

**A COMPARATIVE STUDY OF ELECTROLYTE
PERFORMANCE IN LASER INDUCED GRAPHENE
SUPERCAPACITORS**

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ABSTRACT

This project investigates the fabrication and performance evaluation of laser-induced graphene (LIG) supercapacitors on polyimide substrates, with a focus on the influence of electrolyte type on device performance. LIG electrodes were prepared using an optimized CO₂ laser engraving process, producing a porous, conductive graphene network directly on the substrate without chemical treatments. Six aqueous electrolytes: two acidic (HCl, H₂SO₄), two basic (NaOH, NaHCO₃), and two neutral (Na₂SO₄, NaCl) were prepared at 1 M concentration and tested. The supercapacitors were assembled with electrolyte-soaked cellulose fiber separators between interdigitated LIG electrodes, and copper contacts were applied for measurement. Electrochemical characterization using an LCR meter measured capacitance and equivalent series resistance (ESR) across a frequency range. Results demonstrate that acidic electrolytes generally deliver the highest capacitance, while neutral salts provide a trade-off between conductivity and stability. These findings highlight the importance of electrolyte selection in optimizing supercapacitor performance for specific applications.

Keywords: Laser-induced graphene, Polyimide, Supercapacitor, Electrolyte performance, Capacitance, Equivalent series resistance

LIST OF ACRONYMS AND ABBREVIATIONS

EDLC: Electric Double Layer Capacitance

ESR: Equivalent Series Resistance

LCR: Inductance, Capacitance, Resistance

LIG: Laser Induced Graphene

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CHAPTER 1

1. INTRODUCTION

1.1 General Introduction

Energy storage technologies have become essential with the rise of portable electronics, electric vehicles, and renewable energy integration. Supercapacitors stand out for their ability to deliver high power density and long cycle life, bridging the gap between batteries and traditional capacitors. Laser-induced graphene (LIG) has emerged as a compelling electrode material due to its high surface area, excellent electrical conductivity, and simple fabrication process on flexible substrates. However, the electrolyte choice plays a crucial role in defining the overall performance of LIG supercapacitors by affecting ion transport, electrochemical stability, and charge storage mechanisms. Comparative studies reveal that different electrolytes acidic, alkaline, or neutral significantly influence capacitance, rate capability, and durability of these devices. Optimizing the electrolyte is therefore key to unlocking the full potential of LIG-based supercapacitors for practical energy storage applications.

1.2 Rationale

While laser-induced graphene (LIG) provides an excellent electrode platform due to its porous structure, high surface area, and conductivity, the overall performance of LIG-based supercapacitors also critically depends on the electrolyte used. The electrolyte controls ion transport, electrochemical stability, and the operating voltage window, all of which directly influence capacitance, power delivery, and cycling durability. Different electrolytes acidic, alkaline, or neutral aqueous solutions interact differently with the LIG electrode's porous network, resulting in varied charge storage behavior and efficiency. Therefore, a systematic comparison of electrolyte performance in LIG supercapacitors is essential to identify optimal electrolyte-electrode combinations for specific applications, including flexible and wearable electronics.

1.3 Objectives

1.3.1 General objective:

To fabricate laser-induced graphene supercapacitors on polyimide tape and evaluate their electrochemical performance with different types of electrolytes.

1.3.2 Specific objectives:

- To fabricate supercapacitor electrodes by direct laser writing on polyimide tape to produce laser-induced graphene.
- To assemble supercapacitor devices using acidic, basic, and neutral aqueous electrolytes.
- To measure and compare the specific capacitance of the supercapacitors with different electrolytes.
- To evaluate and compare the equivalent series resistance (ESR) of the supercapacitors across the various electrolytes.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Overview of Supercapacitors

Supercapacitors, or electrochemical capacitors, fill the gap between conventional capacitors and batteries by offering fast charge-discharge rates and higher energy storage capacity. They store charge electrostatically at the electrode-electrolyte interface, enabling rapid energy delivery and excellent cycle life. This combination makes them suitable for applications such as portable electronics, electric vehicles, and renewable energy systems requiring quick energy bursts and long-term durability (Simon & Gogotsi, 2008).

2.2 Charge Storage Mechanisms

Supercapacitors primarily store energy through electric double layer capacitance (EDLC) and pseudocapacitance. EDLC relies on charge separation at the electrode-electrolyte interface without electron transfer reactions, providing long cycle life but moderate capacitance. Pseudocapacitance involves reversible redox reactions at or near the electrode surface, offering higher capacitance but sometimes reduced stability. Many devices utilize both mechanisms to optimize energy density and cycling performance (Conway, 1999).

2.3 Electrode Materials for Supercapacitors

The electrode's properties critically affect supercapacitor performance. Ideal electrodes combine high specific surface area for charge storage, excellent electrical conductivity for fast electron transport, chemical stability, and a porous structure facilitating ion movement. Carbon materials like activated carbon, carbon nanotubes, and graphene derivatives dominate due to their tunable porosity and conductivity (Wang, Zhang, & Zhang, 2017).

2.4 Graphene and Laser-Induced Graphene (LIG)

Graphene's single-layer, hexagonal carbon structure offers exceptional surface area ($\sim 2630 \text{ m}^2/\text{g}$) and conductivity, but challenges like restacking limit accessible surface area. Laser-induced graphene (LIG) overcomes this by directly converting polyimide surfaces into a porous 3D graphene network via laser irradiation. This process is scalable, environmentally friendly, and mask-free, producing electrodes with high conductivity, large surface area, and mechanical flexibility suitable for flexible and wearable electronics.

2.5 Fabrication Techniques for LIG Electrodes

Direct laser writing for LIG fabrication allows tuning pore size and morphology by adjusting laser power, speed, and pulse parameters. This flexibility enables customization of electrode properties without additional chemical processing, optimizing electrochemical performance for specific applications.

2.6 Applications and Challenges of LIG-Based Supercapacitors

LIG supercapacitors have been integrated into flexible electronics, wearable sensors, and miniaturized energy storage due to their flexibility and excellent electrochemical properties. However, challenges like improving energy density and enhancing electrolyte compatibility remain crucial for practical deployment. Addressing these requires advances in electrode structure, electrolyte optimization, and interface engineering.

2.7 Electrolytes in Supercapacitors

Electrolytes provide the ionic medium for charge transfer and profoundly influence supercapacitor performance. They are classified mainly into aqueous and organic types, with aqueous electrolytes further divided into acidic, alkaline, and neutral categories. Acidic electrolytes such as sulfuric acid offer high ionic conductivity and wide voltage windows but can be corrosive and reduce device lifespan. Alkaline electrolytes provide good ionic mobility and stability but may degrade electrodes over time. Neutral

electrolytes like sodium sulfate are safer and more environmentally friendly but generally have lower conductivity and narrower voltage windows, affecting capacitance and energy density. Organic electrolytes expand the voltage window further, increasing energy density but at the cost of lower ionic conductivity, higher cost, and toxicity concerns. Selecting the right electrolyte balances ionic conductivity, electrochemical stability, safety, and compatibility with the electrode material to optimize device performance.

CHAPTER 3

3. MATERIALS AND METHODS

3.1 Materials

The materials and equipment used in this project include:

- **Substrate:** 50 μm Polyimide (polyamide) tape, laminated in three layers to form a 150 μm thick substrate.
- **Laser Engraver:** GCC Mercury III 60W CO₂ laser cutter.
- **Design Software:** SolidWorks and CorelDRAW for electrode pattern design and laser processing.
- **Electrolytes:**

Acidic: Hydrochloric acid (HCl), Sulfuric acid (H₂SO₄)

Basic: Sodium bicarbonate (NaHCO₃), Sodium hydroxide (NaOH)

Neutral: Sodium sulfate (Na₂SO₄), Sodium chloride (NaCl)

- **Electrochemical Testing:** LCR meter for capacitance and ESR measurements.
- **Standard Laboratory Equipment:** Copper tape, Glassware, isopropanol for cleaning, and cellulosic fibers for electrolyte retention.

3.2 Methods

3.2.1 Substrate Preparation

Three layers of 50 μm polyimide tape were laminated to achieve a 150 μm thick substrate. The laminate was cleaned thoroughly with isopropanol to remove dust and oils that could affect laser engraving quality.



Figure 1: Prepared polyimide substrate before laser engraving

3.2.2 Laser Engraving of LIG Electrodes

Prior to finalizing the laser engraving parameters, a systematic optimization process was conducted to identify the ideal laser power, speed, and defocus settings that produce high-quality laser-induced graphene (LIG) on the polyimide substrate. This optimization involved varying laser power and speed across several test patterns and analyzing the resulting surface morphology at 30x magnification to assess porosity, uniformity, and absence of substrate damage.

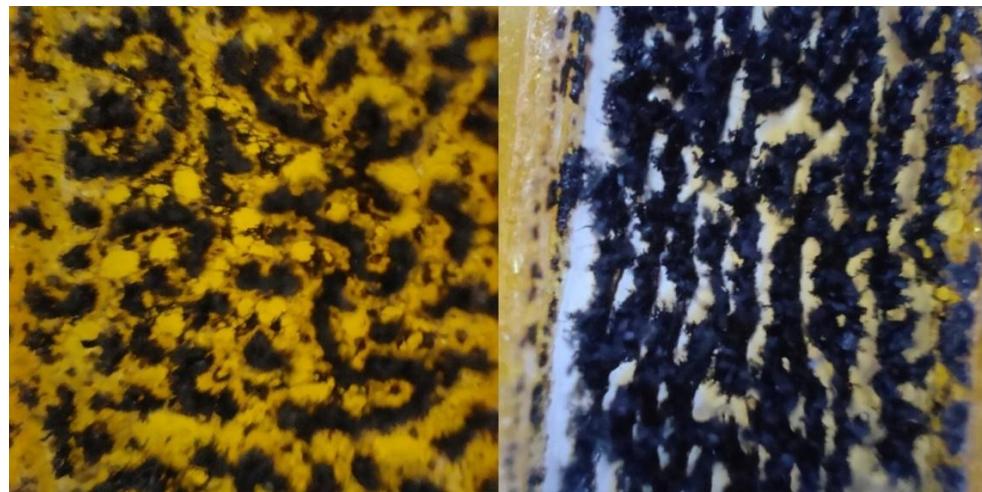


Figure 2: LIG surface at 30x magnification before optimization



Figure 3: LIG surface at 30x magnification after optimization

Electrode patterns designed in SolidWorks and CorelDRAW were transferred to the GCC Mercury III 60W CO₂ laser cutter. The following optimized parameters were used:

- Laser type: CO₂ infrared laser (wavelength 10.6 μm)
- Number of passes: 3
- Defocus: 4 mm below focal plane
- Speed: 58%
- Power: 24%
- Raster resolution: 600 dpi
- Scanning resolution: 1200 ppi
- Fill method: Manual colour fill

These settings ensured precise conversion of the polyimide surface into a porous, conductive LIG network without damaging the substrate.



Figure 4: GCC Mercury III CO₂ laser cutter used for LIG fabrication

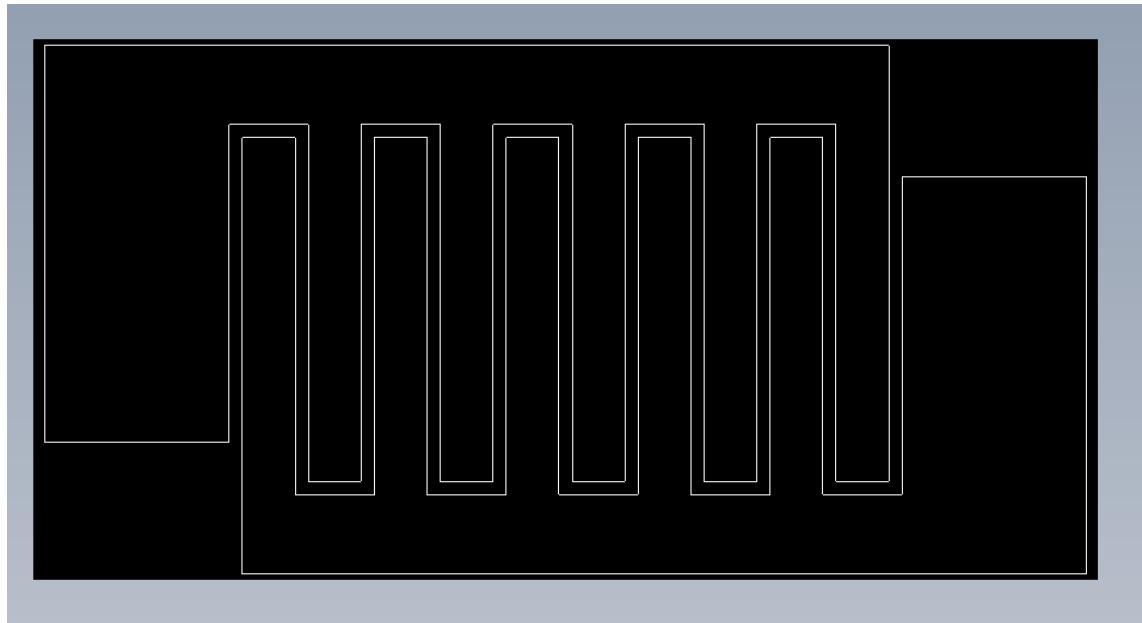


Figure 5: DXF layout of interdigitated electrode design for LIG fabrication

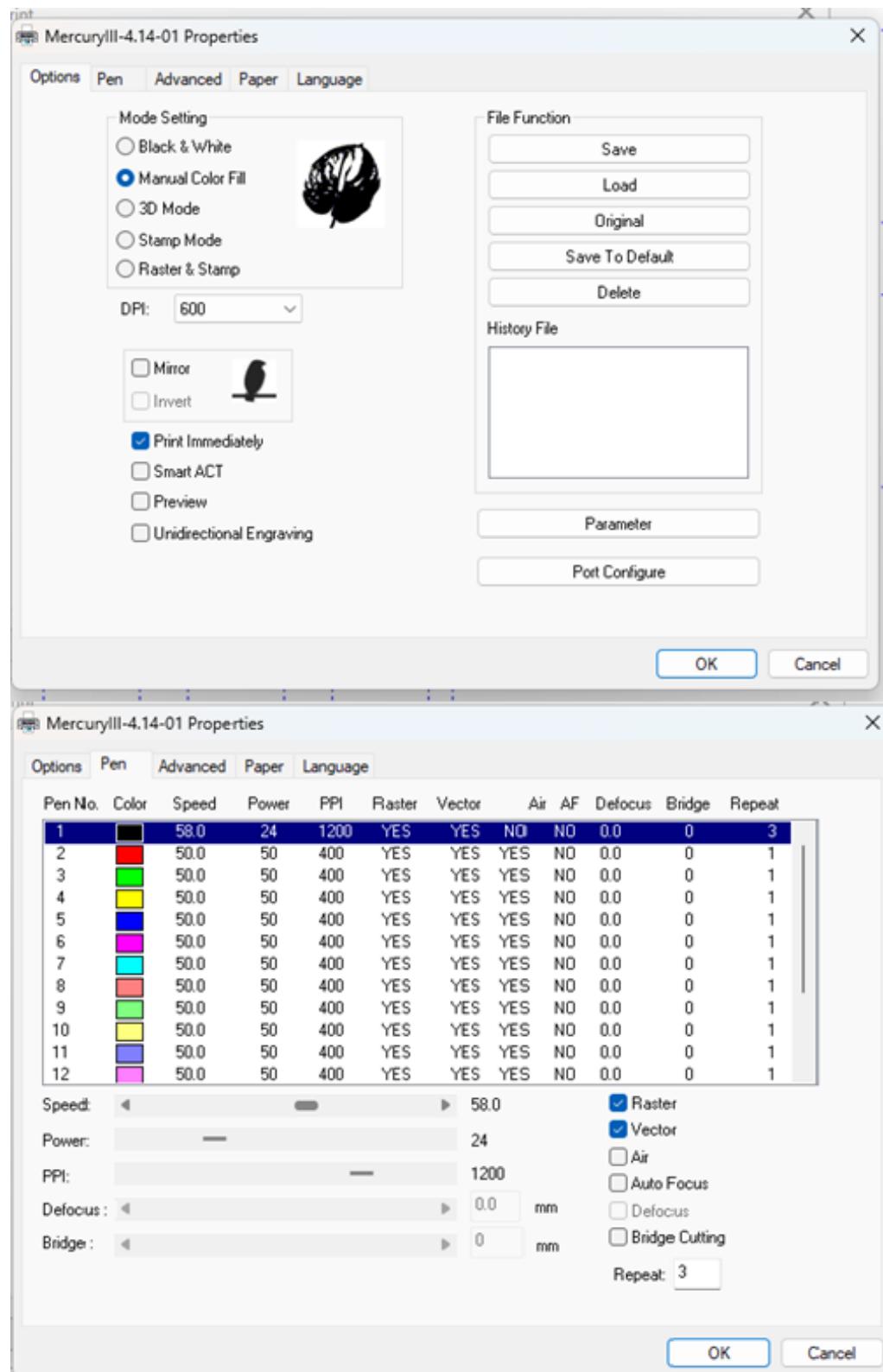


Figure 6: Laser engraving settings for LIG fabrication

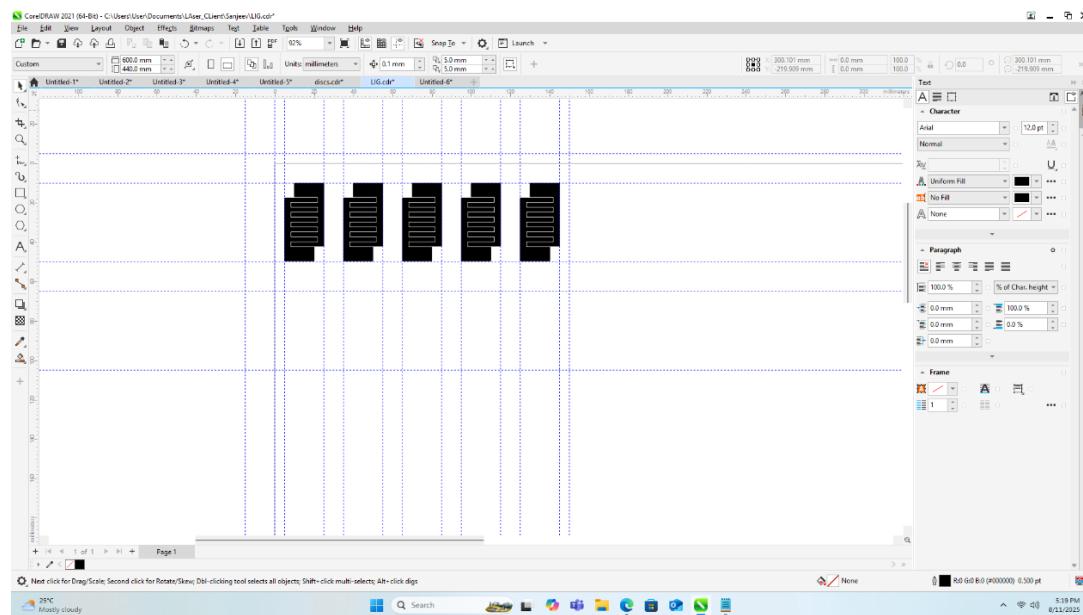


Figure 7: CorelDRAW design prepared for laser engraving

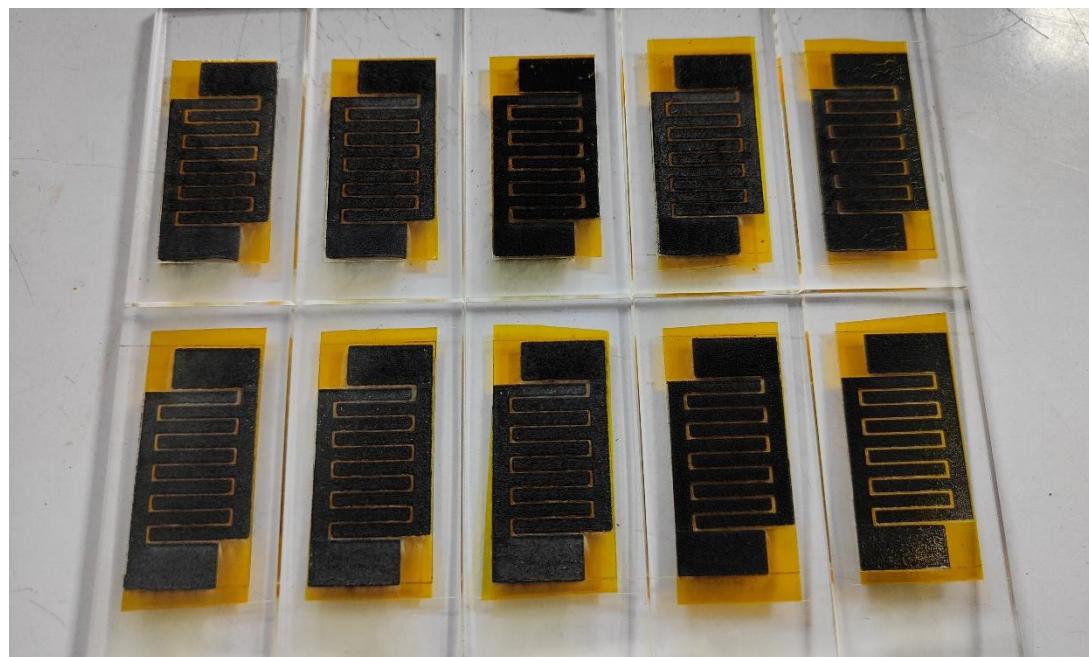


Figure 8: Final LIG electrode pattern on substrate mounted on acrylic base

3.2.3 Post-Fabrication Handling

After laser engraving, the LIG patterns remain firmly on the polyimide substrate and are not peeled off. The substrate with the LIG pattern was handled carefully to avoid contamination or mechanical damage to the graphene surface.

3.2.4 Preparation of Electrolyte Solutions

Each electrolyte was prepared at a concentration of 1 M using the following procedure:

- **Acidic Electrolytes:**

Hydrochloric acid (HCl, 36% w/w) and sulfuric acid (H₂SO₄, 20% w/w) were diluted to 1 M concentration

- **Basic and Neutral Electrolytes:**

Sodium bicarbonate (NaHCO₃), sodium hydroxide (NaOH), sodium sulfate (Na₂SO₄), and sodium chloride (NaCl) were weighed accurately and dissolved in deionized water, then diluted to 1 M final volume.

All solutions were freshly prepared before use to ensure consistency.

3.2.5 Supercapacitor Assembly

Cellulose fiber layers saturated with the respective electrolyte were placed directly over the interdigitated LIG electrodes. Copper tape pieces were attached to electrode ends for electrical connections during testing.

3.2.6 Measurement of Capacitance and ESR

The capacitance and equivalent series resistance (ESR) of each supercapacitor were measured using an LCR meter at a fixed frequency of 100 kHz. Prior to measurement, each device was fully discharged by shorting the terminals for at least 15 minutes to remove any residual charge and minimize dielectric absorption effects. For easy and reliable electrical connection, two small copper tapes were carefully attached to the

terminals of each supercapacitor, ensuring stable contact during testing. The LCR meter was calibrated according to the manufacturer's procedure before starting the measurements to ensure accuracy and consistency across all devices.

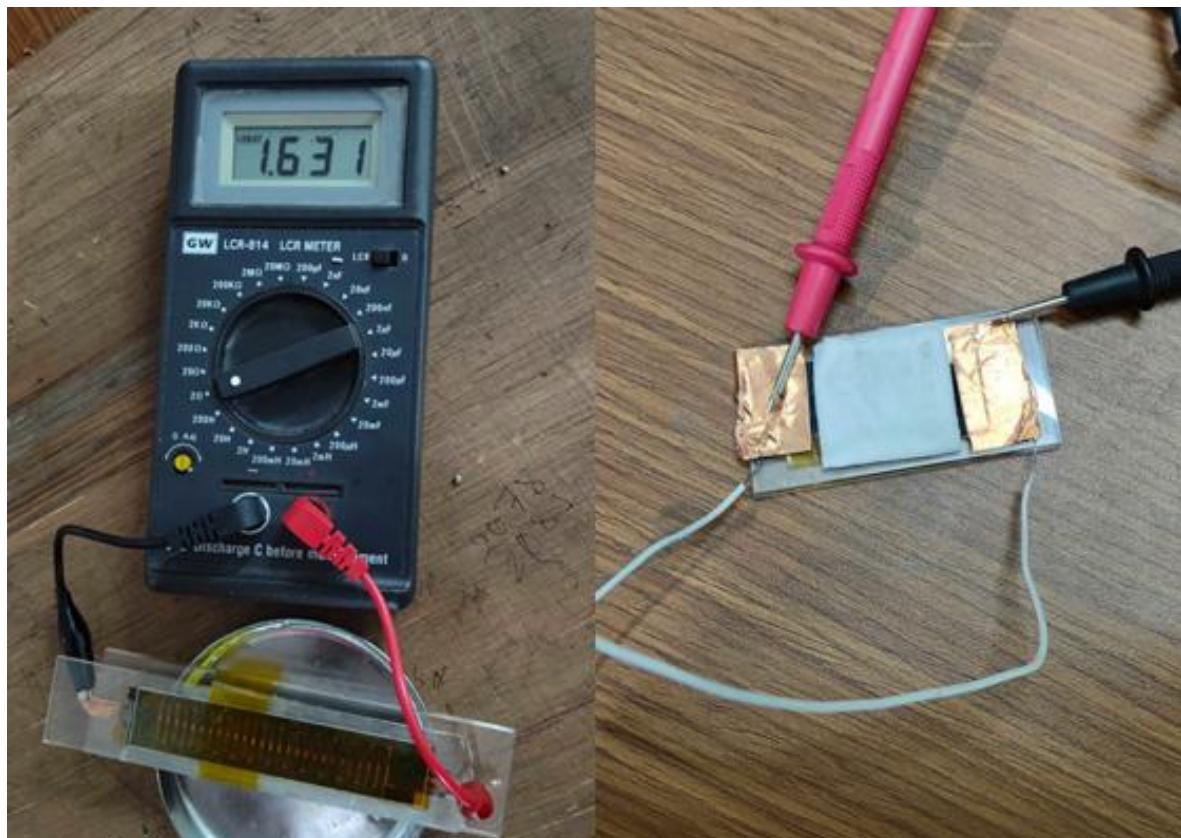


Figure 9: LCR meter and Supercapacitor



Figure 10: Measurement Setup

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1 Capacitance and ESR of LIG Supercapacitors

The performance of the fabricated laser-induced graphene (LIG) supercapacitors was evaluated using various 1 M aqueous electrolytes. Table 4.1 summarizes the measured device capacitance (C), areal capacitance, and equivalent series resistance (ESR) for each electrolyte.

Table 1: Capacitance and ESR for Different Electrolytes

Electrolyte (1 M)	Device C (μF) (2.45 cm^2)	Areal C ($\mu\text{F}/\text{cm}^2$)	ESR (Ω)(100 kHz)
H_2SO_4	263	107	1.35
HCl	315	129	6.37
NaOH	268	109	5.56
NaHCO_3	12	5	15.32
Na_2SO_4	122	50	10.02
NaCl	30	12	25.63

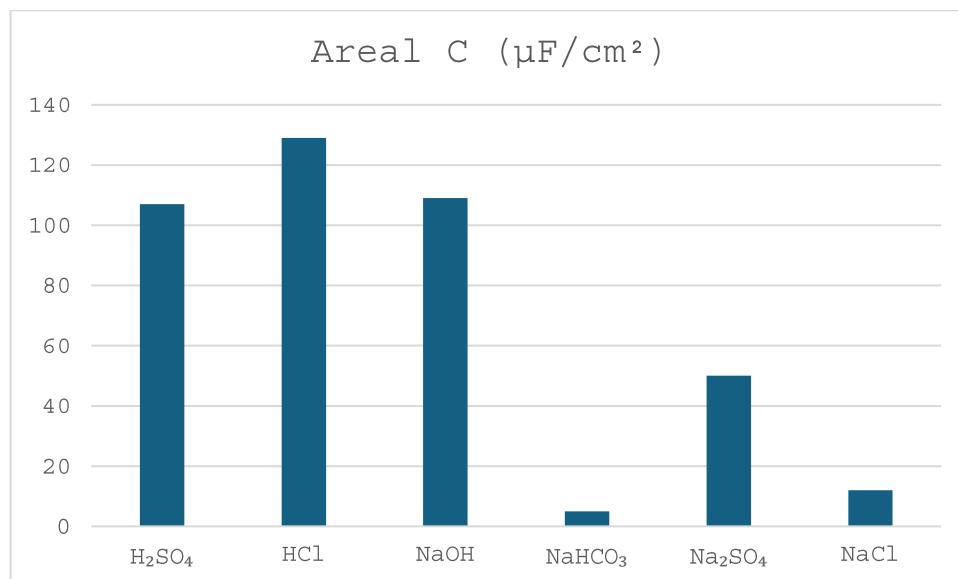


Figure 11: Bar Chart of Areal Capacitance for Different Electrolytes

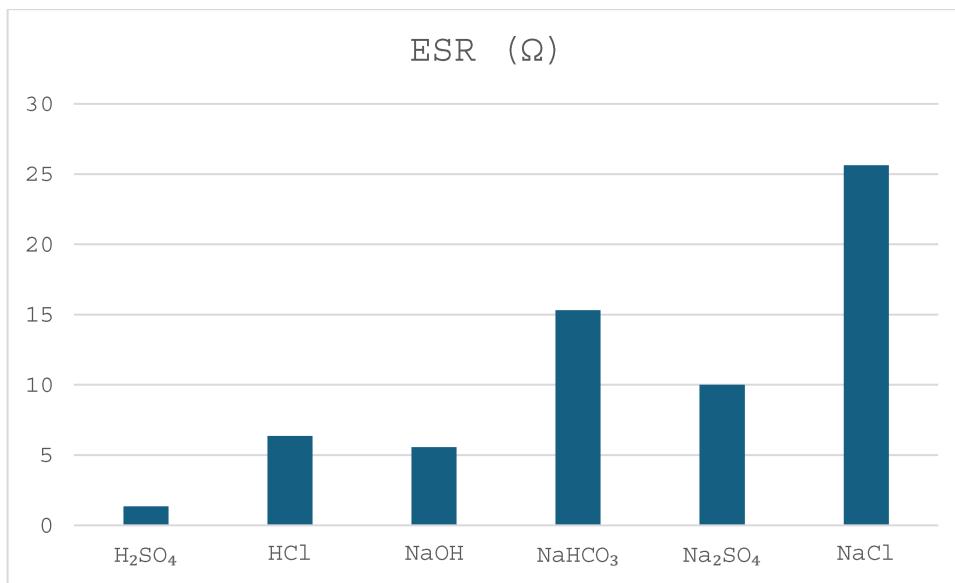


Figure 12: Bar Chart of ESR for Different Electrolytes

4.2 Discussion

4.2.1 Effect of Electrolyte Type on Capacitance

The highest areal capacitance was observed with HCl ($129 \mu\text{F}/\text{cm}^2$), followed closely by H_2SO_4 ($107 \mu\text{F}/\text{cm}^2$) and NaOH ($109 \mu\text{F}/\text{cm}^2$). This trend is consistent with the high ionic conductivity and small hydrated ion size of H^+ and OH^- ions, which can easily penetrate the porous LIG structure, forming an effective electric double layer at the electrode–electrolyte interface.

In contrast, neutral salts such as Na_2SO_4 and NaCl, as well as the weak base NaHCO_3 , showed significantly lower capacitance. NaHCO_3 exhibited the lowest value ($5 \mu\text{F}/\text{cm}^2$), likely due to limited ionic mobility and poor charge accumulation in the pores of LIG. This indicates that the chemical nature of the electrolyte strongly influences the ability to store charge in LIG supercapacitors.

4.2.2 Effect of Electrolyte on ESR

The ESR values were lowest for H_2SO_4 (1.35Ω), indicating minimal internal resistance and excellent ion transport in the acidic medium. HCl and NaOH showed slightly higher ESR (6.37Ω and 5.56Ω , respectively), but still lower than the neutral salts. NaHCO_3 , Na_2SO_4 , and NaCl exhibited higher ESR (25.63Ω), which can be attributed to slower ion

migration, larger hydrated ionic radii, and weaker interaction with the LIG electrode surface.

The ESR data align with the capacitance results: electrolytes with lower ESR generally exhibit higher capacitance due to reduced energy loss during charge–discharge cycles.

4.2.3 Comparison between Acidic, Basic, and Neutral Electrolytes

- **Acidic electrolytes (H_2SO_4 , HCl):** High capacitance and low ESR make them ideal for high-performance supercapacitors. H_2SO_4 particularly provides the best balance of low ESR and good capacitance.
- **Basic electrolytes (NaOH , NaHCO_3):** NaOH shows comparable capacitance to H_2SO_4 but slightly higher ESR, while NaHCO_3 performs poorly in both metrics.
- **Neutral electrolytes (Na_2SO_4 , NaCl):** Moderate to low capacitance and high ESR indicate limited performance, suggesting that neutral electrolytes are less effective for LIG electrodes under these conditions.

CHAPTER 5

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusions

- Laser-induced graphene (LIG) electrodes were successfully fabricated on polyimide substrate using a CO₂ laser, with optimized parameters (power, speed, and defocus) resulting in a uniform porous structure.
- Acidic electrolytes, particularly HCl and H₂SO₄, exhibited the highest areal capacitance (129 μF/cm² and 107 μF/cm², respectively) and low ESR, demonstrating superior charge storage and low internal resistance.
- Basic electrolyte NaOH showed good performance, whereas weak bases (NaHCO₃) and neutral salts (Na₂SO₄, NaCl) exhibited significantly lower capacitance and higher ESR.
- The study confirms that electrolyte type strongly influences supercapacitor performance, and proper tuning of the electrode-electrolyte combination is essential for optimal results.
- Optimization of laser parameters played a crucial role in ensuring the LIG electrodes were conductive, mechanically stable, and porous, which directly impacted the electrochemical performance of the supercapacitors.

5.2 Novelty and National Prosperity aspect of Project work

The project demonstrates a simple, scalable, and environmentally friendly method for fabricating LIG electrodes without requiring chemical treatments or masks. By conducting a comparative study of different electrolytes, it provides valuable insights for designing efficient, low cost, and locally manufacturable supercapacitors. This research has potential applications in renewable energy storage, portable electronics, and affordable energy solutions in Nepal, contributing to national technological development and promoting energy self-reliance.

5.3 Limitations of the work

- The study focused only on 1 M aqueous electrolytes, which limits the generalization to other concentrations or non-aqueous systems.
- Only a single laser system (GCC Mercury III 60W CO₂) was used; results may vary with other laser types or powers.
- Long-term stability, cyclic performance, and real world durability of the supercapacitors were not tested.
- Device area and electrode geometry were fixed; scaling effects were not investigated.

5.4 Recommendations for further work

- Explore different concentrations and mixed electrolytes to further enhance capacitance and reduce ESR.
- Investigate non-aqueous and ionic liquid electrolytes to expand the operational voltage window and energy density.
- Study long term cycling stability and real-world applications to assess durability.
- Experiment with different laser systems, powers, and pulse patterns to further optimize LIG morphology and conductivity.
- Consider scaling up the device size and exploring flexible or wearable configurations for practical applications.

