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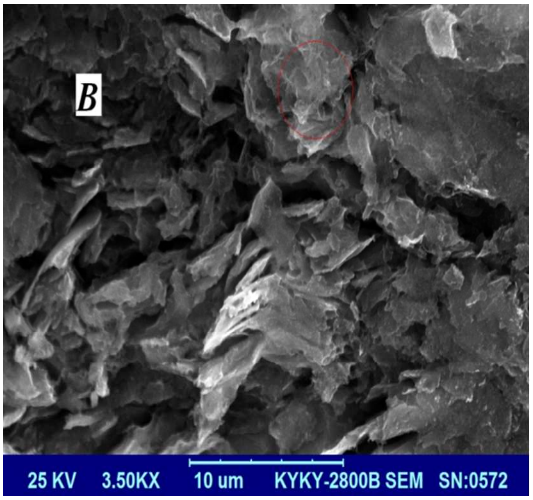
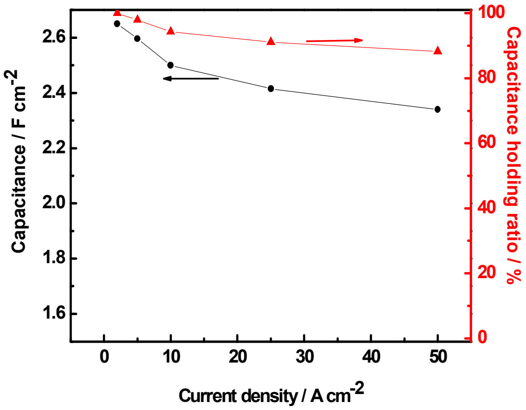
Graphical abstract





Inspite of little thready PANi on the PANi/MGE, the composite electrode possesses an excellent pseudo-capacitive performance and ratio characteristics, with an apparent specific capacitance reached up to 2.65 F cm^{-2}, which might attributed to the synergistic effect between PANi and MGE.

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ARTICLE TYPE

Investigation on the capacitive performance of the polyaniline/modified graphite composite electrodes

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The polyaniline/modified graphite composite electrode (PANi/MGE) was prepared through the electrochemical deposition. In spite of no apparent thread PANi, the electrochemical tests demonstrate that the PANi/MGE possesses an excellent pseudo-capacitive performance and ratio characteristics, with an apparent specific capacitance reached up to 276 F g^{-1}, which might attributed to the synergistic effect between PANi and MGE.

Supercapacitors, which possess high power density, excellent reversibility, and have longer cycle-life as compared to batteries, have been gaining momentum for the last decade.[1] Because of the preferable pseudo-capacitive characteristic, the noble metal oxides and electrically conducting polymers greatly pushed the development of supercapacitors in recent years.[2-3]

As a common conductive polymer, the polyaniline (PANi) attracts more attentions because of its inexpensive raw material, simple preparation method, high electrical conductivity, excellent chemical stability and electrochemical reversibility.[3] Along with the fast transformation between the doped and dedoped polyaniline in the polymer film, a highly reversible redox reaction occured during the charge/discharge process. Therefore, a large pseudo-capacitance is generated due to the high density charge in the interface even the entire volume of the polymer, which makes PANi as a research focus of electrode material for supercapacitors.

With the advantages of low cost, high chemical stability, good conductivity and large surface area, Carbon materials such as activate carbon, carbon aerogel, carbon fiber, carbon nanotubes and graphene are often used as electrode materials for double layer capacitor.[4] In consideration of the large double layer capacitance of carbon material with a high surface area, in addition to the good pseudo-capacitance of PANi, the specific capacitance may be vastly improved through the preparation of a composite material of both carbon material and PANi included. The benefits of introducing carbon materials into conducting polymers through chemical 'in-situ' polymerisation have been intensively studied, with many interesting properties and behaviors of the composites having been discovered. Jang et al obtained the polyaniline/carbon nanofibers composite materials by vapor deposition polymerization, the results showed that the thickness of deposit for the polymer film was about 20 nm and the specific capacitance was high up to 264 F g^{-1}, which mainly ascribed to the faraday pseudo-capacitance of PANi.[5] PEDOT/CNTs was prepared through direct chemical oxidation and electrochemical polymerization by Frackowiak et al, the capacitive characteristic of the composite material was examined both in aqueous solution and organic electrolyte, with a specific capacitance from 60 to 160 F g^{-1}.[6] Béguin et al synthesized the PANI/CNTs and PPy/CNTs by direct chemical oxidation method, it was found that not only the potential range and system conditions, but also the assembly method had significant effects on the specific capacitance of the composite materials.[7] Hu et al deposited PANi on graphite electrode (GE) by cyclic voltammetry (CV), the specific capacitance is greatly improved.[8]

In the previous work,[9-10] in spite of a fairly low surface area (6 m^2 g^{-1}), the modified graphite electrode (MGE) prepared by recurrent galvanic pulses presented an excellent pseudo-capacitive performance, which mainly due to the plenty of the active groups such as the hydroxyl, carbonyl and carboxyl groups, suggesting a promising electrode material for pseudo-capacitor. On this basis, the PANi is in-situ deposited on the MGE by electrochemical deposition in this communication, the electrochemical performance of the PANi/MGE composite material is evaluated by CV, galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS).

The PANi/MGE composite electrode was prepared by electrochemical deposition. The MGE, obtained in the previous work,10 was assembled as the working electrode (1 cm^2 surface area) in Flat Cell K0235 (AMETEK Princeton Applied Research, USA), which was a three-electrode cell configuration immersed in the mixed solution with 2.0 M H_2SO_4 and 0.5 M aniline. A 10 cm^2 platinum sheet and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. All potentials reported here were referred to SCE. No attempt was made to eliminate O_2 from the electrolyte.

The aniline was in situ polymerized on MGE by CV test, cycling 6 times from -0.2 to 0.8 V, with a scan rate of 50 mV s^{-1}, then the PANi/MGE was obtained. The load capacity of PANi was measured through weighting the mass of the MGE before and after the electrochemical deposition. The micro-domain morphology of PANi/MGE was observed by scanning electron microscopy (SEM; KYKY-2800B). In order to evaluate the pseudo-capacitive performance, the CV tests were performed on PANi/MGE within a range of -0.35−1.0 V at different scan rates. Here, a pre-polarization was conducted at -0.2 V for 200 s before each CV test. Galvanostatic charge-discharge tests with different current density were also carried out to investigate the ratio characteristics of the composite material. The EIS were measured with different polarization potential, with ±5 mV potential amplitude and a frequency range of 10 kHz–10 mHz. All electrochemical measurements were carried out using an EG&G PAR Model 2263 Potentiostat/Galvanostat at ambient temperature.

Generally, the PANi could prepared by chemical oxidation or electrochemical method.[3] As a result of the unique advantage that the proton acids doping and electrosynthesis occur in one step, in addition to the high purity of the synthetic product, it is preferred to synthesize PANi by electrochemical method. Chronopotentiometry, chronoamperometry and CV are often used in the polymerization process of PANi on the porous carbon materials. In this work, CV test was employed and Fig. 1 is the CV curves of electrochemical polymerization for PANi at the surface of MGE with different circles. As shown in Fig. 1, the current response constantly reinforces with the increase of cycle number, suggesting the amount of PANi deposited on MGE is ever-increasing. The current density reaches an relative steady state at 5-6 circles, meaning the accomplishment of the polymerization of PANi on MGE, and the electropolymerization PANi might cover the entire surface of MGE. Two pairs characteristic redox peak of PANi are also observed, one correspond to the redox process from non-conducting fully reduced PANi to conductive intermediate oxidized PANi, the other peak is the redox process from the further oxidation PANi to fully oxidized PANi.[11]

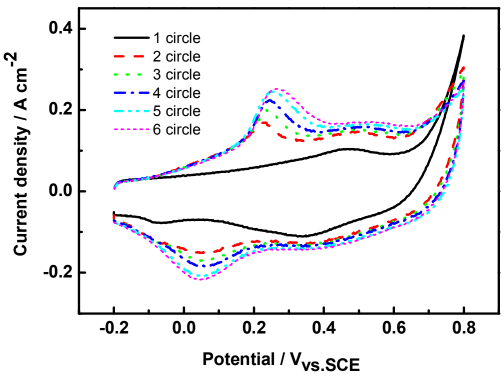

Fig. 1 CV curves of electrochemical polymerization for PANi at the surface of MGE with different circles.

Different with the smooth and compact graphite, MGE presents an obviously porous and rough three-dimensional active layers with microcrystalline flake structure.[9] Fig. 2 is the SEM images of PANi/GE (A) and PANi/MGE (B) composite electrodes. Although the same electrochemical polymerization was used, the morphologies of PANi/GE and PANi/MGE are entirely different. Unlike the Cross-linked reticular fiber structure of PANi/GE as shown in Fig. 2A, the obvious fibers PANi is not observed for PANi/MGE in Fig. 2B (little fibers could be seen in the solid line circle). Compared with the SEM image of MGE,[9] it is found that the sheeting structure at the edge side is apparently thickened which mean the PANi film is deposited on the surface of MGE. In addition, some spherical agglomeration exists in local region, the results illustrated that the special physical structure and chemical compositions of MGE have an important effect on the polymerization process and the morphology of product. Therefore, it was thought that the abundant surface oxide and/or the porosity effect changed the way PANi growing, so the growth of the PANi is along the flat of MGE, and the layered or flaky structure of PANi was obtained on the surface of MGE, instead of the fiber structure. Almost the same phenomenon has been reported in the literature,[8] and the author explained it with a similar viewpoint.

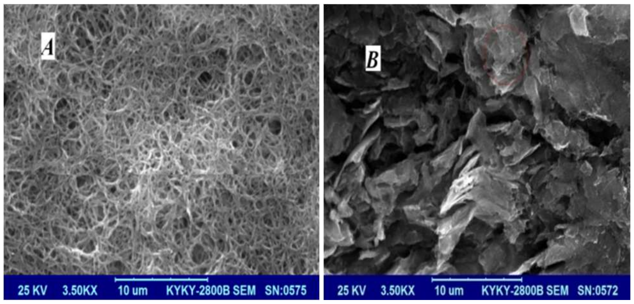

Fig. 2 SEM images of PANi/GE (A) and PANi/MGE (B) composite electrodes

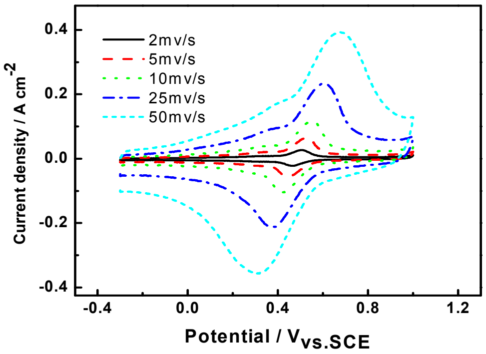

Fig. 3 CV curves of PANi/MGE at different scan rate in 2.0 M H_2SO_4 solution.

CV tests were performed to evaluated the electrochemical performance of PANi/MGE. In the previous work,[9] it was known that a couple of redox peaks appear at 0.4 V in the CV curve of MGE, which mainly attributed to the continuous reversible redox reactions among the hydroxyl, carbonyl and carboxyl groups. As shown in Fig. 3, CV curves of PANi/MGE in 2.0 M H_2SO_4 solution present a more wide redox peaks at 0.5 V, compared with that of MGE at the same scan rate. The large peak area and substantially symmetric redox peaks indicate a favorable pseudo-capacitive character. The main redox peaks of PANi at 0.5 V is so strong that the redox peaks among the surface oxide of MGE are almost covered. In addition, the potential difference between the redox peaks at 0.5 V increased with the increase of the scan rate, the probable reason for that is the redox reaction of PANi involve the transformation of proton and the diffusion of anion, which make the diffusion step as the rate controlling step at higher scan rate, consequently the active particles in bulk solution have not enough time to diffuse to the surface of the electrode and the polarized voltage is enlarged.

The specific capacitance of PANi/MGE can be calculated from the voltammetric charge by CV curve according to Eq. (1):[9,12]

$$C = \frac{q_a + |q_c|}{\Delta V} \qquad (1)$$

where C , q_a, q_c and ΔV are the specific capacitance, the anodic and cathodic voltammetric charge during anodic and cathodic scans, and the potential range of CV, respectively. Here C represents the specific capacitance with an apparent area of 1 cm^2, and it was calculated as high as 2.28 to 2.62 F cm^{-2} with the current density from 2 to 50 mV s^{-1}. Compared with the apparent specific capacitance 1.73 F cm^{-2} of MGE with the current density 50 mV s^{-1}, it was almost increased by half, and the corresponding mass specific capacitance of PANi/MGE was 276 F g^{-1} with the subtraction method which used in the previous work.[9] In addition, the mass of the deposited PANi is about 2.5 mg. With the consideration of the mass specific capacitance of 192 F g^{-1} for MGE,[9] the mass specific capacitance of PANi is about 42000 F g^{-1} if there is only a simple superposition and nothing interaction existed between the PANi and MGE. However, it is unpractical in fact, although a large variety of the capacitance values have been reported (range from 200 F g^{-}1 to more than 500 F g^{-1}),[13-15] the capacitance more than 1000 F g^{-1} has never been heard. Therefore, it was thought that the enhanced capacitance is attributed to the synergistic effect between PANi and MGE. The possible synergistic effect is shown as Fig. 4. It is to say, during the oxidation process, the notrigen atom in the delocalized π bond of the undoped PANi was closely integrated with the carboxyl groups on the MGE through the hydrogen bond, and in the reduction process, the electronegative oxygen atom was also greatly interacted with the amidogen of the doped PANi.

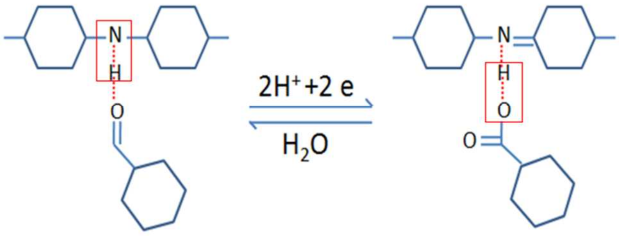

Fig. 4 The schematic diagram of the s synergistic effect between PANi and MGE

Galvanostatic charge/discharge curves at different currents in 2.0 M H_2SO_4 were constructed to further investigate the capacitive behavior of PANi/MGE. Good symmetry of charge and discharge curves in Fig. 5 also suggests a favorable capacitive character of PANi/MGE, and the slope of the charge/discharge curve changes obviously, meaning a predominant pseudo-capacitance, which is consistent with the CV results. Moreover, the charge/discharge curves still present symmetric even the current density up to 50 mA cm^{-2}, indicating an excellent capacitive property of PANi/MGE and a promising application in the high power field.

The specific capacitance of MGE can be calculated from the charge by the galvanostatic charge–discharge curves according to eqn (1):[16]

$$C = (i \times dt)/dE \qquad (2)$$

where C, i, dt and dE are the specific capacitance, the discharge current, discharge time, and the potential range of discharge process, respectively. Here C represents the specific capacitance with an apparent area of 1 cm^2. The apparent specific capacitance at different current density was calculated using eqn (1) and its relationships of discharge current density with capacitance (-●-) and capacitance holding ratio (-▲-) in 2.0 M H_2SO_4 shown as Fig. 6. Along with the current density increasing from 2 to 50 mA cm^{-2}, the apparent specific capacitance changed from 2.65 to 2.34 F cm^{-2}, eighty eight percent of the capacitance remained means a favorable ratio characteristic. In addition, the apparent specific capacitance of PANi/MGE (2.51 F cm^{-2} at 10 mA cm^{-2}) is greatly improved compared with MGE (1.63 F cm^{-2} at 10 mA cm^{-2}),[9] revealing a significant enhancement on the capacitive performance maybe ascribed to the synergistic effect between PANi and MGE, well consistent with the results of CV.

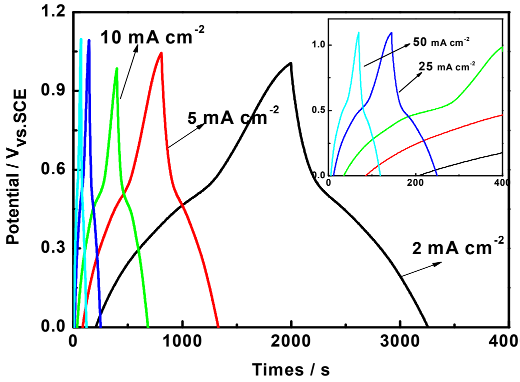

Fig. 5 Galvanostatic charge/discharge curves at different currents in 2.0 M H_2SO_4 (including an enlarged graph).

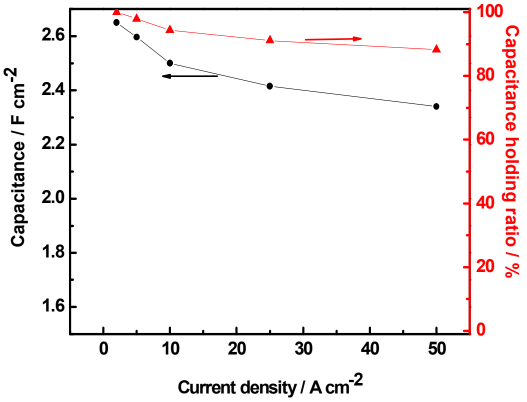

Fig. 6 Relationships of discharge current density with capacitance (-●-) and capacitance holding ratio (-▲-) in 2.0 M H_2SO_4.

The synthesis condition, polarization potential, film thickness and coverage of PANi have an importance effect on the resistance response, consequently the AC impedance spectroscopy of PANi/MGE is quite complicated.[17] Nyquist diagram of PANi/MGE measured at different potential in 2.0 M H_2SO_4

solution. It is noticed that nearly vertical lines are observed in the whole frequency range with a relative low polarization potential, revealing an excellent capacitive character. An approximate line with a 45° slope is visible at medium-high frequency (see the red circle in the enlarged graph in Fig. 7), which was attributed to the diffusion process, in according with the transmission line model.[18] In addition, the approximately vertical increase in the imaginary part at low frequency demonstrated the typical capacitive characteristic, which was mainly governed by a faradaic process of the electroactive material. In the meanwhile, the resistance response at high frequency almost unchanged with the increase of polarization potential, indicating the excellent conductivity of MGE make up for the lack of PANi on the electronic conductivity. However, the resistance response at low frequency have a maximum at 0.4 V with the increase of polarization potential, it can be seen that the capacitance of PANi/MGE is variational with the potential and the maximum corresponding to the coupling potential of redox peaks for PANi and MGE at 0.4–0.5 V. Therefore, the composite material possess a markedly pseudo-capacitive character, and the EIS results are also agree with CV tests. Furthermore, the nyquist plot did not present a vertical line at low frequency when the dc potential is 1.0 V, suggesting an irreversible electrochemical process or an limited diffusion process occurred. So the preferable potential range of PANi/MGE in 2.0 M H_2SO_4 is -0.2–0.8 V, and the composite electrode presents an excellent pseudo-capacitive performance within the potential range.

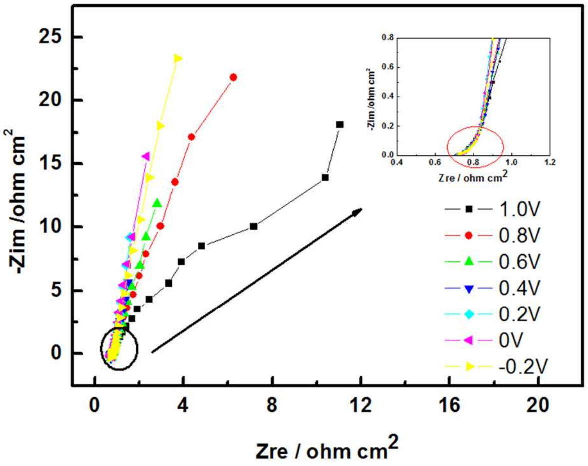

Fig. 7 Nyquist diagram of PANi/MGE measured at different potential in 2.0 M H_2SO_4 solution.

The electrochemical performance of PANi/MGE 2.0 M H_2SO_4 is preliminarily examined by different electrochemical measurements. After the deposion of PANi on MGE, the apparent specific capacitance is greatly improved (2.65 to 1.73 F cm^{-2}), about 1.6 times compared with that of MGE. The excellent pseudo-capacitive performance and ratio characteristics might attributed to the synergistic effect between PANi and MGE.

In addition, deeper problems such as how did the PANi and MGE combine, the mechanism of synergistic effect between PANi and MGE are still in research, and should be further studied.

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