Fabrication and Characterization of Laser Scribed Supercapacitor based on Polyimide for Energy Storage

TAYYABA Malik\textsuperscript{a}, SHAYAN Naveed\textsuperscript{b}, MUHAMMAD Munir\textsuperscript{c}, MOHAMMAD Ali Mohammad\textsuperscript{d,}\textsuperscript{*}

School of Chemical and Materials Engineering (SCME), National University of Sciences and Technology (NUST), Sector H-12, Islamabad 44000, Pakistan

\textsuperscript{a}tayyaba.malik16@gmail.com, \textsuperscript{b}shayan_nse@scme.nust.edu.pk, \textsuperscript{c}muneer@scme.nust.edu.pk, \textsuperscript{d}dr.ali@scme.nust.edu.pk

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Abstract. Recently, supercapacitors have attracted a tremendous amount of attention as energy-storage devices due to their high-power density, fast charge–discharge ability, excellent reversibility, and long cycling life. In this research work, we demonstrate a laser scribed super capacitor based on polyimide (PI) substrate for the storage of electrical energy. PI substrate of thickness 200µm and area 1cm × 1cm was reduced by a laser engraver with a 450 nm wavelength in the form of stackable supercapacitor electrodes. Although, PI itself exhibits non-conductive behavior; however, by laser irradiation we change the surface properties of PI and reduce its resistance. The chemical property of irradiated PI was characterized with XRD where the carbon peak was observed at 2*theta = 25.44, which confirms the reduction of PI material in to a graphene-like substance. The electrical conductivity was analyzed with a probe station and observed to be 1.6mS. Two conductive regions were assembled into a capacitor device by sandwiching a PVA/H\textsubscript{3}PO\textsubscript{4} electrolyte in between. During the charging and discharging characterization of the capacitor device, current density was observed to be 1.5mA/cm\textsuperscript{2}. Capacitance versus voltage analysis was carried out and the device showed 75mF/cm\textsuperscript{2} against a voltage sweep of ±2V. The galvanostatic charging and discharging curve shows a symmetric behavior with respect to time exhibiting the stability and durability of the device.

Introduction

Energy generation and storage is a topic of great contemporary importance and hence efforts are being made across the globe to develop solutions in this domain. For energy storage, a wide range of devices have been proposed which vary in application area, storage capacity, retention, charge/discharge speed, form, size, etc. Besides batteries and electronic memory devices, supercapacitors are a very famous device for the energy storage [1]. It has the ability to store energy and it has high-power density and long cycling life [2]. Supercapacitors are expected to impact consumer electronics, electrical power grids, transport and military applications, and various types of electrical instruments for commercial and industrial uses. Supercapacitors are mostly formed of graphene and graphene like material, which have yielded favorable results in terms of power density and long cycling life. Graphene based materials have a porous three dimensional structure with a large surface area due to which it has the ability to store energy and hence highly desirable for supercapacitors[3]. These supercapacitors not only shows high surface area but also shows good electrical conductivity which is very important parameter for large energy and power. They can be used in flexible electronics devices. Graphene based supercapacitors are very beneficial but graphene is expensive and its synthesis process is complex [4]. For graphene synthesis many chemical steps are required and on commercial scale its yield is not very high. Other than graphene based supercapacitors, direct laser writing on graphite oxide [5, 6], light scribed DVD drive [7] and CO\textsubscript{2} laser based techniques are used to fabricate the supercapacitors[8]. In these techniques, graphene oxide is converted in to the reduced graphene oxide using laser beams which results in a porous structure with a surface amenable for electron transport and charge storage. Laser induced
graphene by laser scribing is a well-known method for the fabrication of supercapacitor electrodes [9]. In the literature it is shown that the capacitance is dependent on its physical geometry and substrate materials [10, 11]. The performance of supercapacitor is also dependent on the intensity of laser power during fabrication, which should be investigated.

In this paper we use a single step and low cost method of producing a carbonized structure by using laser technology. A small laser setup is used to change the surface of polyimide. It is an insulating polymer and has non-conductive properties. Upon irradiation by a laser, its surface is converted into carbonized material which has high porosity. Now this reduced polyimide (rPI) has high conductive properties as compared to a simple polyimide sheet. Having high density, porous structure, and good conductivity, rPI is used for supercapacitor applications. By using this simple laser set up flexible supercapacitor of different types can be formed. Here we checked the behavior and capacitance of our device by changing the design, size, scan rate and laser intensity. In addition, previously silver paste and copper type was used for electrode contacts due to which some kind of resistance existed and to avoid a loss of performance due to this resistance, in this paper we have made some changes in the design. The electrodes are also formed by the same material (reduced polyimide), due to which there is no change or loss of conductivity. These kinds of supercapacitors are flexible, smaller and cheaper in price for consumer purpose. For its design there is no need of any lithography technique, and any kind of design can be imported into the software. By using its simple software, the laser intensity and carving time can be varied. The intensity used in this paper is 111mW and 139mW. At a higher intensity we get better electrochemical results.

Experimentation

Fabrication of Supercapacitor. The fabrication of the supercapacitors was performed by using commercial polyimide of 200µm thickness. A laser engraver of 450 nm wavelength and maximum power 500 mW [12] was used to reduce the surface of PI and convert the irradiated area in to a carbonized structure. Fig. 1(a) shows a photograph of the instrument. It is a 2D laser setup in which the laser moves in the X-Y direction by using stepper motors. This instrument does not require any mask for the fabrication and arbitrary designs can be drawn by importing a customized structure into the control software. By changing the laser intensity different types of stacked supercapacitors were formed with differing characteristics. In stack type supercapacitor, an area of 1cm × 1cm of PI was reduced by the laser which converts it into the carbonized material having a porous structure. An additional elongated area, measuring 0.2cm × 1cm, was reduced besides the 1cm × 1cm square which acts as an electrode to connect to external measurement apparatus. A polymeric electrolyte PVA/H$_3$PO$_4$ is sandwiched in between two 1cm × 1 cm areas and laminated to form a packaged prototype (schematically shown in Fig. 1(b)). The polymeric electrolyte PVA/H$_3$PO$_4$ was made by mixing and stirring 10ml of DI water, 1ml of H$_3$PO$_4$ and 1g PVA and heated at 80ºC overnight [12, 13]. As a result, a gel type electrolyte is formed, which is coated on rPI and then placed in an oven at 50ºC for 45 minutes to remove the excess water present in the electrolyte.

Characterization

Electrochemical testing of the assembled supercapacitor device was done by using an ECI workstation and EC-lab software. The conductivity test of rPI electrodes was performed using a two-point probe station. X-Ray Diffraction (XRD) data for PI and rPI was obtained using a STEO theta-theta diffractometer. Similarly, Fourier Transform Infrared Spectroscopy (FT-IR) data for PI and rPI was obtained using a BRUKER Alpha. High resolution SEM images of various rPI regions were obtained using a JEOL Analytical SEM (JSM-6490A).
Results and Discussion

The reduced polyimide electrodes were characterized by optical microscopy, SEM, XRD, FT-IR, and electrical two-point probing. Fig. 1 (c) shows an optical micrograph of a rPI electrode after laser irradiation. The surface is converted from a brownish solid form into a black porous form which resembles a carbonized area. Fig. 2(a) shows a SEM image of the reduced PI by laser scribing of PI substrate in which it is clearly shown that the surface morphology of PI gets changed after the laser irradiation. A zoomed image of reduced PI in Fig. 2(b) shows the flakes and porous carbon like material which have higher surface density and interconnections with each other. This porous surface look like a honeycomb structure that is very useful for storage purposes. The roughened surface with interconnected pores enables excellent electrolyte contact and contributes towards a high capacitance value. Fig. 2(c) shows the cross sectional view of reduced PI on PI substrate which shows that the structure increases in thickness following laser irradiation.

PI is a non-conductive polymer and when it is reduced by laser irradiation, it becomes conductive [15]. Fig. 2(d) shows the conductivity graph in which it is shown that by using a two probe station with a 0-2V sweep, PI shows a maximum current output of 0.1pA, whereas rPI shows a maximum current output of 3.2mA and a linear graph. The relative magnitude of current output and the linear graph shows the conversion of insulating PI material into conductive rPI material. By using Ohm’s law, we find the value of resistance and subsequently calculate the approximate conductance value which is equal to 1.6mS.
XRD patterns of PI and rPI material is shown in Fig. 2 (e). PI substrate shows a very high intensity peak at $2\theta = 25.44$ and after laser irradiation the reduced PI material shows a small low intensity peak at $2\theta = 25.44$ which indicates the reduction into the graphene like material. In Fig. 2 (f) FTIR spectra of PI shows peaks from 620-1779 cm$^{-1}$ and this matches with commercial polyimide FTIR results having stretching and bending modes of the C-O, C-N and C=C bonds [9]. FTIR spectra of laser reduced PI shows a large change in its peaks from 620-1780 cm$^{-1}$. These changes indicate that the bond structure has changed in the region of interest and especially the disruption of C-O structure indicates reduction.

Fig. 3 shows the electrochemical testing results that were conducted using electrochemical lab setup. Cyclic Voltammetry and charge discharge measurements was taken for the supercapacitor devices made at different laser intensities. Cyclic voltammetry measurements were taken on different scan rates. By changing the scan rate the capacitance value also changes. There are two parameters which we varied and on which we checked the supercapacitor value. The first one is the intensity of the laser, and the second one is the scan rate.

![Graphs](image-url)

Fig. 3. (a) Capacitance vs current analysis of the proposed supercapacitor, (b) Capacitance vs. scan rate for two different laser intensities, (c) Current vs voltage sweep at 138 mW intensity and at various scan rates, (d) charging and discharging cycles analysis of the device fabricated at 138mW laser intensity, (e) Current vs. voltage sweep at 111 mW intensity and at various scan rates, and (f) charging and discharging cycles analysis of the device fabricated at 111mW laser intensity.

Laser reduced PI capacitor exhibits a maximum capacitance value of 75mF/cm$^2$ at the intensity value of 138mW and a minimum value of 35mF/cm$^2$ at an intensity of 111mW. CV results shows that by increasing the scan rate the capacitance values decrease and by increasing the laser intensity to an optimum value we get better capacitance value as shown in Fig. 3(a,b). By using equation (1) and (2) [16] we calculate the capacitance value, where I is the average current, A is the surface area of electrode which is 1cm$^2$ and $dv/dt$ is the scan rate in mV/s.
There is another type of equation used in this paper for the calculation of capacitance. Using equation (3), the capacitor value is calculated from the CV curve. Here I(V) is the total current enclosed in the CV curve in mA, S is the specific active area of electrodes which is $1 \text{ cm}^2$, $\frac{dV}{dt}$ is the scan rate in mV/s and $V_f$ and $V_i$ are the voltage limits.

\[
C_A = \frac{1}{2 \times 5 \times (V_f-V_i) \times \frac{dV}{dt}} \int_{V_i}^{V_f} I(V) dV
\]  

These supercapacitors show excellent cyclic stability; the capacitance remains unchanged after 100 cycles of charge/discharge at a current density of 2.6mA/cm$^2$ and at a scan rate of 100mV/cm$^2$. Galvanostatic charge and discharge cycles are shown in Fig. 3(d,f) at different current values which displays symmetric triangular plots throughout with increasing time.

Conclusions

In this work, we have reported the fabrication and characterization of a supercapacitor which uses laser reduced polyimide as the electrodes. Laser reduction is a low cost and relatively straightforward method to reduce PI and convert a surface layer into a carbonized material having high porosity. Reduced PI has a high storage capacity and we have analyzed the performance of our rPI/(PVA+H$_3$PO$_4$)/rPI supercapacitor by varying the laser intensity from 83mW to 167mW. We found that 138mW is the optimum power for the stacked supercapacitor geometry on a 200µm thick PI substrate and a maximum capacitance value of 75mF/cm$^2$ was obtained. From this we concluded that by changing the intensity of the laser to an optimum condition one can change the capacitance value. Further, by increasing the laser intensity, the capacitance value increased. At different scan rates, the capacitance value is different and increasing the scan rate decreases the capacitance value.

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References


