Oxygen functional groups and electrochemical capacitive behavior of incompletely reduced graphene oxides as a thin-film electrode of supercapacitor

Young Joon Oh a, b, Jung Joon Yoo a, Yong Il Kim a, Jae Kook Yoon a, Ha Na Yoon a, Jong-Huy Kim a, *, Seung Bin Park b, 1

a Energy Storage Department, Korea Institute of Energy Research (KIER), #152 Gajeong-ro, Yuseong-gu, Daejeon, 305-343, Republic of Korea
b Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), #291 Daehak-ro, Yuseong-gu, Daejeon, 305-701, Republic of Korea

A R T I C L E   I N F O
Article history:
Received 6 August 2013
Received in revised form 6 November 2013
Accepted 6 November 2013
Available online 20 November 2013

Keywords:
Oxygen functional groups
Reduced graphene oxide
Thin-film electrode
Pseudocapacitance
Supercapacitor

A B S T R A C T
For incompletely reduced graphene oxides (RGOs), an effect of oxygen functional groups such as carboxyl, phenol, carbonyl, and quinone on electrochemical capacitive behavior was studied. To prepare RGO thin-film electrodes, a simple fabrication process by (i) dropping and evaporating the graphene oxide (GO) solution, (ii) irradiating pulsed light, and (iii) heat-treating at 200 ~ 360 °C was applied. It was notable that the pulsed light irradiation was effective to prevent the disfiguring of deposited GO thin-film during the thermal reduction. From XRD analyses, interlayer distances of the RGOs were gradually decreased from 0.379 to 0.354 nm. As increasing the thermal reduction temperature from 200 to 360 °C, XPS O 1s spectra analyses showed that the atomic percentages of carboxyl and phenol of the RGOs were sustained as 5.40 ± 0.36 and 4.77 ± 0.41 at% respectively. Meanwhile, those of carbonyl and quinone of the RGOs were gradually declined from 3.10 to 1.81 and from 1.32 to 0.65 at% with different thermal reduction temperature respectively. For all RGO thin-film electrodes, the specific capacitance from the CV measurement in 6 M KOH was sustained as ca. 220 F g⁻¹ at the scan of 5 mV s⁻¹. However, in 1 M H₂SO₄, the specific capacitance was gradually decreased from 171 to 136 F g⁻¹. After 100,000 cycles in 6 M KOH, 1 M H₂SO₄, and 0.5 M Na₂SO₄, the RGO (200 °C) electrodes showed ca. 92, 54, and 104% of the initial capacitances respectively. The atomic percentages of the oxygen functional groups involved in the pseudocapacitive Faradaic reaction were decreased after the cycle test. Especially in 1 M H₂SO₄, quinone group was decreased to ca. 48% of initial atomic percentage, which seems to be a main reason for the drastic reduction of capacitance. The specific pseudocapacitance per unit atomic percentage for either carboxyl or phenol group in 6 M KOH was obtained as 12.59 F g⁻¹ at%. For carbonyl group in 1 M H₂SO₄, it was a slightly deviated value as 13.55 F g⁻¹ at%. For quinone group in 1 M H₂SO₄, it was 27.09 F g⁻¹ at%.

1. Introduction
Comparing with the secondary battery, the supercapacitor has some distinctive and advantageous performances such as high power density, excellent charge-discharge cycle, and environmentally friendliness. The supercapacitor is classified into an electric double layer capacitor (EDLC) and a pseudocapacitor. Charge storage mechanism of the EDLC is based on the electrostatic adsorption of charge separated ions on the surface of an electrode material.

As electrode materials for the EDLC, carbon-based materials such as activated carbon, carbon nanotube, carbon aerogel, and carbon fiber are used in general. For the pseudocapacitor, it is based on very fast and fully reversible Faradaic redox reactions at the interface between the electrode and electrolyte. As electrode materials for the pseudocapacitor, some metal oxides (e.g. MnO₂, NiO, RuO₂) and conductive polymers (e.g. polyaniline, polypyrrole) are used.

In recent years, the graphene has been emerged as one of attractive electrode materials for supercapacitors. The graphene, defined strictly, is one atom-thick layered crystalline with honeycomb structure of sp²-bonded carbon. Because of its excellent physical properties such as extremely large surface area (2,630 m² g⁻¹) [1], electrical conductivity (~10^6 S cm⁻²) [2], thermal conductivity (~5,000 W m⁻¹ K⁻¹) [3], Young’s modulus (E = 1.0 ± 0.1 TPa) [4], and optical transmittance (~97.7%) [5], the graphene has been widely...
studied for applications to sensor [6–8], transistor [9–11], semiconductor [12,13], transparent conductive electrode [14–16], and lithium-ion battery [17–19].

By using the outstanding characteristic of the graphene, lots of researches on the graphene for supercapacitor electrodes are being conducted. It is announced that the electric double layer capacitance per unit specific surface area can be up to ca. 21 μF cm⁻² and so a maximum specific capacitance can be ca. 550 F g⁻¹ when the surface area of a graphene is 2.675 m² g⁻¹ [20]. However, it is not practical to use such a high specific surface area of monolayered graphene powder for the supercapacitor electrode. In general, graphene powders which were produced from a chemical or a thermal reduction process of oxidized graphites do not have a monolayered- but a multilayered-graphene morphology because of restacking graphene layers during the reduction process. When the reduced graphene oxide (RGO) is not completely reduced, the RGO contains some oxygen functional groups. Here, it is presumable that the RGO with oxygen functional groups may have not only an electric double layer capacitance but also a pseudocapacitance [21–23]. For instance, a prominent redox peak is usually observed in the cycle voltammetry (CV) of the RGO electrode in H₂SO₄ electrolyte. It is known that quinone groups of the RGO are responsible for the pseudocapacitive Faradaic redox reaction in H₂SO₄ electrolyte [24,25]. However it is not enough to understand the electrochemical capacitive behavior of the RGO containing other oxygen functional groups in alkaline electrolytes.

In this study, we intended to understand what and how the oxygen functional group of the RGO affects electrochemical capacitive behavior. For this purpose, a new method to fabricate the RGO thin-film electrode was developed at first. The method is simple and effective to prepare the RGO thin-film electrode and to control oxygen functional groups quantitatively. Aqueous solutions of 6 M KOH, 1 M H₂SO₄, and 0.5 M Na₂SO₄ were used as alkaline, acidic, and neutral electrolytes so as to investigate some differences of electrochemical capacitive behavior caused by oxygen functional groups.

2. Experimental

2.1. Synthesis of the graphene oxide (GO)

The GO was prepared by a modified Hummers method. 12.0 g of graphite powder (< 20 μm, Sigma-Aldrich), 10.0 g of K₂S₂O₃ (> 99.0%, Sigma-Aldrich), and 10.0 g of P₂O₅ (97%, Sigma-Aldrich) were immersed little by little in 48.0 ml of H₂SO₄ (95%, OCI Company Ltd.) and stirred at 80 °C for 4 hours, and then cooled down to the room temperature. After adding DI water until pH of the mixed solution to be ca. 5, the solution was filtered with a membrane (0.2 μm, Nylon, Whatman) by vacuum suction and dried at the room temperature in air for 12 hours to obtain a preoxidized graphite powder. The preoxidized graphite powder was transferred to a beaker containing 480 ml of H₂SO₄. Then, 60 g of KMnO₄ (> 99%, Sigma-Aldrich) was added little by little to the beaker in an ice bath very carefully. After stirring at 35 ± 5 °C for 2 hours, 3,800 ml of DI water was added to the solution and stirred overnight. Subsequently, 80 ml of H₂O₂ (ca. 30%, Junsei Chemical) was slowly added to the solution of the beaker in the ice bath. After vigorous stirring for 50 minutes, the solution was filtered and transferred to 2 L of 5% HCl (35.0%, Junsei Chemical), and stirred for 130 minutes. Then, it was washed and filtered again so as to be a GO slurry. After dissolving the GO slurry in DI water, the GO solution was centrifuged at 14,000 rpm for 20 minutes and the precipitated GO was removed. Particle sizes of the precipitated GO are too large to be few tens layered graphene oxide at least. Final pH and concentration of the centrifuged GO solution were ca. 3.6 and 0.16 mg ml⁻¹ respectively.

Deposition of GO

Fig. 1. Schematic diagram of preparing RGO electrode.

For analyses of physical properties of the GO, the GO solution was centrifuged and dried at 50 °C in a vacuum oven for 48 hours and it is denoted as a pristine GO in this study.

2.2. Preparation of working electrode

Procedure for fabricating the RGO thin-film electrode is a simple as illustrated in Fig. 1. The prepared GO solution was dropped on a weighted Au current collector (18 mm diameter of Au plate disk) on a hot plate adjusted at 90 °C. After evaporating water and self-assembling the GO flakes to deposit GO thin-film, the GO thin-film was exposed under a pulsed flash-light device (76 MZ-5 digital, Metz-Werke GmbH & Co KG, 290 W). Above processes were repeated until the deposited GO mass to be ranged between 0.8 and 0.9 mg. The pulsed flash-light irradiated GO thin film is deposited on the Au current collector is denoted as GO (90 °C). In order to reduce the GO, the deposited GO thin-film was thermally treated at 200, 240, 310, and 360 °C in a box furnace (ThermVac Engineering Co.) for 8 hours. The temperature was increased with the rate of 3 °C min⁻¹. The prepared samples are denoted as RGO (200 °C), RGO (240 °C), RGO (310 °C), and RGO (360 °C) respectively. By means of a microbalance (MSA27.5–0000–DF, Satorius, 0.1 μg of resolution) equipped in an electrostatically shielded glove box, a mass for each sample of RGO thin-film electrode including the Au current collector was precisely measured and compared with a readily measured mass of Au current collector. The measured mass of RGO thin-films were ranged within 0.5 to 0.6 mg. The thickness of RGO thin-films measured by a micrometer gage (Mitutoyo) were not uniform but less than ca. 2 μm.

2.3. Properties of the RGO thin-film

Thickness of the pristine GO flake was measured by using an atomic force microscope (AFM, XE-100, Park Systems, PSIA). To observe microstructures of RGO thin-film samples, a scanning electron microscope (SEM, S–4800, Hitachi) was used. Thermogravimetric analyzer (TGA, Setaram) was used to see a mass variation depended on temperature. The RGO thin-film sample was heated up to 1,000 °C in N₂ atmosphere with the rate of 5 °C min⁻¹. Crystallographic structure of the sample was analyzed by X-ray diffraction (XRD, D/MAX–2500PC, Rigaku) at the scanning rate of 1° min⁻¹. Existence of oxygen functional groups were examined by Fourier transform infrared spectroscopy (FTIR, JFS66 V/S & HYPERION 3000, BrukerOptiks). X-ray photoelectron spectroscopy (XPS, MultiLab 2000, Thermo) measurements and analyses were conducted to obtain more quantitative information on the oxygen functional groups for each RGO thin-film sample.

2.4. Electrochemical cell tests

For the electrochemical cell test, the three electrode systems with 6 M KOH (95.0%, OCI Company Ltd.), 1 M H₂SO₄ (95.0%, OCI Company Ltd.), and 0.5 M Na₂SO₄ (99.0%, Sigma-Aldrich) aqueous solutions as electrolytes were set up. As a counter electrode, activated carbon (Kansai Coke), PVDF–HFP (KYNAR 2801), and Super-P
(TIMCAL) were mixed in NMP (Junsei Chemical) with the ratio of 8:1:1, and then pasted on the Au current collector. Then, the counter electrode was dried at 120 °C in vacuum for 12 hours. Total mass of loaded materials for the counter electrode was ca. 7 mg. Au wire (diameter 1.0 mm) was used as a reference electrode and a glass-fiber membrane (diameter 18 mm, Whatman GF/B) was used as a separator. Cell test kit (ECC-AQU, EL-CELL, Germany) was used for the three electrode system. After assembling test cell including electrodes and separator with a selected electrolyte in the kit, the assembled cell was treated in a vacuum desiccator for 30 minutes for soaking. The cyclic voltammetry (CV) was carried out by using a Versastat device (Princeton Applied Research). Potential windows were set up in the rage of -1.1 to -0.2 V vs. Au) in 6 M KOH, -0.5 to 0.4 V (vs. Au) in 1 M H₂SO₄, and -0.6 to 0.3 V (vs. Au) in 0.5 M Na₂SO₄. Scan rates were 5, 10, 20, 30, 50, 100, 200, 300, 400 and 500 mV s⁻¹ for each electrolyte. Cycle-life tests for the RGO (200 °C) in 6 M KOH, 1 M H₂SO₄, and 0.5 M Na₂SO₄ electrolytes were conducted at the scan rate of 500 mV s⁻¹ until 100,000 cycles.

3. Results and discussion

3.1. Effect of pulsed flash-light irradiations

In different way of fabricating graphene electrodes for supercapacitors [25-27], RGO thin-film electrodes were simply fabricated without using any binder and conductive materials in this study. Fig. 2 shows photograph images of thermally reduced GO thin-films at 200 °C without pulsed flash-light irradiations (a) and with pulsed flash-light irradiations (b). In the case of without irradiations, the deposited RGO thin-film after the thermal reduction is detached in part from the Au current collector. But the irradiated RGO thin-film is well adhered to the Au current collector. The possible mechanism for the reduction of the graphene oxide by the radiation of light energy is reported by P. Kumar et al. [28] as;

\[ \text{GO} + h\nu \rightarrow \text{GO} + \text{h}^+ + e^- \] (1)

\[ 4\text{h}^+ + 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ \] (2)

\[ 4\text{e}^- + \text{GO} + 4\text{H}^+ \rightarrow \text{RGO} + 2\text{H}_2\text{O} \] (3)

where \( h \) is Planck’s Constant \( (= 6.626 \times 10^{-34} \text{ J s}) \), \( \nu \) is frequency \( (\text{s}^{-1}) \), \( \text{h}^+ \) is hole, and \( e^- \) is electron.

In equation (3), recombination of electron and hole pairs of the GO produces the reduced graphene oxide and water molecules. The fleeing water molecules produced as in equation (3) may form some pathways without detaching the RGO sheet from the current collector during the thermal reduction step. Therefore, the flash-irradiated RGO sheet can be stably adhered to the current collector. In this study, each RGO film was irradiated by the pulsed flash-light before the thermal reduction of heat treatment.

3.2. AFM and SEM images

Based on a typical AFM image as shown in Fig. 3(b), the pristine GO prepared in this study is confirmed as not a monolayered but few tens layered and ca. 0.8 μm length of flake-like shapes. Fig. 3(c, d, e) shows SEM images of the pristine GO, GO (90 °C), and RGO (200 °C) surfaces. In contrast to the pristine GO, GO (90 °C) shows many wrinkles. It is considered as these wrinkles are generated from a self-assembling of GO thin-film deposition during the evaporation and pulsed flash-light irradiation. RGO (200 °C) shows more crumpled morphology by thermal reduction at 200 °C. It can be explained that residual water molecules are eliminated in the mean time of the heating up to 200 °C and also some locally defected lattices of GO layers are being adjusted according to a negative thermal expansion coefficient of the graphene [29]. At higher reduction temperatures over 200 °C, the crumpled surface morphology of the RGOs were not obviously distinguished from that of the RGO (200 °C) by SEM images.

3.3. TGA analyses

From the TGA analyses, mass changes of the graphite, pristine GO, GO (90 °C), RGO (200 °C), RGO (240 °C), and RGO (310 °C) are plotted in Fig. 4. No mass change is observed for the graphite. But the mass of the pristine GO is drastically decreased up to 200 °C. The first mass decrement up to 100 °C is ascribed to the evaporation of water molecules and the second mass decrement ranging from 160 °C to 200 °C is resulted from taking off residual water molecules along with some oxygen functional groups [30,31]. Mass retention ratios for the pristine GO and GO (90 °C) up to 200 °C are 64.0 and 75.6% respectively. The reason for the higher mass retention ratio of the GO (90 °C) over the pristine GO can be explained as more water molecules have been readily removed by the evaporation and the flash-light irradiation. Meanwhile, the RGOs with thermal reductions above 200 °C are much more thermally stable either than the pristine GO or the GO (90 °C), because residual water molecules in the interlayered space of RGOs are eliminated and only a few portion of the oxygen functional group at the interlayer surface of RGO is remained between the RGO layers after the thermal reduction.

**Fig. 2.** Photographs of thermally treated GO at 200 °C without pulsed flash-light irradiations (a) and with pulsed flash-light irradiations (b).
2. and detected at RGOs

\[ \text{RGOs} \]

In equation (4), the incident planes are (002) and (200). In XRD analyses, both the graphite and pristine GO were used as the state of powders and the others of RGO samples were used as thin-films deposited on the Au current collector. Hence, the Au peaks in the XRD spectra for the RGOs are unveiled. In the graphite, a very strong peak is observed at 26.4° assigning to (002) plane, which indicates that the graphite is highly crystalline phase (the intensity was 10 times downscaled in Fig. 5). The (002) plane peak for the pristine GO is shifted to 10.9° and it becomes broader. Interlayer distance between crystalline planes under a wave field is calculated by the following Bragg's equation (4) [32].

\[ 2d \cdot \sin \theta = n\lambda \]  

(4)

where, \( d \): interlayer distance, \( \theta \): scattering angle, \( \lambda \): wavelength of incident X-ray (= 1.54 Å).

The interlayer distance of the graphite and pristine GO crystalline planes are 0.337 and 0.811 nm respectively, which are in accordance with those in previously reported literatures [33–35]. The repulsive force due to water molecules and oxygen functional groups between the oxidized graphene layers contributed to widen the interlayer distance [33]. The interlayer distance of GO (90 °C) is somewhat shortened to be 0.747 nm. It is able to explain that the repulsive force in GO (90 °C) becomes a slightly weaker since water molecules and oxygen functional groups are less than those in the pristine GO after the evaporation and pulsed flash-light irradiation. The (002) plane peaks of the RGOs are shifted to 24° again and changed to be more broadened. In comparison with GO (90 °C), the interlayer distance of RGO (200 °C) is drastically shortened to be 0.379 nm because residual water molecules and much more oxygen functional groups are removed by the thermal reduction. Besides the main peak at 24°, a shoulder peak is detected near 20° for the RGO (200 °C) and RGO (240 °C), which is coincident with previously reported researches [36,37]. As reported in S. H. Huh's research [37], the peak of GO at 11° shifts to higher angle as increasing the thermal reduction temperature. The shoulder peaks of the RGO (200 °C) and

![Image](image1.png)

**Fig. 3.** AFM image (a) and thickness profile of GO(b) and SEM images of pristine GO (c), GO (90 °C) (d), and RGO (200 °C) (e).

![Image](image2.png)

**Fig. 4.** TGA results of graphite, pristine GO, GO (90 °C), RGO (200 °C), RGO (240 °C), and RGO (310 °C).

![Image](image3.png)

**Fig. 5.** XRD results of graphite, pristine GO, GO (90 °C), RGO (200 °C), RGO (240 °C), RGO (310 °C), and RGO (360 °C).
RGO (240 °C) at ~20° were caused by increased thermal reduction temperature up to 240 °C.

As increasing the thermal reduction temperature from 200 to 360 °C, the interlayer distance is decreased gradually from 0.379 to 0.354 nm, which shows the similar tendency with B. Zhao et al.'s research (from 0.378 nm (200 °C) to 0.359 nm (400 °C)) [33].

### 3.5. FTIR analyses

The FTIR spectra of the graphite, pristine GO, GO (90 °C), RGO (200 °C), RGO (240 °C), RGO (310 °C), and RGO (360 °C) are shown in Fig. 6. For all samples except the graphite, the peaks indicated as C=O stretching vibration in carboxylic group peaks are observed ca. 1730 cm⁻¹ [38–40]. Strong peaks of the pristine GO and GO (90 °C) at 3375 and 3246 cm⁻¹ are corresponding to O-H stretching vibration owing to residual water molecules [40]. For the pristine GO, the peaks of O-H bending vibration [40], C-O-C [25], and C-O stretching vibration [41] are shown at 1371, 1225, and 1051 cm⁻¹. From the fact that the peaks of O-H bending vibration and C-O-C bonding for GO (90 °C) are not observed, since some portion of oxygen functional groups are eliminated by the evaporation and pulsed flash-light irradiations as described before. Another weak peak of C-O in carboxylic group for GO (90 °C) is observed at 1165 cm⁻¹. C=C stretching vibration peaks for the pristine GO and GO (90 °C) are detected at ca. 1600 cm⁻¹. But, for all RGOs, these peaks are shifted to 1570 cm⁻¹, as reported by Y. Fang et al. [39]. For all RGOs except RGO (360 °C), the peak of C-O bonding in carboxylic group is also observed at 1165 cm⁻¹.

### 3.6. XPS analyses

Plotted results of XPS 1 s spectra for the RGO (200 °C), RGO (240 °C), RGO (310 °C), and RGO (360 °C) are shown in Fig. 7. Binding energy values of the O 1 s orbital for these analyses have been referred to readily reported literatures [42,43]. XPS O 1 s spectrum in Fig. 7 is used to calculate an atomic percentages (at%) of each oxygen functional group, since quinone group is not exhibited in a XPS C 1 s spectrum. Atomic percentages from dissected spectra of XPS O 1s for the RGO (200 °C), RGO (240 °C), RGO (310 °C), and RGO (360 °C) are listed in Table 1. As increasing the thermal reduction temperature, as shown in Fig. 8, the atomic percentages for carboxyl and phenol groups are sustained as 5.40 ± 0.36 and 4.77 ± 0.41 at% respectively. But, for carboxyl and quinone groups, atomic percentages are gradually declined from 3.10 to 1.81 and from 1.32 to 0.65 at% respectively as increasing the thermal reduction temperature. Throughout XPS analyses, it is found that all RGOs after the heat treatment of thermal reduction up to 360 °C are not fully reduced but incompletely reduced since a few portion of the oxygen functional group is still remained in the RGOs.

![Fig. 6. FTIR spectra of graphite, pristine GO, GO (90 °C), RGO (200 °C), RGO (240 °C), RGO (310 °C), and RGO (360 °C).](image)

![Fig. 7. Fitted results of XPS O 1 s spectra of RGO (200 °C) (a), RGO (240 °C) (b), RGO (310 °C) (c), and RGO (360 °C) (d).](image)
Table 1
Dissected results of XPS O 1s spectra of graphite, pristine GO, GO (90°C), RGO (200°C), RGO (240°C), RGO (310°C), and RGO (360°C).

<table>
<thead>
<tr>
<th></th>
<th>Atomic percentage (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RGO (200°C)</td>
</tr>
<tr>
<td>Quinone</td>
<td>1.32</td>
</tr>
<tr>
<td>O = C-OH (carboxyl)</td>
<td>5.35</td>
</tr>
<tr>
<td>C = O (carbonyl)</td>
<td>3.10</td>
</tr>
<tr>
<td>C-O</td>
<td>4.75</td>
</tr>
<tr>
<td>C-OH (phenol)</td>
<td>4.36</td>
</tr>
<tr>
<td>Chemisorbed oxygen</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>RGO (240°C)</td>
</tr>
<tr>
<td>Quinone</td>
<td>1.02</td>
</tr>
<tr>
<td>O = C-OH (carboxyl)</td>
<td>5.04</td>
</tr>
<tr>
<td>C = O (carbonyl)</td>
<td>2.77</td>
</tr>
<tr>
<td>C-O</td>
<td>2.18</td>
</tr>
<tr>
<td>C-OH (phenol)</td>
<td>5.01</td>
</tr>
<tr>
<td>Chemisorbed oxygen</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>RGO (310°C)</td>
</tr>
<tr>
<td>Quinone</td>
<td>0.74</td>
</tr>
<tr>
<td>O = C-OH (carboxyl)</td>
<td>5.62</td>
</tr>
<tr>
<td>C = O (carbonyl)</td>
<td>2.66</td>
</tr>
<tr>
<td>C-O</td>
<td>3.00</td>
</tr>
<tr>
<td>C-OH (phenol)</td>
<td>5.18</td>
</tr>
<tr>
<td>Chemisorbed oxygen</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>RGO (360°C)</td>
</tr>
<tr>
<td>Quinone</td>
<td>0.65</td>
</tr>
<tr>
<td>O = C-OH (carboxyl)</td>
<td>5.76</td>
</tr>
<tr>
<td>C = O (carbonyl)</td>
<td>1.81</td>
</tr>
<tr>
<td>C-O</td>
<td>2.34</td>
</tr>
<tr>
<td>C-OH (phenol)</td>
<td>4.48</td>
</tr>
<tr>
<td>Chemisorbed oxygen</td>
<td>1.67</td>
</tr>
</tbody>
</table>

is confirmed that charge-discharge currents for the bare Au current collector are negligibly small enough in each electrolyte. In 6 M KOH electrolyte, as shown in Fig. 9(a), flatly roundish shapes of redox peaks are observed, while the Faradaic redox peaks in the 1 M H2SO4 electrolyte in Fig. 9(b) are obviously observed in the potential range between −0.1 to 0.0 V (vs. Au). However, as shown in Fig. 9(c), all CV curves in the 0.5 M Na2SO4 electrolyte are maintained as EDLC-like rectangular shapes without the Faradaic redox peaks. In 6 M KOH and 0.5 M Na2SO4 electrolyte, for all RGO electrodes, no significant difference of CV patterns are exhibited as shown in Fig. 9(a, c). But, in 1 M H2SO4, CV patterns as shown in Fig. 9(b) are being shrunken as increasing the thermal reduction temperature. Fig. 9(d) shows a comparison of CV curves for RGO (200°C) electrode in three different electrolytes at the scan rate of 20 mV s⁻¹. The shape and current values of CV curves are fairly different.

CV curves of RGO (200°C) electrode at different scan rates from 5 to 500 mV s⁻¹ in three different electrolytes are shown in Fig. 10(a, b, c). These CV curves are not deformed but proportionally enlarged as increasing the scan rates up to 500 mV s⁻¹. It seems that electrochemical behavior in 6 M KOH and 1 M H2SO4 reveal a hybrid type of both a pseudo capacitive and an electric double layer capacitive. For an electrode showing a capacitive behavior, regardless what type of capacitance, the specific capacitance (Csp) as a resultant capacitance

Fig. 9. CV patterns of RGO electrodes measured in 6 M KOH (a), 1 M H2SO4 (b), 0.5 M Na2SO4 (c) at scan rate of 20 mV s⁻¹ and CV curves of RGO (200°C) in three electrolytes at scan rate of 20 mV s⁻¹ (d).

3.7. Cycle voltammetries and the specific capacitances

Fig. 9 shows CV curves of the bare Au current collector and RGO electrodes in three different electrolytes of 6 M KOH (a), 1 M H2SO4 (b), and 0.5 M Na2SO4 (c) at the scan rate of 20 mV s⁻¹. It
can be obtained by applying the following equation (5) to its CV curve data.

$$C_{sp} = \frac{1}{S \cdot m \cdot \Delta V} \int_{V_1}^{V_2} i dV$$ (5)

where, $C_{sp}$: specific capacitance (F g$^{-1}$), $S$: scan rate (V s$^{-1}$), $m$: mass of active material (g), $\Delta V$: voltage difference (Volt), $i$: current (Amp), $V_1$: lower voltage limit (Volt), $V_2$: upper voltage limit (Volt).

The specific capacitance variation of RGO (200 °C) electrode on the scan rate is shown in Fig. 10(d). The specific capacitance in 0.5 M Na$_2$SO$_4$ electrolyte is much smaller than those in either 6 M KOH or 1 M H$_2$SO$_4$. In 0.5 M Na$_2$SO$_4$ electrolyte, there is no pseudocapacitance but an electric double layer capacitance. It is able to describe that an electric double layer capacitance in 0.5 M Na$_2$SO$_4$ of neutral electrolyte is occurred at first by the electrostatic adsorption of charge-separated ions of Na$^+$ (ionic diameter = 0.204 nm) and SO$_4^{2-}$ (0.533 nm) on the edge plane of multilayered RGO (200 °C) flakes. Instantly, the adsorbed ions begin to insert into the interlayered space of RGO (200 °C) and then adsorb on the surface of interlayers. Since the electrochemical kinetics of the electrostatic adsorption is slower than that of the pseudocapacitive Faradaic reaction, the declining trend of the specific capacitance at higher scan rates in 0.5 M Na$_2$SO$_4$ is rather steeper than those in 6 M KOH and 1 M H$_2$SO$_4$. As shown in this study has few tens layered and ca. 0.8 µm length of flake-like shapes, an effective specific surface area of RGO (200 °C) with the interlayer distance of 0.379 nm is not able to be higher as much as a mono- or few-layered graphene. Thus, the specific capacitance of electric double layer capacitance for RGO (200 °C) electrode in 0.5 M Na$_2$SO$_4$ shows a relatively lower value of 92.03 F g$^{-1}$ at the scan rate of 5 mV s$^{-1}$.

The result of cycle-life test for the RGO (200 °C) electrode is plotted in Fig. 11. After 100,000 cycles at the scan rate of 500 mV s$^{-1}$ in 6 M KOH, 1 M H$_2$SO$_4$, and 0.5 M Na$_2$SO$_4$ electrolytes, the RGO (200 °C) electrode showed 91.89, 53.91, and 104.27% of the initial capacitance, respectively.

3.8. Oxygen functional groups and pseudocapacitances

As shown in Fig. 12, as increasing the thermal reduction temperature from 200 to 360 °C, the specific capacitance at the scan rate of 5 mV s$^{-1}$ for all RGO electrodes in 6 M KOH electrolyte is maintained at 220.45 ± 5.36 F g$^{-1}$. In 1 M H$_2$SO$_4$ electrolyte, however, the specific capacitance is decreased from 171.03 to 136.45 F g$^{-1}$. In 0.5 M Na$_2$SO$_4$ electrolyte, the specific capacitance for all RGO electrodes are almost constantly maintained as ca. 93 F g$^{-1}$.

The oxygen functional group of RGO can be classified into two groups depending on their acidic or basic nature of aqueous solution. One is an acidic functional group such as carboxyl, lactone, phenol, and lactol. The other is a basic functional group including ketone, quinone, and carbonyl [43,44]. It is known that the acidic
Table 2
Atomic percentages of oxygen functional groups of the RGO (200 °C) electrode before and after 100,000 cycles in 6 M KOH, 1 M H2SO4, and 0.5 M Na2SO4 electrolytes.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Before cycle test</th>
<th>After cycle test in 6 M KOH</th>
<th>After cycle test in 1 M H2SO4</th>
<th>After cycle test in 0.5 M Na2SO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinone</td>
<td>1.32</td>
<td>1.28</td>
<td>0.63</td>
<td>1.32</td>
</tr>
<tr>
<td>O = C-OH (carboxyl)</td>
<td>5.35</td>
<td>2.96</td>
<td>5.66</td>
<td>5.58</td>
</tr>
<tr>
<td>C = O (carbonyl)</td>
<td>3.10</td>
<td>5.70</td>
<td>2.13</td>
<td>3.35</td>
</tr>
<tr>
<td>C-O</td>
<td>4.75</td>
<td>7.15</td>
<td>5.28</td>
<td>4.89</td>
</tr>
<tr>
<td>C-OH (phenol)</td>
<td>4.36</td>
<td>3.33</td>
<td>4.27</td>
<td>4.48</td>
</tr>
<tr>
<td>Chemisorbed oxygen</td>
<td>1.70</td>
<td>1.59</td>
<td>1.48</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Fig. 12. Specific capacitances at scan rate of 5 mV s⁻¹ for RGO electrodes as increasing thermal reduction temperature.

Fig. 13. Fitted results of XPS O 1s spectra of the RGO (200 °C) electrodes before (a) and after 100,000 cycle tests in 6 M KOH (b), 1 M H2SO4 (c), and 0.5 M Na2SO4 (d).

Functional group reacts with hydroxyl ions (OH⁻) in the alkaline aqueous solution and the basic functional group reacts with protons (H⁺) in the acidic aqueous solution [39,43]. Faradaic redox reactions with carboxyl and phenol groups observed in 6 M KOH electrolyte are depicted as following equations (6) and (7) respectively [39,43]. Therefore, it is able to describe that the flatly roundish redox peaks (cathodic and anodic) as shown in Fig. 9(a) and 10(a) are revealing the pseudocapacitive Faradaic redox reaction with carboxyl and phenol groups.

\[
\text{C} + \text{OH} \Leftrightarrow \text{C} + \text{OH}_2^+ + e^-
\]

(6)

\[
\text{C} + \text{OH} \Leftrightarrow \text{C} + \text{H} + e^-
\]

(7)

Faradaic redox reactions with carbonyl and quinone groups in 1 M H2SO4 electrolyte are depicted as following equations (8) and (9) respectively [43,45]. Thus, it is able to describe that the prominent redox peaks in 1 M H2SO4 electrolyte as shown in Fig. 9(b) and 10(b) are revealing the pseudocapacitive Faradaic redox reaction with carbonyl and quinone groups. In the neutral solution of 0.5 M Na2SO4, since there is no Faradaic redox reactions resulted, it is not able to obtain a pseudocapacitance.

\[
\text{C} = \text{O} + \text{H}^+ + e^- \Leftrightarrow \text{C} + \text{OH}
\]

(8)
To find the changes of atomic percentage of oxygen functional groups after the cycle tests, we analyzed and compared the XPS O 1s spectra of the oxygen functional groups for the RGO (200 °C) before and after the 100,000 cycles with the scan rate 500 mV s⁻¹ in 6 M KOH, 1 M H₂SO₄, and 0.5 M Na₂SO₄ electrolytes. As shown in Fig. 13 and Table 2, after the cycles in 6 M KOH, the atomic percentages (5.35 and 4.36 at%) of carboxyl and phenol groups for the RGO (200 °C) were decreased to 2.96 and 3.33 at% respectively. In 1 M H₂SO₄, 1.32 and 3.10 at% of quinone and carbonyl groups were decreased to 0.63 and 2.13 at% after the cycle test respectively. It is notable that atomic percentages of oxygen functional groups worked in the pseudocapacitive Faradaic reaction have been decreased after the cycle tests. Especially, in 1 M H₂SO₄ electrolyte, ca. 48% depletion of quinone group seems to be a major reason of the capacitance decrement as shown in Fig. 11. However, in 0.5 M Na₂SO₄ electrolyte, the atomic percentages are not significantly changed since oxygen functional groups are not involved in the pseudocapacitive Faradaic reaction.

In order to estimate the pseudocapacitance for RGO electrodes, we assumed as (i) no other functional groups but four oxygen functional groups of carboxyl, phenol, carbonyl, and quinone in RGO thin-films contribute to the pseudocapacitance. Since it is known that the electric double layer capacitance is generated at edge plane rather than basal plane in most carbon structure, we considered that the interlayer distance of the RGOs is not dominant. Hence, we assumed the ion size effect for the thin-film electrode of RGO flakes with the same interlayer distance is not crucial to the electric double layer capacitance in this study. Therefore, it can be assumed that (ii) the electric double layer capacitance for all RGO electrodes in either 6 M KOH or 1 M H₂SO₄ is the same as in 0.5 M Na₂SO₄.

As listed up in Table 3, the specific pseudocapacitance for each RGO electrode is calculated by subtracting the electric double layer capacitance in 0.5 M Na₂SO₄ from the total specific capacitance of each RGO electrode as shown in Fig. 12.

A quinone group generates two times larger capacitance than the other oxygen groups, because two electrons (e⁻) per one quinone group take part in the pseudocapacitive Faradaic redox reaction as in the equation (9). Therefore, two times larger atomic percentage of quinone has to be substituted in calculating a fraction of the specific pseudocapacitances for each carbonyl and quinone group. As an example for RGO (200 °C) electrode in 1 M H₂SO₄, the specific pseudocapacitance for carbonyl and quinone groups are calculated as following equations (10) and (11) respectively:

\[ 79.0 \text{ F g}^{-1} \times 3.10 / (3.10 + 2 \times 1.32) = 42.67 \text{ F g}^{-1} \text{ (for carbonyl)} \]

\[ 79.0 \text{ F g}^{-1} \times (2 \times 1.32) / (3.10 + 2 \times 1.32) = 36.33 \text{ F g}^{-1} \text{ (for quinone)} \]

In order to find how much pseudocapacitance is generated by each functional group with respect to unit mass of each RGO thin-film, a parameter that the specific capacitance per unit atomic percentage of an oxygen functional group is defined as ‘the specific pseudocapacitance per unit atomic percentage’ with its unit as [F g⁻¹ at%⁻¹].

<table>
<thead>
<tr>
<th>RGO electrodes</th>
<th>Specific capacitance at 5 mV s⁻¹ (F g⁻¹)</th>
<th>Specific capacitance at 5 mV s⁻¹ by a functional group (F g⁻¹)</th>
<th>Specific pseudocapacitance per unit at% at 5 mV s⁻¹ (F g⁻¹ at%⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 M KOH</td>
<td>136.45</td>
<td>127.43</td>
<td>116.45</td>
</tr>
<tr>
<td>1 M H₂SO₄</td>
<td>147.92</td>
<td>147.43</td>
<td>146.92</td>
</tr>
<tr>
<td>0.5 M Na₂SO₄</td>
<td>91.92</td>
<td>91.43</td>
<td>90.92</td>
</tr>
</tbody>
</table>
For each oxygen functional group, the specific pseudocapacitance per unit atomic percentage can be estimated from dividing the calculated specific pseudocapacitance for each functional group by its atomic percentage as in Table 3. The specific pseudocapacitance per unit atomic percentage of carboxyl or phenol group in 6 M H2SO4 is obtained as 12.59 F g−1 at%−1. For carboxyl group in 1 M H2SO4, a slightly deviated value as 13.55 F g−1 at%−1 is obtained. For quinone group, 27.09 F g−1 at%−1 is obtained.

4. Conclusions

For incompletely reduced graphene oxides (RGOs), an effect of oxygen functional groups such as carboxyl, phenol, carbonyl, and quinone on electrochemical capacitive behavior was studied. To prepare RGO thin-film electrodes containing the oxygen functional group, a simple fabrication process by (i) dropping and evaporating graphene oxide (GO) solution on Au current collector, (ii) irradiating intensive pulsed flash-lights on the deposited GO thin-film, and then (iii) heat-treating the irradiated GO thin-film with different reducing temperatures at 200, 240, 310, and 360 °C was successively applied. From AFM image, the pristine GO that the GO solution was dried at 50 °C in a vacuum oven for 48 hours was observed as not a monolayered but few tens layered and ca. 0.8 μm length of flake-like shapes. It was notable that the pulsed flash-light irradiation was effective to form and maintain some pathways for taking off residual water molecules without disfiguring the deposited GO thin-film during the thermal reduction. Thus, the RGO thin-film after the heat treatment of thermal reduction up to 360 °C could be adhered stably on the current collector.

From XRD analyses, it was found that 0.811 nm of the interlayer distance of crystalline for the pristine GO was slightly decreased to 0.747 nm by the evaporation at 90 °C and pulsed flash-light irradiation and then rapidly decreased to be 0.379 nm after the thermal reduction at 200 °C. As increasing the thermal reduction temperature from 200 to 360 °C, the interlayer distance of RGO (360 °C) was gradually decreased to be 0.354 nm. From XPS O 1 s spectra analyses, for all RGO thin-films, the atomic percentage for each carboxyl and phenol was sustained as 5.40 ± 0.36 and 4.77 ± 0.41 at% respectively. But, for carbonyl and quinone groups, atomic percentages are gradually declined from 3.10 to 1.81 and from 1.32 to 0.65 at% respectively as increasing the thermal reduction temperature.

For all RGO thin-films, the specific capacitance in 6 M KOH electrolyte was sustained as ca. 220 F g−1 at the scan of 5 mV s−1. However, in 1 M H2SO4 electrolyte, the specific capacitance at the same scan rate was gradually decreased from 171 to 136 F g−1 as increasing the thermal reduction temperature. As a result of cycle-life test for the RGO (200 °C) electrodes after 100,000 cycles at the scan rate of 500 mV s−1 in 6 M KOH, 1 M H2SO4, and 0.5 M Na2SO4 electrolytes, ca. 92, 54, and 104% of the initial capacitances were shown. The atomic percentages (5.35 and 4.36 at%) of carboxyl and phenol groups before the cycle test were decreased to 2.96 and 3.33 at% respectively after cycle test in 6 M KOH. In 1 M H2SO4, 1.32 and 3.10 at% of quinone and carbonyl groups were decreased to 0.63 and 2.13 at% after the cycle test respectively. It is notable that atomic percentages of oxygen functional groups worked in the pseudocapacitive Faradaic reaction have been decreased after the cycle tests. Especially, in 1 M H2SO4 electrolyte, ca. 48% depletion of quinone group seems to be a major reason of the drastic decrement of the capacitance. However, in 0.5 M Na2SO4 electrolyte, the atomic percentages are not significantly changed since oxygen functional groups are not involved in the pseudocapacitive Faradaic reaction.

Assuming as (i) no other functional groups but four oxygen functional groups of carboxyl, phenol, carbonyl, and quinone in the RGO thin-film electrodes contribute to the pseudocapacitance and (ii) the electric double layer capacitance in either 6 M KOH or 1 M H2SO4 is the same as in 0.5 M Na2SO4, the specific pseudocapacitances generated by carboxyl and phenol groups in 6 M KOH electrolyte were 67.80 and 55.25 F g−1 respectively, and also those by carboxyl and quinone groups in 1 M H2SO4 electrolyte were 42.67 and 36.33 F g−1 respectively. As a parameter how much pseudocapacitance is generated by an oxygen functional group for unit mass of each RGO thin-film, the specific pseudocapacitance per atomic percentage of carboxyl or phenol group in 6 M KOH was 12.59 F g−1 at%−1. For carboxyl group in 1 M H2SO4, it was a slightly deviated value as 13.55 F g−1 at%−1. For quinone group in 1 M H2SO4, 27.09 F g−1 at%−1 was obtained.

Acknowledgements

Authors would like to express lots of gratitude for the research grant from the KIER and the Korea Research Council of Industrial Science and Technology (ISTK) based on Cooperative Research Program for National Labs.

References

[15] H. Bi, F. Huang, J. Liang, X. Xie, M. Jiang, Transparent conductive graphene films synthesized by ambient pressure chemical vapor deposition used as the front electrode of C60 solar cells, Advanced Materials 23 (2011) 3202.


