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Progress on Preparation and supercapacitance

Performance of Graphene/polyaniline Composites

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Abstract: In Recent years, and graphene / polyaniline composites with excellent electrochemical performance have aroused Extensive concern of domestic andforeign scholars . Graphene is of Large specific surface Area and double layer capacitance characteristics , polyaniline are with High faradaic Pseudocapacitance, Synergy to both makes this supercapacitance Performance to the Composites increase greatly . The preparation methods of the graphene/polyaniline compositesand The Influence Factors to the capacitance Performance were introduced , The constructing methods of Three-dimentional structure of graphene/polyanilineComposites were Summarized, The future trends of the composites In supercapacitor fields were prospected as Down .

Keywords: three- dimensional structure; graphene; polyaniline ; composite; capacitance performanceprogress

1. Primer say

since Geim[m] Since the discovery of graphene , scholars have done a lot of research on it . recent years , Research on graphene matrix composites has become a new hot topic , and has also caused great repercussions .. Although graphene has a high specific surface area , carrier mobility and intensity etc can , However, its easy to reunite defects and the low capacitance characteristics of the electric double layer can not meet the practical needs of the application . and graphene with high electrification active and conductive polyaniline composite , The synergistic effect of the capacitance characteristics of polyaniline with its double layer capacitor , can improve the composites

capacitance performance of . on the one hand , polyaniline reduces graphene stacking and reunion , increased surface area and graphene stability , improve electronicMigration rate ; another _ Aspect , Graphene improves the collapse or dissolution of polyaniline due to volume expansion or contraction , improves the cycle of composite materials stability . composite good capacitance characteristics , make it more widely used in capacitor parts .

2. Graphite Brightening / Preparation of polyaniline composites

Graphene / Polyaniline Composites are prepared in different ways , There are also differences in the structure and performance of composites for . current , method mainto have in-place aggregation , Layers Self-assembly , hydrothermal synthesis , Dilution Aggregation , Interface Aggregation , covalent grafting and electrochemical coprecipitation methods .

2.1 in-place aggregation

in-situ polymerization is the uniform dispersion of graphene into aniline solutions , To aggregate the two reactions , The is covered with polyaniline on the graphene surface. , makes the The structure of graphene does not change [0] . currently , Most of the composites are prepared by in- situ polymerization , is a more mature preparation method , but reac-

tion time between longer , Experimental procedure is more complex .

Wang , and so on [3] Composite of flexible graphene with polyaniline by in-situ polymerization , to use the fabricated composite as a supercapacitor electrode , Its electrochemical performance is higher than that of pure single components , in the 1000 to maintain the service life of the after the secondary loop 84% and 1126 F / G The specific capacitance of the ; Power-Tight degrees larger than pure material , maximum reach 141.1 W/kg . Ya_n etc [H] provides energy density by in-situ polymerization Wh/kg, work Rate of , kW/ kg Graphene nano plate / polyaniline Composite . Shini etc [0] preparation of graphene by in-situ polymerization method / polyaniline compositematerial , The material has a nanotube structure and high electrochemical properties . Yau Jun Wang Leize The also uses the same method for preparing graphene / Polyaniline Composite .

Ran Yanli All Convert natural graphite to an improved hummers Graphite oxide is prepared by the method , Preparation of Polyaniline by in- situ chemical oxidation polymerization / Graphene oxide (PANI / Go) complex material ,- diagram 1 is a composite of SEM Photo , PANI The particles are uniformly covered in the Go Surface ,through the table sign ,go can increase PANI electrochemical performance and looping characteristics of . the specific capacitance of the material used as the electrode of the supercapacitor is 413.28 F /g, more pure PANI The value of is higher than 90.72 F / G , passes 1000 after the cyclic charging and discharging of , Its capacity can still remain in 70%.

Zang , and so on On depositing the graphene fabric on a silver wire with polyethylene terephthalate. , and dips it as a working electrode into the containing HCl " aniline solution " , In- Place Electrical aggregation under the condition that the voltage is 0.8 V , to prepare a flexible graphene / Polyaniline Composite fabric film and apply to supercapacitor electrodes , with good stability and flexibility , in the process of deformation, electrochemical performance has not decreased instead of the power to lift the capacity high to original value 118%, The use of this thin film electrode can produce new portable wearable nano devices . in- situ polymerization makes the binding of the material between the the stronger , reduces the use of oxidants and surfactants , reduces pollution to the environment ; Composite material prepared by in-situ polymerization of polymers The shape of the material is difficult to control .

2.2 Layers Self-assembly

The layer self-assembly method of is the preparation of a composite film by the interaction of positive and negative charges . the layer self-assembly method has the "" method Simple , _ in aqueous solution or aqueous dispersions , reducing organic solvent use The advantages of,, and the thin film thickness can be controlled . chen yu ze M to oxidize graphene under alkaline conditions , Water-hydrazine restore , to make graphene with carboxyl groups on the surface (CCG) disperse , put CCG with acid DopingPANI as assembly unit for layer self-assembly , successfully prepared (CCG /PANI) "" Uniform film . (CCG/PANI) ten film with has good stability , Its electrochemical stability diagram 2 shows , detected discovery , Film has good electrochemical performance , for ascorbic acid also _ Set electrocatalytic activity .

Zhu Zhengyu [611] A negatively-charged graphene after modification of polyacrylic acid dispersed in water using a layer self-assembly technique (PAA -^ GR) with positive Electric polyaniline composite , prepare to get {PAA-5~GR / PANI } " Composite film , Detected , Composite film to H2O2 has good oxygen reductive catalytic performance , stability and reproducibility . Sun June etc 612 take Hummers Preparation of graphite oxide , and then after a series of chemical reactions the polyacrylic acid non covalent modified graphene (PAA -;r) , PAA -; R replaces graphene oxide as assembly unit , and Polyaniline layer self-assembly , Get graphene / polyaniline {PAA~Gr /PANI } " Composite film ." Composite film to the H2O2 have electrocatalytic activity and good uniformity , so you can the applies to the sensor realm . Lee wait [613] Layer-by-layer self-assembly of graphene oxide and polyaniline , The film obtained by IS formed after heat treatment is also Original Graphene / polyaniline Composite film , Detect Discovery , Has a good loop stability , Heat-treated composite film in 0.5 A / G Discharge current density The shows a good ratio of capacitance 375. 2 F / G .

2.3 hydrothermal synthesis

Zhong Wenbin [4] To have polyaniline nanofibers (PANI ^ F)with go to assemble , Preparation of polyaniline nano-fibers by hydrothermal reaction after / also graphene oxide (PANI ~ F / RGO)composite [,RGO Uniform Package on PANI~ F Surface . The experiment shows that , when PANI ^F vs RGO 's quality quantity ratio is m (PANI-F):m(rGO)) =10:1 when , on 1 a/g [] (NO) (no) (NO)(+) flow density , composite capacitance is 517 F / G , composites than Capacitor and stability higher ,to apply to electrode material . Min Yonggang etc M Mix poly (furfuryl alcohol) with graphite oxide using hydrothermal reaction the method of the preparation of graphene oxide by / poly Alcohol gel , Remove poly (furfuryl alcohol) and get three -dimensional graphene and disperse it in acidic solution , and then add a to the dispersion into aniline and oxidizer for hydrothermal reaction , finally successfully prepared with Three-dimensional graphene with higher than capacitance / Polyaniline composites , when scan speed The rate is Ten MV / s , MV / s , MV / s , MV / s , MV / s and MV /s , composites have a maximum ratio of capacitors to 1151 F / G . semantic ^. 8 etc [through hydrothermal synthesis $CoFe_2$ 0 4 and graphene and polyaniline compound ,Preparation of ultra high performance electrode material material , With a capacitance of 1133.3 卩 ^ (1 Claw 乂), on 1000 cycles After charging and discharging the capacitor loses the 4%. Feng etc [E7] Use hydrothermal synthesis to Prepare graphene / Polyaniline / porous Silicon composite , when Graphene content to 50% , the higher than capacitance of the composite to the highest , In the current density is 0.8 A / G When the capacitor is 405 F / G . hydrothermal synthesis minus less use of reductant ,the composites prepared by are mostly gel-like , Although the preparation process is simple , but has strict requirements for reaction temperature and time . 2.4 other method

except for a few of the above methods , There are other ways to prepare graphene / Polyaniline Composite . Wang etc Using diluted aggregation reaction to polyaniline nanowire array with flexible polystyrene microspheres / Reduction graphene (PS/ rgn) film Comp , Remove polystyrene microspheres , prepare single Vertical Three-dimensional rgn/PANI Composite membrane , detection results , at current density 0.5 A/ g when , its ratio capacitance is / , When the current density is Ten A / G , constant charge-discharge loop 1000 After the capacitor remains 87%, applications in supercapacitors have great potential .

Lv , and so on [M] sulfonated Graphene nanoparticles prepared by interfacial polymerization / Layered laminated composites of polyaniline supported by multi-walled carbon nanotubes , Check test results show , on The 1000 Cycle is still the original value of the capacitor 91.4%. Li etc [M] preparation of Polyaniline by covalent grafting /Graphene oxide material composite ,PANI and Go creates hierarchies under synergistic effects and enables composites to obtain excellent electrochemical properties and large specific surface areas , in the sensor , This material can be used in areas such as energy storage and catalysis . Zhang etc [M] preparation of graphene oxide by electrochemical deposition method / Polyaniline composites , improving electrochemical properties by regulating mass concentration . due to the excellent electrochemical properties of the composites , can be used to prepare supercapacitors Electrodes , electrochemical deposition is an efficient , Green Preparation method . Chen etc [122]Polyaniline prepared by Intercalation Composite method / Restore oxidation Graphene composites , is to insert polyaniline into a good dispersibility of oxidized graphene. ,finally convert graphene oxide , resulting composite in current density 0. 1 A / G The has a specific capacitance of 764 F / G .

Overall , Composite materials prepared by in-situ polymerization can be mass-produced , But graphene has poor compatibility , makes it less evenly dispersed ideal ,reaction time long b " ;" ; layer self-assembly does not require complex devices , Green , to prepare film with controllable thickness [M] , Its assembly structure order _ [M] ; The hydrothermal method is mostly prepared with gels , Has a good dispersion , reduces the use of organic solvents in the preparation process . Three preparation methodsmore than , layer self-assembled composites have the lowest specific capacitance but better catalytic performance ; Flexibility of composite materials prepared by in-situ polymerization better . is currently used to prepare go/PANI The method of composites is generally based on in-situ polymerization as the main .

3. Impact Factor

3.1 Surfactant

Dongjie [M] studied nonionic surfactant triple-block copolymer P 123 as a surfactant on graphene / Polyaniline Composite effect . in acidic solution with P 123 , with in-place aggregation synthesis go/ PANI composite , The effects of the different content of the P123 on the microstructure and capacitance characteristics of composites are studied ,P123 The content has no effect on the crystalline structure of the composites , but composite ratio surface area , Capacitance and aperture with P 123 The increase in content increases first and then decreases by , describes the microstructure of the composite and the P 123 has a certain amount of relationship , and when P 123increases the content of , The composite effect of the material is also preceded by the difference , when P 123 and PANI The molar ratio of the N (P123) / n (PANI) =0.0108 ,Go and PANI has the best composite effect , loop stability is good , maximum surface area and aperture , capacitance performance is also the most good , in loop 1000 The capacitor retention rate is still after the time 8%, When current density is ? mA/g when , is than capacitor 215. 8 F[]/ g .

3.2 oxidizer

Liu Zhiseng [M] to make graphene oxide into a dispersing liquid , Porous Graphene is prepared by hydrothermal method using graphite oxide dispersions as raw materials, and then with P-MnO_2 and ammonium sulfate to oxidant , graphene by in-situ polymerization / Polyaniline Composite . oxidizer p-MnO_2 vs. Ammonium sulfate , low cost ,more environmentally friendly , simultaneous P- MnO_2 crystal structure and oxidation benefit the synthesis of polyaniline materials , oxidizer - P- Mn 0 2 The material for has better electrochemical performance , can reach than capacitance All F / G , capacitance retention is A . 7%, simultaneous magnification performance and discharge capacityhigher .

3.3 RGO Restore degree of

Zhang Yan LAN [127] Graphite oxide made from flake graphite , Graphene oxide is made by ultrasonic dispersion , by chemically restoring restore degrees different rGO,make by in-place aggregation RGO Composite Preparation with aniline monomer RGO / PANI Composite , and renders the layer structure , polyaniline nanofibers evenly distributed in rGO surface . with a different degree of reduction rGO keep adding , in a specific capacitor , Loop Stable and magnification features composites compared to pure PANI , because The degree of restore differs from RGO , when rGO added content of oxygen functional groups , Reduced PANI Reunion and provide double layer capacitor , provides a favorable condition for the movement of electrons . and with rGO restore level into One Step increase , Oxygen Functional group decreases , The increase in polyaniline reunion , cause the capacitor to drop .

3.4 Graphene Type

Han Xu [M] with an improved hummers The use of the method and the chemical oxidation process of polyaniline and oxidized graphene , reduction of graphite oxide composite , To separate prepared polyaniline / oxidized graphene , Polyaniline / to reduce the doping of graphene oxide . PANI/rGO and PANI/go Microscopic junction of composite materials structure similar to graphene's flake structures , not much changed , and PANI the renders the form of granular and nanowire respectively . for composites measure , found that the different types of graphene affect the microstructure and electrochemical properties of the PANI , where PANI/ rGO has good capacitance performance , available on Super capacitor .

3.5 Raw material matching

Wang Yu I by adjusting the mass ratio of polyaniline to graphene under acidic conditions , a series of different components including are prepared by in-situ polymerization amount of pani / Graphite oxide composite . experimental results show that , polyaniline successfully covered on graphene surface , and with the content of the polyaniline Add , composite X X-ray diffraction peaks increasingly tend to pure polyaniline , Renders a amorphous clustered structure . The quality of polyaniline and graphene is greater than the effect on the electrochemical properties of composites ,

when the ratio of polyaniline to graphene increases continuously , composite capacitance rendering increases first after Decrease Trend , when ratio is Ten , The ratio of the composite to the maximum , scan rate is Ten MV / s , than the capacitor is162.2 F / G .

can be found by comparing , The effect of surfactants on the microstructure of the composite is mainly the size of the aperture and the specific surface area ; different types of stone Graphene and polyaniline composite , different forms of polyaniline in composite materials ; as the content of polyaniline is too large , , produce class on graphene surface like pure polyaniline bar structure . The effect of oxidants on the electrochemical properties of composite materials is less ; reductive oxidation of graphene in different reduction degrees The effect of the content of the Oxygen functional groups on the capacitance of the material is significant , With the number of functional groups increasing , capacitive increase first and then reduce . to produce a super high performance graphene / the polyaniline Composite should not only consider the above factors , and choose the best condition , to produce super power with high specific capacitor Container to meet the needs of the actual application .

4. Three-dimensional graphene / Polyaniline Composite

The agglomeration and stacking of graphene have always affected its application in capacitors , Many researchers have produced large specific surface areas and porous Three-dimensional graphene , and compound three-dimensional graphene with polyaniline , form foam , Nano Film and reticular structure to improve graphene on Storage applications . Three-dimensional graphene / The main methods of preparing polyaniline composites are : In- situ aggregation , electrochemical polymerization and self-assembly Law, and so on .

Yu , and so on [M] to reduce the flexibility of graphene oxide foam (frgo^F)) immersed in aniline monomer aqueous solution , make polyaniline perpendicular nanowires through Jane single in-situ polymerization uniformly deposited on layered mesoporous materials Graphene foams (Frgo~F/PANI), concentration of aniline monomer can control polyaniline nanowires , to enable material to be controlled at the time of preparation , Composite SEM photo as shown 3 shows . three-dimensional frgo^F inherited porous structure of all _ Sex and controllability , Graphene foams with synergistic three-dimensional double continuous multistage pore structure are effective skeletons of polyaniline nanowires . " specific capacitance for this material " , current density the , power density and cycle stability are higher .

Xu in situ polymerization of fibrous polyaniline deposited in carbon nanofibers / Graphite oxide (CNF / Go) template on , prepared to CNF/go /PANI Composite film ,synthetic PANI cosmetic CNF /go, Show three-dimensional layered nanostructures , benefit electrolyte ion diffusion to the inside of the active material , to make composite films into high-performance layer electrodes , at the scan rate of Ten MV / s , The specific capacitance of the electrode is 450.2 F / G . Sun Hongjuan etc prepared three-dimensional reduction of graphite graphene / polyaniline composite , The three-dimensional structure is made from reductive oxidation of graphene / polyaniline / reduction of graphene oxide composite , Polyaniline nanoparticles disperse evenly between layers of reduced graphene oxide sheets , To form a three-dimensional mesh structure , its special point is larger than surface area , good dispersibility , good conductivity and structural stability .

Fig. 3 sem image of three-dimension reduction of Fig. 4 SEM images of three-dimension

Graphene/polyaniline composites graphene/polyaniline composites

Mr Tang preparation of three-dimensional graphene using calcium carbonate as a template / Polyaniline Composite , The material's SEM photo as shown 4 shows , has mutual Through hole structure , High cycle stability under low voltage conditions ; Preparation of three-dimensional porous graphene by crosslinking method , Polyaniline growth by in-situ polymerization in three-dimensional porous graphene hole wall and surface , The composite's SEM photos as shown 4 show , with High cycle stability ,larger than capacitor .

Wang , and so on % Graphite - mesoporous silicon composites as templates , Preparation of mesoporous

polyaniline on ultrafine graphene nanoparticles using in-situ polymerization , Composite cycle stability is good . Qiang Zhao etc M preparation of three-dimensional ordered structure of polyaniline by in-situ polymerization / graphene nanocomposites Material , polyaniline nanorods uniformly vertical growth in graphene , Graphene plays a supporting role , the specific surface area of the material is large ,Excellent magnification performance , in current density 0.5 A / G , can reach than capacitance 358 F / G , The current density increases to Ten A / G , With a capacitor retention rate of . 3%. Xu Kin-June [M] Graphene prepared by in-situ polymerization and freeze-drying method / Polyaniline composite sponge has high specific capacitance and has three-dimensional porous mesh knot construct , as the content of polyaniline increases, , The specific capacitance of the composite increases gradually. , up to 487 F/ G , can be applied to the supercapacitor realm . Lo Jianping etc B [7] The also uses the same method to synthesize the three-dimensional porous structure of graphene /Polyaniline Composite , Graphene is not restored before the composite material Less stable , at current density of 0.5 A / G , The specific capacitance of the composite is 321.91 F / G , is higher than the before the restore 81.53 F / G . Yu etc all Preparation of graphene by electrochemical polymerization method / manganese dioxide /polyaniline Three-dimensional coaxial nanometer array structure , the three-dimensional array structure in current density 0.5 A The specific capacitance of the /g is the 755 F/ G , passes 1000 after charging and discharging , capacitor remains 87%. Liu people through in-place The method of chemical oxidation polymerization is prepared with three-dimensional highly ordered polyaniline in aqueous solution / Graphene Composites , as a supercapacitor electrode , higher than capacitor to reach / . Liu etc [A The three-dimensional ordered Polyaniline was successfully prepared by the in-situ chemical oxidation polymerization method - Stone
Graphene Composite , The electrode materials used by the as supercapacitors exhibit extremely high specific capacitance , When the current density is 1.0 A / G under the condition of , than capacitance up to 1295 f/g .

8 Dagger 3 , and so on [A] two-step preparation of molybdenum disulfide / polyaniline / The specific capacitance of the graphene oxide aerogels can be reached 618 F /G , in To The capacitor maintenance rate after the secondary cycle charge is 96%. Fan etc [all] the graphene oxide is prepared by electrostatic self-assembly / Polyaniline microspheres , last electrochemical reduction of reduced oxide graphene / sulfonated polyaniline Hollow microspheres , detected by electrochemical detection , When the current density is 1. 0 A/ g When the capacitor is up to 614 f/g , passes The capacitor retention rate is after the secondary cycle charge 90%, The composite has good cycling stability qualitative . Zhengyuan etc [through KCKERMG emulsion polymerization to produce polyaniline with unique hollow structure - Graphene microspheres , When the current density is 1. 0 A/ g under the condition of , The specific capacitance of the microsphere reaches 480.59 f/g , and two-dimensional structure of the graphene /Polyaniline Composite compared to , Hollow microspheres than The capacitor is relatively raised 103.5%.

5. knot language

Graphene / Large specific surface area of polyaniline composites , cyclic stability and excellent electrochemical performance , makes it a hot for domestic and foreign scholars to study door Topics , relevant theoretical research and practice development are also of great significance . But there are still a lot of questions to be addressed. ,including (1) reduce Composites reunion to improve electrochemical performance and cycling stability ;(2) Explore simpler , Green , low cost , Preparation of high-performance composites method ;(3) Implementation of graphene / microstructure regulation of polyaniline composites ; (4) improve its performance to meet application development requirements . Although the gather The composite of aniline and graphene improves capacitance performance , But the specific surface area of the composite is , structure Stability , aperture size and capacitance characteristics are still does not satisfy the actual application , based on the above questions , to produce High specific surface area , High electrochemical performance , , structurally stable graphene / Polyaniline composite material material will be the main direction of future research . believe that as the research continues ,, composite Performance Improvement , Graphene / Polyaniline Composite The material as electrode material will play a greater role in the Supercapacitor field .

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