

Carbon nanotubes/Polyaniline Composite Preparation and electrochemical energy storage performance

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Abstract: using powder carbon nanotubes (CNT) and carbon nanotube network with connection points (cntnis) as a template, through the polyaniline (PANI) limited domain aggregation got CNT/PANI and CNTn/PANI₂ species composite. using a transmission electron microscope and a scanning electron microscope for the shape of the material. Look at the description, using nitrogen adsorption-desorption. The pore structure parameters of the material are studied by the desorption analysis. Electrical conductivity of the material using a dual-electric four-probe Tester To test, using constant current charge and discharge, cyclic voltammetry, Electrochemical test methods such as cyclic lifetime and AC impedance characterize the electrochemical storage of materials performance. The results indicate that, CNTn/PANI composite than CNT/PANI composite exhibit better conductivity and electrochemical energy storage performance, Its discharge is greater than capacity 143.2 f/g (Organic liquid).

Keywords: carbon nanotubes; Carbon Nanotube network; finite domain aggregation; Composite; Electrochemical Storage performance Map category number O641.1 document Marker A

electrochemical Super Capacitor (ESC) has greater capacity than general capacitor, faster charge and discharge speed and extra long cycle use lifetime, so much attention now. One of the main research directions for ESC is to further improve ESC capacitance. The focus of the study is its electrode material. in ESC electrode material^[4,5], Carbon nanotubes (CNT) material with unique one-dimensional hollow structure, Good conductive Thermal performance, Excellent mechanical properties and high stability are widely concerned with, and attractive applications in the field of composite materials before. View but CNT standalone use as ESC electrode material when, shows lower capacitance depending mainly on dual-layer storage, only, F/G (organic electrolyte)^{B1}. Polyaniline (PANI) materials as ESC when electrode material is higher than capacity, low cost, Synthetic method. Single benefits, thus also being concerned about. But because it varies significantly in volume during repeated charge and discharge, Poor stability, and the conductivity is more than low, affect performance^{E0}. A. combines CNT and PANI₂ Composite material Benefits--CNT/PANI^{E3}~to avoid CNT and PANI The respective disadvantages of the, get better electrochemical performance. In recent years CNT/PANI Research Base for composite electrode materials This set in 2 Aspects: first to study the composition of the two to improve their overall performance[^]~, Two is to change the PANI The appearance structure of the ISI Improve overall performance^{^3}~. But the basic research in the current study is the powder CNT directly with PANI to compound, does not consider powder CNT connection, greatly reduces CNT Electrical and mechanical properties of composite materials.

Research Discovery, takes the CNT electrodeposition on the array substrate PANI The method is prepared by the CNT/PANI composite exhibit good electrochemical storage performance[^], but CNT Harsh preparation conditions for arrays, is not easy to control, affects its large scale application. This topic group²⁷²⁸ use the with connected carbon nanotubes network (cntn) new material fixes this problem. This article is based on the cntnis as a template, uses a finite field Aggregation Method (cntn/PANI Composite, and studied its electrochemical energy storage performance. The results

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indicate that, that is prepared under the same conditions CNT/PANI than CNT/PANI Composites exhibit better electrochemical energy storage performance.

1. Experiment Section

1.1 Reagents and instruments

CNT for self-control²⁹; 1.0 mol/L HClO_4 /Vinyl carbonate (EC)+diethylcarbonate (DEC) V(EC):V(DEC)=1:1] electrolyte (Shenzhen new State company); Celgard 2400 diaphragm (United States Celgard Company); ammonium persulfate, phosphoric acid,

aniline, Toluene and ethanol (Chengdu Kelon Reagent Co., Ltd.); reagent all analytical pure.

jeol JEMCX type transmission electron microscope (TEM) and jeol jsmj001F type scanning electron microscope (SEM) (Japanese day company); DM4000 Optical microscope (German lycra company); RTS- double-probe conductivity tester (Guangzhou four probe public Division); quadrasorb si Automatic independent multi-station specific surface area and porosity Analyzer (American Health Tower); ZF- constant Potential/Henderson current meter (Shanghai Square); CT-3008W-5V TenMA-S4 Battery Tester (Shenzhen new company); LK2006 type electrochemistry workstation (Tianjin Rand Corporation).

1.2 Preparation of composite materials

The preparation of uses finite field in-situ polymerization⁷¹, To do the following: will add 0.025 mol/L H_2SO_4 ammonium with 0.1 mol/L mixed solution of phosphoric acid, Stir 1 h. To disperse aniline into organic solvent toluene, Form 0.1 mol/L Benzeneamine-Toluene solution. adds the above processed CNT and its solution slowly join the aniline-Toluene Solution, controls temperature in $0 \sim 5^\circ\text{C}$, is constantly stirring the reaction, in-place growth PANI. rinse filter products with ethanol and deionized water repeatedly, until you wash the liquid is colorless to transparent. Remove, Vacuum cryogenic drying to get CNT/PANI Thin Film composite, where $m(\text{CNT}):m(\text{PANI}) = 1:24$. to compare, follows the same experimental method and condition, with powder CNT is the base, To prepare powdery CNT/PANI Composite, and $m(\text{CNT}):m(\text{PANI}) = 1:24$. The that the will eventually get CNT/PANI dispersed in ethanol, Vacuum filter with CNT/PANI film Composites, dry, pending.

1.3 characterization of the material

take the TEM and SEM Characterize the morphology of the prepared materials. test the thickness of the resulting material using an optical microscope. Test the conductivity of the resulting material using a conductivity tester.

using specific surface area and porosity analyzer at Liquid nitrogen temperature (K) adsorption of material-curve tested, take the Brunauer-Emmett-Teller (BET) The method calculates the surface area, porosity in relative pressure p/p_0 . The measured under, take the Density functional theory (DFT) aperture analysis method parse aperture distribution. before testing the material before the CV vacuum degassing H.

1.4 electrochemical performance test

because of the resulting 2A composite is a macroscopic material with a thin film structure, So you can hit the slice directly, Is used as a ESC of, Negative every. with 1.0 Mol/L HClO_4 /EC+decv (EC): V(DEC) = 1:1] is electrolyte, Celgard 2400 is diaphragm, is filled within the glove box for argon to simulate ESC.

cyclic voltammetry (CV) test on ZF- constant potential/, on constant current meter. to use the assembled directly ESC, uses two-electrode mode, scan speed 5 mV/s. with 3.4 a/g charge/Discharge current density, in $0 \sim 2$ V The test voltage range of is on the battery tester for electrochemical storage performance tests. AC impedance test performed on electrochemical workstations (exchange amplitude is Ten MV, Test frequency range is

kHz \sim 0.1 Hz).

2. Results and discussions

2.1 topography Representation

diagram1(A) to purify CNT for TEM Photo. Visible, for CNT surface is smooth, wraps around, basically no impurities, Tube od approximately ~ 25 -nm. diagram1(B) is CNT for SEM Photo. Visible, CNT The original in the CNT Evenly distributed, pipe size and figure1(A) consistent in, is about ~ 25 nm, But in these original CNT a new with a short, slightly smaller diameter growing between CNT (as shown in the arrow show). These short, small growth CNT (, CNT when, To grow CNT The growth time is set to Ten min, is growing original CNT $1/6$) The is primarily the original where the connection is adjacent or intersecting CNT, to form a three-dimensional network structure macro-body material, To increase the effects of material mechanics and conductivity^{127,8}. diagram1(C) is a that is prepared by the finite-domain aggregation method CNT/PANI Composite SEM Photo. to see, Composite is tubular distribution, diameter is $45\sim 60$ nm. PANI Evenly Overlay CNT Surface. diagram1 (D) is CNT/PANI composite SEM photo. Visible, The material is predominantly tubular, But poor uniformity, There are some linear with slightly smaller diameters material interspersed between tubular materials. Compared to the figure1(C), CNT The material is under the same method as the PANI The uniformity of the composite is greater than the CNT Difference. can be considered primarily because of the finite field in-situ synthesis, needs to be as decentralized as possible CNT, but CNT is a macro-body material, on PANI composite procedure, always exist as a whole, Cannot be spread out, to affect its uniformity. But the resulting material is a Macro Overall, no further film processing. and this structure is conducive to improving the overall electrical and mechanical properties of the material, To affect its

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Pore size distribution curves calculated by DFT method (B)

Table 1 is CNT/PANI and CNT/PANI composite surface area and pore structure parameters. consists of the table 1 Know, 2 kind of composite material has an average aperture of 5.62 and 4.90 nm, the further proves that the composite material is composed mainly of mesoporous; CNT/PANI specific surface area of 604.3 m^2/g , relative to CNT/PANI (374 m^2/g) increased 62% , This shows that under the same aggregation method, CNT base The bottom has a larger impact. and powdery CNT compared to, growing after CNT in the original CNT The connection between creates a new hole, To make the table area into one step up, and the resulting holes are all mesoporous, for electrochemical storage.

2.2 electrochemical profiling

diagram 3 is CNT/PANI and CNT/PANI Composites are assembled into the ESC for CV Graph. Visible, 2 kind of composite material, CV curves all show significant redox peaks, to indicate that the composite can contain a pseudo capacitor stored energy. but CNT/PANI in the

-0.482 and 0.506 V Place A to redox peaks, and CNT/PANI The redox peaks of the appear in the -0.339 and 0.380 V Place. Is well known, as PANI signature of redox peaks, at scan speed in the case of, The migration of peak potentials with the ions of the material Diffuse speed about, spread faster, The larger the migration^{B^h} #. so, to think of the figure 3 CNT/PANI migration of redox peaks and CNT has a direct relationship to. and CNT/PANI compared to, CNT/PANI in CNT creates a more stable, Higher conductivity Conductive network, Improve the overall ion diffusion speed of materials, to cause redox peaks to move. To further observe the 2 kind of compound material CV curve know, CNT/PANI Composite CV The curve is surrounded by an area that is more than CNT/PANI to large, description compared to CNT/PANI, CNT/PANI has higher electrochemical capacity. at the same time CNT/PANI response to redox peaks of composite materials flow significantly stronger than CNT/PANI Composite, This is mainly due to CNT The connection of CNT has an excellent conductivity in the composite. Network skeleton action, and with PANI after a composite, because of the good synergy between the, to make composite electrochemistry The energy storage performance is greatly improved..

diagram 4 to assemble a with the prepared material ESC constant current charge/discharge curve after. Know, the charge and discharge curves for composite materials are nearly triangle-like symmetric shapes, but not good linearity, they embody the Faraday pseudo capacitance feature. CNT/PANI and CNTn/PANI Composite Material The discharge time is 1922 and 3437 s. According to the literature can be, CNTn/PANI The specific capacity of the composite is approximately 143.2 F/g (Single electrode quality is 4.8 mg, Organic Electrolyte), compared to CNT/PANI Composite (109.8 F/g, Single electrode quality for 3.5 mg) has a significant improvement over capacity. At the same time, it also makes it clear from the diagram that, consists of the CNTn/PANI Composite of the ESC The discharge instantaneous pressure drop (IR Drop) significantly better than by CNT/PANI The material consists of ESC Small, The description consists of the CNTn/PANI Makes up on ESC equivalent series resistors less than CNT/PANI of the system, This is closely related to the conductivity of the electrode material itself., with the above conductance rate test results are consistent. shows, CNTn connections within are more likely to use electronic transport, The increase in connection points greatly shortens the electronic transmission distance, Lower by The system internal resistance value of the ESC-electrode material. CNTN can form a richer conductive network, Improved Composite in PANI Microscopic morphology and dispersion of particles.

diagram 5 is CNT/PANI and CNTn/PANI Composites are assembled into ESC Cycle Life Graph. Know, passes secondary charge/discharge cycle, the specific capacity of the material is somewhat attenuated: CNT/PANI The capacity attenuation rate for composites is 6.1%, and CNTn/PANI The capacity attenuation rate for composites is only 4.2%. explains that under the same charge and discharge conditions, with CNTn/PANI Composite as electrode material ESC has better loop stability. This is primarily because the CNTn A connection point within the causes the with better mechanical properties, to make composites more stable. CNT exists, especially with connection points CNTN The presence of, can significantly improve PANI The disadvantages of a material being unstable during repeated charge and discharge.

diagram 6 is CNT/PANI and CNTn/PANI The electrode is assembled with the ESC The electrochemical impedance spectra measured under a dual-electrode system diagram. Visible, 2 Nyquist (Nyquist) diagram with similar shapes, All by HF area semicircle, High frequency to low frequency transition area close to 45° and low frequency area close to 90° The slash form. where CNTn/PANI The value of the curve of the in the High-frequency region and the axes intersection (15.6 (1) ratio CNT/PANI (52.9 (1) small, The description consists of the CNTn/PANI The consists of ESC system equivalent series resistor' smaller, This is the same as the above conductivity test and constant current charge/discharge curve IR drop, results consistent. by using the resulting material Nyquist semicircle Curve

fit, To draw CNT/PANI and CNTn/PANI The half arc diameter of the in the High-frequency region is 18.12 and 10.46, This description CNTn/PANI The charge transfer resistance caused by the charge transfer reaction in the system is smaller. synthesizes The above two points, Description CNTn/PANI Conductive of the system better, electrode reaction relatively easy. The curve extends from the semicircle of the High-frequency region to the low-frequency, all appear with a skew angle of about 45° Line (Warburg Curve), This is the reactant or product of the electrode reaction in the charge and discharge process caused by the roughness of the surface of the porous electrode and the inhomogeneity of the pores's proliferation control behavior due to compared to CNT/PANI, CNTn/PANI for Warburg curve close to 45°, Description CNTn/PANI The system has a smaller resistance caused by ion diffusion, Higher ion diffusion speed, This is preceded by the CV The test results for are consistent. for CNTn/PANI the capacitor system for, The AC impedance curve in the lower frequency area appears close to the virtual axis of the line, and CNT/PANI The curve shows thenot obvious, This description CNTN/PANI The capacitance performance of is more pronounced, Higher capacitance utilization.

To summarize, with powder CNT and with connection points CNTn is a template, through the PANI The finite-domain aggregation of has been evenly complex All materials. 2 Composite materials all exhibit Electrochemical Energy storage performance by, but CNTn/PANI composites than CNT/PANI Composite material has better electrochemical storage performance, The discharge ratio of the electrical capacity in the organic electrolyte to reach the 143.2 F/G, and has a

good following ring performance, reason is CNTN than CNT has better electrical and mechanical properties, so that the composites have a better overall guide electrical performance vs. stable performance, thus better electrochemical storage performance.

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