Sensors and Materials, Vol. 36, No. 11 (2024) 4915–4926
MYU Tokyo

S & M 3839

Fabrication of Single-layer Graphene-doped Electric Double-layer Capacitor and Effects of Annealing, Platinum Deposition, and Gel Electrolyte on Its Performance

Zhan-Sheng Yuan,[1] Kao-Wei Min,[2*] Jin-Yao Lai,[3]
Ming-Ta Yu,[4] Chi-Ting Ho,[4] and Teen-Hang Meen[3**]

[1]Marine Information Engineering College, Jimei University, Xiamen 361021, China
[2]Department of Electronic Engineering, Lunghwa University of Science and Technology, Taoyuan City 333, Taiwan
[3]Department of Electronic Engineering, National Formosa University, Huwei, Yunlin 632, Taiwan
[4]Department of Mechanical Design Engineering, National Formosa University, Huwei, Yunlin 632, Taiwan

(Received April 30, 2024; accepted October 10, 2024)

Keywords: supercapacitors, gel, electrolytes, graphene, activated carbon

We fabricated a single-layer graphene-doped electric double-layer capacitor (EDLC) consisting of glass, indium tin oxide, graphene layers, gel electrolyte, deposited platinum, and a conductive separator. To find the appropriate doping materials and compositions of the EDLC, we conducted experiments using single-layer graphene and ZnO as doping materials. We also varied the doping concentrations of single-layer graphene to find the optimal concentration. The single-layer graphene EDLC was fabricated with different annealing and platinum deposition methods. Different electrolytes were also tested to determine the appropriate compositions and methods to fabricate the EDLC. The performance of the EDLC was assessed by measuring the capacitance, charge–discharge efficiency, charge–discharge cycle, and hysteresis area of cyclic voltammogram (CV). The results revealed that single-layer graphene was better than ZnO for doping the EDLC, and the appropriate concentration was 0.07 wt%. Annealing the single-layer graphene, depositing platinum, and using a gel electrolyte of 10 wt% polyvinyl alcohol (PVA) and 6 M potassium hydroxide (KOH) helped improve the performance of the single-layer graphene EDLC. The capacitance and charge–discharge efficiency were increased by 9.4–72.2 and 3.2–158.6%, respectively, depending on the methods and materials tested in this study. The charge–discharge cycle and hysteresis area were enhanced by 11.5–26.4 and 11.0–24.6%, respectively. Therefore, the annealed single-layer graphene-doped EDLC with deposited platinum and a gel electrolyte is recommended for use in electric vehicles (EVs) and advanced sensors because of its improved performance.

1. Introduction

Supercapacitors (or electrochemical supercapacitors) have attracted widespread attention and research as they are used in energy storage devices. Supercapacitors have the characteristics of

*Corresponding author: e-mail: x56784834@gmail.com
**Corresponding author: e-mail: thmeen@gs.nfu.edu.tw
https://doi.org/10.18494/SAM5112

electrolytic capacitors and batteries in terms of energy and power density. Electrochemically active materials or porous substances are used to manufacture supercapacitors that better store energy. The structure of the supercapacitor is similar to that of the electrolytic capacitor and batteries but they offer a longer cycle life, higher power and energy density, simpler charging mechanism, more rapid charge–discharge capability, and easier maintenance and operation than the electrolytic capacitor and batteries.(1–3)

Supercapacitors are categorized as electric double-layer capacitors (EDLCs) and pseudocapacitors depending on the method of storing and charging energy. In the electrodes of EDLCs, carbon-based materials are used as they have high specific surface areas. The material for the electrode must have enough sites for charge adsorption but not be chemically reactive with the electrolyte. In pseudocapacitors, on the other hand, continuous Faradaic redox reactions occur between the electrode surface and the electrolyte to store electrical energy.

In EDLCs, two materials are used to improve the structure and conductivity of electrodes: high-surface-area carbon powder and high-surface-area carbon fiber. The properties of carbon materials are decisive in determining the performance and manufacturing of EDLCs. Other key factors of the electrode material influencing EDLC performance include surface area, particle size distribution, and electrochemical stability and conductivity. Various carbon materials have been identified to meet these requirements, including porous activated carbon powder, nanocarbon fibers, carbon aerogels, carbon nanotubes, reticular activated carbon structures, and carbonization products of organic substances in polymers. Presently, porous activated carbon is predominantly used for carbonaceous electrodes. Although porous activated carbon has a large specific surface area, it has poor crystallinity, inadequate conductivity, and limitations in electron transfer during electrode transmission. Such properties lower the capacitance of the device with porous activated carbon. Moreover, it self-discharges at a high potential. Thus, it is vital to enhance the conductivity and capacitance of porous activated carbon when using it for EDLCs. Therefore, graphene has been studied extensively for EDLCs. Graphene has excellent electrical and thermal conductivitites of up to 5000 W/mK and a large surface area of 2630 m^2/g. Additionally, graphene boasts electron mobility of up to 200000 cm^2/Vs.(2,4) By using graphene, manufacturing costs can also be reduced. These characteristics make graphene an excellent material for carbon electrodes of EDLCs.

To use EDLCs as the capacitors of electric vehicles (EVs), a high energy and power density, a long cycle life, a short charge–discharge time, high reliability, and enhanced safety are mandatory along with a low manufacturing cost, as EVs require high power, fast charging, optimal operating temperature, and longer lifespan of batteries. Therefore, supercapacitors with high power density, ultrashort charge–discharge times, excellent cycle life, and high reliability are required for EVs. In EVs, other than supercapacitors, various sensors must be used to enable more functional and efficient operations. In general, sensors are placed around supercapacitors to gain the following advantages.(5,6)

1. Rapid response: Supercapacitors deliver power quickly, which requires sensors to swiftly perceive and respond to changes in the external environment.
2. Stability: Supercapacitors provide stable power output, which is monitored and controlled using stable and reliable sensors.

3. Longevity: Supercapacitors must have a long life and durability, which demands an extended lifespan of the sensor system.
4. Energy efficiency: To store and discharge high power effectively, supercapacitors must have the characteristics of fast charging, optimal operating temperature, extended lifespan, and enhanced energy-saving to prolong battery life. These are monitored using the sensor system.

The integrated supercapacitor and sensor system is also used for smart cities, intelligent transportation, health monitoring, and environmental monitoring for the efficient and reliable operation of devices and equipment. Such systems are also used in the energy supply, transportation, mobile communication, aerospace, and defense industries.[7–10]

Regarding the manufacture of supercapacitors and sensors that meet the above-mentioned requirements for diverse uses, we investigate how to fabricate the EDLC with improved overall performance in this study. We experimented with single-layer graphene and zinc oxide (ZnO) to explore which doping material improved the performance and efficiency of the EDLC. Then, we also experimented with the doped EDLC to investigate the effect of platinum deposition and gel electrolytes on the performance of the doped EDLC. Platinum deposition improved the performance of the doped EDLC by increasing the hysteresis area, while gel electrolytes enabled the doped EDLC to have a shorter time in reaching the highest potential, a longer cycle at a higher capacitance, and enhanced charge–discharge efficiency. Owing to its excellent electrochemical performance, environmental friendliness, and low cost, single-layer graphene was chosen for supercapacitors, while platinum deposition and gel electrolytes helped the single-layer graphene-doped EDLC enhance its performance significantly. The fabricated supercapacitor in this study meets the high-power requirements of EVs and can also be used in high-performance sensors for various purposes.

2. Methods

2.1 Fabrication of EDLCs

A supercapacitor consists of electrodes and an electrolyte. Platinum electrodes are usually used as current collectors since supercapacitors must store much energy and have a large surface area (at least 2630 m^2/g).[2,4] In this study, we doped single-layer graphene, acquired from wood-driven activated carbon, and ZnO to the EDLC. The pores of the activated carbon are mesoporous, reducing the resistance to ion transport. In addition, the activated carbon has high conductivity and mechanical strength, making it appropriate for fabricating single-layer graphene. The supercapacitors with the single-layer graphene-doped EDLC can have better performance than those with activated carbon or carbon-nanotube-doped EDLCs.

In the preparation of EDLCs, indium tin oxide (ITO) transparent conductive glass is commonly used. For the fabrication of EDLCs, we cut the ITO glass into sizes of 4×4 cm^2 or 5×6 cm^2 using a glass cutter. Platinum electrodes were prepared using an electron beam evaporator. The ITO glasses were cleaned to deposit carbon paste on them. Any contaminants on the ITO glass were removed before doping. To prepare the paste of single-layer graphene for doping, 1 g of wood-driven activated carbon was heated to 500 ^{o}C in a furnace for two hours.

Polyvinyl butyral (PVB) and dimethylacetamide (DMA) were mixed in the appropriate proportions as an adhesive. This adhesive was then mixed with annealed and unannealed graphenes. The graphene was annealed at 500 °C. The mixture was stirred using a magnetic stirrer for two hours. The paste of single-layer graphene was prepared by adding 20 wt% of conductive carbon slurry to DMA solvent and stirring for two hours. The paste of ZnO was prepared by combining the ZnO nanoparticles with polyvinylidene fluoride (PVDF) and N-methyl-2-pyrrolidone (NMP). The final concentration of ZnO in the paste was 20 wt%.

We used a spin coater to apply the paste to the EDLC. First, a cleaned ITO transparent conductive glass with a working area of 2.5 × 3 cm^2 was prepared. The glass was then placed on the vacuum chuck of the spin coater, and the prepared paste was dropped onto it. Then, the paste was spread on the glass. The speeds and durations of the spin coater were set to 2000 rpm for 10 s and 3000 rpm for 20 s. The glass with the paste was baked at 150 °C for 10 min in an oven to remove organic solvents. Next, the paste was applied again and baked to finish the preparation of the doped EDLC. The electrolyte of the supercapacitor was prepared using solutions of 10 wt% polyvinyl alcohol (PVA) and 6 M potassium hydroxide (KOH). Ten milliliters of each solution were mixed thoroughly until the mixed solution became transparent.

The structure of the fabricated EDLC is illustrated in Fig. 1. The electrodes were perforated using physical or chemical methods to create two holes with diameters of 1–2 mm. Then, a conductive separator (membrane) was inserted between two platinum plates. The separator was an isolation layer with 1 nm of platinum coated on each side. Subsequently, the gel electrolyte consisting of PVA mixed with 6 M PVA-KOH was injected into the interlayer of the capacitor through the holes. Once filled, the holes were sealed for encapsulation. The liquid electrolyte was a mixture of tetraethylammonium tetrafluoroborate in acetonitrile.

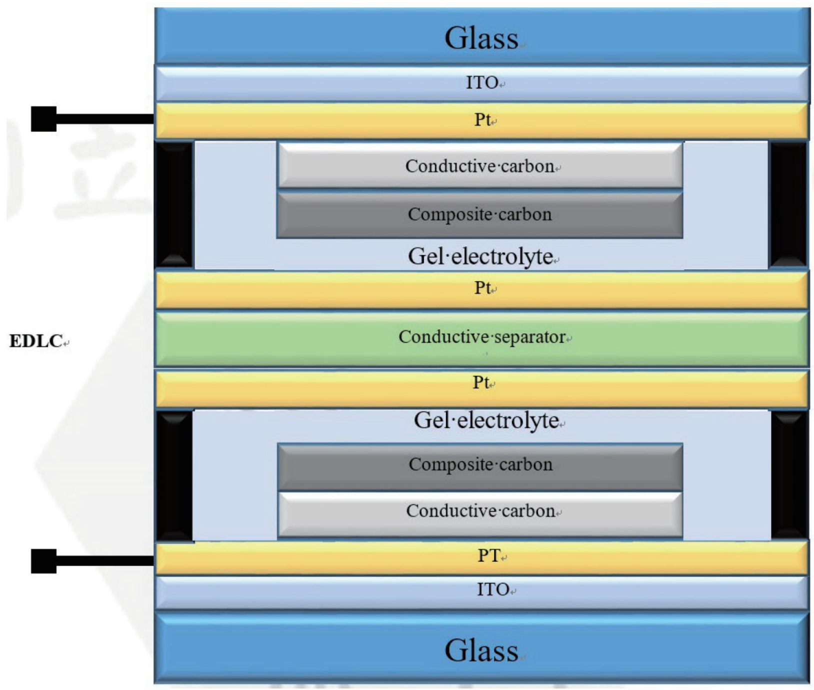

Fig. 1. (Color online) Structure of fabricated EDLC.

2.2 Measurements

Cyclic voltammetry is often used for cyclic potential scans in electrochemical experiments. In this study, we also used cyclic voltammetry to measure the potential of the doped EDLC. Using one EDLC as the working electrode and the other as a counter and reference electrode, we measured the changes in current to draw a cyclic voltammogram (CV) at a fixed voltage (±0.5 V for aqueous electrolytes) and a scan rate of 20 mV/s. The capacitance was calculated using

$$C = \frac{dQ}{dV} = \frac{1}{mv\Delta V}\int_{V_1}^{V_2} I\left(V\right)dV , \tag{1}$$

where $\int_{V_1}^{V_2} I\left(V\right)dV$ represents the area enclosed by CV between voltages V_1 and V_2 (cyclic voltammetry hysteresis area), v denotes the scan rate, ΔV represents the voltage range, and m denotes the total weight of the electrode material.

As the EDLCs are not affected by electrode potential, their cyclic voltammogram is rectangular. Pseudocapacitors usually exhibit modified rectangular shapes in CV because of their dependence on electrode potential. The shape of the CV varies depending on the capacitor. Thus, the lifetime of the EDLCs was estimated using constant-current charge–discharge cycles. The supercapacitors were charged to 0.5 V at different currents and then discharged to 0 V. The charge–discharge efficiency of the supercapacitors was calculated using

$$\eta = \frac{Q_{dch}}{Q_{ch}} \times 100\% = \frac{t_{dch}}{t_{ch}} \times 100\% , \tag{2}$$

where Q_{dch} is the discharge capacity, Q_{ch} is the charge capacity, t_{dch} is the discharge time, and t_{ch} is the charge time.

3. Results and Discussion

3.1 Effect of doping materials

The effects of doping with single-layer graphene and ZnO on EDLCs were assessed by measuring and comparing the capacitances of carbon electrodes. Figure 2 shows the cyclic voltammetry of the EDLCs doped with single-layer graphene (black line) and ZnO nanoparticles (red line) (Fig. 2). The scan range was −0.5 to 0.5 V in 1 M KOH electrolyte, and the scanning rate was 20 mV/s. The area enclosed by the CV of the single-layer graphene-doped EDLC was 2.63×10^{-2}, while that of ZnO-doped EDLCs was 5.5810^{-3}. The capacitance of the single-layer graphene-doped EDLC was 402.3 F/g, while that of the ZnO-doped EDLC was 232.44 F/g. The single-layer graphene-doped EDLC showed a larger area in CV and high capacitance, indicating better performance than the ZnO-doped EDLCs.

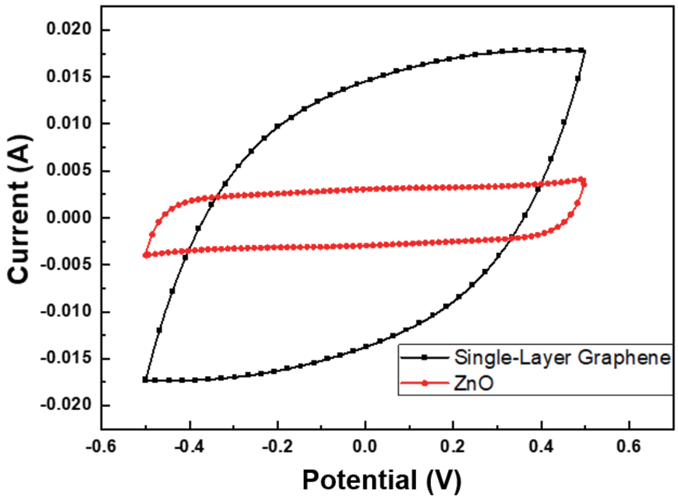

Fig. 2. (Color online) Cycling voltammetry of single-layer graphene- and ZnO-doped EDLCs.

The current charge–discharge curves of the doped EDLCs are shown in Fig. 3. The applied current was 1 mA, and the EDLCs were charged and discharged between 0 and 0.5 V. The charge–discharge efficiencies of the single-layer graphene-doped and ZnO-doped EDLCs were 83.5 and 65.8%, respectively. Therefore, single-layer graphene allowed the EDLC to have a higher charge–discharge efficiency than ZnO and enhanced the overall performance of the supercapacitor.

3.2 Effect of concentration of single-layer graphene

We investigated the effect of the concentration of the single-layer graphene doped on the EDLC. We compared the capacitance, charge–discharge efficiency, cycle, and hysteresis area of the single-layer graphene-doped EDLC at various concentrations of single-layer graphene from 0.01 to 0.07 wt%. As the doping concentration increased, all parameters improved significantly except for the charge–discharge efficiency, which increased with concentration but slightly decreased at the concentration of 0.07 wt%. Such results were attributed to the low density and large volume of graphene (Table 1). Field emission scanning electron microscopy (FE-SEM) images showed an increase in the number of wrinkles of the single-layer graphene with an increase in its doping concentration (Fig. 4). At higher concentrations, more activated carbon particles adhered to the wrinkles, and the number of wrinkles increased especially when annealed at 500 °C. The annealed single-layer graphene also exhibited a bulklike structure. The high concentration and annealing helped improve the performance of the single-layer graphene-doped EDLC.

3.3 Effect of annealing of single-layer graphene

The effect of thermal annealing of single-layer graphene on the capacitance of the EDLCs was explored in the experiment. Figure 4 shows the cyclic voltammetry curves of the doped

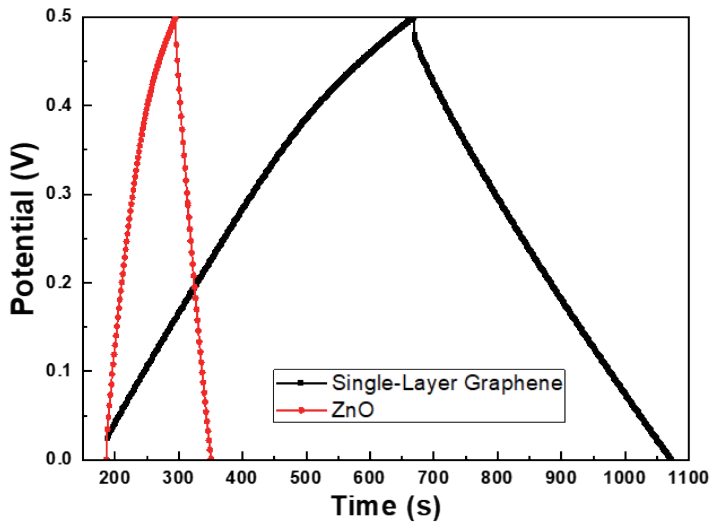

Fig. 3. (Color online) Charge–discharge curves of single-layer graphene- and ZnO-doped EDLCs.

Table 1
Analysis results of the effects of single-layer graphene doping concentration.

Concentration (wt%)	Capacitance (F/g)	Charge–discharge efficiency (%)	Cycle (s)	Hysteresis area
0.01	272.60	79.99	490.1	1.28×10^{-2}
0.03	308.15	83.03	485.2	1.63×10^{-2}
0.05	330.08	83.69	654.15	1.87×10^{-2}
0.07	402.3	83.82	888.69	2.63×10^{-2}

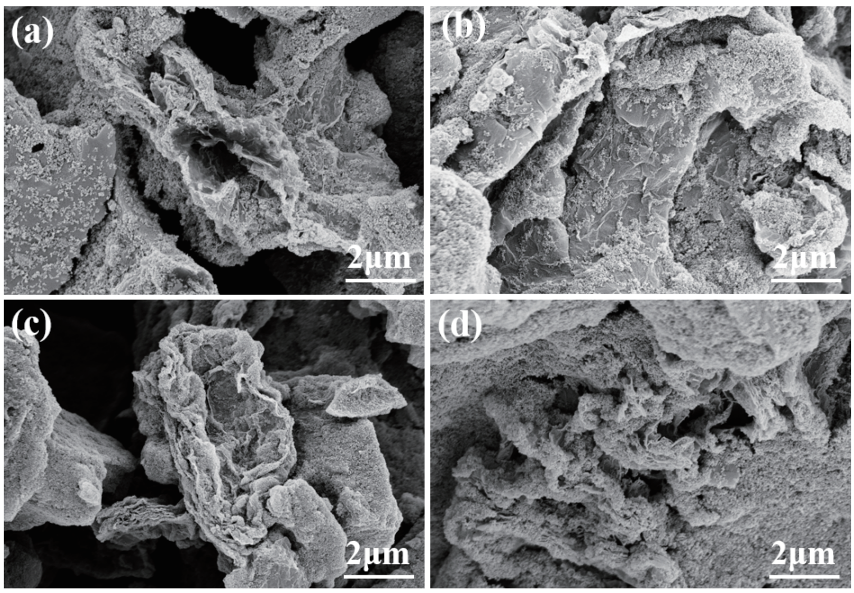

Fig. 4. (Color online) FE-SEM images of EDLCs with different concentrations of single-layer graphene doping: (a) 0.01 wt%, (b) 0.03 wt%, (c) 0.05 wt%, and (d) 0.07 wt%.

EDLCs with annealed and unannealed single-layer graphenes (black and red lines) (Fig. 5). The capacitance of the EDLCs doped with annealed single-layer graphene was 347.8 F/g, while that with nonannealed graphene was 365.8 F/g. The charge–discharge curves showed that the cycle of the EDLC doped with annealed single-layer graphene was shorter than that in the case of doping with nonannealed graphene. The charge–discharge efficiency of the EDLC doped with annealed single-layer graphene was 87.3%, while that of the EDLC with nonannealed graphene was 80.8%. The time taken to reach the maximum potential of the EDLC doped with annealed single-layer graphene was 332.4 s, while that of the EDLCs doped with nonannealed single-layer graphene was 700.7 s (Fig. 6). The results revealed that the EDLC doped with annealed single-layer graphene showed a shorter charge–discharge cycle, a shorter time to charge, and a higher charge–discharge efficiency. Such improvements were related to the effect of thermal annealing, which caused the disruption of the single-layer structure of graphene into a bulklike structure that increased resistivity but decreased conductivity. Annealing also has the effect of improving the electrical properties of graphene by removing contaminants.

3.4 Effect of platinum deposition

Platinum has high conductivity, electrochemical stability, catalytic activity, and resistance to oxidation or reduction, which effectively inhibits the oxidation and reduction of the EDLC. Thus, platinum is often used to enhance the surface area and capacitance of the EDLC. We deposited platinum of 1 nm thickness on both sides of the conductive separator of the single-layer graphene-doped EDLC and measured the effect of the platinum deposition. As a result, an increase in the hysteresis area was observed with platinum deposition (Fig. 7). Additionally, the charge–discharge efficiency and lifecycle also increased (Fig. 8). These findings indicated that platinum effectively suppressed the oxidation–reduction reactions of electrons, thereby

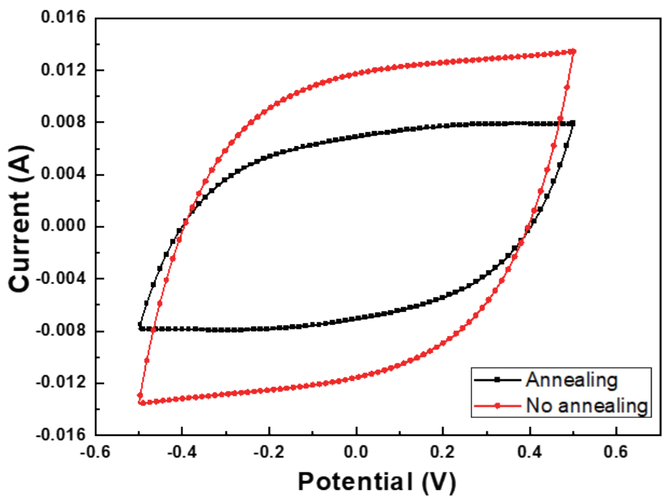

Fig. 5. (Color online) Cyclic voltammetry curves of EDLCs doped with annealed and nonannealed single-layer graphene.

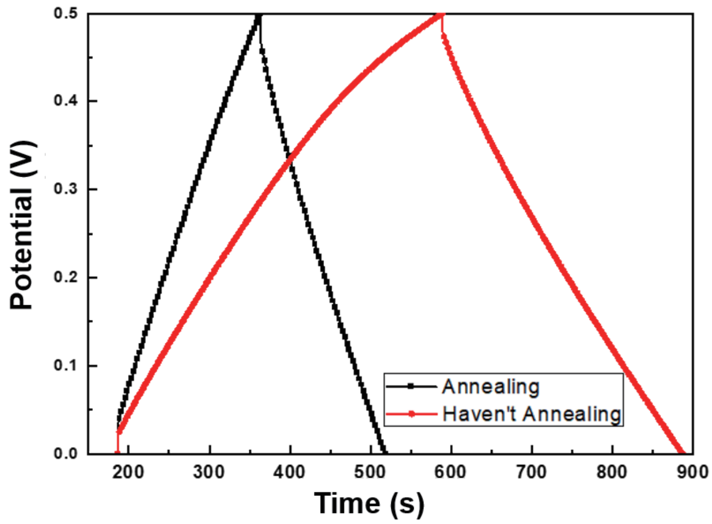

Fig. 6. (Color online) Charge–discharge curves of EDLCs doped with annealed and nonannealed single-layer graphene.

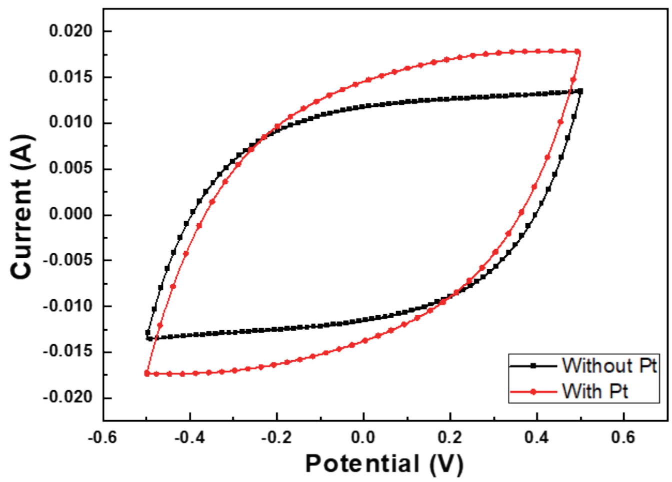

Fig. 7. (Color online) Cyclic voltammetry of single-layer graphene-doped EDLCs with and without platinum deposition on conductive separator (Pt: platinum deposition).

enhancing the efficiency of the single-layer graphene-doped EDLC. The capacitance and charge–discharge efficiency of the single-layer graphene-doped EDLC with and without platinum deposition are shown in Table 2. The single-layer graphene-doped EDLC with platinum deposition showed an improvement of capacitance by 9.4%, charge–discharge efficiency by 3.2%, charge–discharge cycle by 26.4%, and hysteresis area by 24.6%. Such results indicated that platinum deposition considerably enhanced the performance of the single-layer graphene-doped EDLC.

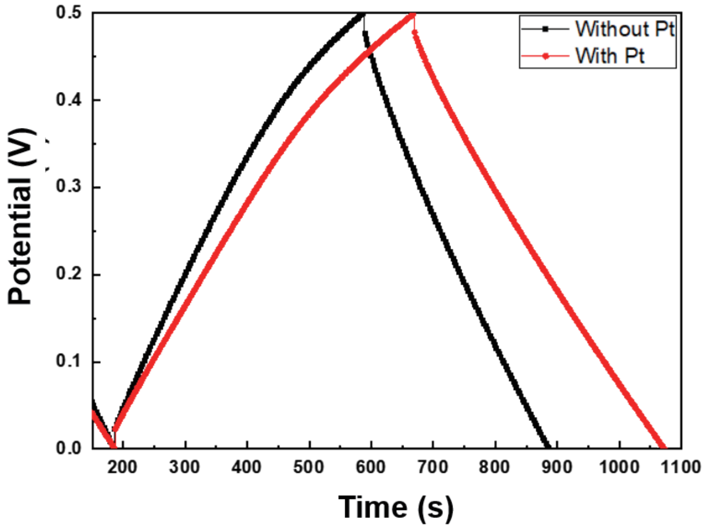

Fig. 8. (Color online) Charge–discharge curves of single-layer graphene-doped EDLCs with and without platinum deposition on conductive separator (Pt: platinum deposition).

Table 2
Capacitance and charge–discharge efficiency of the single-layer graphene-doped EDLCs with and without platinum deposition.

EDLC	Capacitance (F/g)	Charge–discharge efficiency (%)	Cycle (s)	Hysteresis area
No platinum deposition	365.79	80.81	700.7	2.03×10^{-2}
Platinum deposition	402.3	83.82	888.69	2.63×10^{-2}

3.5 Effect of gel electrolyte

The gel electrolyte possesses liquid and solid characteristics at the same time. While it maintains a solidlike structure, it facilitates the ion conduction of liquid electrolytes. Compared with the liquid electrolyte, the gel electrolyte exhibits significantly higher resistance. Thus, it is difficult for the gel electrolyte to gain electrons from platinum counter electrodes, leading to reduced electron transfer rates. We measured a charge–discharge cycle of the single-layer graphene-doped EDLC with gel and liquid electrolytes (Fig. 9). The electrolytes of 6 M KOH in liquid and gel forms at a concentration of 10 wt% were used in the experiment. The hysteresis area of the single-layer graphene-doped EDLC with gel electrolyte reached the maximum potential in less than 700 s, while that with liquid electrolyte required longer than 800 s. After 1,000 s, the operating temperature of the single-layer graphene-doped EDLC with the gel and liquid electrolytes increased. However, the evaporation of liquid electrolyte cannot be prevented, and the single-layer graphene-doped EDLC with liquid electrolyte showed fast discharge and decreased efficiency (Table 3). When using the gel electrolyte, the capacitance of the single-layer graphene-doped EDLC increased by 10.8% compared with that in the case using the liquid electrolyte. The charge–discharge efficiency, charge–discharge cycle, and hysteresis area were enhanced by 158.6, 11.5, and 11.0%, respectively.

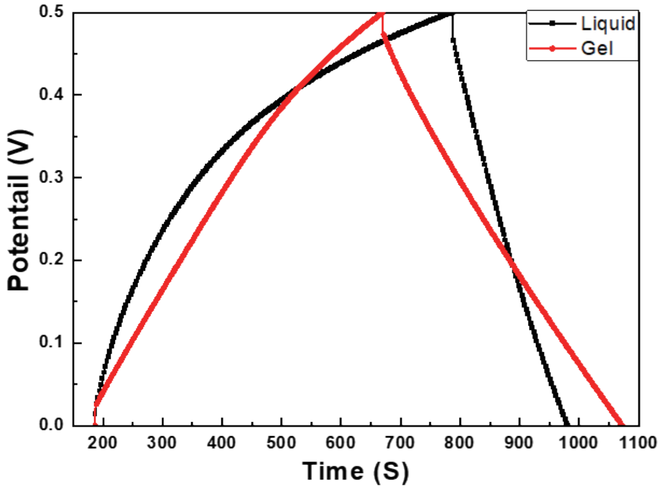

Fig. 9. (Color online) Charge–discharge curves of single-layer graphene-doped EDLCs using gel and liquid electrolytes.

Table 3
Capacitance and charge-discharge efficiency of single-layer graphene-doped EDLCs with gel and liquid electrolytes.

Electrolyte	Capacitance (F/g)	Charge–discharge efficiency (%)	Cycle (s)	Hysteresis area
Liquid	361.23	32.26	794.1	2.28×10^{-2}
Gel	402.3	83.82	888.69	2.63×10^{-2}

4. Conclusions

To fabricate an EDLC with improved performance, we evaluated the performance of the EDLCs with different doping materials (single-layer graphene and ZnO) and various doping concentrations of single-layer graphene. Single-layer graphene EDLCs fabricated by different annealing and platinum deposition methods and with different electrolytes were investigated to determine the appropriate compositions and methods for fabricating the optimal EDLC. The performance was evaluated by measuring the capacitance, charge–discharge efficiency, charge–discharge cycle, and the hysteresis area of CV. The results showed that single-layer graphene doping improved the performance of the EDLC more than ZnO doping, and the appropriate doping concentration of single-layer graphene was found to be 0.07 wt%. Single-layer graphene doping enabled the capacitance and charge–discharge efficiency of the EDLC to be improved by 72.2 and 26.8%, respectively, compared with ZnO doping. When the EDLC was doped with annealed single-layer graphene, its capacitance and charge–discharge cycle were improved by 5.2 and 110.8%, respectively, compared with the EDLC doped with unannealed single-layer graphene. The single-layer graphene-doped EDLC with platinum deposition showed improvements of capacitance, charge–discharge efficiency, charge–discharge cycle, and hysteresis area by 9.4, 3.2, 26.4, and 24.6%, respectively, compared with the EDLC without platinum. Finally, the single-layer graphene-doped EDLC with the gel electrolyte had parameters enhanced by 10.8, 158.6, 11.5, and 11.0%, respectively, compared with the single-layer graphene-doped EDLC with the liquid electrolyte. Such results provide an important reference for the manufacture of EDLCs with improved performance, which can be used as supercapacitors for EVs and advanced sensors.

References

1 L. L. Zhang and X. Zhao: Chem. Soc. Rev. **38** (2009) 2520. https://doi.org/10.1039/B813846J
2 C. Liu, Z, Yu, D. Neff, A. Zhamu, and B. Z. Jang: Nano Lett. **10** (2010) 4863. https://doi.org/10.1021/nl102661q
3 H. Peng: Fiber-shaped integrated device, Fiber-Shaped Energy Harvesting and Storage Devices (Springer, Berlin Heidelberg, 2015) 179–197. https://doi.org/10.1007/978-3-662-45744-3
4 D. A. Brownson, D. K. Kampouris, and C. E. Banks: Chem. Soc. Rev. **41** (2012) 6944. https://doi.org/10.1039/C2CS35105F
5 B. Tawiah, R. K. Seidu, B. K. Asinyo, and B. Fei: J. Power Sources **595** (2024) 234069. https://doi.org/10.1016/j.jpowsour.2024.234069
6 H. Sheng, Y. Ma, H. Zhang, J. Yuan, F. Li, W. Li, E. Xie, and W. Lan: Adv. Mater. Technol. **9** (2024) 2301796. https://doi.org/10.1002/admt.202301796
7 Q. Huang, Y. Yang, R. Chen, and X. Wang: EcoMat. **3** (2021) e12076. https://doi.org/10.1002/eom2.12076
8 M. Yaseen, M. A. K. Khattak, M. Humayun, M. Usman, S. S. Shah, S. Bibi, B. S. U. Hasnain, S. M. Ahmad, A. Khan, N. Shah, A. A. Tahir, and H. Ullah: Energies **14** (2021) 7779. https://doi.org/10.3390/en14227779
9 M. E. Sahin, F. Blaabjerg, and A. Sangwongwanich: Energies **15** (2022) 674. https://doi.org/10.3390/en15030674
10 M. Czagany, S. Hompoth, A. K. Keshri, N. Pandit, I. Galambos, Z. Gacsi, and P. Baumli: Materials **17** (2024) 702. https://doi.org/10.3390/ma1703070