Research status and Prospect of graphene/MnO₂ composites for supercapacitors

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Abstract: The latest research progress of graphene/MnO₂ composites in supercapacitors is reviewed. The theoretical specific capacitance of MnO₂ is as high as 1370 F/g, but the actual specific capacitance is far less than the theoretical value due to the limitation of MnO₂ layer thickness. The combination of graphene and MnO₂ and the anchoring of MnO₂ nanostructures between graphene nanosheets can effectively inhibit the stacking of graphene and enhance the interfacial charge transfer. With the help of the synergistic effect of the two, it is expected to achieve high specific capacitance, high conductivity and good cycle stability. The preparation method and electrochemical performance of graphene/MnO₂ composite were introduced. The electrochemical performance was further improved due to the introduction of conductive polymer. Finally, it is pointed out that graphene/MnO₂ composites and devices still face a series of problems such as safety and reliability, large-scale production and cost reduction. With the continuous maturity and breakthrough of technology, it is expected to be applied in industry, transportation and daily electronic devices.

1. Introduction

Supercapacitor is a new type of energy storage device, which has the advantages of high power density, short charging time, long cycle life and environmental protection. It can be used in energy storage device, power supply system and many electronic equipment. According to the different energy storage mechanisms, supercapacitors can be divided into two categories: one is electric double-layer capacitors (EDLCs) with carbon as electrode material, which can store electric energy by electrostatic way by forming Helmholtz layer between electrode and electrolyte; The other is Faraday capacitor, which uses metal oxide and conductive polymer as electrode materials, also known as quasi capacitor or pseudo capacitor, which uses redox reaction to store electric double-layer energy in an electrochemical way. The composite capacitor combines the advantages of electric double-layer capacitor and pseudo capacitor in the selection of electrode materials[1].

The Faraday pseudocapacitance produced by oxidation-reduction reaction of transition metal oxides is much higher than that of carbon materials [2]. Therefore, researchers at home and abroad focus on transition metal materials. Manganese dioxide (MnO₂) is a typical green electrode material with high theoretical specific capacity (1370 F/g), rich natural content, low price and environmental friendliness[3]. Graphene is a kind of carbon material with two-dimensional structure. It has ideal thickness of monoatomic layer, theoretical specific surface area of 2630 m²/g, good conductivity and chemical stability. It is considered as an ideal electrode material for electric double-layer capacitor. However, the presence of van der Waals force makes graphene easy to agglomerate, thus reducing the specific surface area and specific capacity of graphene.
2. Graphene/MnO$_2$ composites

2.1. Solvothermal(hydrothermal) method

Solvothermal (hydrothermal) method is a synthesis process which takes high pressure reactor as reactor, solvent (water) as reaction medium, using hydrolysis crystallization of metal salts under high temperature and high pressure. Dai et al.\cite{4} successfully prepared fibrous MnO$_2$/graphene composites with graphene and KMnO$_4$ as raw materials under hydrothermal treatment at 160°C for 12 h, and the effects of different contents of MnO$_2$ and graphene on the electrochemical properties of the composites were investigated. The one-dimensional fibrous MnO$_2$ in the composite can not only prevent the aggregation of two-dimensional sheet graphene, but also optimize the electrochemical properties of the composite. The results show that the composite with 90% graphene content has the best electrochemical performance (in the three electrode test system, the maximum specific capacitance of the composite is 170 F/g, and the capacitance retention rate is 97.1% after 1000 charge discharge cycles). Sun et al.\cite{5} used KMnO$_4$ and graphene as raw materials to prepare MnO$_2$/graphene composite under the hydrothermal condition of 120°C. The micro morphology of MnO$_2$/graphene composite is shown in Fig. 1. When the current density is 0.2 A/g, the specific capacitance of the composite is 169 F/g. After 1000 cycles, the capacitance retention rate is 75.5%.

![Figure 1. Micromorphology of MnO$_2$/graphene composites](image)

2.2. Electrochemical deposition method

Electrochemical deposition refers to the process that under the action of electric field, in a certain electrolyte solution, the ions in the solution are deposited on the cathode or anode surface through redox reaction. Composite electrodes in supercapacitors usually need adhesives. Xiong et al.\cite{6} prepared 3D MnO$_2$/RGO composites by electrodeposition, electrophoresis and thermal reduction. RGO is introduced into MnO$_2$ electrode material to form a stable 3D composite structure. At the same time, MnO$_2$ can prevent the stacking of RGO, resulting in porous morphology and double-layer structure, increasing the specific surface area. Ghasemi et al.\cite{7} synthesized needle like MnO$_2$ nanostructures with potassium bromate and manganese sulfate. Nano MnO$_2$ coated with graphene oxide (GO) was prepared by electrostatic precipitation method. MnO$_2$ and GO generate positive and negative charges respectively, and precipitate after electrostatic attraction. MnO$_2$/RGO nanocomposites were prepared by electrochemical reduction of MnO$_2$/GO on stainless steel mesh. MnO$_2$/RGO has high capacitance (375 F/g, 1 A/g) and good cycle stability. The results show that this morphology can provide a suitable interface for cation exchange and charge storage.

2.3. Microemulsion method

Microemulsion method refers to two insoluble solvents which form emulsion under the action of surfactants\cite{8}. After obtaining nucleation, coalescence, heat treatment, nanoparticles are obtained, and the particle size and stability of nano materials are precisely controlled. The dispersity and interface of particles are good\cite{9}. LIU et al.\cite{10} dispersed graphene oxide (GO) and KMnO$_4$ in distilled water and added oleic acid by ultrasonic
wave. MnO₂/graphene nanocomposites were obtained by microemulsion method. MnO₂ flower like nanospheres are uniformly dispersed, as shown in Fig.2. The concavoconvex surface of MnO₂ nanospheres can not only increase the specific surface area, but also contact more electrolytes, which contributes to better cycle stability and higher specific capacitance. When the current density is 1.0 A/g, the specific capacitance of the composite is as high as 250.6 F/g. after 1000 cycles of constant current charge discharge, the capacitance loss is small and the retention rate is about 91.18%.

2.4. Chemical reaction method
Qian et al [11] used sodium polystyrene sulfonate (PSS) as modifier in the reduction process of GO, which not only improved the dispersion of graphene in solution, but also facilitated the uniform adsorption and growth of metal ions on graphene sheets. The specific capacitance of the composite prepared by this method is 324 F/g at the scanning rate of 10 mV/s in the three electrode system, and the specific capacitance decreases only 3.2% after 1000 charge discharge cycles. Choi et al [12] used polystyrene spheres (PS) as templates to introduce uniform macropores on the surface of graphene to improve its ion transport efficiency. Then granular MnO₂ was loaded on the graphene surface. In the three electrode system, the maximum specific capacitance of the composite was increased to 389 F/g. The asymmetric supercapacitors with maximum energy density of 44 Wh/kg were obtained by using the composite and three-dimensional macroporous graphene as electrodes. The maximum specific capacitance of MnO₂/graphene composite was 280 F/g in the three electrode system.

2.5. Microwave assisted method
When microwave radiation is used to synthesize nano metal oxides, the penetration depth is high, the nucleation rate is fast, the thermal gradient of reaction medium is small, and the synthesis time is short. Due to the high concentration of local heat, very fine nanocrystalline particles are usually produced, which can be repeatedly synthesized into crystalline metal oxide nanomaterials[18]. Vimuna et al [13] prepared MnO₂/GO composites by microwave radiation self limited deposition method. Under microwave irradiation in water isopropanol system, needle like MnO₂ crystals deposited on the surface of go lamellae are helpful to improve the electrochemical properties of the composites. The specific capacitance is 280 F/g. Yan et al [14] synthesized MnO₂/graphene composites by microwave irradiation, in which MnO₂ accounted for 78%. The specific capacitance is 310 F/g at 2.0 mV/s and 228 F/g at 500 mV/s, which is almost three times of that of pure graphene (104 F/g) and pure MnO₂ (103 F/g).

3. Graphene/manganese dioxide/conductive polymer composites
As a new electrode material, conductive polymer has the characteristics of high specific capacitance, energy density and power density. Because of its good flexibility and light weight, the main research direction is applied to the design and manufacture of energy storage devices, but the disadvantage is poor electrochemical
stability. Poly (3,4-ethylenedioxythiophene): polystyrene sulfonic acid (PEDOT:PSS) Coating MnO2 surface can not only increase the specific capacitance of the pseudocapacitor electrode, but also increase the conductivity of the electrode material by providing additional electron transmission channels. Hareesh et al. [17] used chemical methods to make PEDOT:PSS coating on the surface of MnO2/RGO composite material, the PEDOT:PSS/MnO2/RGO compound material. When the current density is 0.5 A/g, the specific capacitance is 633 F/g. after 5000 cycles, the capacitance still remains 100% and the cycle stability is excellent. Wu et al. [18] prepared MnO2/PANI/graphene nanobelts (MnO2/PANI/GNRs) ternary composites with three-dimensional porous structure by chemical method. As shown in Figure 3 (a), GNRs are encapsulated by PANI and polymerized for the first time. At the same time, MnO2 nanorods were introduced, and GNRs were crosslinked with MnO2 and embedded in PANI. As shown in FIG.3 (b)~(d), MnO2/PANI/GNRs have a three-dimensional porous structure, which provides an effective channel for ion transport. From Fig.3 (e)~(h), MnO2 and GNR are uniformly distributed in PANI array. When the current density is 1.0 A/g, the specific capacitance is 472 F/g. After 5000 cycles, the capacitance retention rate is 79.7%. At 10 A/g, the specific capacitance is 306 F/g, and the capacitance remains 65%.

4. Conclusion and Prospect
With the continuous development of super capacitor technology, its application scope has been extended from the initial electronic equipment field to the power field and energy storage field. Although great progress has been made in the development of supercapacitors in China, there is still a certain gap in mastering the core technology (electrode and electrolyte) compared with the leading countries. Pure graphene electrode only uses the double layer energy storage mechanism, so its capacitance is limited. The specific capacitance of Faraday pseudocapacitor material is larger, but the internal resistance is also large, so the cycling stability is poor under the condition of fast charge and discharge. The combination of graphene with metal oxide and conductive polymer can give full play to their advantages and improve the overall performance of the electrode. MnO2/graphene composites with conducting polymers and other pseudo capacitor materials, which take advantage of the synergy of the three, and through the control of microstructure and morphology, such as three-dimensional porous or cross-linked structure, are expected to bring better conductivity and electrochemical performance. Compared with other metal resources, MnO2 has high abundance, low cost and obvious competitive advantage. However, the electrode materials with high energy density, high cycle stability, light weight, safe operation and low cost need to be further developed and improved. Among them, the key to improve the electrochemical performance of the electrode materials is to optimize the composition and preparation process of the composite materials.

References
[1] Liu W J, Kao T W, Dai Y M, et al. Ni-based nanocomposites supported on graphene nano sheet (GNS) for supercapacitor applications[J]. Journal of Solid State Electrochemistry, 2014, 18(1):189-196.

[2] Choudhary N, Li C, Moore J, et al. Asymmetric Supercapacitor Electrodes and Devices [J]. Advanced Materials, 2017, 29(21):1605336.

[3] Liu K, Anderson M A. Porous Nickel Oxide/Nickel Films for Electrochemical Capacitors[J]. Mrs Online Proceedings Library Archive, 1996, 393(1):124-130.

[4] Dai X, Shi W, Cai H, et al. Facile preparation of the novel structured α-MnO2/Graphene nanocomposites and their electrochemical properties[J]. Solid State Ences, 2014, 27:17-23.

[5] SUN H B, GU H Z, CHEN Y. Preparation and electrochemical properties of graphene/MnO2 nanocomposites for supercapacitors[J]. Key Engineering Materials, 2018, 768: 102-108.

[6] XIONG C Y, LI T H, ZHAO T K, et al. Three-dimensional graphene/MnO2 nanowalls hybrid for high-efficiency electrochemical supercapacitors[J]. NANO, 2018, 13(1): doi: 10.1142/s1793292018500133.

[7] Ghasemi S, Hosseini S R, Booretalari O. Sonochemical assisted synthesis MnO2 RGO nanohybrid as effective electrode material for supercapacitor[J]. Ultrasonics Sonochemistry, 2018 40( Pt A):675-685.

[8] XU J, CHEN Y, DONG Z, et al. Facile synthesis of the Ti3+-TiO2-RGO compound with controllable visible light photocatalytic performance: GO regulating lattice defects[J]. Journal of Materials Science, 2018, 53(18):12770-12780.

[9] LIU C L, GUI D Y, LIU J H. Process dependent graphene-wrapped plate-like MnO2 nanospheres for high performance supercapacitor[J]. Chemical Physics Letters, 2014, 614: 123-128.

[10] Qian Y, Lu S, Gao F. Preparation of MnO2/graphene composite as electrode material for supercapacitors[J]. Journal of Materials Ences, 2011, 46(10):3517-3522.

[11] Choi B G, Yang M H, Hong W H, et al. 3D Macroporous Graphene Frameworks for Supercapacitors with High Energy and Power Densities[J]. Acs Nano, 2012, 6(5): 4020-4028.

[12] FALCAO E H L, BLAIR R G, MACK J J, et al. Microwave exfoliation of a graphite intercalation compound[J]. Carbon, 2007,45(6):1367-1369.

[13] VIMUNA V M, ATHIRA A R, XAVIER T S, et al. Microwave assisted synthesis of graphene oxide-MnO2 nanocomposites for electrochemical supercapacitors[J]. AIP Conference Proceedings,2018, 1953(1): doi: 10.1063/1.5032471.

[14] YAN J, FAN Z J, WEI T, et al. Fast and reversible surface redox reaction of graphene-MnO2 composites as supercapacitor electrodes[J]. Carbon, 2010, 48(13): 3825-3833.

[15] WANG K, LI L W, XUE W, et al. Electrodeposition synthesis of PANI/MnO2/graphene composite materials and its electrochemical performance[J]. International Journal of Electrochemical Science,2017, 12(9): 8306-8314.

[16] LIU W J, SUN X Z, HAO Q L. Electrochemical deposition of MnO2/PEDOT:PSS composite and its capacitance characteristics[J]. Energy Storage Science and Technology, 2018, 7(2): 262-269.

[17] HAREESH K, SHATEESH B, JOSHI R P, et al. Ultra high stable supercapacitance performance of conducting polymer coated MnO2 nanorods/RGO nanocomposites[J]. RSC Advances, 2017, 7(32):20027-20036.

[18] WU T, WANG C N, MO Y, et al. A ternary composite with manganese dioxide nanorods and graphene nanoribbons embedded in a polyaniline matrix for high-performance supercapacitors[J]. RSC Advances, 2017, 7(35): 33591-33599.