



ARTICLE

Effects of Polypyrrole / Graphene Oxide Composites with Different Reaction Times on Electrochemical Performance

Minzhen Feng Wei Lu* Ranran Zhen Ya Wang Yun Zhou

Chongqing Key Laboratory of inorganic Function Materials, College of Chemistry, Chongqing Normal University, Chongqing, 401331, China

ARTICLE INFO

Article history

Received: 10 February 2020

Accepted: 10 February 2020

Published Online: 30 April 2020

Keywords:

Graphene oxide

Polypyrrole

Supercapacitors

ABSTRACT

Graphene oxide (GO) was prepared using the modified Hummers method and used as a template for polypyrrole. Polypyrrole was polymerized in situ on the surface of GO to finally obtain the polypyrrole/graphene oxide composite material. The effects of different reaction times on the electrochemical performance of polypyrrole/graphene oxide in the second step were studied. It was obtained that the composite material had optimal properties when the reaction time was 24 h.

1. Introduction

With the development of today's society, people's demand for energy is increasing. The development and application of new energy are imminent. As a new type of energy storage device, supercapacitor has been widely used in various fields such as electric vehicles, communications, and industrial production. Because of its advantages such as fast charging speed and high power density, it has been widely used in various fields such as electric vehicles, communications, and industrial production^[1-3]. It is well known that supercapacitors correspond to different electrode materials according to different energy storage mechanisms^[4-6]. At present, common electrode materials include carbon nanotubes, biomass carbon and other high specific surface area carbon materials, metal oxides, and high-molecular

conductive polymers. Conductive polymers have attracted much attention because of their good electrical conductivity and higher specific capacitance. Among many conductive polymers, polypyrrole is considered to be one of the most valuable electrode materials due to its characteristics of cheap raw materials, simple synthesis, and high theoretical capacitance. However, due to its poor mechanical properties, the polypyrrole has a significant change in volume after multiple charge and discharge tests at high rates, and its conductivity decreases. As a result, the polypyrrole exhibits a poor capacitance retention rate and a rapidly decaying capacitance^[7-10].

In order to improve the shortage of pure polypyrrole, polypyrrole can be combined with carbon materials to improve its performance. Such as graphene oxide, biomass carbon, activated carbon and so on. Among many carbon

*Corresponding Author:

Wei Lu,

Chongqing Key Laboratory of inorganic Function Materials, College of Chemistry, Chongqing Normal University, Chongqing, 401331, China;

Email: mailluwei666@126.com

materials, graphene oxide has a wrinkled surface, which results in graphene oxide having a large specific surface area. In addition, the surface of graphene oxide has a large number of oxygen-containing functional groups, so that it has better water solubility, which is conducive to better dispersion of graphene oxide in water. In order to provide more active sites for polypyrrole, the polypyrrole nanospheres are embedded on the graphene oxide substrate. However, the reaction time for the synthesis of polypyrrole has a great impact on the morphology of polypyrrole and its performance in super capacitors. In this paper, modified Hummers method was used to prepare graphene oxide^[11]. Polypyrrole nanospheres were prepared on the surface of graphene oxide by in-situ polymerization. At the same time, the optimal reaction time of polypyrrole were discussed.

2. Experimental Part

2.1 Experimental Reagent

Hydrogen peroxide, Potassium hydroxide, Graphite, Sodium nitrite, Sulfuric acid, Potassium permanganate, Absolute ethanol, Chlorhydric acid, Pyrrole, Ammonium persulfate(APS), N-methylpyrrolidone, Acetylene black, Carbon paper. All medicines were purchased from research technology suppliers and used without further purification.

2.2 Experimental Process

(1) Synthesis of graphene oxide by improved Hummers method^[11]. 60 ml of dilute hydrochloric acid was mixed with 20 ml of ethanol solution, and 36 mg of graphene oxide solid powder was added thereto. The above mixed solution was dispersed uniformly by ultrasound, and then pyrrole monomer was added.

(2) Take a certain amount of APS and dissolve it in 20 ml of dilute hydrochloric acid to obtain the pre-prepared mixed solution.

The above two solutions were stirred in a water bath below 0°C. Slowly add the pre-prepared mixed solution to the liquid mixed with graphene oxide, and react the mixed solution in the ice bath for 6 h, 12 h, 18 h, and 24 h. Finally, the resulting solution was suction filtered and washed with dilute HCl, ethanol and deionized water in this order. Dry in a vacuum oven at 60°C for 10 h. The obtained product was a polypyrrole/graphene oxide composite (PPy/GO).

2.3 Test Equipment

Cyclic voltammetry and constant current charge and dis-

charge tests were performed on all samples using H₂SO₄ as electrolyte in Shanghai Chen Hua CHI660E. The cyclic voltammetry test voltage is -0.2~0.8 V, Ag/AgCl is the reference electrode, Pt sheet electrode is the counter electrode, and the test sample is the working electrode; Charge/discharge test voltage selection range is 0~0.8 V.

3. Results and Discussion

3.1 Electrochemical Testing of Materials

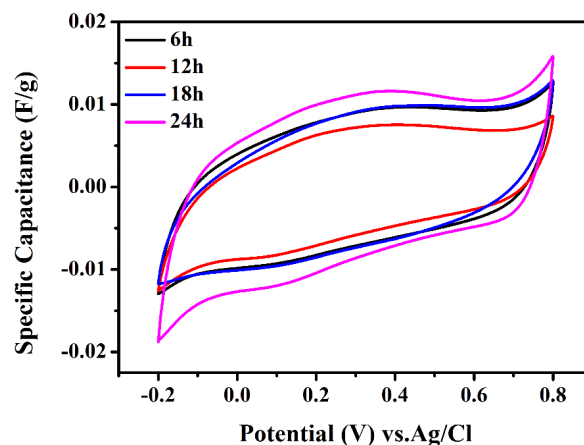


Figure 1. Cyclic voltammetry curves of PPy/GO with different reaction times

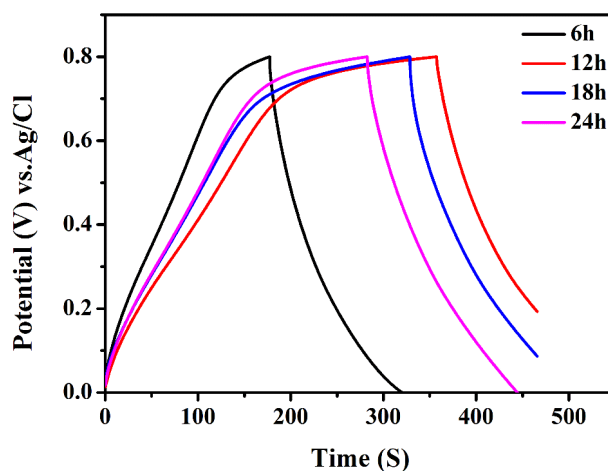


Figure 2. Charge/discharge of PPy/GO with different reaction times

Figure 1 is a cyclic voltammetry diagram of PPy/GO prepared at different reaction times. The scan rate is 20 mv s^{-1} , and the test voltage is -0.2 V to 0.8 V. It can be seen that the shapes of all the curves are almost the same. Protrusions appear on the scan curves. This is because during the test, the sample has undergone a redox reaction and exhibited a redox peak. It can also be seen from Fig-

ure 1 that when the reaction time is 24 h, the area enclosed by the CV curve is the largest. This shows that under this reaction time, the sample has a larger specific capacitance [12-13].

Figure 2 is a GCD chart of samples prepared at different reaction times. It can be seen from the figure that the performance of PPy/GO with a reaction time of 24 h is the best. Although the discharge time of PPy/GO with a reaction time of 24 h is lower than that of the 12 h and 18 h samples, the reaction discharge part of the former two is not fully discharged, which has a greater impact on the stability of the sample [14-15].

4. Conclusions

In short, graphene oxide prepared by the improved Hummers method has a large specific surface area. The effects of different reaction times on the electrochemical performance of PPy/GO composites were discussed. It was finally obtained that the PPy/GO composite had the best electrochemical performance when the reaction time was 24 h. In general, as the research continues, the optimization of PPy/GO will become more in-depth. I believe that PPy/GO will definitely become one of the most popular electrode materials in the future.

Acknowledgements

This work was supported by national natural science foundation of China (21504010); Open project of engineering research center of active material biotechnology, ministry of education, Chongqing normal university (AS201609).

References

- [1] Wang Y., Shi Z., Huang Y., et al. Supercapacitor Devices Based on Graphene Materials[J]. *Journal of Physical Chemistry*, 2009, 113(30): 13103-13107.
- [2] Frackowiak, Elzbieta. Carbon materials for supercapacitor application[J]. *Physical Chemistry Chemical Physics*, 2007, 9(15): 1774-0.
- [3] Snook G A , Kao P., Best A S.. Conducting-polymer-based supercapacitor devices and electrodes[J]. *Journal of Power Sources*, 2011, 196(1): 1-12.
- [4] Yang H , Kannappan S , Pandian A S , et al. Graphene supercapacitor with both high power and energy density[J]. *Nanotechnology*, 2017, 28(44): 445401.
- [5] He Y., Chen W., Li X., et al. Freestanding Three-Dimensional Graphene/MnO₂ Composite Networks As Ultra light and Flexible Supercapacitor Electrodes[J]. *ACS NANO*, 2013, 7(1): 174-182.
- [6] Borenstein A , Hanna O., Attias R., et al. Carbon-Based Composite Materials for Supercapacitor Electrodes: A Review[J]. *Journal of Materials Chemistry A*, 2017, 5(25).
- [7] Siuzdak K., Bogdanowicz R.. Nano-engineered diamond-based materials for supercapacitor electrodes: A review[J]. *Energy Technology*, 2017.
- [8] Carratalá-Abril J., Rey-Martínez L., Beneito-Ruiz R., et al. Development of Carbon-based Composite Materials for Energy Storage[J]. *Materials Today: Proceedings*, 2016, 3: S240-S245.
- [9] Liu Y., Nie C., Liu X., et al. Review on carbon-based composite materials for capacitive deionization[J]. *RSC Adv.* 2015, 5(20): 15205-15225.
- [10] Ke Q., Wang J.. Graphene-based Materials for Supercapacitor Electrodes - A Review[J]. *Journal of Materials*, 2016: S2352847816000022.
- [11] Hummers W S, Offeman R E. Preparation of Graphitic Oxide[J]. *Journal of the American Chemical Society*, 1958, 208: 1334-1339.
- [12] Zhang X., Ma L., Gan M., et al. Fabrication of 3D lawn-shaped N-doped porous carbon matrix/polyaniline nanocomposite as the electrode material for supercapacitors[J]. *Journal of power sources*, 2017, 340(FEB.1): 22-31.
- [13] Rasouli H., Naji L., Hosseini M G.. 3D structured polypyrrole/reduced graphene oxide (PPy/rGO)-based electrode ionic soft actuators with improved actuation performance[J]. *New Journal of Chemistry*, 2018, 42.
- [14] Liu W., Fang Y., Xu P , et al. Two-Step Electrochemical Synthesis of Polypyrrole/Reduced Graphene Oxide Composites as Efficient Pt-Free Counter Electrode for Plastic Dye-Sensitized Solar Cells[J]. *ACS Applied Materials & Interfaces*, 2014, 6(18):16249-16256.
- [15] Fan X., Yang Z., He N.. Hierarchical nanostructured polypyrrole/graphene composites as supercapacitor electrode[J]. *RSC Advances*, 2015, 5(20): 15096-15102.