Redox Molecule Adsorbed Graphene Films with Compact Structure for Electrochemical Energy Storage

Yucan Zhu, Xingke Ye, Hedong Jiang and Chunyang Jia*

School of Electronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, China

*Corresponding author: cyjia@uestc.edu.cn

Abstract. Graphene films with compact structure and high ion accessible surface are essential to achieve dense energy storage with high-performance. Thus we prepared hydroquinone (HQ) adsorbed reduced graphene oxide (HQ-rGO) films with high packing density by capillary pressure. Hence, sulphuric acid was pre-intercalated between graphene sheets to reduce ion transport resistance, and adsorbed HQ molecules provide abundant pseudocapacitance. Finally, the two materials play a synergistic effect, significantly improving the capacitance performance. The resulting HQ-rGO films exhibit high volumetric capacitance of ~189.4F cm\(^{-3}\) at 1mA cm\(^{-2}\), and after current density increase to 30mA cm\(^{-2}\), its capacitance retention can achieve 54% of original value, which demonstrates excellent rate performance of the device. Clearly, this strategy is great promising for fabrication of electrode material with high performance.

1. Introduction

With the rapid development of wearable electronic equipment, advanced energy storage becomes more and more important [1]. Thus, supercapacitors (SCs), as a class of emerging energy-storage device, have aroused wide concern due to their advantages of high power density, long cycle life, safety and reliability [2]. Electrode material, which determines the device’s performance, becomes a research hotspot to obtain high-performance SCs.

Graphene film is considered as a promising material for SCs’ electrode because of its excellent electrochemical stability, great electronic conductivity as well as mechanical strength [3]. However, graphene film exhibits lower specific surface area due to the irreversible π-π stacking of graphene sheets, resulting in a mediocre capacitance performance of the device. Therefore, plenty of techniques that suppresses the agglomeration of graphene sheets were developed to prepare high-performance graphene-based films, such as constructing fluffy/porous graphene films [4]. Prepared graphene-based films by these works show high gravimetric capacitance and wonderful rate performance. Unfortunately, their volumetric capacitance is always unsatisfactory owing to the loose structure [5]. Apparently, it is a major challenge that how to achieve high specific capacitance in the case of a compact structure of the SCs’ electrode.

In this work, we employed capillary pressure of graphene hydrogel (GH) films to implement high packing density graphene film electrode. Specifically, the mixed aqueous solutions of hydroquinone (HQ) and sulfuric acid (H\(_2\)SO\(_4\)) were intercalated between graphene nanosheets. After capillary
contraction, H$_2$SO$_4$ as the barrier is used to prevent the stacking of graphene sheets and provide high speed ion transport channel, meanwhile, HQ can provide additional pseudocapacitance. Finally, the prepared HQ adsorbed reduced graphene oxide (HQ-rGO) films with high packing density not only exhibit high specific capacitance values, but also show excellent rate performance.

2. Experimental section

2.1. Materials
Natural graphite powder was purchased from Shanghai Hua Yi Group HuaYuan Chemical Industry Co., Ltd. Other chemical reagents were purchased from Chengdu Chron Chemicals Co., Ltd.

2.2. Fabrication of HQ-rGO films
GO suspensions was prepared from natural graphite powder by a modified Hummers method. Subsequently, the suspensions was diluted to 1mg mL$^{-1}$ with deionized water. Zn foil is immersed into the GO suspensions for interfacial gelation for 24h. Then obtained GH films was detached from Zn surface by using 20 fold diluted hydrochloric acid solution. Finally, the free-standing GH films was soaked in a deionized water for 12h to remove Zn and acidic impurities.

90mg HQ was added into 30mL of H$_2$SO$_4$ (0.1 M), followed by ultrasonic for 1h to obtain mixed solution. After that, prepared GH films were immersed into the above mixed solutions for 12h. Subsequently, it was clipped by two glass panels and moved to a vacuum oven for drying to obtain HQ-rGO films. As a control, the GH films were also immersed into 0.1 M H$_2$SO$_4$ solution and deionized water, respectively. Finally, the obtained films were named as S-rGO and rGO films, respectively.

2.3. Characterization
The morphologies of graphene films were characterized by field emission scanning electron microscopy (SEM, JEOL JSM-7600F). The structure of materials was performed by X-ray diffraction (XRD, Bruker D8 ADVANCE A25X) using Cu-Ka radiation ($\lambda$=1.5418Å). Fourier transform infrared spectroscopy (FTIR, PerkinElmer Frontier) was characterized by at room temperature.

2.4. Electrochemical measurements
Electrochemical performance of the films, such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), were characterized by using electrochemical workstation (CHI660E) in the symmetric SCs system.

The gravimetric ($C_m$, F g$^{-1}$) and volumetric ($C_V$, F cm$^{-3}$) specific capacitance of the films were calculated from the GCD curves, as follows:

\[
C_m = \frac{2I\Delta t}{m\Delta V}
\]
\[
C_V = \frac{2I\Delta t}{V\Delta V}
\]

Where $m$ (g) and $V$ (cm$^3$) are the mass and volume of a single film electrode, respectively. $I$ (A) stands for the galvanostatic discharging current, $\Delta t$ (s) is the discharging time, $\Delta V$ (V) is the potential window.

The volumetric energy ($E_V$, Wh cm$^{-3}$) and power ($P_V$, W cm$^{-3}$) density were calculated from the Equation (3) and (4), respectively.

\[
E_V = \frac{C_AV^2}{28800}
\]
\[
P_V = 3600E_V/\Delta t
\]
Where $U(V)$ is the operation potential.

3. Results and Discussion

As shown in Figure 1a, depositional GH films are first detached from the surface of Zn foil. Figure 1b shows that the cross-section SEM image of the GH films exhibits fluffy porous structure. This structure favours electrolyte ion transport, but it usually shows poor value of $C_V$ due to loose structure. Then aqueous solution within the GH films is displaced by the mixture solution of the H$_2$SO$_4$ and the HQ, meanwhile, the HQ molecule also adsorbs on graphene sheets. Finally, the HQ-rGO films are obtained through capillary contraction of GH films with water evaporation. Its cross-section SEM image in Figure 1c displays dense layered structure, which facilitates achieving high $C_V$ value. Besides, Figure 1d shows the smooth and compaction surface of the HQ-rGO, which is caused by glass panel.

Figure 1. (a) Schematic diagram of preparation process of the HQ-rGO films. The cross-sectional SEM images of (b) the GH films and (c) the HQ-rGO films. (d) The surface SEM image of the HQ-rGO films.

Figure 2a shows FTIR spectra of HQ molecule and HQ-rGO film. The peaks at 1501, 1093, and 753 cm$^{-1}$ result from the skeletal vibration of benzene, vibration of C-H and –OH, respectively. All of the peaks are observed from the spectra of the HQ molecule and HQ-rGO film, respectively, demonstrating the uniform mixing of the HQ and rGO [6]. The XRD patterns in Figure 2b show that peak positions of the rGO, S-rGO and HQ-rGO films are ~25.3°, ~24.4°, ~23.6°, corresponding to the interlayer spacing of ~3.52Å, ~3.65Å, ~3.77Å, respectively. Compared with that of the rGO film, S-rGO and HQ-rGO films exhibit a slightly larger interlayer spacing, demonstrating the intercalation effect of H$_2$SO$_4$ and HQ molecule. In addition, interlayer spacing of HQ-rGO film is greater than that of the S-rGO film, which suggests that the presence of the HQ further increases layer spacing. This result also implies that the HQ molecule plays a role for suppressing the agglomeration of nanosheets.

As shown in Figure 3a, CV curve of the HQ-rGO film shows a maximum integral area at scan rate of 50 mV s$^{-1}$ with 1 M H$_2$SO$_4$ electrolyte, and the curve of the rGO film exhibits the smallest integral area and poor current response, demonstrating the worst performance of the rGO film. These results suggest that the intercalated H$_2$SO$_4$ inhibits the agglomeration of graphene sheets and provide great ion transport channel. Besides, the redox peaks at ~0.1V is observed at CV curve of the HQ-rGO film, revealing the pseudocapacitance characteristics of the HQ molecule. According to Figure 3b, we found that the discharge time of the S-rGO film is longer than that of the rGO film, which suggests that H$_2$SO$_4$ improves electrode material utilization. At 0.5A g$^{-1}$, the HQ-rGO film shows the maximum
discharge time, and its $C_m$ value is up to ~111.6 F g$^{-1}$. In addition, Nyquist plots of the rGO films in Figure 3c displays sloping line in the low-frequency region, and the S-rGO and HQ-rGO films show almost vertical lines. This also indicates that the presence of H$_2$SO$_4$ provides high-speed ions transport channels within the film electrodes, and a certain amount of the HQ molecule doesn’t obviously affect the electrolyte ions transport.

**Figure 2.** (a) FTIR spectra of the HQ molecule and HQ-rGO film. (b) XRD patterns of the rGO, S-rGO and HQ-rGO films.

The CV is also important indicator for estimating practical applications of electrode materials. Figure 3d exhibits that the rGO, S-rGO and HQ-rGO films show the $C_V$ values of 19, 64.6, and 189.4 F cm$^{-3}$ at 1mA cm$^{-2}$, respectively. Compared with rGO film, the $C_V$ value of the S-rGO film can be improved significantly, further demonstrating the effect of the intercalated H$_2$SO$_4$. The HQ-rGO film shows higher $C_V$ value than that of the S-rGO film, which suggests the HQ molecule contributes extra pseudocapacitance. Besides, the rate performance of the HQ-rGO film based device is inferior to that of S-rGO film, which is due to the loss of capacitance for the HQ molecule at high current density. In addition, the $E_V$ and $P_V$ values of the device based on the HQ-rGO film are also impressive, corresponding to ~6.6Wh L$^{-1}$ and ~2500W L$^{-1}$, respectively (Figure 3e). Finally, the cycling stability of the SCs shown in Figure 3f exhibit the excellent capacitance retention rate of ~87.5% at 5A g$^{-1}$ after 5000 cycles. Furthermore, the coulombic efficiency of the devices also almost maintains ~100% in the process of charging and discharging.

**Figure 3.** Electrochemical performance of the rGO, S-rGO, and HQ-rGO films (a-d). (a) CV curves at 50mV s$^{-1}$, (b) GCD curves at 0.5A g$^{-1}$, (c) Nyquist plots, and (d) CV values at different current densities. (e) Ragone plot and (f) cycling stability of the SCs based the HQ-rGO films.
4. Conclusion
In summary, HQ-rGO films with high packing density are prepared by capillary pressure. The adsorbed HQ molecule and intercalated H$_2$SO$_4$ provide extra pseudocapacitance and high-speed ions channels, respectively. They achieve synergy and improve the capacitance performance of the rGO film, simultaneously achieving high $C_V$ values and excellent rate performance of graphene films.

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