Reduced graphene oxide aerogel for supercapacitor electrode

Ngo Van Hoanh[1], Phung Xuan Thinh[2], Le Huu Thanh[1],
Le Trung Hieu[1], Ngo Tien Quyet[3], Nguyen Tran Hung[1*]

[1]Institute of Chemistry and Materials, Academy of Military Science and Technology;
[2]Deparment of Education, Academy of Military Science and Technology;
[3]University of Science, Vietnam National University, Ha Noi.
[*]Corresponding author: nguyentranhung28@gmail.com
Received 16 Dec. 2022; Revised 20 Feb. 2023; Accepted 08 Aug. 2023; Published 25 Aug. 2023.
DOI: https://doi.org/10.54939/1859-1043.j.mst.89.2023.67-72

ABSTRACT

In this study, the rGO aerogel material was successfully fabricated by freeze-drying combined with high-temperature reduction method. The characteristics of rGO aerogel were investigated by modern techniques such as SEM-EDX, XRD, Raman, N_2 adsorption and desorption. Electrochemical properties were studied through cyclic potential scanning (CV), charge-discharge (GCD) and electrochemical Imdependance Spectroscopy (EIS) methods in 6M KOH electrolyte solution. Research results show that rGO aerogel has a large specific surface area and pore volume of 162.4 m^2/g and 0.237 cm^3/g, respectively, and a large specific capacitance of 90 F/g at a current density of 0.1 A/g and long charge-discharge life with specific capacitance reaching 87.5% after 500 charge-discharge cycles.

Keywords: Graphene aerogel; Supercapacitor; Capacity; Electrode.

1. INTRODUCTION

Electrochemical capacitors (supercapacitors) with high of power density, fast of charge/discharge rates and long of cycle life have been become main complements to secondary batteries [1, 2]. Depending on the charge storage mechanisms, supercapacitors can be distinguised into two classes: the electrochemical double layer capacitor with carbonaceous active materials as electrodes, while the other is pseudocapacitor or redox supercapacitors with transition-metal oxides or conducting polymers electrodes [3, 4] .

Electrochemical double-layer capacitors (EDLCs) show fast charging performance and excellent charge-discharge stability among the energy storage devices. EDLCs store electrical charge on high surface area conductive materials [5].

Reduced graphene oxide (rGO), has been widely studied as a electrode material for supercapacitor due to its high conductivity and stable cycling propety. The rGO in an aerogel structure show high surface area and porosity that enable the easy access of electrolyte ions. Various methods have been studied to enhance rGO aerogel as a supercapacitor electrode, such as aerogel composite formation with transition metal oxide (TMO), conductived polymers, or heteroatom (nitrogen, sulfur) doping in rGO aerogel [6, 7].

In this study, a simple approach is applicated to synthesis rGO aerogel which used as supercapacitor electrode material. GO, as the aerogel precursor, was produced by freeze-drying method and used for the rGO aerogel formation by high temperature reducing. The material performance and electrochemical properties of rGO aerogel electrode material was investigated.

2.EXPERIMENTAL

2.1 Chemicals and raw materials

Graphit powder (99%, Merck), H2SO4 (98%, Sigma Aldrich), H3PO4 (85%, Aladdin), KMnO4 (AR, Merck), H2O2 solution (30%, Aladdin), HCl solution (37 %, Aladdin), Deionized water.

2.2. Preparation of rGO aerogel

rGO aerogel was produced by ice-template method. Fist, 1 g of graphite was oxidized with a mixture of 90 mL H_2SO_4 (98%), 10 mL of H_3PO_4 (85%) and 6 g of $KMnO_4$ at 5 ^oC for 15 min. The mixture was stirred for 3 h at 70 ^oC. The oxidation was stopped with 50 mL H_2O_2 (30%) and the solution transfer to brown. Centrifugation at 4000 r/min was applied to wash mixture 5 times with HCl solution (37%) followed by 200 mL deionized water until the pH was neutral. GO dispersion was obtained after exfoliated through sonication for 30 minutes. GO dispersion (10 mg/mL) was frozen at -40 ^oC and freeze-dryed at -80 ^oC for 48 h. The resultant rGO aerogel was obtained by reducting GO aerogel at 900 ^oC for 4 h under Ar gas.

2.3. Materials characterization

The crystal structure of rGO aerogel was identified by X-ray diffractometer on a Bruker D8-Advance (Germany) with CuKα radiation in the angle range 2θ from 10^o to 70^o. The specific surface area and porosity distribution of rGO aerogel were investigated by a N_2 adsorption-desorption isotherm using a Tri Start 3000 at 77K with a degasing temperture at 200 ^oC for 5 h. The surface morphology and elemental compositon were studied by a scan electron microscope with an energy-dispersive X-ray analysis at an accelerating voltage of 15 kV (SEM-EDX).

2.4. Supercapacitor electrodes preparation and electrochemical mesurements

To obtain the electrochemical mesurements of the prepared sample, the two-electrode configurations were used. The nickel foil was pretreated with absolute ethanol and dried at 80 ^oC for 3 h. The supercapacitor electrodes were made of rGO aerogel, conductive (Carbon super-P), and the binder: PVDF in 8:1:1 ratio using N-methyl-2-pyrrolidone as solvent. After milling by ball mill for 8 hours, the mixture was coated on the nickel foil with a size ϕ= 8 mm. The prepared electrode were then dried at 100 ℃ in vacuum for 12 hours to remove solvent. An aqueous solution of 6M KOH was used as the electrolyte. Electrodes made by the method mentioned above were immersed into the electrolyte. Then, two electrodes were assembled in a cell-lock.

The electrochemical performances of rGO electrodes were investigated by Cyclic Voltammetry (CV), Gavanostatic Charging- Discharging (GCD) and Electrochemical Imdependance Spectroscopy (EIS) measuraments, which were carried out by Autolab PGSTAT309n (Metrohm, Switzerland). The specific capacitance (Cs) of the electrodes materials and energy density of supercapacitor (E) were calculated vis Eq.(1) and Eq.(2), respectly [8].

$$C_s = \frac{2I \times \Delta t}{m \times \Delta V} \quad (1)$$

Where I (A), Δt (second), ΔV (V), m (mg) is current, discharging time, potential window and the mass of the active material on electrode, respectively.

$$E = \frac{C \times \Delta V^2}{2} = \frac{C_s \times \Delta V^2}{8} \quad (2)$$

Where E is the energy density (Wh/kg).

3. RESULTS AND DISCUSSION

3.1. Characterization of rGO aerogel

Morphological properties of rGO were investigated by a scanning electron microscope. The water removal during the reducing process forms the pores in rGO aerogel. As seen in figure 1, the interconnected pore in material can be observed.The carbon wall of aerogel was formed by several stacking layers of the rGO sheet that increase the mechanicals strength of the aerogel structure. The EDX results showed that, the major compositon of rGO is C (81,18 wt%) and O (18,50 wt%) with C/O ratio is 4.38, which contributes to the excellent performance of rGO

aerogel for supercapacitor electrode [9].

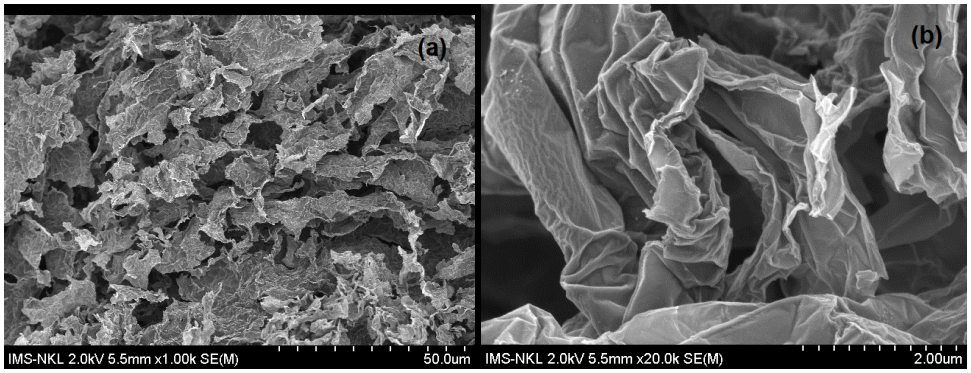
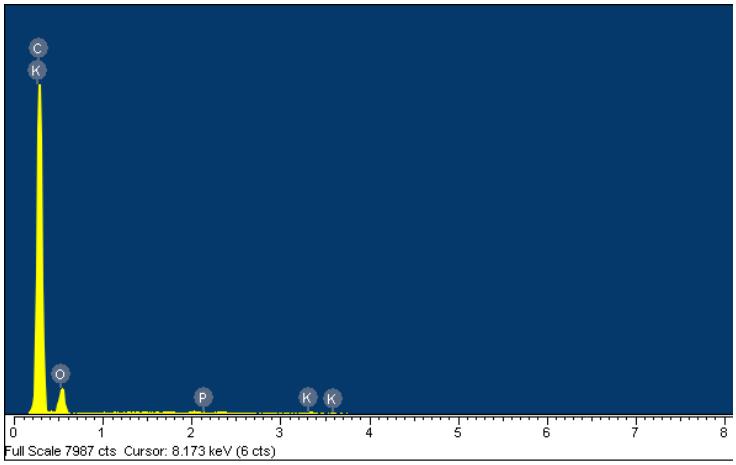


Figure 1. *SEM images at 1000x (a) and 20000x (b) for rGO aerogel.*



C (wt%)	O (wt%)	C/O
81.18	18.50	4.38

Figure 2. *EDX pattern for rGO aerogel.*

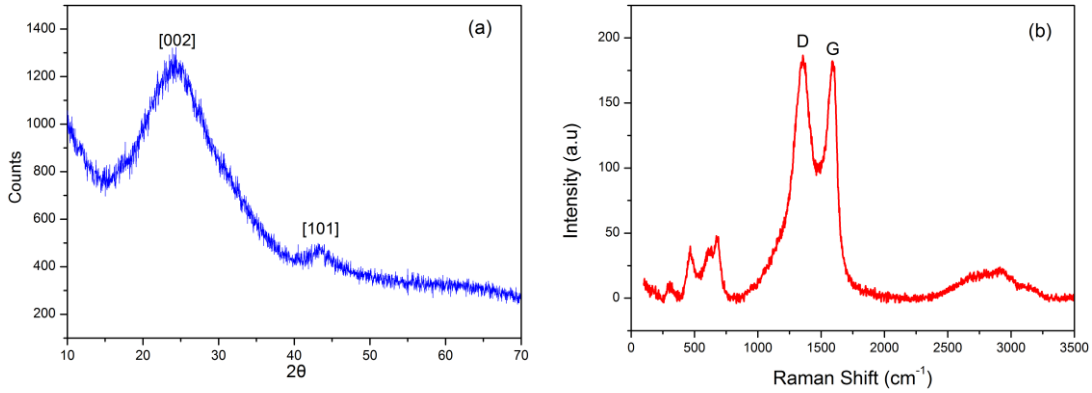


Figure 3. *(a) XRD pattern and (b) Raman spectra for rGO aerogel.*

XRD pattern of rGO aerogel shows the major peaks at 2θ= 25.6° and 42.9°, associated with diffraction of graphitic carbon of (002) and (101), respectively. Accounting on the (002) peak, the interlayer spacing of material (d) were 3.5 Å, which indicates the oxygen containing groups removal from GO surface (2θ=10.27°, d=9.05Å) [10]. The stacking of rGO sheets can be divided

into parallel and nonparallel structure. The peak (101) and (002) nonparallel can be used for explaining the parallel and nonparallel stacking of rGO aerogel, respectly. The high peak area ratio of (002)/(101) shows the major stacking of rGO is parallel [9].

Raman spectra was shown in Fig. 3b, show two major peaks at 1355 cm^{-1} and 1590 cm^{-1}. The D peak around 1355 cm^{-1} reflects the vibration of the sp^3 carbon-carbon of the hexagonal layer and sp^2 carbon with other functional groups which contain oxygen atom. The G peak at 1590 cm^{-1} is attributed of of sp^2-bonded carbon atoms [11, 12]. The I_D/I_G ratio of rGO aerogel is 1.02. Compared with other carbon materials, rGO aerogel show higher value ratio of I_D/I_G. During the reduction process, the surface carbon atoms of rGO aerogel were carried off slowly and disorderedly, thus, leaving the free bond at the surface and forming a disordered carbon structure [13].

The N_2 adsorption-desorption cycle of rGO aerogel was presented in Fig. 4 show that the isotherm of material can be classified into type II model which is characteristic for macroporous materials. The adsorption of N_2 on the rGO sheets surface in the aerogel includes monolayer and multilayer adsorption process. The N_2 adsorption volume at the low P/P° area show that a significant overlapping of monolayer adsorption and the beginning of multilayer adsorption. The increase of adsorption volume at the P/P°=1 due to macroporous pore and multilayer N_2 diffusion and adsorption behavior [14]. The rGO aerogel has high specific surface area S_{BET}=162.4 cm^2/g and pore volumn V_p =0.237 cm^3/g.

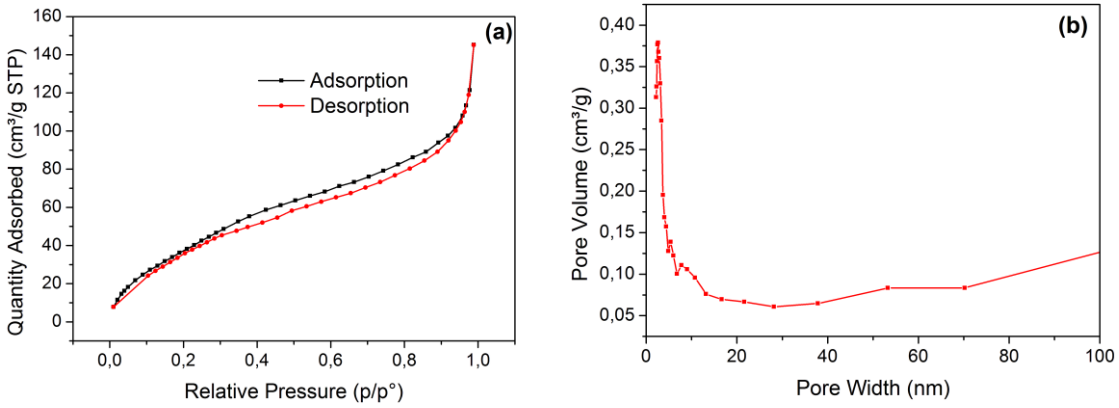


Figure 4. *(a) N_2 adsorption-desorption isotherm and (b) pore size distrubution.*

3.2. Electrochemical properties

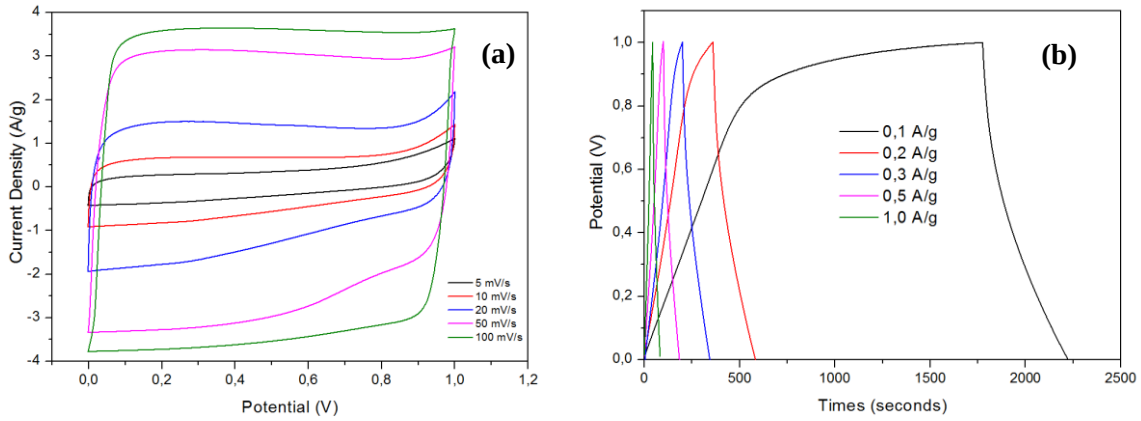


Figure 5. *(a) CV curves and (b) GCD cures of rGO aerogel at different current densities.*

The electrochemical properties of rGO aerogel were studied by CV technique. The CV cycle of rGO aerogel at different scan rate from 10 mV/s to 100 mV/s were showed in Fig. 5a. The CV

curves of the material exhibit an EDLC behavior by showing a rectangular CV shape with a large area, indicating distinct capacitive behavior and reversibility.

The galvanostatic charge-discharge test were used to evaluate the electrochemical performance of rGO aerogel under the operational conditions as a supercapacitor. Fig.5b shows the (GCD) graphs at different current density from 0.1 to 1 A/g in the potential range from 0 to 1 V. The specific capacitance of each electrode was calculated from the discharge curve slope vis Eq.1. The rGO aerogel shows an excellent specific capacitance of 90 F/g at 0.1 A/g and 80 F/g at 1 A/g. The capacitor has a pretty energy density about 11.25 Wh/kg.

The Nyquist plot representing the resistance of the rGO aerogel electrode is shown in Figure 6a. Nyquist plot of electrode samples with starting point at Z'= 0.3 Ω shows that the rGO aerogel electrode has a relatively low internal resistance and solution resistance Rs. The 45° inclined line representing the Warburg impedance of the rGO sample is very short, indicating that ions can easily move through the pores of the material.

The GCD test procedure was repeated with sets of 500 cycles. The capacitance retention of the capacitor (Fig.6b) shows that rGO aerogel exhibit outstanding stability. The capacitance retention of rGO aerogel remains 85.7% after 500 charge-discharge cycles. It is possible that the rGO aerogel materials have lost their original structure and porosity, which has affected their conductive and charge-discharge properties.

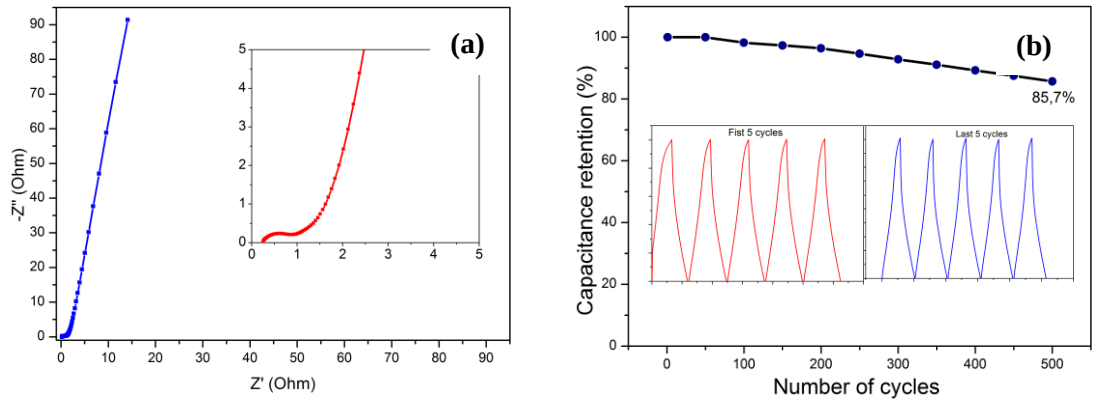


Figure 6. *(a) Nyquist plot of rGO aerogel*

and (b) Cycling performance of rGO electrodes at 1.0 A/g.

4. CONCLUSIONS

rGO aerogel was successfully prepared, the characterization and electrochemical performance of rGO aerogel were studied. The obtained rGO shows high specific surface area S_{BET}=162.4 cm^2/g and pore volumn V_p=0.237 cm^3/g. The structural properties contribute to the electrochemical properties of the rGO aerogel (90 F/g at 0.1 A/g) with high cycles stability (85.7% capacitance retention for 500 cycles). This study provides a promising route to prepare rGO aerogel as highly efficient electrodes materials for supercapacitors.

REFERENCES

[1]. Liu, B., Q. Zhang, Z. Wang, et al., "*Nitrogen and Sulfur-Codoped Porous Carbon Nanospheres with Hierarchical Micromesoporous Structures and an Ultralarge Pore Volume for High-Performance Supercapacitors*". ACS Applied Materials & Interfaces. **12**(7): p. 8225-8232, (2020).

[2]. Fan, W., C. Zhang, W.W. Tjiu, et al., "*Graphene-Wrapped Polyaniline Hollow Spheres As Novel Hybrid Electrode Materials for Supercapacitor Applications*". ACS Applied Materials & Interfaces. **5**(8): p. 3382-3391, (2013).

[3]. Yang, X., Y. Li, P. Zhang, et al., "*Hierarchical hollow carbon spheres: Novel synthesis strategy, pore structure engineering and application for micro-supercapacitor*". Carbon. **157**: p. 70-79, (2020).
[4]. Bavio, M.A., G.G. Acosta, and T. Kessler, "*Polyaniline and polyaniline-carbon black nanostructures as electrochemical capacitor electrode materials*". International Journal of Hydrogen Energy. **39**(16): p. 8582-8589, (2014).
[5]. Huang, G., Q. Geng, B. Xing, et al., "*Manganous nitrate -assisted potassium hydroxide activation of humic acid to prepare oxygen-rich hierarchical porous carbon as high-performance supercapacitor electrodes*". Journal of Power Sources. **449**: p. 227506, (2020).
[6]. Zang, P., S. Gao, L. Dang, et al., "*Green synthesis of holey graphene sheets and their assembly into aerogel with improved ion transport property*". Electrochimica Acta. **212**: p. 171-178, (2016).
[7]. Sethi, M., H. Bantawal, U.S. Shenoy, et al., "*Eco-friendly synthesis of porous graphene and its utilization as high performance supercapacitor electrode material*". Journal of Alloys and Compounds. **799**: p. 256-266, (2019).
[8]. Simon, P. and Y. Gogotsi, "*Materials for electrochemical capacitors*". Nature Materials. **7**(11): p. 845-854, (2008).
[9]. Wu, X., J. Zhou, W. Xing, et al., "*High-rate capacitive performance of graphene aerogel with a superhigh C/O molar ratio*". Journal of Materials Chemistry. **22**(43): p. 23186-23193, (2012).
[10]. Lee, S.P., G.A.M. Ali, H. Algarni, et al., "*Flake size-dependent adsorption of graphene oxide aerogel*". Journal of Molecular Liquids. **277**: p. 175-180, (2019).
[11]. Zhao, G., C. Chen, D. Yu, et al., "*One-step production of O-N-S co-doped three-dimensional hierarchical porous carbons for high-performance supercapacitors*". Nano Energy. **47**: p. 547-555, (2018).
[12]. Wei, G., J. Yu, M. Gu, et al., "*Dielectric relaxation and hopping conduction in reduced graphite oxide*". Journal of Applied Physics. **119**: p. 224102, (2016).
[13]. Chaunchaiyakul, S., T. Yano, K. Khoklang, et al., "*Nanoscale analysis of multiwalled carbon nanotube by tip-enhanced Raman spectroscopy*". Carbon. **99**: p. 642-648, (2016).
[14]. Thommes, M., K. Kaneko, A.V. Neimark, et al., "*Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)*". **87**(9-10): p. 1051-1069, (2015).

TÓM TẮT

Vật liệu rGO aerogel ứng dụng trong điện cực siêu tụ điện

Trong nghiên cứu này, vật liệu rGO aerogel được chế tạo thành công bằng phương pháp đông khô kết hợp khử ở nhiệt độ cao. Đặc trưng của rGO aerogel được khảo sát bằng các kỹ thuật hiện đại như SEM-EDX, XRD, Raman, hấp phụ giải hấp N_2. Tính chất điện hóa được nghiên cứu qua phương pháp quét thế vòng (CV), xạc - xả (GCD) và đo tổng trở (EIS) trong dung dịch điện phân KOH 6M. Kết quả nghiên cứu cho thấy, rGO aerogel có diện tích bề mặt riêng và thể tích lỗ xốp lớn lần lượt là 162,4 m^2/g và 0,237 cm^3/g, điện dung riêng lớn đạt 90 F/g ở mật độ dòng 0.1 A/g và tuổi thọ xạc xả lớn với điện dung riêng đạt 87.5% sau 500 lần xạc xả liên tục.

Từ khoá: Graphen; Aerogel; Siêu tụ điện; Tính chất điện hóa.