

MoS₂/Reduced Graphene Oxide-Based 2D Nanocomposites for Boosting the Energy Density of Electric Double-Layer Capacitor

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ABSTRACT

A method for synthesizing and structuring 2D-MoS₂/rGO (molybdenum disulfide/reduced graphene oxide) nanocomposite-based electric double layer capacitor (EDLC) that has a slower discharge rate and higher energy density than rGO-based EDLC (RG-EDLC) is reported. The rGO electrode and the nanocomposite were characterized using powder XRD and SEM for their physical and structural properties. Cyclic voltammetry (CV) was used to analyze the electrochemical behavior of the EDLCs. A maximum current density at which the MoS₂/rGO nanocomposite-based EDLC (MRG-EDLC) can charge and discharge was 2.5 A/g, while it was 1A/g for the RG-EDLC. The specific capacitance of the MRG-EDLC was 14.52 F/g at 0.5 A/g with an energy density of 8.06 Wh/kg.

INTRODUCTION

An electric double-layer capacitor or supercapacitor can store energy with exponential charge and discharge behavior in comparison to standard capacitors. Although double-layer capacitors have high electrical conductance, they still possess a low potential of not more than 3V. Continuous research is underway to develop novel active materials and membranes to boost their energy and power densities.

Storing charge in supercapacitors depends on the formation of an interfacial double layer on active electrode materials [1]. Recently, several research works have been reported on EDLCs with reduced graphene oxide as the electrode material [2–5] because of its excellent life cycle, high electric conductivity and chemical stability [6, 7]. Electrolytes such as potassium hydroxide, organic electrolyte, and ionic liquids were used in the EDLCs to improve their specific capacitance [8–11], energy and power densities. In particular, a graphene-based supercapacitor with a curved morphology was reported to possess high energy density with a capacitance of 154.1 F/g at 1 A/g current density [12]. On that basis, Yanwu et al. [13] modified this process and improved the capacitance properties using the same ionic liquid. However, the reduction of their graphene oxide in powder or sheet form made use of hydrazine. Without using a reducing chemical, graphene oxide powder has also been reduced under high temperatures at about 1000°C [14]. During our investigation, it was found that rGO nanosheets would lose its physical properties above 350°C. As such, rGO nanosheets were prepared by thermally reducing them at 350°C in nitrogen ambient without using a toxic chemical in this work.

MoS₂, an archetypal layered transition metal sulfide, has three atomic layers (S-Mo-S) stacked and fused together using van der Waals bonding. This two-dimensional transition-metal dichalcogenide (2D-TMD) has a 2H phase crystal structure with a monolayer bandgap of ~1.9 eV. As such, bare MoS₂ was not used as an electrode material for EDLCs due to its semi-insulating property. Our objective is to nano-blend rGO nanosheets with molybdenum disulfide

(MoS₂) first and later to explore its thermal and chemical stability. We report a two-dimensional (2D) nanocomposite (MoS₂/rGO) prepared by a simple chemical process, which serves as a promising electrode material for use in EDLCs. Commercially available Celgard membrane and propylene carbonate were used to evaluate the properties and the validity of MoS₂/rGO nanocomposite-based EDLCs.

METHODS

Synthesis of reduced graphene oxide solution

The graphene oxide (GO) suspension was prepared using the modified Hummers method [15]. In brief, a mixture of graphite powder and sodium nitrate was placed in an ice bath to which concentrated H₂SO₄ was added subsequently under stirring, and then potassium permanganate was added gradually. This mixture was stirred at 50°C for 2 h, and then DI water was added. Next, some more DI water and a 30% H₂O₂ aqueous solution were added slowly into the mixture in order to stop the reaction. The final solution mixture was washed with HCl solution in a centrifuge twice to remove the metal residues. Thereafter, the solution was further washed with DI water until the pH value became neutral. A graphene oxide suspension (2 mg/ml) was prepared by diluting the washed powder with DI water. For preparing the GO nanosheets, the GO suspension was cast on a glass-substrate and dried under vacuum at 60°C overnight. Thus-formed GO nanosheets were transformed into a conductive nanosheet after being calcined at 350°C inside an oven in nitrogen ambient.

Synthesis of MoS₂/rGO nanocomposite

The MoS₂ suspension was prepared by mixing the commercially available MoS₂ powder with N-Methyl-2-pyrrolidone (NMP) solution at a concentration of 0.5 g/ml, and sonicated for 12 hours. The rGO suspension was added along with the MoS₂-NMP mixture in a weight ratio of 1:1 and sonicated for 3 hours, which resulted in a highly homogenous mixture. This mixture was then filtered using an anodic aluminum oxide (AAO) template and dried at 100°C for 12 hours in order to obtain thin-film nanosheets.

Assembly of EDLCs

The EDLCs were assembled inside a 2032 coin cell with either the rGO or MoS₂/rGO nanocomposite at each end as electrodes, a membrane at the center and an electrolyte solution (e.g., potassium hydroxide) in between the electrodes and the membrane. A commercially available Celgard membrane was used as-received without further treatment.

RESULTS AND DISCUSSION

The rGO SEM image in Figure 1(a) shows μm -scale rippled morphology of the typical multilayered sheet. The inclusion of MoS₂ nanosheets resulted in a rough surface (Figure 1(b)), logically due to co-stacking of MoS₂ nanosheets over the rGO nanosheets. This sheet-roughness helps increase the surface-area of the nanocomposite sheet membrane and in turn the charge-transfer throughout the membrane-matrix. In order to understand the structural properties of the

as-prepared rGO and the nanocomposite, an XRD analysis (Figure 1(c)) was performed. The (002) diffraction peak-position shift in the XRD pattern signifies that the GO was chemically reduced to rGO. For the MoS₂/rGO nanocomposite, the presence of (002), (103) and (105) diffraction peaks indicates a layered structure of MoS₂. The diffraction peaks indicate the amount of MoS₂ material present in the nanocomposite.

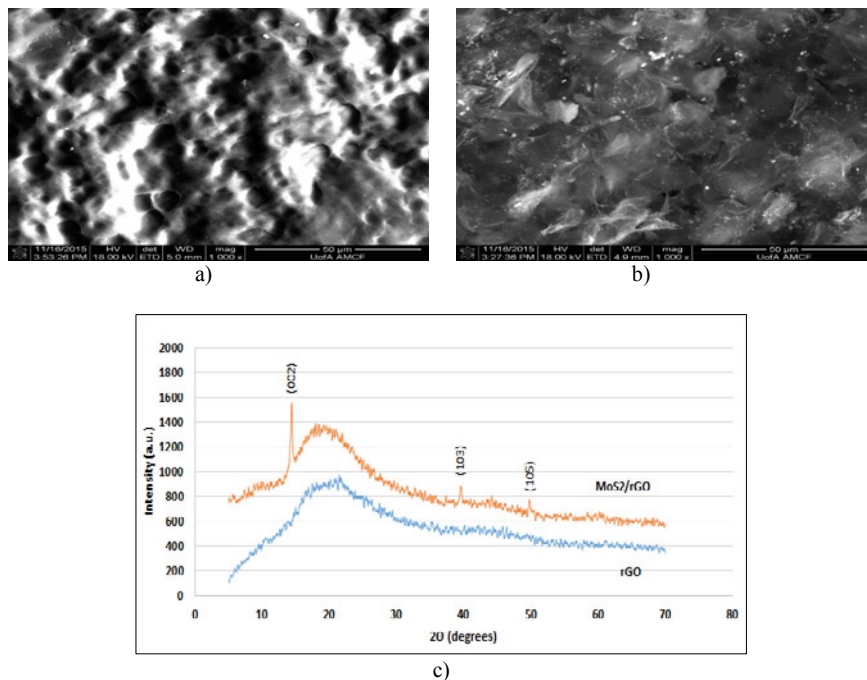
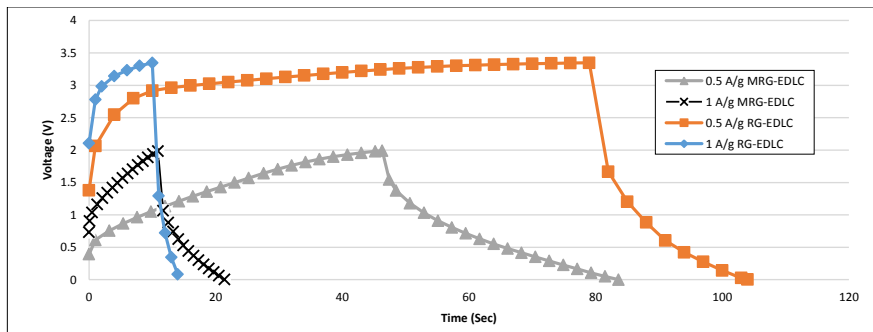
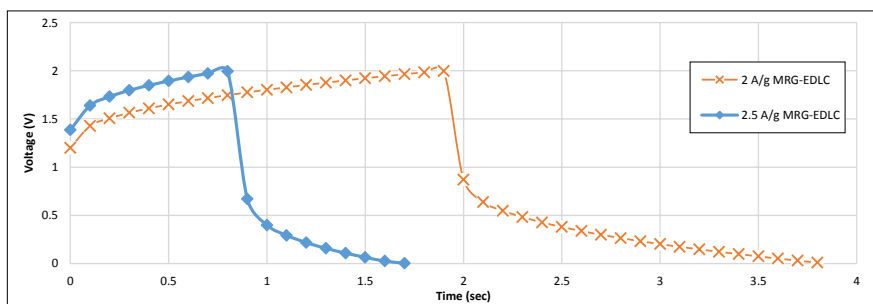


Figure 1 SEM images of (a) rGO and (b) MoS₂-rGO nanosheets, and (c) XRD patterns for samples (a) and (b)

The galvanostatic charge-discharge curves with slope variations as a function of time (Figure 2) indicate the electrochemical adsorption and desorption at the electrode-electrolyte interface. Figure 2(a) shows the comparison of RG-EDLC and MRG-EDLC at 0.5 A/g and 1 A/g. It can be seen that the RG-EDLC discharges faster in comparison to the time taken to charge it at a current density of 0.5 A/g. A similar kind of behavior was observed even at a current density of 1.0 A/g, the maximum current density for the RG-EDLC to charge and discharge. In MRG-EDLC, the time taken to charge and discharge were almost the same and discharging of MRG-EDLC at current densities of 0.5 A/g and 1 A/g were at a much slower rate in comparison to RG-EDLC. A similar phenomenon of charging and discharging time being equal was also observed at current densities of 2 A/g and 2.5 A/g as shown in Figure 2(b).

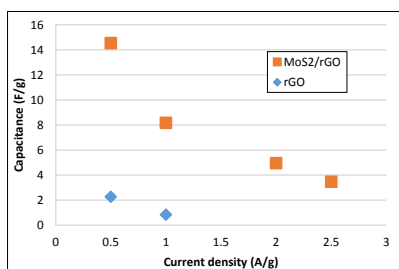


(a)

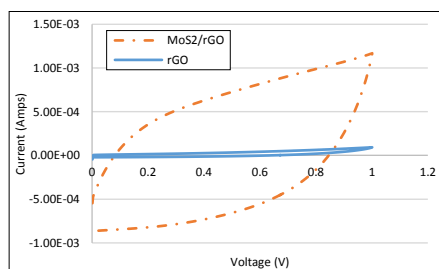


(b)

Figure 2 Typical galvanostatic charge-discharge curves for (a) RG-EDLC and MRG-EDLC at 0.5 A/g and 1 A/g current density and (b) MRG-EDLC at 2 A/g and 2.5 A/g current density.



(a)



(b)

Figure 3 Electrochemical characterization of nanosheet film-based EDLCs. Specific capacitance at various discharge current densities (a) and cyclic voltammetry curves (b) of RG-EDLC and MRG-EDLC at a current density of 0.5 A/g.

The maximum potential for MRG-EDLC is 2V and for the RG-EDLC is 3.35V. But the specific capacitances were 14.52 F/g and 8.17 F/g at 0.5A/g and 1 A/g of MRG-EDLC (Figure 3(a)), respectively, which is almost 6-10 times higher in comparison to RG-EDLC with specific capacitances of 2.26 F/g and 0.825 F/g at 0.5 A/g and 1 A/g, respectively (Figure 3(a)). In addition, the maximum operating current density for the MRG-EDLC is 2.5 A/g, whereas it is just 1 A/g for RG-EDLC. Cyclic voltammetry (CV) measurements are used to determine the capacitive behavior of the EDLCs. As the area of the hysteresis loop in the CV curve widens for an EDLC, it indicates a higher capacitance. Figure 3(b) shows the CV plots of the RG-EDLC and MRG-EDLC. Clearly, the area of the hysteresis-loop for the MRG-EDLC is much greater from a higher capacitance, whereas in RG-EDLC, the small loop area is less, indicating a low capacitance.

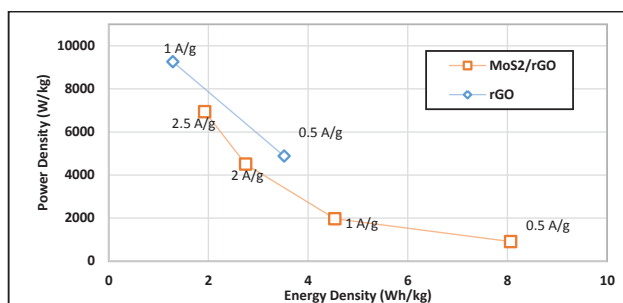


Figure 4 Power density versus energy density for RG-EDLC and MRG-EDLC

The increase in charge-discharge time leads to an increase in capacitance, which in turn leads to an increase in energy density in these EDLCs. The power density depends on the discharge time (t_d). The energy density and the power density can be calculated using the formula:

$$\text{Energy density} \quad E = \frac{CV^2}{2} \quad (1)$$

$$\text{Power density} \quad P = \frac{E}{t_d} \quad (2)$$

where C is the capacitance and V is the potential window. It can be seen from Figure 4 that at a current-density of 0.5 A/g, the energy-density of MRG-EDLC (8.06 Wh/kg) has increased more than 2 times than that of the RG-EDLC (3.52 Wh/kg). At a current density of 1.0 A/g, the energy-density has increased 3.5 times, from 1.28 Wh/kg in RG-EDLC to 4.53 Wh/kg for the MRG-EDLC. The power-density of MRG-EDLC increases as the current density increases with a minimum of 907.5 W/kg at 0.5 A/g and a maximum of 6,940 W/kg at 2.5 A/g.

CONCLUSION

In this work, rGO nanosheets were successfully nano-blended with molybdenum disulfide (MoS₂) sheets at a temperature of 350°C in nitrogen ambient for EDLC applications.

The specific capacitance of the MRG-EDLC increased twice compared to that for the RG-EDLC, which in turn led to a 2 times increase in energy-density at a current-density of 0.5 A/g. The current-density at which the EDLC can operate also increased from 1.0 A/g to 2.5 A/g. Under this inspiration, we will further advance the rechargeable supercapacitor technology using this 2D-MoS₂/rGO nanocomposite.

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