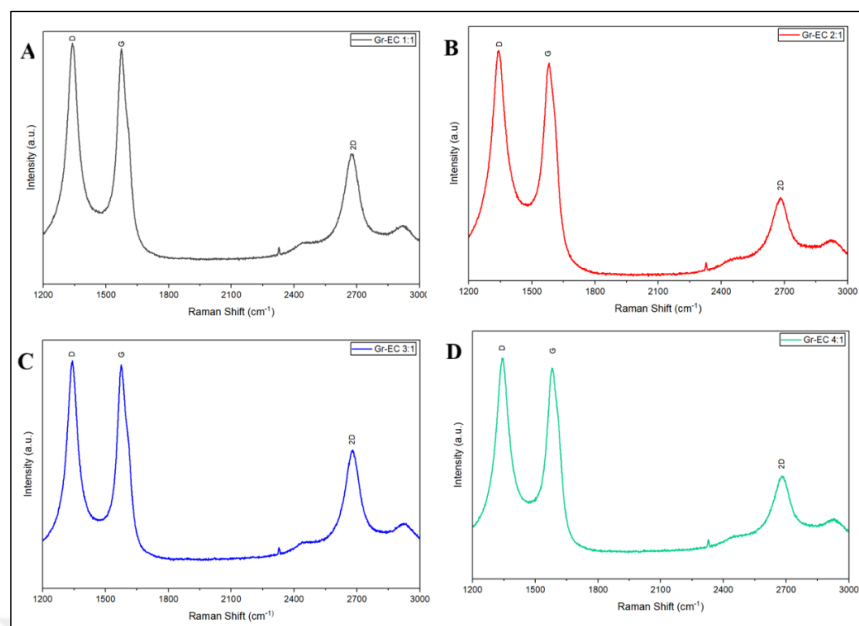


Figure 10.9: Raman spectroscopy analysis of Gr-EC at different ratios.

Differences between samples are primarily examined through the comparative intensities of the bands and the distinctness of the 2D band. In the Gr-EC (1:1) sample (**Figure 10.9A**), the D band is more pronounced due to its higher binder ratio compared to the others, but the 2D band is observed to have a weak and broad structure. This situation is associated with increased areas of amorphous carbon and structural disorder. With the increase in the graphene ratio in **Figure 10.9 (B-C)**, a more balanced Raman spectrum was obtained. Particularly in the Gr-EC (3:1) sample, a more consistent intensity distribution between the D and G bands and a distinct, symmetric 2D band were observed. These results indicate that the continuity of the graphene network and the crystalline order are better preserved.

In general, Raman spectroscopy results indicate that the Gr-EC ratio has a significant effect on the order of the carbon structure. Specifically, the 3:1 ratio provides the most balanced equilibrium between defect density and graphitic structure, revealing that this ratio creates the most structurally suitable composition.

10.1.2. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analyses conducted to investigate the surface chemical composition and carbon bonding states of Gr-EC composite electrodes clearly demonstrate the effects of various graphene/ethyl cellulose ratios on surface chemistry (**Figures 10.10 and 10.11**). In the XPS survey spectra (**Figure 10.10**),

characteristic peaks for carbon (C1s, ~284 eV) and oxygen (O1s, ~532 eV) elements were observed in all samples. Additionally, very weak nitrogen (N1s, ~400 eV) signals were also detected.

Survey spectra (**Figure 10.10A-D**) reveal that the carbon/oxygen (C/O) atomic ratio on the surface changes regularly with increasing graphene content. In the Gr-EC (1:1) example, the O1s peak is more pronounced than the C1s peak. This indicates that oxygen-containing functional groups on the surface are dominant due to the high binder content. Increasing the graphene ratio to 2:1 and 3:1 creates a change in the C1s peak intensity. This indicates that the graphitic properties on the surface are strengthened. The highest C/O ratio was observed in the Gr-EC (3:1) sample. This indicates that this compound is rich in graphene content and has a more limited surface chemistry in terms of oxygen functionality. In contrast, an increase in the O1s signal was observed in the Gr-EC (4:1) sample, despite the nominally higher graphene content. This is thought to be due to the interaction of reactive defect sites on the surface with oxygen, caused by agglomeration resulting from overloading with graphene.

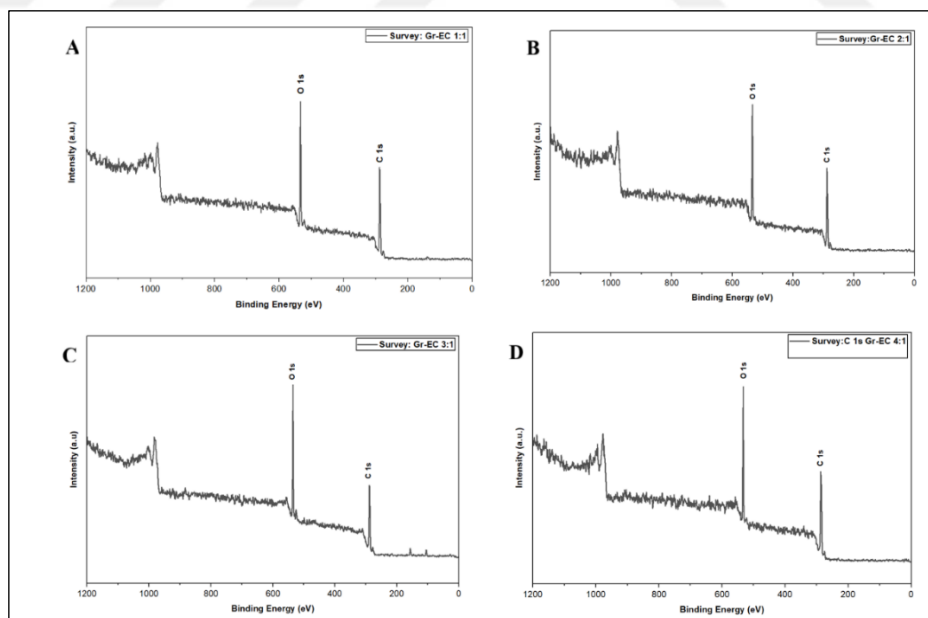


Figure 10.10: XPS survey graph of Gr-EC at different ratios.

Analysis of the C1s spectra reveals that the carbon bonding states change regularly with the Gr-EC ratio (**Figure 10.11A-D**). The distinct peak detected at approximately

284.5 eV in all samples is associated with sp^2 hybridized C=C bonds and suggests the presence of a graphite like carbon structure. The C–C/C–H components found in the 285.0–285.2 eV range, on the other hand, carry the characteristics of sp^3 hybridized carbon and defective areas. The C–O bonds in the 286.2–286.8 eV range are associated with binding ether and hydroxyl groups and partially oxidized graphene surfaces. The C=O (≈ 287.8 eV) and O–C=O (≈ 289.0 – 289.5 eV) components observed at higher binding energies indicate the presence of carbonyl and carboxyl groups.

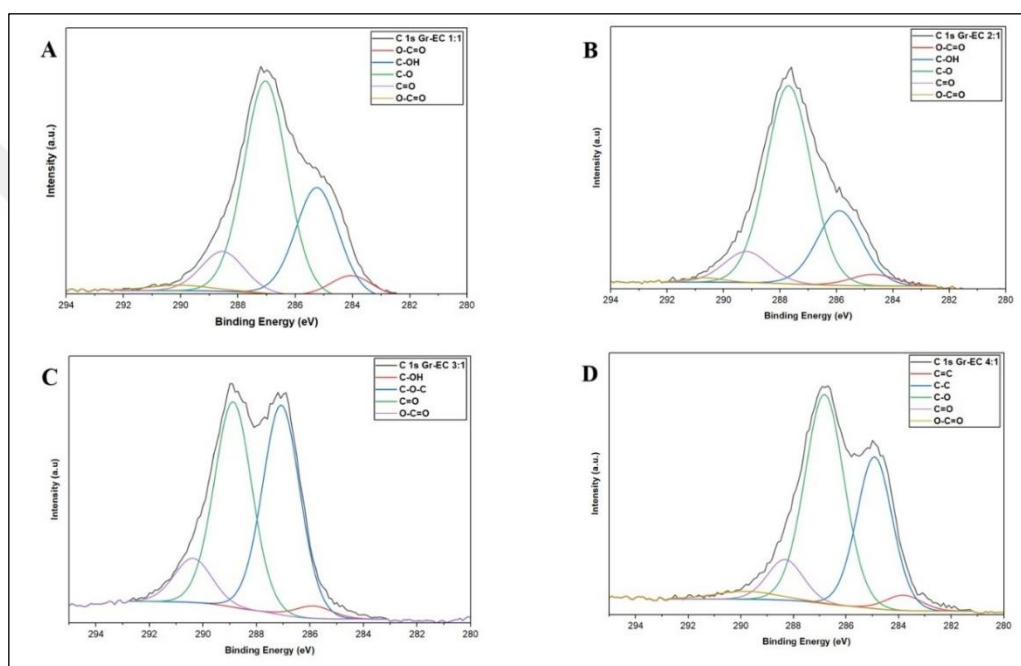


Figure 10.11: XPS C1s analysis of Gr-EC at different ratios.

In the Gr–EC (1:1) sample (**Figure 10.11A**), the high total contribution of the C–O, C=O, and O–C=O components can be associated with a significant effect on the surface chemistry of the binder phase. With increasing graphene ratio, particularly in the 2:1 and 3:1 samples, an increase in the sp^2 C=C component and a noticeable decrease in oxygen-containing functional groups were observed. The Gr–EC (3:1) (**Figure 10.11C**) sample, having the highest sp^2 carbon content and simultaneously exhibiting the lowest oxygen functionality, stands out as the composition in which the graphitic structure is best preserved on the surface.

In contrast, a decrease in the sp^2 component and an increase in the amount of oxygen-containing components were observed in the Gr–EC (4:1) (**Figure 10.11D**) sample.

This is associated with agglomeration, disordered packing, and an increase in defect density caused by the high graphene ratio.

Generally, XPS data suggest that the proportion of graphene to binder is important for determining the electrode's surface chemical composition; however, XPS also shows that the 3:1 Gr-EC ratio produces the best overall surface chemistry as measured by a balance of graphitic carbon content and oxygen functional groups, which is crucial to the structural integrity of the binder to support the continuity of the graphene network and therefore consistent with the structural-chemical relationships seen with the electrochemical properties of the electrodes.

10.1.4 X-ray Diffraction (XRD)

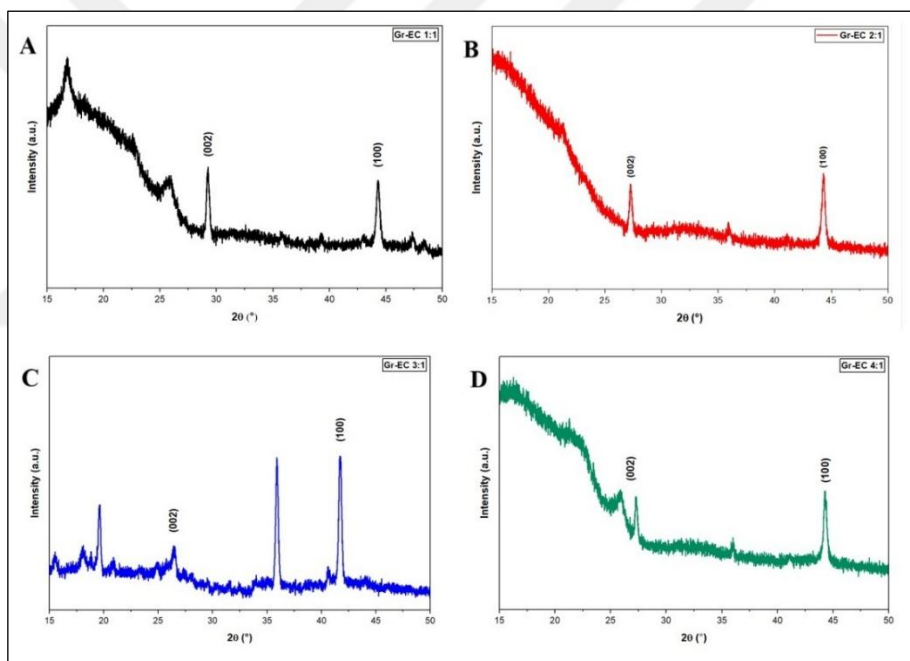


Figure 10.12: XRD analysis of Gr-EC at different ratios.

X-ray diffraction (XRD) analyses conducted to examine the crystalline structural properties of Gr-EC composite electrodes show that the graphitic carbon structure is preserved in all graphene/ethyl cellulose samples with different ratios (**Figure 10.12**). The (002) diffraction peak observed at approximately $2\theta \approx 26^\circ$ in all compositions belongs to graphene layers and indicates that graphene obtained from LIG by mechanical exfoliation retains its sp^2 carbon structure after the ink preparation and printing stages. This peak value indicates that graphene layers are partially rearranged

during the film formation process and that the graphitic phase is preserved within the composite structure.

Furthermore, we note that the weak (100) reflection observed around $2\theta \approx 43-44^\circ$, particularly in samples with high graphene content, indicates that the in-plane order in the graphitic carbon structure is partially preserved. The (100) peak provides a typical reflection of the hexagonal carbon structure of graphene. This indicates that the graphene obtained from LIG does not completely lose its structural integrity after the processing step.

The broad, low-intensity peaks observed in the XRD pattern are expected to appear in composite electrode structures. The amorphous nature of the ethyl cellulose binder partially prevents the regular alignment of graphene layers. However, it appears that the graphitic phase is successfully formed at all Gr–EC ratios and is preserved in the composite electrode structure. The main reason affecting the performance differences between the electrodes is the morphological factors. In particular, the continuity of the graphene network, the distribution of binders, and agglomeration tendencies determine this situation. These factors have been analyzed more concretely through SEM observations and electrochemical measurements.

10.2. Electrochemical Characterizations

10.2.1. Cyclic Voltammetry (CV)

The Graphene–ethyl cellulose (Gr–EC) microsupercapacitor electrodes were fabricated with four different graphene-binder ratios: 1:1, 2:1, 3:1, and 4:1. Cyclic voltammetry measurements were performed in the potential window of 0–1.0 V at a scan rate of 0.1 V/s. The quasi-rectangular profile without noticeable redox peaks confirms dominant electric double-layer capacitance (EDLC) behavior; however, there is clear evidence of varying current responses due to the varying amounts of ethyl cellulose (binder) present in each sample.

The lowest current response was exhibited by the 1:1 sample ($\sim 30 \mu\text{A}$); in addition, this sample exhibited the smallest voltammetric area, indicative of the lowest capacitance.

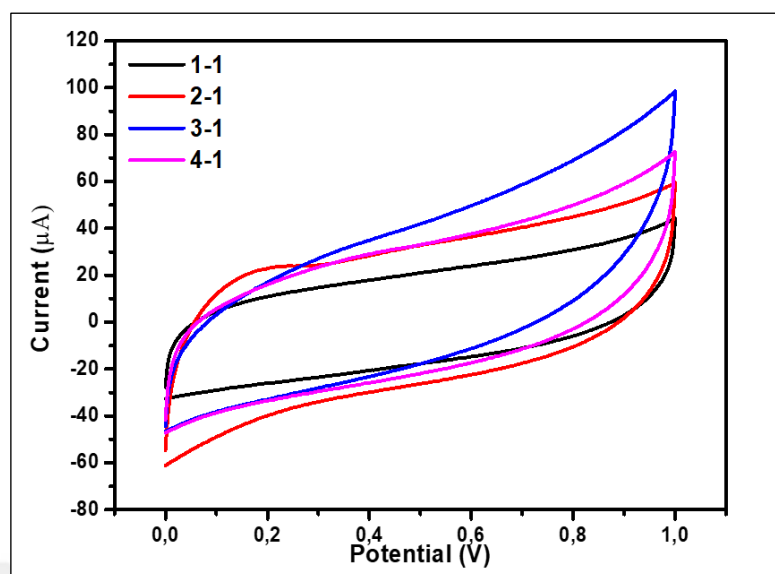


Figure 10.13: CV measurements of symmetric microsupercapacitor electrodes at different Gr- EC ratios.

In contrast to the 1:1 sample, an increase in the amount of graphene to a 2:1 ratio resulted in a substantial improvement in current response ($\sim 50 \mu\text{A}$). In addition, the CV curves exhibited better symmetry than those observed for the 1:1 sample, which may indicate improved charge storage capabilities. Although the 2:1 electrode showed improved current response, the electrochemical performance was still lower than that of the 3:1 electrode.

The electrode with the 3:1 graphene-to-binder ratio exhibited the best current response ($\sim 90\text{--}100 \mu\text{A}$) and the largest CV area, indicating the highest capacitance and most efficient charge storage behavior among all samples examined. The well-defined quasi-rectangular profile further confirms the efficient charge storage characteristics of the 3:1 electrode. The improved electrochemical performance of the 3:1 sample can be associated with the formation of a more continuous and porous graphene network, facilitating enhanced ion accessibility and electrical conductivity.

Conversely, the decrease in the current response exhibited by the 4:1 sample ($\sim 60\text{--}70 \mu\text{A}$) can be attributed to insufficient binder content, leading to poor mechanical integrity and increased internal resistance.

The calculated electrochemical parameters derived from CV curves are summarized in **Table 10.1**. The 3:1 electrode exhibits the highest areal capacitance among all samples, confirming its superior electrochemical performance.

Table 10.1: CV-derived electrochemical parameters of Gr–EC electrodes at varying ratios.

Gr-EC	Scan rate V/s	Potential range $\Delta V(V)$	Specific Capacitance $C_s(\mu F/cm^2)$	Specific Energy $E(\mu Wh/cm^2)$
1:1	0.1	1	88.490	27.65
2:1	0.1	1	138.330	43.23
3:1	0.1	1	146.673	45.84
4:1	0.1	1	123.820	38.69

Overall, the CV analysis confirms that the 3:1 Gr–EC composition achieves the optimal balance between conductivity and structural integrity, resulting in superior areal capacitance and energy density. Therefore, this ratio was selected as the optimal formulation for the subsequent electrochemical evaluation.

10.2.2. Galvanostatic Charge-Discharge (GCD)

Figure 10.14 shows the galvanostatic charge-discharge (GCD) curves for symmetric micro-supercapacitor electrodes with different Gr-EC weight ratios (1:1, 2:1, 3:1, and 4:1) under a constant current value of 10 μA and within a potential range of 0–1 V. Examining the triangular and linear voltage-time graphs determined for all samples reveals that the charge storage mechanism predominantly exhibits electric double layer capacitance (EDLC) characteristics and that the charge-discharge process is reversible in nature.

Looking at the discharge times in Table 10.2, it is clear that the performance ranking is 3:1 > 4:1 > 2:1 > 1:1. The shortest discharge time was recorded at a ratio of 1:1 (18.3 s) and showed the lowest surface capacitance value of 45.750 $\mu F/cm^2$. This may be related to the high binder content limiting the active graphene surface area and ion flow.

Increasing the graphene ratio has resulted in an increase in discharge time and capacitance values. Measurements taken at a 2:1 ratio determined that the discharge

time was 27.7 seconds and the surface capacitance was 69,250 $\mu\text{F}/\text{cm}^2$. The highest performance was achieved at a 3:1 ratio; in this case, the discharge time was 45.1 seconds, and the capacitance value was 112,750 $\mu\text{F}/\text{cm}^2$. This composition also achieved the highest energy density at 15.7 $\mu\text{Wh}/\text{cm}^2$. The symmetric and linear structure of the curves indicates low internal resistance and good charge-discharge stability.

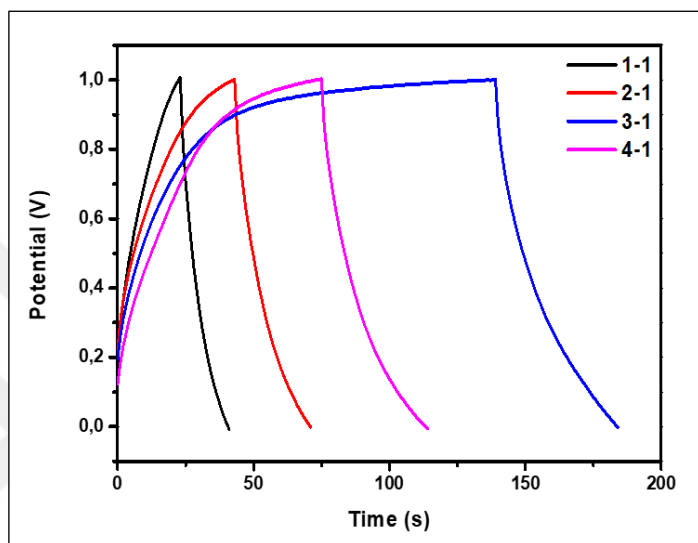


Figure 10.14: GCD curves of symmetric microsupercapacitor electrodes at different Gr-EC ratios.

Increasing the graphene content to a 4:1 ratio resulted in a partial decrease in performance (38.8 s; 97,000 $\mu\text{F}/\text{cm}^2$; 13.5 $\mu\text{Wh}/\text{cm}^2$). This can be explained by the fact that insufficient binder quantity reduces the mechanical strength of the electrode structure and increases contact resistance.

The fact that the power density remained constant at 1250 $\mu\text{W}/\text{cm}^2$ in all samples indicates that the measurements were performed under similar current conditions and that a fair evaluation could be made between different compositions.

In conclusion, GCD analyses show that the 3:1 Gr-EC ratio offers the most balanced electrochemical performance, with the highest discharge time, surface capacitance, and energy density.

Table 10.2: Specific capacitance, energy density, and power density values of the symmetric supercapacitor with a Gr-EC different weight ratio.

Gr-EC	i (A)	Δt (s)	ΔV (V)	Area cm^2	$C_s(\mu\text{F}/\text{cm}^2)$	$E(\mu\text{Wh}/\text{cm}^2)$	$P(\mu\text{W}/\text{cm}^2)$
1:1	0.00001	18.3	1	4.000	45.750	6.4	1250.0
2:1	0.00001	27.7	1	4.000	69.250	9.6	1250.0
3:1	0.00001	45.1	1	4.000	112.750	15.7	1250.0
4:1	0.00001	38.8	1	4.000	97.000	13.5	1250.0

10.2.3. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is an important characterization method for analyzing the internal resistance components, charge transfer kinetics, and ion diffusion behavior of supercapacitors. In this study, the impedance responses of symmetric microsupercapacitor electrodes with various graphene-ethyl cellulose (Gr-EC) ratios (1:1, 2:1, 3:1, and 4:1) were investigated using the Randles equivalent circuit model (**Figure 10.15**).

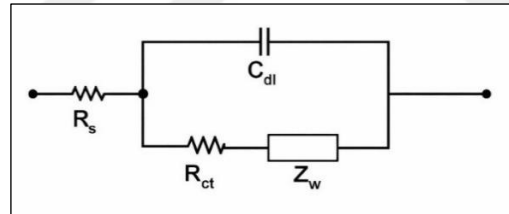


Figure 10.15: EIS characterization using the Randles equivalent circuit impedance model.

The equivalent circuit used includes the total ohmic resistance (R_s), effective interfacial resistance (R_{ct}), double-layer capacitance (C_{dl}), and Warburg diffusion element (W). In this microsupercapacitor structure, where planar and EDLC behavior is prominent, the specified parameters are used not as absolute physical values but for the purpose of comparing different electrode formulations with each other in terms of electrochemical performance. They have been effectively examined as fitting parameters.

In Nyquist diagrams, the intersection point with the real axis in the high-frequency region indicates R_s . This value reflects the total ohmic contribution, which includes the electrode volume resistance, current collectors, and contact resistances in addition

to the electrolyte resistance. The semicircular shape of the curve in the frequency band of a half cycle is due to R_{ct} and is indicative of the electron transfer limitations as they occur in the electrode/electrolyte interface. At lower frequencies, the portion of the curve that has a slope is a representation of the ionic and diffusional transport properties within the system, and the sharp rise at extremely low frequencies indicates an ideality for capacitance (see Figure 10.16).

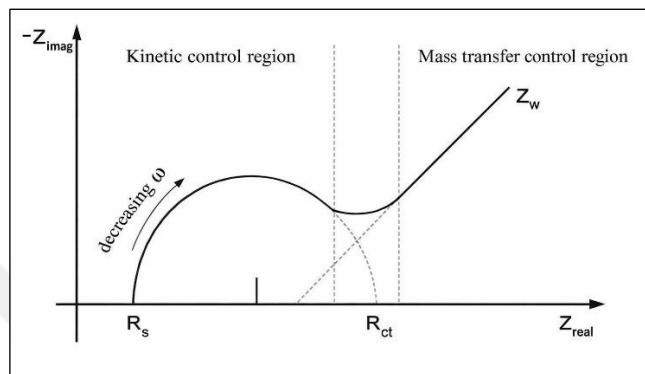


Figure 10.16: Schematic representation of the Nyquist diagram.

The electrode with a Gr-EC ratio of 1:1 exhibits low electrochemical performance. According to the data in Table 2, quite high values such as $R_s = 8696.92 \, \Omega$ and $R_{ct} = 20256.86 \, \Omega$ were observed for this sample. This indicates significant ohmic losses and pronounced surface interface limitations. An extremely low C_{dl} value ($4.8839 \times 10^{-8} \, F$) indicates that the electrochemically active surface area is quite limited.

The big semi-circle is visible in the Nyquist plot, and there is an apparent departure from the ideal rectangular response at low frequency, which indicates that the poor performance of the electrode is evident through these observations. The results indicate that the high binder content (at a 50% EC ratio) has electrically isolated the graphene layers from each other; therefore, the integrity of the conducting network was disrupted, and ion access to the network was restricted.

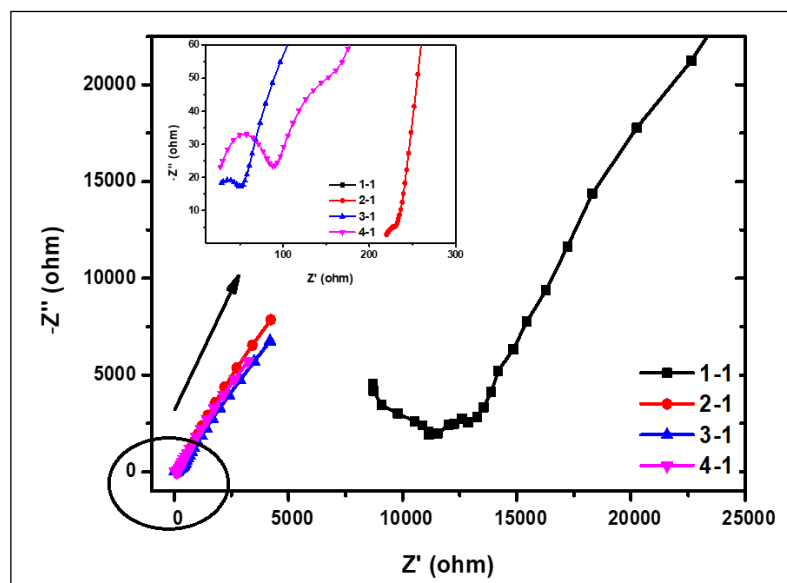


Figure 10.17: Fitted impedance spectra of symmetric microsupercapacitor electrodes at different Gr-EC ratios.

With the increase in graphene ratio and the transition to the 2:1 composition, a significant improvement in impedance parameters has been observed. The R_s and R_{ct} values decreased to 219.87 Ω and 230.22 Ω , respectively, while the C_{dl} value increased to 5.0733×10^{-5} F. This indicates the formation of a more continuous conductive network and more effective functioning of the electrode-electrolyte interface. At the same time, the observation of a distinct semicircle in the Nyquist diagram, indicating non-ideal low-frequency behavior, suggests that the system is not yet fully optimized and that microstructural limitations such as graphene agglomeration still exist.

The highest electrochemical performance was observed in the composition with a 3:1 ratio. For this sample, the lowest R_s (28.4 Ω) and R_{ct} (48.86 Ω) values were determined, while the C_{dl} value was also quite high, measured at 2.4738×10^{-7} F. The near disappearance of the semicircle in the Nyquist diagram and the steepening of the curve at low frequencies indicate that this electrode exhibits ideal capacitive behavior with minimal resistance losses. The decrease in diffusion constraints in the low-frequency range indicates that ion transport occurs quite effectively. These findings reveal that the 3:1 ratio provides an ideal balance between conductivity and structural stability.

A decline in performance is observed when the graphene ratio is further increased at the composition 4:1. While the R_s value is still relatively low (27.2Ω), the R_{ct} value has risen to 87.63Ω and the C_{dl} value has dropped to $1.1008 \times 10^{-7} \text{ F}$. There are also deviations from ideal capacitive behavior that occur in the low frequency region of the Nyquist diagram. These are attributed to factors such as aggregation of graphene, loss of structural integrity, and low adhesion resulting from inadequate binder content.

Table 10.3: Fitted EIS spectrum data of symmetric microsupercapacitors fabricated with nanocomposite electrodes at different Gr-EC weight ratios.

Gr-EC	$R_s (\Omega)$	C_{dl}	$R_{ct} (\Omega)$	W
1:1	8696.92	4.8839E-8 F	20256.86	4.6209E-7
2:1	219.87	5.0733E-5 F	230.22	1.3168E-4
3:1	28.4	2.4738E-7 F	48.86	2.4516E-4
4:1	27.2	1.1008E-7 F	87.63	4.1042E-4

The data from the EIS results show that the performance of the micro-supercapacitor depends heavily on the Gr-EC mass ratio. The data indicate that when the binder-to-carbon material mass ratio is too high (1:1), the binder will disrupt the conductivity of the electrode. Conversely, a lower binder to carbon mass ratio (4:1) leads to structural instability in the electrodes. Therefore, based on these results, it can be inferred that a Gr-EC mass ratio of 3:1 produces an electrode with the most desirable characteristics for both minimum electrical impedance and maximum capacitive behavior, as well as the ideal capacitive behavior demonstrated through the Nyquist diagrams.

10.2.4. Long-Term Cycling Performance of the Optimized Gr-EC (3:1) Electrode Scanning Electron Microscope

Optimized Gr-EC (3:1) symmetric micro-supercapacitor's long-term electrochemical stability and rate capability were systematically assessed utilizing cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements. These analyses were conducted to investigate the effects of scan rate, operating voltage range, applied current density, and long-term cycles on the electrochemical properties of the device. The overall electrochemical performance of the optimized electrode is presented in **Figure 10.18** and **Tables 10.4-10.6**.

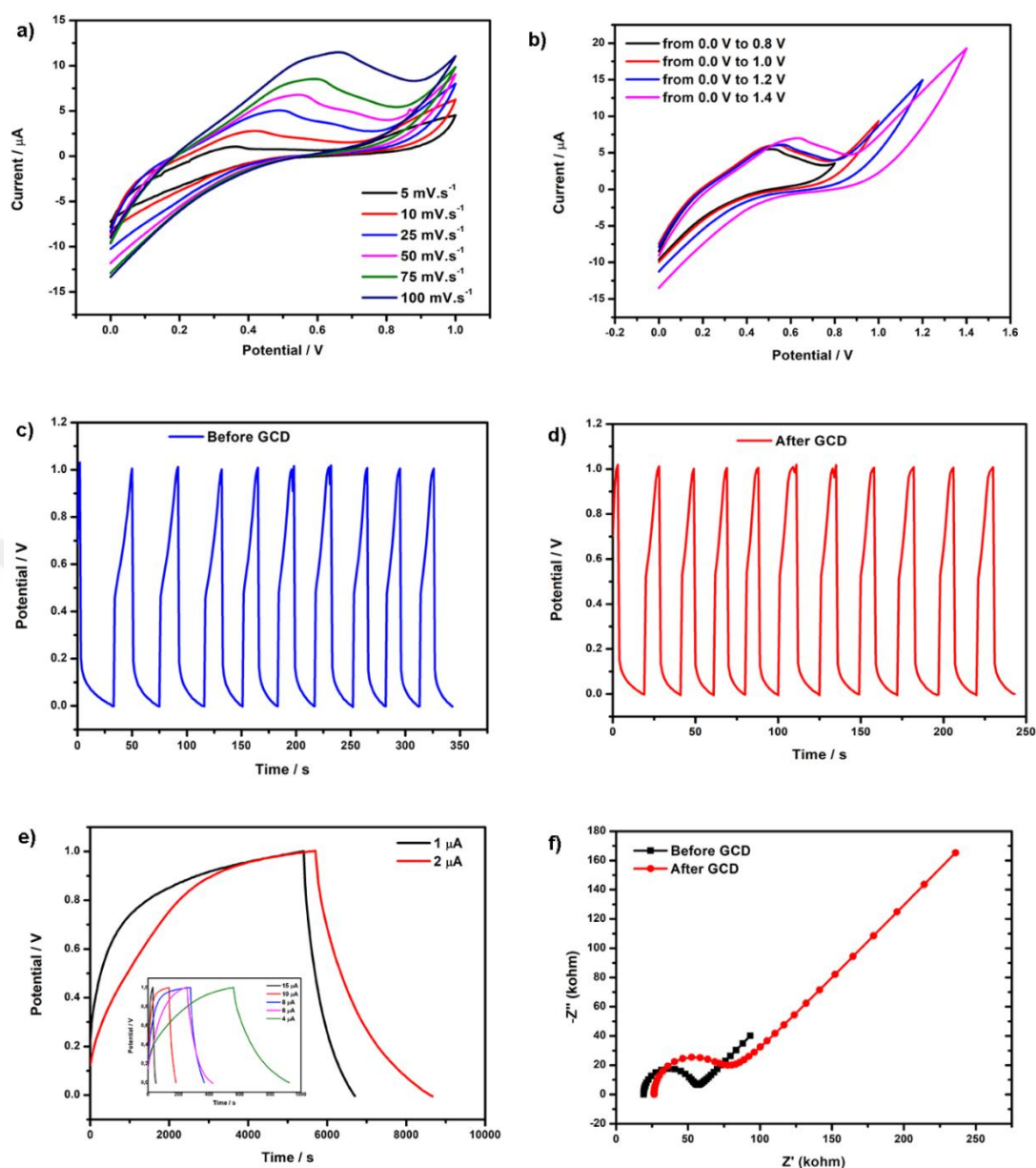


Figure 10.18: a) Cyclic voltammograms recorded at different scan rates for the Gr-EC weight ratio 3:1 symmetric supercapacitor, b) cyclic voltammograms recorded at different operating potentials ranges, c) 10-cycle GCD curves recorded before the cyclic stability test, d) 10-cycle GCD curves recorded after the cyclic stability test, e) GCD curves recorded at different current densities, and f) Nyquist plots recorded before and after the cycle stability test.

As shown in **Figure 10.18a**, CV curves obtained at various scan rates ranging from 5 to 100 mV s⁻¹ maintain a nearly rectangular shape without significant distortion. This behavior demonstrates the effective ion transport capability of the electrode structure

and confirms that the charge storage mechanism is essentially an electrical double-layer capacitive one even at higher scan rates. Maintaining the symmetry of the curve reveals that the optimized electrode possesses both low internal resistance and high-speed capability.

The gradual decrease in the voltammetric area with increasing scan rate can be attributed to limited ion diffusion at shorter time scales, a characteristic feature of porous electrode materials. The area capacitance and corresponding energy density values obtained using these CV curves are presented in **Table 10.4**.

Table 10.4: Specific capacitance and energy density values of a 3:1 weight ratio Gr-EC symmetric supercapacitor.

Scan rate V/s	Potential range $\Delta V(V)$	Specific capacitance $C_s(\mu F/cm^2)$	Specific Energy $E(\mu Wh/cm^2)$
0.005	1	790.500	247.03
0.010	1	631.500	197.34
0.025	1	385.300	120.41
0.050	1	235.350	73.55
0.075	1	184.100	57.53
0.100	1	146.673	45.84

Figure 10.18b shows the CV responses obtained when the operating voltage range is gradually expanded from 0–0.8 V to 0–1.4 V. The curves remain largely symmetric without distinct redox peaks. This indicates that the device operates with a primarily non-Faradaic charge storage mechanism within the tested voltage range.

The increased voltage range and expansion of the closed area indicate an expected increase in the stored charge, confirming the electrochemical stability of the electrode under extended potential conditions.

The GCD profiles obtained before and after the cyclic stability test are shown in **Figures 10.18c-d**, respectively. The nearly triangular and symmetrical structure of the charge-discharge curves indicates that it exhibits reversible capacitive behavior with high coulombic efficiency.

The lowest change observed in slope and discharge time after the cycle demonstrates that the electrode structure remains stable during continuous use. This result indicates

that the optimized 3:1 electrode exhibits good mechanical durability and stable electrochemical performance during repeated charge-discharge cycles.

Figure 10.18e displays the GCD curves obtained at different current levels. As expected, increasing the applied current shortens the ion diffusion time, thereby reducing the discharge time. This is consistent with the operating principle of capacitive energy storage systems.

Despite this decrease, the charge-discharge curves remain quite symmetrical and demonstrate good speed performance with low polarization effects.

The area capacitance, energy density, and power density values obtained from GCD measurements are shown in **Table 10.5**.

Table 10.5: Specific capacitance, energy density, and power density values of the symmetric supercapacitor with a Gr : EC weight ratio of 3:1.

I (μA)	$\Delta t(\text{s})$	$\Delta V(\text{V})$	Area cm^2	Cs($\mu\text{F}/\text{cm}^2$)	E($\mu\text{Wh}/\text{cm}^2$)	P($\mu\text{W}/\text{cm}^2$)	P($\mu\text{W}/\text{cm}^2$)
1	2986	1	4.000	746.500	103.7	0.1	125.0
2	1306	1	4.000	653.000	90.7	0.3	250.0
4	371	1	4.000	371.000	51.5	0.5	500.0
6	169	1	4.000	253.500	35.2	0.8	750.0
8	89	1	4.000	178.000	24.7	1.0	1000.0
10	45.1	1	4.000	112.750	15.7	1.25	1250.0
15	20	1	4.000	75.000	10.4	1.9	1875.0

Nyquist plots taken before and after the cyclic stability test are shown in **Figure 10.18f**. The impedance spectra exhibit a small semicircle in the high-frequency range, followed by a linear tail characterized by capacitive behavior in the low-frequency region.

The slight change observed after the cyclic test indicates that the overall capacitive characteristics are preserved and that there are some minor differences in the load transfer resistance. Equivalent circuits matching parameters, such as solution resistance (R_s), load transfer resistance (R_{ct}), double-layer capacitance (C_{dl}), and Warburg impedance (W), are summarized in **Table 10.6**.

In general, electrochemical characterization studies reveal that the optimized Gr–EC (3:1) electrode exhibits consistent capacitive behavior under different scan rates, voltage ranges, and applied current conditions. The minimal changes observed in GCD profiles and impedance responses after cycling indicate that the electrode possesses

robust structural integrity and the presence of effective ion transport pathways. These findings demonstrate that the optimized composition offers reliable and long-term electrochemical performance for flexible micro-supercapacitor applications.

Table 10.6: EIS fitting parameters of the Gr-EC (3:1) electrode before and after cycling.

Before	After
$R_s=19122.0\ \Omega$	$R_s=26423.0\ \Omega$
$C_{dl}=2.971E-8\ F$	$C_{dl}=2.389E-8\ F$
$R_{ct}=34201.0\ \Omega$	$R_{ct}=45483.0\ \Omega$
$W=2.2273E-5\ Mho^{(1/2)}$	$W=5.4018E-6\ Mho^{(1/2)}$

To investigate long-term electrochemical durability in greater depth, the CV curves obtained at the 1st and 5000th cycles are compared in **Figure 10.19**. The overall shape and enclosed area of the curves are largely preserved after a long cycling process. This indicates that the optimized device has good capacitance retention and consistent electrochemical performance.

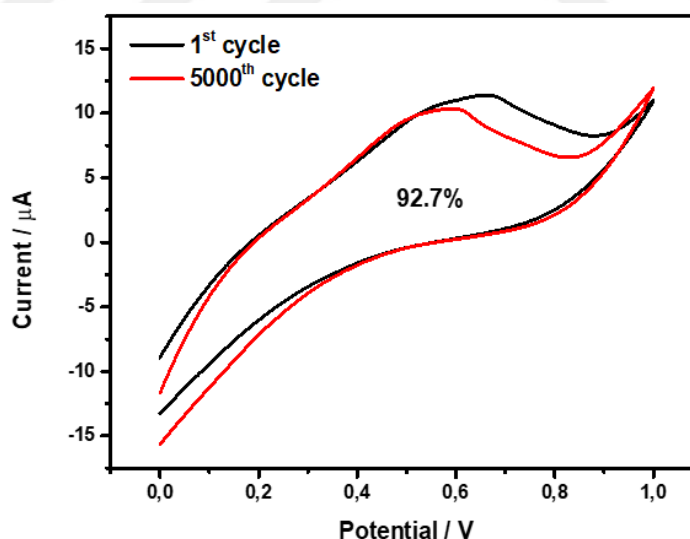


Figure 10.19: Gr-EC weight ratio 3:1 electrode charge-discharge performance tests of a symmetric microsupercapacitor device over 5000 cycles.

A capacitance retention of approximately 92.7% after 5000 cycles further demonstrates the excellent cycling stability and structural integrity of the optimized electrode.

The slight decrease in current response observed after a long cycle can be attributed to minor electrode/electrolyte interface rearrangements, which are commonly seen in long-term cycling tests.

These findings demonstrate that the optimized Gr-EC (3:1) electrode possesses excellent rate capability, exhibits stable electrochemical properties, and provides high cycle durability. Furthermore, it proves that this electrode is suitable for high-performance flexible micro-supercapacitor applications.

10.2.5. Ragone Plot Analysis and Comparative Energy-Power Performance Comparison

A Ragone plot has been prepared to evaluate the practical energy and power performance of the optimized Gr-EC (3:1) symmetric microsupercapacitor. This plot helps determine the system's position among energy storage technologies. The gravimetric energy and power densities included in the Ragone analysis were calculated by converting the values obtained on an areal basis to kg units, taking into account the total active material mass. Considering the symmetric device architecture, the total active mass of both electrodes was used as the basis for the calculations.

As shown in **Figure 10.20**, the designed device falls within the performance range of typical symmetric supercapacitors. The results reveal that the system has a lower energy density compared to battery and fuel cell technologies, but provides a significantly higher power density. This indicates that microsupercapacitors offer advantages in high-power applications, particularly in areas requiring rapid charging and discharging.

In the Ragone plot, the decrease in energy density along with current density and the increase in power density align with the expected behavior of supercapacitor systems. Achieving longer discharge times at low current densities enables more effective electrochemical reactions, thereby allowing higher energy densities to be attained. This trend is consistent with GCD analysis results and supports the system's performance under internal resistance and ion diffusion constraints.

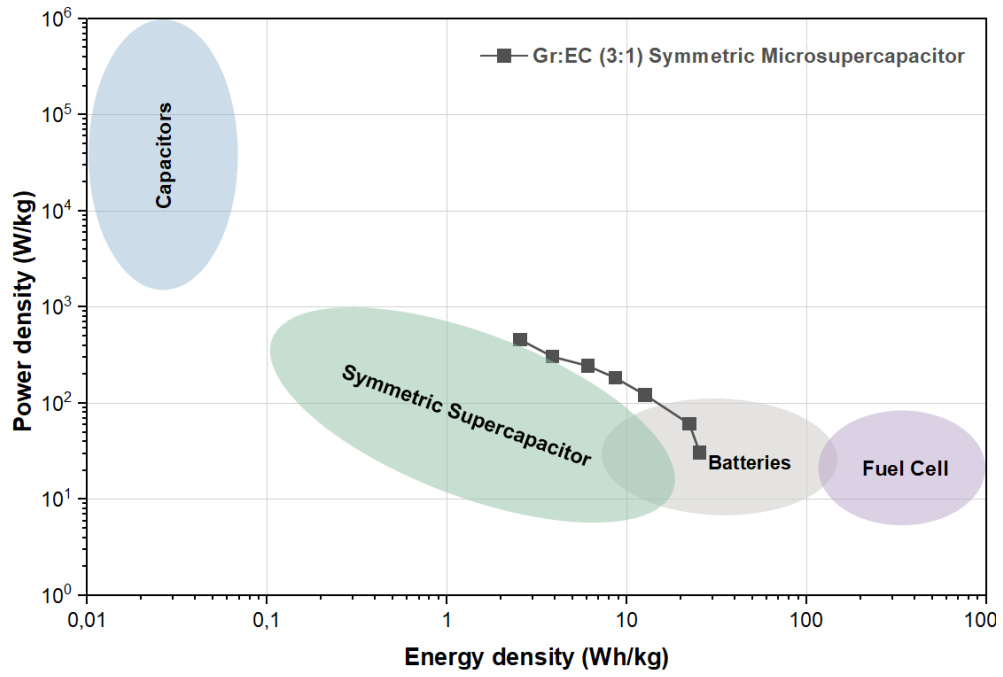


Figure 10.20: Ragone plot of the optimized Gr-EC (3:1) symmetric MSC.

As a result, the electrode structure with a 3:1 Gr-EC ratio exhibits a balanced energy and power characteristic, possessing both sufficient energy storage capacity and high power transfer capability. The obtained results are consistent with CV, GCD, and EIS analyses and demonstrate that the optimized composition is suitable for practical energy storage applications.

11. CONCLUSION

In this study, graphene powder derived from laser-induced graphene (LIG) layers obtained on a polyimide (PI) substrate using a CO₂ laser was effectively utilized in the production of conductive inks by blending it with ethyl cellulose (EC) binder at different ratios. The ratios are 1:1, 2:1, 3:1, and 4:1. These inks were then used to produce symmetric micro supercapacitor electrodes via the screen printing method. The effects of the binder ratio on the microstructural, structural, and electrochemical properties of the electrodes were systematically investigated.

SEM and EDS analyses revealed that increasing the graphene content resulted in a more homogeneous surface and facilitated the formation of conductive networks with high carbon content. However, the high binder ratio (1:1) formed a percolation network, while insufficient binder at the 4:1 ratio resulted in noticeable agglomeration and weakened structural integrity. The 3:1 composition produced the most homogeneous pore structure and provided an optimal conductive network structure. Raman, XPS, and XRD analyses confirmed that the graphitic structure improved further with the increase in graphene content.

The electrochemical characterization results revealed that all electrodes exhibited typical electric double-layer capacitance (EDLC) behavior, forming an almost rectangular CV curve. Among all compositions, the 3:1 electrode exhibited the highest overall electrochemical performance. At a scan rate of 100 mV s⁻¹, the highest surface capacitance of 146.67 $\mu\text{F cm}^{-2}$ and energy density of 45.84 $\mu\text{Wh cm}^{-2}$ were obtained. GCD measurements supported excellent charge-discharge characteristics with low internal resistance and good reversibility. In contrast, while the 1:1 electrode restricted excessive binder content, limited ion transport, and disrupted the conductive percolation network, insufficient binder content weakened mechanical integrity and increased contact resistance in the 4:1 electrode, negatively affecting the electrochemical performance.

Electrochemical impedance spectroscopy (EIS) analysis based on the Randles equivalent circuit has shown that both the solution resistance (R_s) and the charge transfer resistance (R_{ct}) are reduced to the lowest levels in the optimized 3:1 electrode. This indicates that the charge transfer kinetics have increased and the surface

properties have improved. On the other hand, the increase in diffusion impedance in the 4:1 electrode indicates that ion movement is restricted in the electrode structure.

Long-term electrochemical tests once again demonstrated the excellent durability of the optimized electrode. The device exhibited strong cycle stability and structural durability, retaining approximately 92.7% of its initial capacitance after 5000 cycles. Additionally, the electrode exhibited stable capacitive properties under different scanning speeds, voltage ranges, and applied current conditions. This confirmed its good rate capability and long-term reliable performance.

In general, the findings reveal that establishing a balanced relationship between graphene and the binder material is extremely important for improving the electrochemical performance of micro supercapacitors produced using the screen printing method. The Gr–EC 3:1 ratio has been identified as the most ideal mixture, offering structural durability, effective ion transfer, low resistance, and high capacitive performance.

This research demonstrates that graphene powders obtained from LIG can be successfully converted into screen-printable conductive inks for the scalable manufacturing of flexible energy storage devices. The results provide important insights for the design and development of next-generation micro supercapacitors for wearable electronics, IoT systems, and on-chip energy storage technologies.

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PUBLICATIONS AND PRESENTATIONS FROM THE THESIS

Tig K., Aydemir N., Effect of Graphene Concentration on the Charge/Discharge Characteristics of Hybrid Supercapacitors, 8th International Conference on Materials Science and Nanotechnology (MSNANO-25), 1–3 September 2025, Istanbul, Turkey (Poster Presentation)

Tig K., Aydemir N., Printed Graphene-Based Supercapacitor for Electronic Applications, GTU 8th Graduate Studies Symposium, 30 May 2024, Kocaeli, Turkey (Poster Presentation)

