CVD-graphene for low equivalent series resistance in rGO/CVD-graphene/Ni-based supercapacitors

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Abstract
Reduced equivalent series resistance (ESR) is necessary, particularly at a high current density, for high performance supercapacitors, and the interface resistance between the current collector and electrode material is one of the main components of ESR. In this report, we have optimized chemical vapor deposition-grown graphene (CVD-G) on a current collector (Ni-foil) using reduced graphene oxide as an active electrode material to fabricate an electric double layer capacitor with reduced ESR. The CVD-G was grown at different cooling rates—20 °C min−1, 40 °C min−1 and 100 °C min−1—to determine the optimum conditions. The lowest ESR, 0.38 Ω, was obtained for a cell with a 100 °C min−1 cooling rate, while the sample without a CVD-G interlayer exhibited 0.80 Ω. The CVD-G interlayer-based supercapacitors exhibited fast CD characteristics with high scan rates up to 10 V s−1 due to low ESR. The specific capacitances deposited with CVD-G were in the range of 145.6 F g−1–213.8 F g−1 at a voltage scan rate of 0.05 V s−1. A quasi-rectangular behavior was observed in the cyclic voltammetry curves, even at very high scan rates of 50 and 100 V s−1, for the cell with optimized CVD-G at higher cooling rates, i.e. 100 °C min−1.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction

Rapid developments in electronic devices in modern society demand fast energy storage and stabilized cycling devices, which can charge rapidly and retain energy over longer periods of time. To meet these conditions, electric double layer capacitors (EDLC), popularly known as supercapacitors or ultracapacitors, store the charge in the form of an electric double layer (EDL) by the adsorption of electrolyte ions on high surface area electrodes with ultra-small separation [1]. Carbon-based materials, for example, activated carbon, carbon nanotubes, carbon fibers, carbon aerogel, and graphene, have a high surface area in addition to other unique properties [2–7]. Among these materials, graphene is an obvious choice as an electrode material due to its distinguishing properties, such as high conductivity, high charge mobility, high

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strength, and a large surface area. Graphene has a surface area of 2630 m$^2$ g$^{-1}$ and an electrical conductivity of 200–3000 s cm$^{-1}$ [8]. As single layer graphene exhibits an intrinsic EDLC capacitance [9] of $\sim$21 $\mu$Fcm$^{-2}$ for the graphene surface, its specific capacitance is estimated to be 550 F g$^{-1}$ if the EDL covers the complete surface of the graphene [9]. On the other hand, reduced graphene oxide (rGO) has also attracted attention as a supercapacitor electrode material because of its low cost mass productivity and excellent electrochemical stability. High specific capacitance is the main focus in supercapacitor-related research, and many reports are available with high specific capacitance using graphene or rGO as an electrode or active material. Yang et al reported that self-stacked multilayered graphene films on an electrode material have a high specific capacitance of 156.5 F g$^{-1}$ at a high current density of 1080 A g$^{-1}$ [10]. Chen et al reported that graphene hydrogels were deposited on nickel (Ni) foam as an electrode material, where the Ni framework shortened the distances of the charge transfer. The electrochemical capacitor exhibited a fast charging/discharging performance at a current density of 50 mAcm$^{-2}$ due to low equivalent series resistance (ESR) $\sim$ 0.9 $\Omega$ [11]. Chen et al reported the specific capacitance of graphene layers, grown via the CVD method on Ni foam, at various cooling rates. The highest specific capacitance was 55.3 F g$^{-1}$ at a slow scan rate of 5 mV s$^{-1}$ with an ESR of $\sim$0.75 $\Omega$ [12]. Wang et al studied the specific capacitance of rGO via gas-based hydrazine reduction to restore the conducting carbon network. They achieved a specific capacitance of 205 F g$^{-1}$ at 1 A g$^{-1}$ with a power density of 10 kW kg$^{-1}$ and an energy density of 28.5 Wh kg$^{-1}$ in an aqueous electrolyte solution, and the lowest ESR was 0.23 $\Omega$ [13]. Bai et al studied the effect of the pH of hydrothermal rGO on supercapacitor performance. The specific capacitance obtained was 230 F g$^{-1}$ at a current density of 1 A g$^{-1}$ at neutral pH, and the reported ESR was $\sim$0.4 $\Omega$ for various pH values [14]. Xu et al studied 3D graphene hydrogel films as an electrode active material with a specific capacitance of 186 F g$^{-1}$ or an areal capacitance of 372 mF cm$^{-2}$ at a current density of 1 A g$^{-1}$, and a high retention of capacitance up to 10 000 charge/discharge (CD) cycles at a current density of 10 A g$^{-1}$, and an ESR greater than 3 $\Omega$ was obtained [15]. Kim et al reported out-of-plane CNTs on graphene as an electrode material with an areal capacitance of 653.7 $\mu$Fcm$^{-2}$ at 10 mV s$^{-1}$, but the ESR was not reported [16]. Jha et al reported a single walled CNT-rGO (1:1) hybrid supercapacitor with a specific capacitance of 222 F g$^{-1}$, an energy density of 94 Wh kg$^{-1}$ at a scan rate of 10 mV s$^{-1}$, and a constant cyclic stability of 1000 cycles at 1 A g$^{-1}$ [17].

All these reports exhibited good capacitance exploiting the high surface area of rGO. However, various other factors contribute to the high performance of graphene-based supercapacitors. These factors include the number of graphene layers, conditions for synthesizing graphene, ESR, the separator, the current collector, and the electrolyte. Among these, the ESR factor is less focused, although it is an important factor in determining the power density of a supercapacitor as high resistance results in low current and undesirable heating during the CD processes. The ESR can be lowered by mitigating the contact resistance between the active electrode material and the current collector. The high conductivity of graphene can be exploited as a contact layer between the active material and current collector to reduce the contact resistance. Recently, it was reported that graphene can reduce the interface resistance between the active material and the current collector [18]. It has been found that the interface resistance can be reduced to as low as 0.93 $\Omega$ using vertically-grown graphene between rGO film as an active material and Ni foam as a current collector [18]. Although the specific capacitance value was 156 F g$^{-1}$ at a current density of 100 A g$^{-1}$, the reported ESR value was large, and there is scope for reducing the ESR.

In this study, CVD-grown graphene (CVD-G) on Ni-foil has been adapted as an interface contact layer between the current collector, Ni-foil, and active electrode material, rGO. CVD-G has been grown at various cooling rates to control the interface resistance leading to a decrease in the overall ESR. The resulting supercapacitors have a fast CD time, quasi-rectangular behavior in the cyclic voltammetry (CV) curves, and a high cycling stability at scan rates of up to 100 V s$^{-1}$.

2. Materials and methods

Graphene was grown on Ni-foil at different cooling rates (20 °C min$^{-1}$, 40 °C min$^{-1}$ and 100 °C min$^{-1}$, abbreviated as CVD-G20, CVD-G40 and CVD-G100, respectively) using the CVD method. The detailed process is discussed in section 1 of the supplementary material (available online at stacks.iop.org/NANO/29/195404/mmedia (figure S1)). The rGO, used as an active electrode material, was obtained by the reduction of graphene oxide (GO) using hydrazine (the reduction details are provided in section 2 of the supplementary material). The rGO obtained can clearly be distinguished by a visual change in the colors of GO and rGO.

3. Electrode cell fabrication

The dispersed rGO was spray-coated onto the surface of the CVD-G deposited Ni-foil (figure S2(e) of the supplementary material), which was fixed on a hot plate at a temperature of 80 °C. The nozzle diameter of the airbrush used was 0.2 mm and the inlet pressure of the nitrogen gas was 2 bar. The mass of the coated rGO on both electrodes was found to be $\sim$0.13–0.18 mg for a sample area of 4 $\times$ 3 cm$^2$. As the CVD-grown graphene films are very thin, they have negligible mass. These film-type cells were assembled into a layered two-electrode system, separated by a glass fiber filter paper with a thickness of 675 $\mu$m (Whatman 1821-025 grade GF/B) soaked with a 6 M KOH electrolyte. A schematic of the symmetric capacitor with two electrodes is shown in figure S3 of the supplementary material.
4. Characterizations

Raman spectroscopy was used to determine the graphene layers and intensity ratio ($I_{2D}/I_G$) of the 2D and G bands. The surface area analysis of the active electrode material was performed by Brunauer–Emmett–Teller analysis at a scanning speed of 5 °C min⁻¹, and the specific area was 366.88 m² g⁻¹ (see figure S2(f) of the supplementary material). The electrochemical characteristics of the cells were analyzed using CV (voltage window 0–1 V), galvanostatic CD (voltage window 0–1 V) and electrochemical impedance spectroscopy (SP-150 potentiostat) at room temperature in the frequency range of 0.1 Hz–100 kHz with an ac amplitude of 5 mV.

5. Structure and morphology

Field emission scanning electron microscopy (FE-SEM, HITACHI S-4700) was used to analyze the surface morphology of the graphene. The FE-SEM images of the CVD-G on Ni-foil at various cooling rates are shown in figures 1(a)–(f), implying that the graphene surface morphology depends on the cooling rate. The surface roughness (coarseness) and the wrinkle distribution vary at the different cooling rates. For CVD-G20 (figures 1(a), (d)), the graphene film formed uniformly on the Ni plane with few wrinkles.

On the other hand, at fast cooling rates, the roughness of the surface increases. The grown graphene wrinkles have certain pores on the surface, as indicated by arrows. With an increase in the cooling rate, the number of wrinkles and their size also increase [12]. The size of these wrinkles at cooling rates of 20 °C min⁻¹, 40 °C min⁻¹ and 100 °C min⁻¹ is approximately 300, 500, and 700 nm, respectively. The formation of the graphene wrinkles is mainly attributed to the different thermal expansion coefficients of the Ni-foil and graphene [19–22], which leads to compressive stress within the graphene layers, resulting in the formation of wrinkles to release stress. In particular, many graphene layer crusts in CVD-G100 were separated from the substrate. This means that as the solubility of the carbon atoms dissolved in the Ni-foil rapidly decreases with fast cooling, the atoms are segregated and rapidly spurt from the Ni surface, forming an irregular shape. On the other hand, in the slow cooling process, the carbon atoms are extruded slowly, forming a flat surface.

6. Raman spectroscopy

Representative Raman spectra of CVD-G on Ni-foil at cooling rates of 20 °C min⁻¹, 40 °C min⁻¹ and 100 °C min⁻¹ are shown in figures 1(g)–(i), respectively. The Raman spectrum indicates the number of layers and defect states of graphene. The disorder-induced D-band (around 1350 cm⁻¹) peaks are very weak, indicating that high quality CVD-G formed on the Ni substrate. As the cooling rate increased, the peak position of the 2D band (around 2710 cm⁻¹) was blue-shifted and the peak shape gradually broadened, indicating that the number of graphene layers increased [12]. In addition, the intensity ratio of the 2D and G bands ($I_{2D}/I_G$) gradually decreased as the cooling rate increased, indicating that thicker graphene was grown, as shown in figure 1(j). The relationship between the cooling rate and the thickness of the CVD-G is a controversial issue. Some previous reports have suggested that the number of graphene layers increases with the cooling rate [12, 19, 23]. However, some other reports insist on an opposite trend, i.e. the number of graphene layers decreases as the cooling rate is increased, suppressing the non-equilibrium precipitation process [21, 24, 25]. Our observations are in agreement with the former. The Raman spectra of the GO and rGO were also analyzed (figures S2(c), (d)). The GO peak (1588.3 cm⁻¹) in the G-band shifted upward compared to the graphite peak (1580 cm⁻¹). This may be ascribed to the presence of an isolated double bond that resonates at a higher frequency than the G-band of graphite [26, 27]. The G-band of the rGO appears at 1581.3 cm⁻¹, which corresponds to the recovery of the hexagonal network of defective carbon atoms [26].

7. Electrochemical characteristics of supercapacitors

7.1. CV analysis

The electrochemical characteristics of the CVD-G-based supercapacitors were studied using CV. The CV curves of CVD-G20, CVD-G40, and CVD-G100-based cells at various scan rates (0.05, 1, 2 and 10 Vs⁻¹) are shown in figures 2(a)–(d). For comparison, the data of the rGO-based cell without CVD-G (abbreviated as no-CVD) are shown together. All the curves exhibit nearly rectangular shapes, indicating ideal supercapacitor behavior at high scan rates of up to 10 Vs⁻¹, without chemical reaction.

At the scan rate of 10 Vs⁻¹, as shown in figure 2(d), the CV curve shape of the no-CVD sample was distorted, while the samples with CVD-G20, CVD-G40, and CVD-G100 maintained rectangular shapes. The specific capacitance was calculated using the following equation:

$$C = \frac{\int_0^\nu IdV}{\nuVm}$$

where, $I$ is the current, $\nu$ is the scan rate, $V$ is the voltage window, $m$ is the mass of the active electrode material (rGO), and $V_1$ and $V_f$ are initial and final voltages, respectively. The specific capacitances calculated from the CV curves for no-CVD, CVD-G20, CVD-G40, and CVD-G100 cells are 144.8 F g⁻¹, 154.30 F g⁻¹, 213.8 F g⁻¹, and 145.6 F g⁻¹ at a scan rate of 0.05 Vs⁻¹, and 48.23 F g⁻¹, 102.03 F g⁻¹, 143.28 F g⁻¹, and 104.20 F g⁻¹ at 10 Vs⁻¹, respectively. It was observed that the capacitances of the CVD-G electrode-based cells are larger than that of the no-CVD cell. The variation of the measured capacitance among the CVD-G cells is ascribed to an experimental error due to the small quantity of the rGO. The increase in capacitance in the
CVD-G-based electrode cells can be attributed to two factors: (1) the increased surface area introduced by wrinkles and pores on the CVD-G surface, and (2) the facilitated charge transport with the introduction of graphene film on the Ni-foil. Considering that the surface area of CVD-G (∼24 cm²) is much smaller than that of rGO (∼659 cm²), the effect of the surface area increment may not be the main reason. Instead of that, the connectivity between the Ni and rGO is important, and charge transport can be facilitated by means of CVD-G. The effect of the facilitated charge transfer is negligible at low scan rates, but it significantly affects the capacitance at higher scan rates. As can be seen from figure 2(e), the capacitance decrement rate is faster for the no-CVD sample as compared to the CVD-G electrode cells, which supports the fact that, with the introduction of graphene layers, the contact resistance is reduced and the capacitance retention is greater. As the scan rate increases from 0.05 V s⁻¹ to 10 V⁻¹, the specific capacitance decrement is 66.6%, 33.8%, 32.9% and 28.4% for no-CVD, CVD-G20, CVD-40 and CVD-100-based electrode cells, respectively. It means that CVD-G100 electrodes...
have maximum stability at a high scan rate, which indicates that the surface of CVD-G100 supports faster electron charge transfer. The CV characteristics of CVD-G100 electrodes were further examined at ultra-high rates, and the electrodes maintained a quasi-rectangular shape, even at a rate of 100 \( \text{Vs}^{-1} \), as shown in figure 2(f), indicating excellent charge transportation at the interface between the current collector and the active layer. This fact is also supported by the lowest IR drop in CVD-G100-based electrodes, as will be discussed later. On the other hand, it was confirmed that the contribution of a Ni substrate to the capacitance was negligible, judging from a test sample with bare Ni substrates.

7.2. Charge/discharge studies

Figures 3(a)–(c) show the CD curves of all the working electrodes at 10, 500, and 1000 \( A \text{g}^{-1} \), respectively. The curves show a very linear and symmetrical shape at a relatively low current density of 10 \( A \text{g}^{-1} \) with a negligible voltage drop for all electrodes. However, as the current density increases to 500 and 1000 \( A \text{g}^{-1} \), the IR drop is found to
increase (figure 3(d)). The IR drop for CVD-G-based electrodes is very small compared to the no-CVD electrode, suggesting that supercapacitors based on CVD-G electrodes can be charged/discharged in a few seconds due to low resistance at the interface of rGO and Ni-foil. The IR drop is approximately proportional to the ESR of the cell [18, 28]. The IR drop was $\sim$0.4 V for the no-CVD electrode, whereas for the CVD-G electrodes, the maximum IR drop was less than 0.1 V at a higher current density of 1000 Ag$^{-1}$. It can be seen that even at high current densities, the CVD-G100 exhibits excellent CD reversibility as it has linear and symmetrical triangular shapes with a low IR drop ($\sim$0.075 V). The low IR drop implies that the roughness of the graphene in the CVD-G100-based electrode facilitates the charge transport between rGO and Ni-foil due to the increased multiple edge contact points, as shown in the schematic in 3(e). It is known that the edge contact has lower resistance than the surface contact in graphene-based devices [29]. The roughness of the graphene with sharp-edged wrinkles, as indicated in the FE-SEM images, acts as a bridge between the rGO and Ni-foil, facilitating charge transport and leading to a reduced IR drop. It has been previously reported that vertically-aligned graphene favors charge transport due to multiple contacts between the current collector and the active electrode material [18]. It was also stated in an earlier report that the wrinkles offer fast electrical paths and a short ion diffusing path [30].

7.3. Electrochemical impedance spectroscopy (EIS) measurements

The resistance at the interface of rGO and Ni-foil was estimated using EIS measurements performed with a 5 mV sinusoidal signal in the frequency range of 0.1 Hz–100 kHz. A Nyquist impedance plot exhibiting the imaginary component of impedance ($Z''$) with respect to the real component of impedance ($Z'$) at the high frequency region is shown in figure 4(a). A typical equivalent circuit is depicted, as shown in figure 4(b), where $R_s$ is the series resistance, $R_{ct}$ is the ion charge transfer resistance, $C_e$ is the interfacial contact capacitance, and $C_{DL}$ is the double layer capacitance. The plots of the CVD-G electrodes show nearly vertical curves with small intercepts on the x-axis, indicating excellent capacitive behavior [11, 12]. The ESR values of all electrodes, determined by intercepts at the real axis in the Nyquist plots [13, 18], are 0.38, 0.40, 0.48, and 0.80 $\Omega$ for CVD-G100,
CVD-G40, CVD-G20, and no-CVD electrodes, respectively, which corresponds with the IR drop results observed in the CD curves. While the data for the CVD-G electrodes is almost a straight line, a semicircle at high frequencies can be seen clearly in the no-CVD electrode, indicating a high charge transfer resistance [13]. Our result contrasts with the earlier report by Chen et al [12], which showed that CVD-G with a lower cooling rate had a lower charge-transfer resistance and improved the CD efficiency of supercapacitors. However, their sample was based on the CVD-G as an active material with Ni foam as an electrode without rGO, and the value of the ESR was in the range of 0.75–0.95 Ω, which is similar to the value for our no-CVD sample. As the Ni foam has a micro porous structure, there may be many bottlenecks for the charges to move through compared with the Ni-foil.

Figure 4(c) shows the phase response of the frequency for different working electrodes. The CVD-G100-based electrode shows a flat plateau region with a ~90° phase at the lowest frequency, indicating a typical capacitive character [18, 31]. While CVD-G20 and CVD-G40 have similar plateaus, the no-CVD electrode has a short and lower plateau region at a phase angle of ~80°. In the intermediate frequency range, the CVD-G-based cells have a wider band as compared to the no-CVD cell, which again supports the fact that CVD-G significantly reduces the charge-transfer resistance.

Figure 4(d) shows the change in the specific capacitance with the number of cycles of the CVD-G100 supercapacitor at a scan rate of 100 mVs⁻¹. The capacitance remained at 98.8%, even after 3000 tests. This shows that the supercapacitors of the CVD-G100-based electrodes have excellent stability, lifetime and a very high level of reversibility in repeated scan cycles.

8. Conclusions

Graphene was directly grown on Ni-foil using the CVD method at various cooling rates to control the interface resistance between the active electrode material, rGO, and the current collector, Ni-foil. It was observed that a faster cooling rate gives a lower ESR (0.38 Ω) with low IR drops. The resulting cells have a high specific capacitance, fast CD time, and quasi-rectangular behavior in CV curves at high scan rates up to 100 V s⁻¹. As the scan rate increases from 0.05 V s⁻¹ to 10 V⁻¹, the specific capacitance retention decrement is 66.6%, 33.8%, 32.9% and 28.4% for no-CVD, CVD-G20, CVD-40 and CVD-100-based electrode cells, respectively. It indicates that the surface of CVD-G100 supports faster electron charge transfer, even at higher scan rates. The CVD-G100 electrode also exhibited better capacitance retention abilities (~99%) after 3000 cycles at a scan rate of 100 mVs⁻¹, which was again corroborated with reduced contact resistance due to multiple contact points between rGO and Ni-foil. Furthermore, CVD-G100-based electrodes also maintained quasi-rectangular behavior, even at a scan rate of 100 V s⁻¹. These electrodes can be very useful in high performance devices working at faster scan rates.

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