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COMPOSITE CATHODE MATERIAL DOPED WITH NANO-GRAPHITE AND PREPARATION METHOD THEREOF.

(57)

The invention relates to the technical field of battery material preparation, and in particular to a composite cathode material doped with nano-graphite and a preparation method thereof. The preparation method comprises the following steps: (1) adding nano-graphite into *Spartina alterniflora* powder, performing primary pyrolysis, cooling and secondary pyrolysis to obtain a mixed carbon material; and (2) treating the mixed carbon material with alkali and acid in turn to obtain the composite cathode material doped with nano-graphite. The preparation method of the invention is simple and convenient, and the nano-graphite doped *Spartina alterniflora* source hard carbon material (composite cathode material) is prepared by the preparation method of the invention. The hard carbon material has a good first coulombic efficiency, and the battery prepared by using the hard carbon material as the cathode has excellent sodium storage performance.

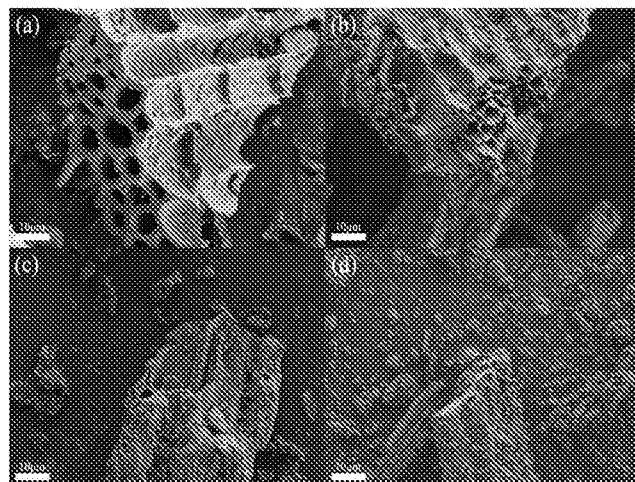


FIG. 2

DESCRIPTION

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**COMPOSITE CATHODE MATERIAL DOPED WITH NANO-GRAPHITE AND
PREPARATION METHOD THEREOF****TECHNICAL FIELD**

The invention relates to the technical field of battery material preparation, and in particular to a composite cathode material doped with nano-graphite and a preparation method thereof.

BACKGROUND

Nano-graphite has a unique sodium storage mechanism. Compared with traditional graphite, nano-graphite can not only store sodium between graphite layers, but also reversibly insert and remove sodium ions in defects, holes and active sites on the edge of graphite. Therefore, nano-graphite has more sodium storage sites than traditional graphite. Due to the larger specific surface area of nano-graphite, nano-graphite-doped anode materials are generally better soaked by electrolyte and have larger contact area. Therefore, the transfer resistance of sodium ions in the process of charging and discharging is lower, and nano-graphite can play a more outstanding role in battery rate and high current and long cycle performance. However, nano-graphite materials also have certain disadvantages. Because of its large specific surface area, nano-graphite must contact with the electrolyte in a larger area during the first cycle, resulting in a larger SEI film area and higher irreversible capacity for the first time. On the other hand, nano-graphite materials are stacked and agglomerated, and the aggregation of a large number of nano-graphite will lead to the increase of local graphite degree, the lower specific surface area and the lower number of active sites, which will affect the sodium storage performance of the materials.

SUMMARY

The purpose of the invention is to provide a composite cathode material doped with nano-graphite and a preparation method thereof, so as to solve the problems existing in the prior art.

To achieve the above purpose, the present invention provides the following solutions:

One of the technical schemes of the invention: a composite cathode material doped with nano-graphite and a preparation method thereof, comprising the following steps:

(1) adding nano-graphite into *Spartina alterniflora* powder, performing primary pyrolysis, cooling and secondary pyrolysis to obtain a mixed carbon material;

(2) treating the mixed carbon material with alkali and acid in turn to obtain the composite cathode material doped with nano-graphite.

Further, the preparation of the *Spartina alterniflora* powder specifically comprises: cutting leaves and stems of *Spartina alterniflora*, drying at 140-160°C for 4-8 h, and crushing to obtain the *Spartina alterniflora* powder.

Further, the doping amount of nano-graphite in *Spartina alterniflora* powder is 0-10wt%, and the doping amount is not 0%.

Further, the primary pyrolysis conditions are argon atmosphere, the temperature is 550-650°C, and the time is 18-22 min; the temperature of the secondary pyrolysis is 1100-1300°C and the time is 2.5-3.5 h.

Further, the alkali treatment specifically comprises: adding the mixed carbon material into potassium hydroxide solution with mass fraction of 8-12%, and heating at 55-65°C for 50-70 min.

Further, the acid treatment specifically comprises: adding the mixed carbon material into hydrochloric acid with a concentration of 2.8-3.2 mol/L, and heating at 55-65°C for 50-70 min.

The second technical scheme of the invention: a composite cathode material doped with nano-graphite prepared by the above preparation method.

The third technical scheme of the invention: an application of the above composite cathode material doped with nano-graphite in electrode preparation.

The invention discloses the following technical effects:

The preparation method of the invention is simple and convenient, and the nano-graphite doped *Spartina alterniflora* source hard carbon material (composite anode material) is prepared by the preparation method of the invention, and the composite anode material has more pores. According to the measurement of electrochemical performance, the first charge-discharge capacity of G-SALC2 can reach 200 mAh g⁻¹ at the current of 20 mA g⁻¹, and the first coulombic efficiency is 67%. In a long cycle, the capacity of 108 mAh g⁻¹ can still be maintained after a thousand cycles with a current of 200 mA g⁻¹, and the capacity retention rate is 88%. In the rate test, the rate capacity of G-SALC2 (nano-graphite-doped composite anode material) is 297, 199,

129,78 and 67 mAh g⁻¹ under the varying currents of 20 mA g⁻¹, 50 mA g⁻¹, 100 mA g⁻¹, 200 mA g⁻¹ and 500 mA g⁻¹, respectively. The battery capacity was measured by variable-speed cyclic voltammetry. It was found that the capacity of G-SALC was controlled by both diffusion capacity and surface capacity, and with the increase of scanning speed, the proportion of pseudo-capacitance in battery capacity increased, which indicated that G-SALC had excellent electrochemical performance and battery capacity at high current and high rate.

The *Spartina alterniflora* (SALC) in the invention is a worldwide invasive species. Using it as a raw material to prepare anode materials can not only provide convenient, cheap and a large number of industrial anode materials, but also bring new solutions and ideas for eliminating and solving invasive species, and achieve the purpose of killing two birds with one stone.

The invention improves the capacity, long cycle performance and multiplying power performance of SALC by doping different amounts of nano-graphite. It was found that the specific capacity of nano-graphite-modified SALC reached 297 mAh g⁻¹, but it still had the capacity of 108 mAh g⁻¹ under the condition of a long cycle of 200 mAh g⁻¹, and the capacity retention rate was 88%, which indicated that G-SALC was a high-performance anode material.

BRIEF DESCRIPTION OF THE FIGURES

In order to more clearly explain the embodiments of the present invention or the technical solutions in the prior art, the following will briefly introduce the drawings needed in the embodiments. The following drawings are only some embodiments of the present invention. For those of ordinary skill in the art, other drawings can be obtained according to these drawings without any creative effort.

Fig. 1 is a schematic diagram of the synthesis process of composite cathode materials doped with nano-graphite in the embodiment of the present invention;

Fig. 2 is a scanning electron microscope (SEM) diagram of cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

Fig. 3 is a high magnification scanning electron microscope (SEM) of the cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

Fig. 4 is a transmission electron microscope (TEM) diagram of cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

Fig. 5 is a high-power transmission electron microscope picture of cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

Fig. 6 is a performance characterization diagram of the cathode materials prepared in Embodiments 1 to 4, in which (a) is XRD, (b) Raman spectrum, (c) nitrogen adsorption-desorption curve isotherm, and (d) pore size distribution;

Fig. 7 shows the carbon composition of the cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

Fig. 8 is the electrochemical performance diagram of the cathode of sodium battery, in which (a) is the first charge-discharge curve at 20 mA g^{-1} , (b) is the ramp and platform capacity of the first charge-discharge, (c) is the short cycle performance of 50 mA g^{-1} , (d) is the rate cycle performance, and (e) is the long cycle performance at 200 mA g^{-1} ;

Fig. 9 is the cyclic voltammograms of the cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

Fig. 10 is an analysis diagram of sodium storage behavior mechanism of the cathode material (G-SALC2) prepared in Embodiment 1 of the present invention, in which (a) is the cyclic voltammetry curve at different scanning rates, (b) is the logarithmic curve relationship between peak current and scanning rate, (c) is the pseudo-capacitance contribution at 1 mV s^{-1} , and (d) is the ratio of capacitance contribution and diffusion contribution at different scanning rates; and

Fig. 11 is the EIS spectrum and equivalent circuit diagram of the cathode materials prepared in Embodiments 1 to 4 of the present invention after the first cycle.

DESCRIPTION OF THE INVENTION

Now, various exemplary embodiments of the present invention will be described in detail. This detailed description should not be taken as a limitation of the present invention, but should

be understood as a more detailed description of some aspects, characteristics and embodiments of the present invention. U502408

It should be understood that the terms mentioned in the present invention are only used to describe specific embodiments, and are not used to limit the present invention. In addition, for the numerical range in the present invention, it should be understood that each intermediate value between the upper limit and the lower limit of the range is also specifically disclosed. Every smaller range between any stated value or the intermediate value within the stated range and any other stated value or the intermediate value within the stated range is also included in the present invention. The upper and lower limits of these smaller ranges can be independently included or excluded from the range.

Unless otherwise stated, all technical and scientific terms used herein have the same meanings commonly understood by those of ordinary skill in the field to which this invention relates. Although the present invention only describes preferred methods and materials, any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention. All documents mentioned in this specification are incorporated by reference to disclose and describe the methods and materials related to the documents. In case of conflict with any incorporated documents, the contents of this specification shall prevail.

Without departing from the scope or spirit of the present invention, it is obvious to those skilled in the art that many modifications and changes can be made to the specific embodiments of the present specification. Other embodiments obtained from the description of the present invention will be obvious to the skilled person. The specification and embodiment of this application are only exemplary.

As used in this invention, "comprising", "including", "having" and "containing" are all open terms, which means including but not limited to.

Embodiment 1

A preparation method of composite anode material doped with nano-graphite;

(1) Washing the leaves and stems of *Spartina alterniflora*, cutting them into strips with a length of 0.5-1.0 cm, putting them in an oven, drying them at 150°C for 4 hours, and crushing them to a particle size of 100 meshes to obtain *Spartina alterniflora* powder.

(2) Mixing nano-graphite with *Spartina alterniflora* powder, so that the doping amount of nano-graphite is 2wt%, pyrolyzing at 600°C for 20 min under argon protective atmosphere to remove tar and impurities in the sample, cooling to room temperature, and then putting it into a tube furnace for pyrolysis again at 1200°C for 3 h, cooling, and obtaining the mixed carbon material.

(3) Grinding the mixed carbon material through a 100-mesh sieve to obtain mixed carbon material powder, adding mixed carbon powder into 10% potassium hydroxide solution, stirring for 15 min, covering with plastic wrap, heating at 60°C for 1 h, filtering, adding into 3 mol/L hydrochloric acid, stirring for 15 min, covering with plastic wrap, heating at 60°C for 1 h, filtering, adding into ethanol, stirring for 15 min, covering with fresh-keeping film, and heating in oven at 40°C for 1 h; filtering, washing with deionized water until the solution is neutral, and drying to obtain composite cathode material doped with nano-graphite (G-SALC2).

Embodiment 2

Same as Embodiment 1, except that the doping amount of nano-graphite in step (2) is 5wt%.

The composite cathode material doped with nano-graphite (G-SALC5) is obtained.

Embodiment 3

Same as Embodiment 1, except that the doping amount of nano-graphite in step (2) is 10wt%.

The composite cathode material doped with nano-graphite (G-SALC10) is obtained.

Embodiment 4

(1) Washing the leaves and stems of *Spartina alterniflora*, cutting them into strips with a length of 0.5-1.0 cm, putting them in an oven, drying them at 150°C for 4 hours, and crushing them to a particle size of 100 meshes to obtain *Spartina alterniflora* powder.

(2) Pyrolyzing *Spartina alterniflora* powder at 600°C for 20 min under argon protection atmosphere, cooling it to room temperature, and then putting it into a tube furnace for pyrolysis at 1200°C for 3 h, and then cooling it to obtain the mixed carbon material.

(3) Grinding the mixed carbon material through sieve to obtain mixed carbon material powder, adding mixed carbon powder into 10% potassium hydroxide solution, stirring for 15 min, covering with plastic wrap, heating at 60°C for 1 h, filtering, adding into 3 mol/L

hydrochloric acid, stirring for 15 min, covering with plastic wrap, heating at 60°C for 1 h, filtering, adding into ethanol, stirring for 15 min, covering with fresh-keeping film, and heating in oven at 40°C for 1 h; filtering, washing with deionized water until the solution is neutral, and drying to obtain composite cathode material doped with nano-graphite (G-SALC0).

Embodiment 5

As in Embodiment 1, the difference is that the leaves of *Spartina alterniflora* are used in step (1), the tissue structure in the leaves is more complex, and it is easy to form high-hardness carbon materials, and the slope capacity of sodium storage capacity is more.

Embodiment 6

As in Embodiment 1, the difference is that the stem of *Spartina alterniflora* is used in step (1), and the specific surface area of stem tissue is larger, so it has more additional sodium storage sites, so the overall sodium storage capacity is larger.

Embodiment 7

Same as Embodiment 1, but in the operation step, the mixing of nano-graphite and *Spartina alterniflora* powder must be completed before pyrolysis, and high temperature is a necessary condition for the combination of the two.

Embodiment 8

(1) Washing the leaves and stems of *Spartina alterniflora*, cutting them into strips with a length of 0.5-1.0 cm, putting them in an oven, drying them at 140°C for 8 hours, and crushing them to a particle size of 100 meshes to obtain *Spartina alterniflora* powder.

(2) Mixing nano-graphite with *Spartina alterniflora* powder, so that the doping amount of nano-graphite is 2wt%, pyrolyzing at 550°C for 22 min under argon protective atmosphere to remove tar and impurities in the sample, cooling to room temperature, and then putting it into a tube furnace for pyrolysis again at 1100°C for 3.5 h, cooling, and obtaining the mixed carbon material.

(3) Grinding the mixed carbon material through a 100-mesh sieve to obtain mixed carbon material powder, adding mixed carbon powder into 8% potassium hydroxide solution, stirring for 15 min, covering with plastic wrap, heating at 55°C for 70 min, filtering, adding into 2.8 mol/L hydrochloric acid, stirring for 15 min, covering with plastic wrap, heating at 55°C for 70 min, filtering, adding into ethanol, stirring for 15 min, covering with fresh-keeping film, and heating

in oven at 40°C for 1 h; filtering, washing with deionized water until the solution is neutral, and drying to obtain composite cathode material doped with nano-graphite (Performance is comparable to that of Embodiment 1).

Embodiment 9

(1) Washing the leaves and stems of *Spartina alterniflora*, cutting them into strips with a length of 0.5-1.0 cm, putting them in an oven, drying them at 160°C for 4 hours, and crushing them to a particle size of 100 meshes to obtain *Spartina alterniflora* powder.

(2) Mixing nano-graphite with *Spartina alterniflora* powder, so that the doping amount of nano-graphite is 2wt%, pyrolyzing at 650°C for 18 min under argon protective atmosphere to remove tar and impurities in the sample, cooling to room temperature, and then putting it into a tube furnace for pyrolysis again at 1300°C for 2.5 h, cooling, and obtaining the mixed carbon material.

(3) Grinding the mixed carbon material through a 100-mesh sieve to obtain mixed carbon material powder, adding mixed carbon powder into 12% potassium hydroxide solution, stirring for 15 min, covering with plastic wrap, heating at 65°C for 50 min, filtering, adding into 3.2 mol/L hydrochloric acid, stirring for 15 min, covering with plastic wrap, heating at 650°C for 50 min, filtering, adding into ethanol, stirring for 15 min, covering with fresh-keeping film, and heating in oven at 40°C for 1 h; filtering, washing with deionized water until the solution is neutral, and drying to obtain composite cathode material doped with nano-graphite (Performance is comparable to that of Embodiment 1).

Comparative embodiment 1

As in Embodiment 1, the difference is that the mass ratio of nano-graphite to *Spartina alterniflora* powder in step (2) is 1:100.

Comparative embodiment 2

As in Embodiment 1, the difference is that the mass ratio of nano-graphite to *Spartina alterniflora* powder in step (2) is 15:100.

Comparative embodiment 3

As in Embodiment 1, the difference is that the mass ratio of nano-graphite to *Spartina alterniflora* powder in Step (2) in Step (1) is 30:100.

Embodiment 1

The cathode materials prepared in Embodiments 1 to 4 were characterized, and the results are shown in Figures 2 to 6 and Table 1.

The characterization method is as follows:

(1) X-ray diffraction (XRD)

XRD is a method to study the crystal structure and phase structure of materials by using the diffraction phenomenon of X-rays in the process of penetrating objects. Generally speaking, when the crystalline state in the body is good, the diffraction peak is strong and sharp. However, when the crystalline state in the object is poor, the diffraction peak is wide. This technology has been widely used in a series of fields such as crystal structure analysis, stress analysis and film preparation. The model of the instrument used in the invention is Bruker Advance D8, and the parameters are: the radiation source is $\text{CuK}\alpha$, the diffraction wavelength λ of $\text{K}\alpha$ is 0.15406 nm, the tube voltage is 40 kV, and the tube current is 35 mA. In practical application, Bragg formula is used to calculate the lattice spacing, and its formula is:

$$2d\sin\theta=n\lambda$$

Where d is the interlayer spacing, θ is the angle between the incident X-ray and the crystal plane, n is the reflection order, and λ is the wavelength of the incident light ($\lambda=0.15406$ nm).

(2) Raman spectrum

Raman spectroscopy is a Raman scattering spectroscopy analysis technology named after Indian scientist Raman. Under the irradiation of incident light, molecules will show scattering spectra with different wavelengths, and then information of molecular vibration and rotation can be obtained. Based on this, the invention can obtain relevant information about molecular structure and properties.

The Raman spectrometer used in the invention is HORIBA Xplora Plus of Japan, with excitation wavelength of 532 nm and scanning range of 600-2000 cm^{-1} .

(3) Specific surface area and pore size distribution

The specific surface area and pore size distribution (BET) mainly depend on the adsorption of gas on the solid surface itself to measure the data of specific surface area, pore size distribution and pore volume of materials. The model of the instrument used in this invention is ASAP2020, and the test is degassed at 200 °C for 2 h, and the temperature during the measurement is -195.850 °C.

(4) Scanning electron microscope

Scanning electron microscope (SEM) is an extremely effective method to study the microscopic surface of matter. The principle is that by focusing the electron beam on the surface of the object, the electrons interact with the atoms on the surface of the object to produce various kinds of information that carry the shape and structure of the object, and then the microscopic technology can generate the image of the surface of the object by detecting and capturing these information. SEM image structure can well reflect the microscopic morphology and distribution of substances, which is beneficial to intuitively and effectively understand the microscopic morphology of substances. The scanning electron microscope used in this invention is Zeiss Sigma 300 produced by Japanese company, and its magnification is 10x-1,000,000x.

(5) Transmission electron microscope

Transmission electron microscope (TEM) is another important microscopic technology. Its principle mainly depends on the transmission electron penetrating the sample to image. The generated image is accepted and amplified by the detector, and finally the transmission image is generated. In order to ensure the clarity and accuracy of the image, it is generally required that the sample be made into a 100 nm ultrathin slice to ensure the transmission effect. Because the electron wavelength used by transmission electron microscope is short, the image produced in this way has a higher resolution, thus reaching a higher magnification. It captures the details of the structure similar to graphite lamellae or fine structure, and infers the disorder and graphitization degree of carbon materials according to these information. The transmission electron microscope used in this invention is jeol2100f, and its main application purpose is to observe information such as microstructure and atomic layer arrangement of *Spartina alterniflora*-derived hard carbon materials. The accelerating voltage is 100 kV.

(6) X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a widely used characterization method to analyze the sample surface. The principle is that when X-rays irradiate the sample surface, the valence electrons or inner electrons in the atom are excited, and then the photoelectron energy in this process is obtained. Spectral data are collected by a detector, based on which the content, proportion and valence of elements in the sample can be obtained through software analysis.

The X-ray photoelectron spectroscopy instrument used in the invention is Thermo Scientific K-Alpha, and its excitation source is Al K α alpha ray ($h\nu=1486.6$ eV). The vacuum degree of the analysis chamber is better than $5.0E-7$ mBar, the working voltage is 12 kV, the filament current is 6 mA, and the step length is 0.05 eV.

Fig. 2 is a scanning electron microscope (SEM) diagram of cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

Fig. 3 is a high magnification scanning electron microscope (SEM) of the cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

As can be seen from fig. 2, the surface of the composite cathode material doped with nano-graphite has more similar wrinkles and extremely small particles compared with the surface of the *Spartina alterniflora* (SALC) material prepared in Embodiment 4, and the substance attached to the surface of the main structure should be the doped nano-graphite. As can be seen from Fig. 2(a), the surface of *Spartina alterniflora* (SALC) material is relatively clean and tidy, without any impurities attached, and it is an original hard carbon structure with a large number of clear tiny pores; as can be seen from Fig. 2(b) that similar structures like lumps and folds began to appear outside the original hard carbon structure, indicating that nano-graphite has been successfully attached to the surface of SALC, forming G-SALC material; as can be seen from fig. 2(c) that a large amount of nano-graphite is attached to the surface of the carbon material, which effectively modifies the properties of the material, and the attached graphite also appears obvious agglomeration phenomenon; As can be seen from Fig. 2(d) that the amount of graphite attached to the surface of SALC reaches the maximum, and a large number of granular nano-graphite with uneven surface is attached to the surface of SALC. At the same time, a large number of nano-graphite are also distributed in the space outside the material, and some nano-graphite obviously agglomerate to form larger graphite blocks.

Fig. 4 is a transmission electron microscope (TEM) diagram of cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

Fig. 5 is a high-power transmission electron microscope picture of cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

It can be seen from Fig. 4 that, compared with SEM pictures, transmission electron microscope (TEM) can more clearly see that the surface of the composite anode material doped with nano-graphite contains a large number of graphitized lamellae, and most of these lamellae are distributed in disorder, formed by disordered, twisted and amorphous carbon fragments. It can be seen from fig. 4(a) that disordered graphite still occupies the main part in Embodiment 4(G-SALC0), and few regular graphitized lamellae appear; it can be seen from Fig. 4(b) that the graphitized lamellae in Embodiment 1(G-SALC2) increased obviously, and a large number of lamellar lamellae existed in G-SALC2 in a spiral structure, and nano-graphite had been doped into the hard carbon structure; as can be seen from Fig. 4(c), Embodiment 2(G-SALC5) has clearer graphite lamellae, which not only increases the number of graphite lamellae, but also increases the occupied area and the number of single lamellae, and nano-graphite has increased in G-SALC. As can be seen from Fig. 4(d), the graphitization degree of Embodiment 3(G-SALC10) is the highest. Not only can a large number of graphite flakes be easily found, but it can be found that graphitized flakes occupy most of the surface area, and graphitized flakes occupy most of the surface area, which is consistent with the phenomenon that nano-graphite is highly adhered to the surface of hard carbon materials in SEM images. The interlayer spacing of G-SALC is 0.341 nm, which fully shows that nano-graphite has been doped into SALC materials.

The XRD properties of the anode materials prepared in Embodiments 1 to 4 are shown in Table 1, and the XRD characterization chart is shown in Fig. 6.

Fig. 6 is a performance characterization diagram of the cathode materials prepared in Embodiments 1 to 4, in which (a) is XRD, (b) Raman spectrum, (c) nitrogen adsorption-desorption curve isotherm, and (d) pore size distribution;

Table 1 XRD properties of 1 G-SALC

LU502408

Samples	$d_{002}(\text{nm})$	$L_c(\text{nm})$	$L_a(\text{nm})$	N_i
G-SALC0	0.358	1.13	2.48	3.15
G-SALC2	0.356	1.17	2.54	3.28
G-SALC5	0.353	1.34	2.83	3.80
G-SALC10	0.347	1.54	3.41	4.45

It can be seen from Fig. 6(a) that there are broad peaks and sharp peaks at 24 degrees and 26 degrees, respectively corresponding to amorphous carbon and attached nano-graphite in typical hard carbon materials. The broad peak at 43 degrees is related to sp^2 hybrid carbon in G-SALC. At the same time, with the increasing amount of doped nano-graphite, the original (002) peak of hard carbon material decreases, while the characteristic peak of graphite at 26.5° becomes stronger, and its intensity is proportional to the content of nano-graphite, which proves that the content of nano-graphite in the sample increases and decreases in disorder. According to the Bragg formula, the interlayer spacing of four groups of samples is 0.358 nm (G-SALC0), 0.356 nm (G-SALC2), 0.354 nm (G-SALC5) and 0.347 nm (G-SALC10), respectively. The decrease of interlayer spacing means the rise of ordered graphite lamellae. At the same time, as shown in Table 1, the average layer thickness (L_c) and plane width (L_a) of the cathode material also increase with the increase of doped nano-graphite materials.

It can be seen from Fig. 6(b) that the cathode material prepared by the present invention has two strong peaks, namely the D peak at 1345 cm^{-1} and the G peak at 1590 cm^{-1} . The appearance of D peak is related to the defect of amorphous carbon caused by sp^3 hybridization, while the G peak is related to graphite-like carbon with sp^2 hybridization. Therefore, the relative ratio of D peak and G peak is a parameter which is helpful to study amorphous carbon and disorder degree in samples. The ratio of I_d/I_g is 1.05, 0.83, 0.74 and 0.47, respectively, which proves that disorder degree of G-SALC decreases and graphitization degree increases. At the same time, with the increase of doped nano-graphite, the G peak gradually approaches from a wide and slow peak to a fine peak, which indicates that the content of graphite crystallites increases.

As can be seen from Fig. 6(c), the specific surface areas of G-SALC0, G-SALC2, G-SALC5 and G-SALC10 are 51.4, 22.23, 25.27 and $38.23\text{ m}^2\text{ g}^{-1}$, respectively, and the nitrogen adsorption-desorption amount obviously increases when the relative pressure is between 0.8-1 (compared with the hard carbon structure of *Spartina alterniflora*). At the same time, there is a

closed circular curve in the relative pressure range of 0.5-0.9, and this curve is a type IV hysteresis loop. The appearance of the IV hysteresis curve means that there are a large number of tiny pores composed of lamellae and carbon blocks in the G-SALC sample, which leads to the hysteresis curve.

It can be seen from Fig. 6(d) that most of the pores about 2 nm of the added nano-graphite anode materials are filled by nano-graphite, and at the same time, with the increase of nano-graphite content, the pore content decreases, indicating that nano-graphite has largely replaced some tiny pores.

Embodiment 2

The carbon element composition of the cathode materials prepared in Embodiments 1 to 4 was measured;

Measurement method: X-ray photoelectron spectroscopy (XPS) was used for measurement, and the results are shown in Fig. 7.

Fig. 7 shows the carbon composition of the cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

In Fig. 7, the solid line represents the actual test data, and the dotted line represents the data fitting value.

As can be seen from Figure 7, the C1s peak is decoupled, and its position is around 285eV. By fitting and dividing the C1s peak, the C1s peak can be divided into four peaks, namely sp^2 , sp^3 , C=O, O=C-O, which are located at 284.6, 285.6, 285.6 and 286.7 eV respectively. Among them, sp^2 peak is generally generated by graphitized carbon, while sp^3 peak is generated by amorphous carbon. By studying the relative ratio of them, the graphitization degree of the sample can be verified. The area of sp^3 is I_{sp^3} , while the area of sp^2 is I_{sp^2} , the ratio of G-SALC0, G-SALC2, G-SALC5 and G-SALC10 is I_{sp^3}/I_{sp^2} . With the increase of doped graphite content, the ratio of I_{sp^3}/I_{sp^2} gradually decreases, which indicates that the amorphous carbon content in G-SALC samples decreases, while the graphitized carbon content gradually increases, which indicates that nano-graphite has been successfully doped into SALC samples, and the order of doping amount is constantly increasing.

Preparation of electrodes and assembly of batteries

(1) preparation of electrode

Like the cathode of lithium battery, the preparation of the electrode of sodium battery is the key step of the whole battery test, and the quality of the electrode directly affects the performance of the battery. The cathode material, binder and conductive carbon black prepared in Embodiments 1-4 were added into agate grinding body in the mass ratio of 8:1:1 for grinding and mixing for 15 min, and then deionized water was added to continue grinding for 25 min until uniform viscous liquid was obtained.

The viscous liquid is coated on the copper foil with a certain thickness by a coater, and the load of the active substance in the electrode ranges from 1.2 to 1.8 mg cm^{-3} . Put the coated copper foil in a vacuum drying oven and dry it at 100°C for more than 1 h. Then, press the pole piece with a tablet press, and dry it in a vacuum drying oven at 100°C for 12 hours, so as to obtain the cathode material (active material) on the carbon cathode sheet with a load range of 1.2 - 1.8 mg cm^{-3} . The carbon cathode sheet is weighed and recorded.

(2) Assembly of batteries

The battery was assembled in a glove box filled with argon, and the contents of oxygen and hydrogen were lower than 1 ppm. The type of sodium ion battery used in the invention is 2032 button cell assembly, wherein the counter electrode is metal sodium, and the diaphragm used is fiber film Whatman Gf/D. The electrolyte is EC-PC mixed liquid containing $1 \text{ mol L}^{-1} \text{ NaClO}_4$ with a volume ratio of 1:1, and 5% fluoroethylene carbonate is added to it. Install the button cell according to the order of negative shell, carbon negative plate, glass fiber diaphragm, positive plate, gasket, spring and positive shell, put the installed battery into a packaging machine for packaging, and stand at room temperature for 12 hours before testing.

(3) Constant current charge and discharge test

Constant-current charging and discharging test is the most commonly used means to test the battery performance. The battery tester used in this invention is Shenzhen New Wales CT-4000, 5 V 10 mA model. The voltage range of the battery is 0.01/3.0 V, and the test environment is room temperature.

In the cyclic test, the current density used in the invention is 50 mA g⁻¹ and 200 mA g⁻¹ respectively. In the rate test, the current density used in this invention is 20 mA g⁻¹, 50 mA g⁻¹, 100 mA g⁻¹, 200 mA g⁻¹ and 500 mA g⁻¹.

(4) Cyclic Voltammetry/AC Impedance Test

Cyclic voltammetry is a commonly used and effective method to study electrochemical system, which mainly depends on the alternating electrochemical reactions of electrodes in different sweep rates and voltage change ranges. The properties of the tested electrochemical system are analyzed by the obtained current-voltage diagram. Generally speaking, the process from high potential to low potential corresponds to the formation of the reduction peak of Na⁺ embedded in the cathode, while the process from low potential to high potential corresponds to the formation of the oxidation peak of Na⁺ released. By observing the peak height, peak area and half-peak width of cyclic voltammetry, a series of information about diffusion coefficient and capacity of electrode materials can be obtained.

AC impedance test is a commonly used electrochemical test method at present. A sinusoidal AC voltage with a certain frequency is added to an electrochemical system, and an AC current signal is fed back from the electrochemical system. According to the information of current and voltage, the relationship between impedance and frequency of the electrochemical system can be obtained by simulation calculation.

The instrument for testing AC impedance used in this invention is CHI 760E, with a frequency range of 0.01-100000 Hz and an amplitude of 10 mV.

Fig. 8 is the electrochemical performance diagram of the cathode of sodium battery, in which (a) is the first charge-discharge curve at 20 mA g⁻¹, (b) is the ramp and platform capacity of the first charge-discharge, (c) is the short cycle performance of 50 mA g⁻¹, (d) is the rate cycle performance, and (e) is the long cycle performance at 200 mA g⁻¹;

It can be seen from fig. 8(a) that the constant current charging and discharging process is under the condition of 0.01~3V voltage at the current density of 20 mg⁻¹. The discharge capacities of G-SALC0, G-SALC2, G-SALC5 and G-SALC10 are 354, 439, 377 and 371 mAh g⁻¹, respectively, while the charging capacities are 208, 297, 261 and 238mAh g⁻¹, and the coulombic efficiency is 58%, 67%, 69% and 68%. Like the first cycle of CV, part of irreversible capacity comes from the consumption of SEI film formation, and the reason for the low first

coulombic efficiency also includes the irreversible reaction process in which some sodium ions are trapped by defects.

According to the adsorption-intercalation theory, the capacity at the high voltage platform mainly comes from the capacity contributed by the edge defects and pores of the carbon layer, while the capacity contributed at the low voltage platform area is mostly the intercalation reaction completed by graphite crystallites. It can be seen from fig. 8(b) that as the amount of doped graphite increases, more capacity contribution comes from the platform area. This result not only accords with the theoretical explanation, but also fully proves that the doped nano-graphite has fully combined with SALC hard carbon materials, which proves the existence of G-SALC.

It can be seen from fig. 8(c) that the initial specific capacities of G-SALC0, G-SALC2, G-SALC5 and G-SALC10 are 132, 198, 177 and 166 mAh g⁻¹, respectively, and the capacity retention rates are 94%, 95% and 166 mah g⁻¹ after the cycle. Although it fluctuates slightly during the cycle, it still maintains a good cycle capacity and capacity retention rate. After 100 cycles, the specific capacity of G-SALC0 is 132 mAh g⁻¹, and its capacity retention rate is 95%, while that of G-SALC2 after 100 cycles is 188 mAh g⁻¹, and its capacity retention rate is 95%. The specific capacity of 100 cycles of G-SALC5 is 177mAh g⁻¹, while the specific capacity of 100 cycles of G-SALC10 is 163mAh g⁻¹. Compared with the anode materials in the prior art, G-SALC has good capacity retention and cycle stability, because the porous and tough *Spartina alterniflora* source is used as the raw material when building the primary skeleton of G-SALC, and it is carried out at a suitable temperature.

It can be seen from Fig. 8(d) that in the rate test, the capacity of G-SALC2 is 20 mA g⁻¹, 50 mA g⁻¹, 100 mA g⁻¹, and 200 mA g⁻¹ and 500 mA g⁻¹ current capacity, and they are 297, 199, 129, 78, 67 mAh g⁻¹ respectively, when the current returns to 20 mA g⁻¹, its capacity can be restored to 273 mA g⁻¹. The capacity of G-SALC increases slowly with the increase of cycle times, and the capacity even exceeds the initial current, and the capacity retention rate reaches 103%. Many cycles activate the battery performance and improve its capacity performance. Moreover, when the amount of nano-graphite is small, the capacity of the material is improved, which is mainly because the doped nano-graphite provides additional intercalation capacity for G-SALC. However, with the increase of graphitization degree, the growth of pseudo-graphite leads to the

decrease of interlayer spacing and sodium ion diffusion channel, which makes the process of sodium ion insertion in G-SALC more difficult. At the same time, the further increase of the number of graphite layers and surface area also means that it is more difficult for sodium ions to intercalate into the pseudo-graphite structure.

It can be seen from fig. 8(e) that the initial capacity of G-SALC2 is 123 mAh g⁻¹, and after 1000 cycles, the final capacity is 108 mAh g⁻¹, with a capacity retention rate of 88%. In this process, the capacity of G-SALC fluctuates, rises or falls during the whole charging and discharging process, but it is still relatively stable in general. Therefore, G-SALC still maintains a good capacity retention capacity under high current, which indicates that G-SALC has excellent material stability and excellent structural stability.

Fig. 9 is the cyclic voltammograms of the cathode materials prepared in Embodiments 1 to 4 of the present invention, in which (a) is Embodiment 4, (b) is Embodiment 1, (c) is Embodiment 2, and (d) is Embodiment 3;

As can be seen from fig. 9, the results of the first three rounds of scanning of G-SALC material under the conditions of scanning speed of 0.1 mV s⁻¹ and voltage range of 0.01-3 V are as above. The strong reduction peak near 0V corresponds to the process of sodium ion embedding. Compared with the first scanning process, the G-SALC has obvious reduction peak between 0 and 1 V, and this phenomenon disappears in the subsequent cyclic voltammetry results, which proves that the strong reduction peak is largely related to the first irreversible capacity. Irreversible capacity comes from two aspects. On the one hand, the electrolyte reacts on the electrode surface to form SEI film; on the other hand, it is related to the irreversible reaction of sodium ions with the electrode surface and defects. Compared with other literatures, the smaller irreversible reduction peak also proves that G-SALC has fewer side reactions at the phase interface during the formation of SEI film, which indicates that G-SALC has higher first coulombic efficiency and first efficiency. The high coincidence of subsequent CV curves also proves that the material has good cyclic stability.

Fig. 10 is an analysis diagram of sodium storage behavior mechanism of the cathode material (G-SALC2) prepared in Embodiment 1 of the present invention, in which (a) is the cyclic voltammetry curve at different scanning rates, (b) is the logarithmic curve relationship between peak current and scanning rate, (c) is the pseudo-capacitance contribution at 1 mV s⁻¹,

and (d) is the ratio of capacitance contribution and diffusion contribution at different scanning rates; 14502408

As can be seen from fig. 10(a), with the increase of scanning speed, a wide reduction peak of G-SALC2 appears around 0.2-0.3 V, which should be related to the mechanism of sodium ion intercalation in high current state. In order to analyze the sodium storage property of G-SALC, the capacity mechanism is analyzed by using the formula $i = av^b$ based on the relationship between peak current i and scanning current v . In the equation, i is the peak current, v represents the scanning rate, and a is the correlation constant. If b is 0.5, the battery is controlled by diffusion behavior. If b is between 0.5 and 1, sodium battery is controlled by both diffusion behavior and capacitance behavior. If b is equal to 1, the battery is controlled by capacitance behavior. By drawing the curve relationship between $\log(i)$ and $\log(v)$, the peak currents of oxidized state and reduced state are calculated respectively (Figure 10(b)), and it is found that the B value of G-SALC is 0.65 and 0.75, respectively. Compared with the previous SALC material, the B value of G-SALC material is obviously improved, which proves that the surface control capacity of battery capacity is increased after doping nano-graphite.

According to the adsorption-embedding theory, the total capacitive charge contribution at a fixed rate can be quantified by decoupling the ratio contribution of diffusion control charge and capacitive charge at any place and finally accumulating. The formula is $i(V) = k_1v + k_2v^{0.5}$, where $i(V)$ represents the current at a certain voltage, k_1v is the surface control capacitance, and $k_2v^{0.5}$ is the diffusion control capacity. The invention uses this to quantitatively analyze the contribution of G-SALC2 pseudocapacitor to the battery. The dark part in Figure 10(c) shows the surface control capacity contribution of G-SALC2 at the scanning rate of 1mV s^{-1} . Through calculation, it is found that the capacity contribution of pseudo-capacitance reaches 30%, 33%, 41%, 59% and 66% under the conditions of 0.1, 0.2, 0.5, 1, 1.5 and 2mV s^{-1} . With the increase of scanning speed, the sodium storage process of charge and discharge in G-SALC is more and more dependent on the surface contribution capacitance, which indicates that G-SALC is very important in rate performance and large current and long cycle.

Fig. 11 is the EIS spectrum and equivalent circuit diagram of the cathode materials prepared in Embodiments 1 to 4 of the present invention after the first cycle.

Electrochemical impedance spectroscopy (EIS) is also used to test the performance of G-SALC, in which the amplitude of sine wave is 10mv and the frequency range is 100000 Hz to 0.01 Hz. As can be seen from fig. 11, the spectrum of G-SALC consists of two parts, a semicircle in the high frequency region and an oblique line in the low frequency region. The semicircle in the high frequency region represents the charge transfer resistance, while the oblique line in the low frequency region represents the ion diffusion resistance inside the cathode material. The rcts of G-SALC0, G-SALC2, G-SALC5 and G-SALC10 are 536, 452, 476 and 638 ω , respectively. Compared with other G-SALC series samples, G-SALC2 has relatively lower electron transfer resistance.

By the formula

$$D_{Na} = 0.5 \left(\frac{RT}{N^2 F^2 A C A_w} \right)^2$$

The ion diffusion coefficient of sodium ion in the cathode material G-SALC can be calculated, where R is the gas constant, T is the absolute temperature, N is the number of electrons transferred in the reaction, A is the active area of the electrode, F is Faraday constant, C is the phase density of sodium ion, and A_w is the slope after z' and $\omega^{-1/2}$ are plotted. The calculated diffusion coefficients of G-SALC0, G-SALC2, G-SALC5 and G-SALC10 are $2.18 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, $2.36 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, 3.85×10^{-13} , $1.05 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. Among them, G-SALC2 has high D_{Na} content and low charge transfer resistance, which proves that the capacity and ion transport performance of G-SALC doped with nano-graphite have been greatly improved.

The preparation method of the invention is simple and convenient, and the prepared *Spartina alterniflora* source hard carbon material (composite cathode material) doped with nano-graphite has excellent performance. The structure and morphology of G-SALC were characterized by BET, XRD, SEM, TEM and Raman. The prepared G-SALC successfully completed the process of doping nano-graphite into SALC carbon materials, and formed a hard carbon material structure with more pores and nano-graphite. After that, the electrochemical performance of G-SALC was measured by charge and discharge, cyclic voltammetry and EIS. Under the condition of 20 mA g^{-1} current, the first charge and discharge capacity of G-SALC2

can reach 200 mAh g^{-1} , and the first coulombic efficiency is 67%. In a long cycle, the capacity of G-SALC2 is 108 mAh g^{-1} can still be maintained after a thousand cycles with a current of 200 mAh g^{-1} , and the capacity retention rate is 88%. In the rate test, the rate capacity of G-SALC2 is 297, 199, 129, 78 and 67 mAh g^{-1} under the varying currents of 20 mA g^{-1} , 50 mA g^{-1} , 100 mA g^{-1} , 200 mA g^{-1} and 500 mA g^{-1} , respectively. In the further measurement of battery capacity by variable-speed cyclic voltammetry, it is found that the capacity of G-SALC is controlled by both diffusion capacity and surface capacity, and with the increase of scanning speed, the proportion of pseudo-capacitance in battery capacity is also increasing, which shows that G-SALC has excellent electrochemical performance and capacity performance under high current and high rate conditions.

Embodiment 4

The electrical properties of composite cathode materials prepared from non-stop raw materials were measured. The preparation method was the same as in Embodiment 1, and the results are shown in Table 2.

Table 2

Material	Capacity performance (mA g ⁻¹)	Coulombic efficiency circulation capacity	Coulombic efficiency circulation capacity
Apple	245	61%	113% (1000 rounds)
Return belt	334	64%	≈95% (300 rounds)
Rice hull	≈210	53%	72% (200 rounds)
Glucose	280	79%	--
Sisal seed	299	71%	93% (1000 rounds)
Corncob	152	31%	86% (100 rounds)
Blue-Green Algae	231	52%	99% (60 rounds)
Garlic shell	258	41%	88% (100 rounds)
Red hairy danpi	≈205	54%	109% (100 rounds)
Sugar	235	70%	76% (100 rounds)
Tin/porous carbon	295	39%	64% (15 rounds)
Tin/tree fiber	339	79%	42% (400 rounds)
Carbon Nano Tube	251	50%	82% (400 rounds)
Embodiment 1	265	67%	110% (1000 rounds)

The above-mentioned embodiments only describe the preferred mode of the invention, but do not limit the scope of the invention. On the premise of not departing from the design spirit of the invention, all kinds of modifications and improvements made by ordinary technicians in the field to the technical scheme of the invention shall fall within the scope of protection determined by the claims of the invention.

CLAIMS

1. A preparation method of composite cathode material doped with nano-graphite, characterized by comprising the following steps:

(1) adding nano-graphite into *Spartina alterniflora* powder, performing primary pyrolysis, cooling and secondary pyrolysis to obtain a mixed carbon material;

(2) treating the mixed carbon material with alkali and acid in turn to obtain the composite cathode material doped with nano-graphite.

2. The preparation method according to claim 1, characterized in that the preparation of the *Spartina alterniflora* powder comprises: cutting leaves and stems of *Spartina alterniflora*, drying at 140-160°C for 4-8 h, and crushing to obtain the *Spartina alterniflora* powder.

3. The preparation method according to claim 1, characterized in that the doping amount of nano-graphite in *Spartina alterniflora* powder is 0-10wt%, and the doping amount is not 0%.

4. The preparation method according to claim 1, characterized in that the primary pyrolysis conditions are argon atmosphere, the temperature is 550-650°C, and the time is 18-22 min; the temperature of the secondary pyrolysis is 1100-1300°C and the time is 2.5-3.5 h.

5. The preparation method according to claim 1, characterized in that the alkali treatment comprises: adding the mixed carbon material into potassium hydroxide solution with mass fraction of 8-12%, and heating at 55-65°C for 50-70 min.

6. The preparation method according to claim 1, characterized in that the acid treatment comprises: adding the mixed carbon material into hydrochloric acid with a concentration of 2.8-3.2 mol/L, and heating at 55-65°C for 50-70 min.

7. A composite cathode material doped with nano-graphite prepared by the preparation method according to any one of claims 1 to 6.

8. An application of the composite cathode material doped with nano-graphite according to claim 7 in electrode preparation.

PATENTANSPRÜCHE

LU502408

1. Ein Verfahren zur Herstellung eines mit Nano-Graphit dotierten Verbundkathodenmaterials, dadurch gekennzeichnet, dass es die folgenden Schritte umfasst:
 - (1) Zugabe von Nano-Graphit zu *Spartina alterniflora*-Pulver, Durchführung von primärer Pyrolyse, Kühlung und sekundärer Pyrolyse, um ein gemischtes Kohlenstoffmaterial zu erhalten;
 - (2) Behandlung des gemischten Kohlenstoffmaterials nacheinander mit Alkali und Säure, um das mit Nano-Graphit dotierte Verbundkathodenmaterial zu erhalten.
2. Das Herstellungsverfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Herstellung des *Spartina alterniflora*-Pulvers umfasst: Schneiden von Blättern und Stängeln von *Spartina alterniflora*, Trocknen bei 140-160 °C für 4-8 h und Zerkleinern, um das *Spartina alterniflora*-Pulver zu erhalten.
3. Das Herstellungsverfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Dotierungsmenge von Nano-Graphit in *Spartina alterniflora*-Pulver 0-10wt% beträgt und die Dotierungsmenge nicht 0% ist.
4. Das Herstellungsverfahren nach Anspruch 1, dadurch gekennzeichnet, dass die primären Pyrolysebedingungen Argon-Atmosphäre sind, die Temperatur 550-650°C beträgt, und die Zeit 18-22 Minuten beträgt; die Temperatur der sekundären Pyrolyse beträgt 1100-1300°C und die Zeit 2,5-3,5 h.
5. Das Herstellungsverfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Alkalibehandlung umfasst: Zugabe des gemischten Kohlenstoffmaterials in eine Kaliumhydroxidlösung mit einem Massenanteil von 8-12 % und Erhitzen auf 55-65°C für 50-70 min.
6. Das Herstellungsverfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Säurebehandlung umfasst: Zugabe des gemischten Kohlenstoffmaterials in Salzsäure mit einer Konzentration von 2,8-3,2 mol/L und Erhitzen auf 55-65°C für 50-70 min.
7. Ein mit Nano-Graphit dotiertes Verbundkathodenmaterial, hergestellt nach dem Herstellungsverfahren nach einem der Ansprüche 1 bis 6.
8. Eine Anwendung des mit Nano-Graphit dotierten Verbundkathodenmaterials nach Anspruch 7 bei der Elektrodenherstellung.

FIGURES

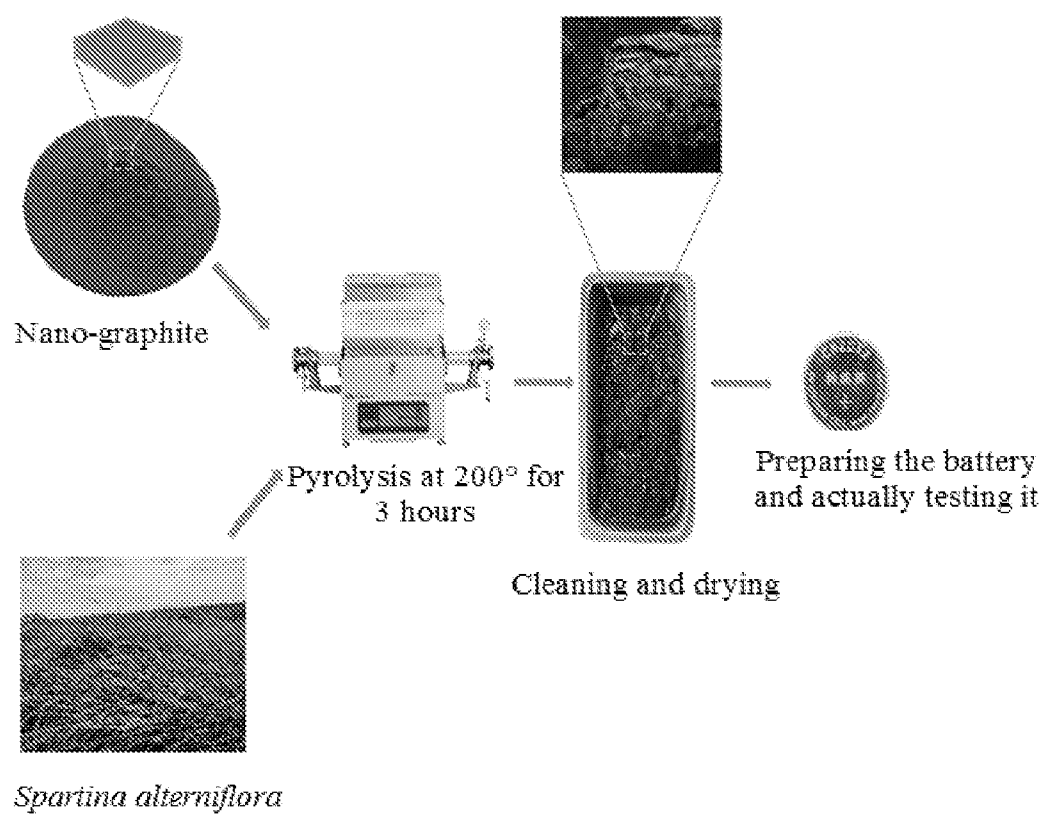


FIG. 1

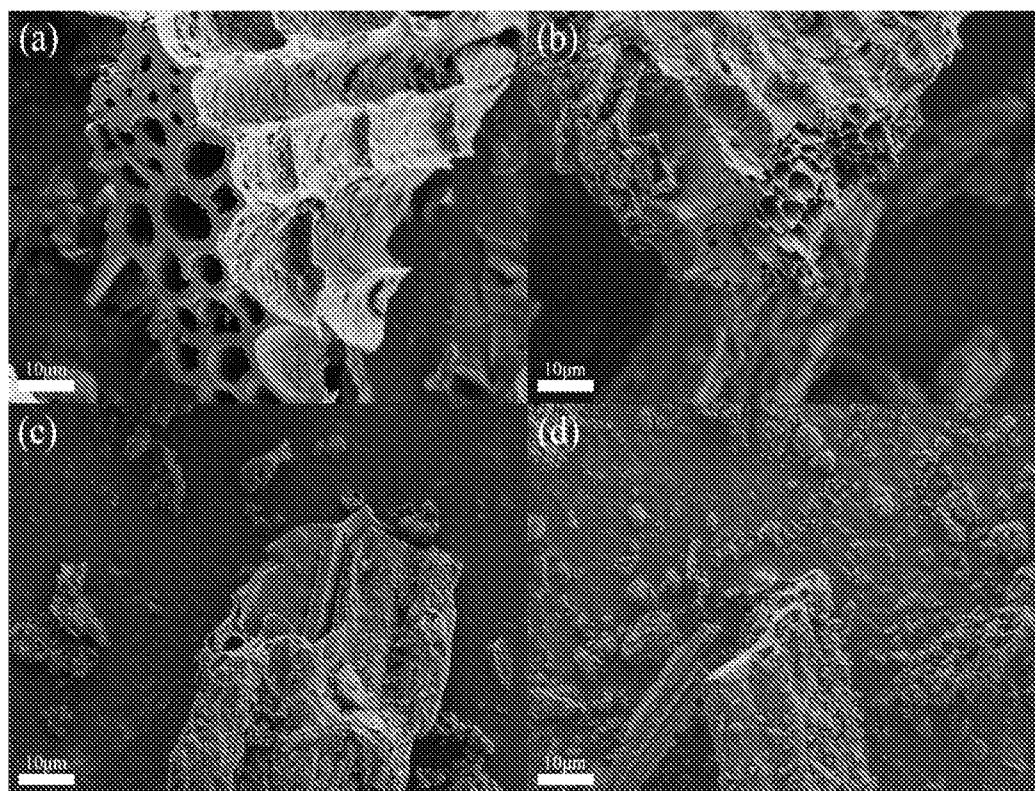


FIG. 2

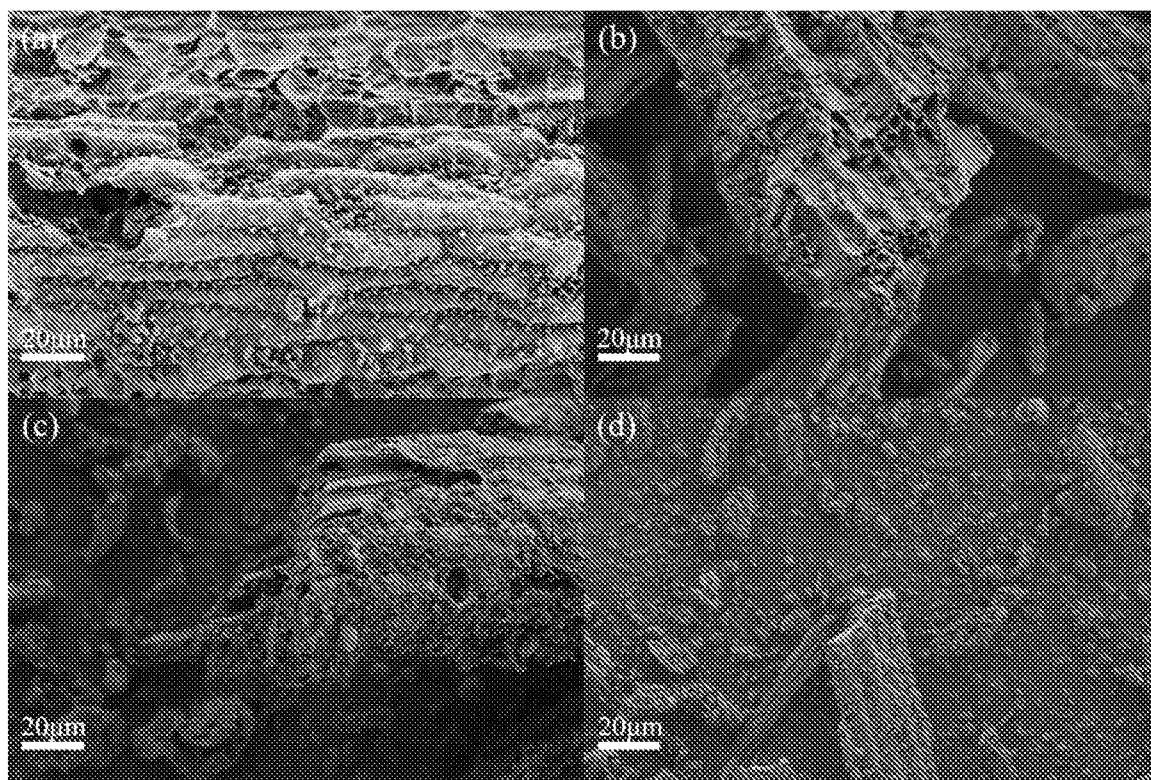


FIG. 3

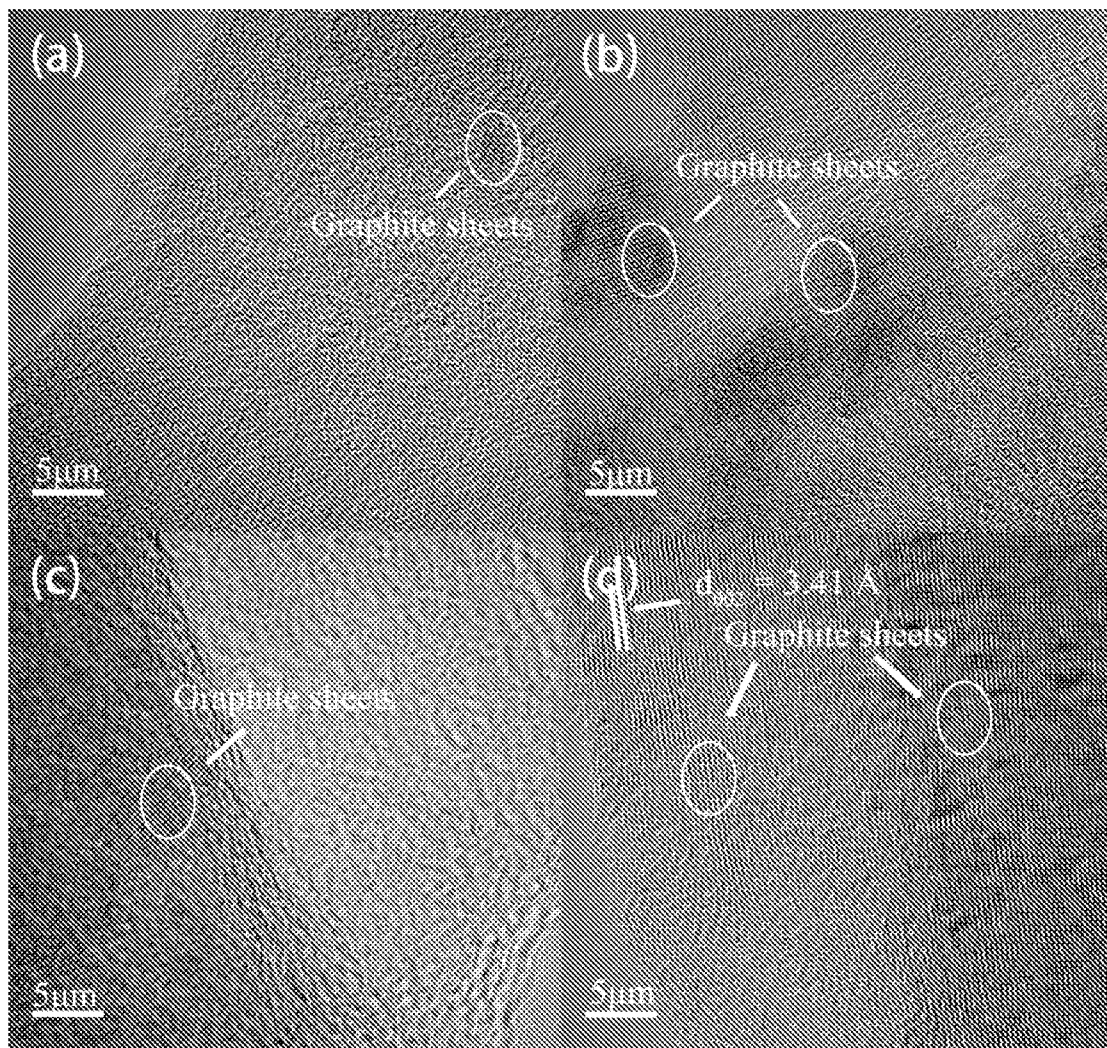


FIG. 4

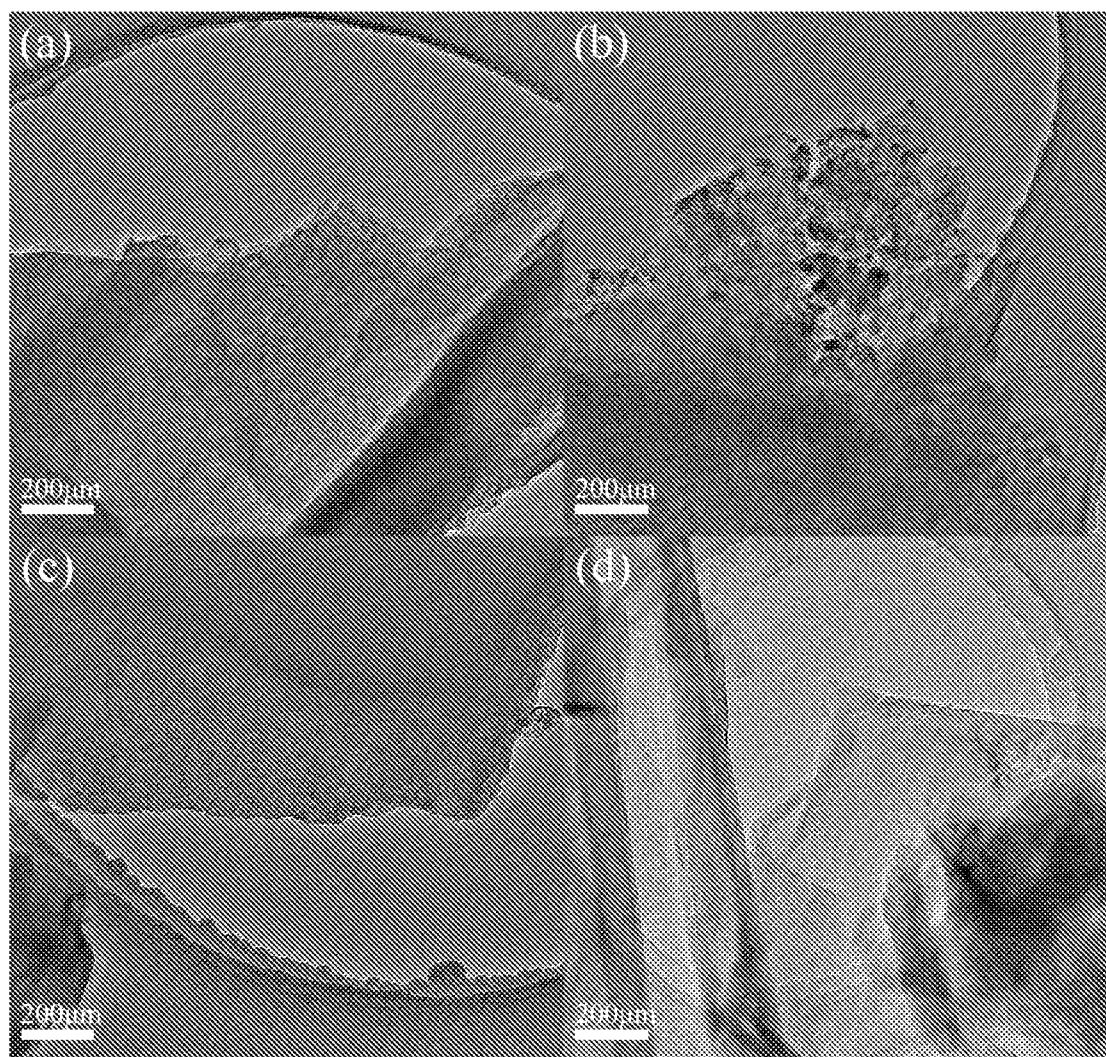


FIG. 5

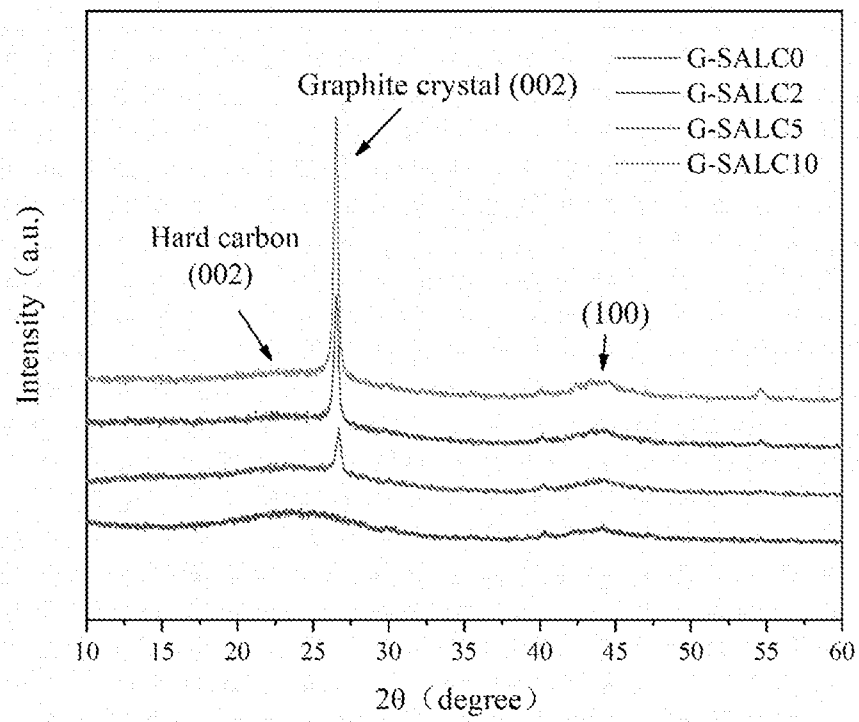


FIG. 6(a)

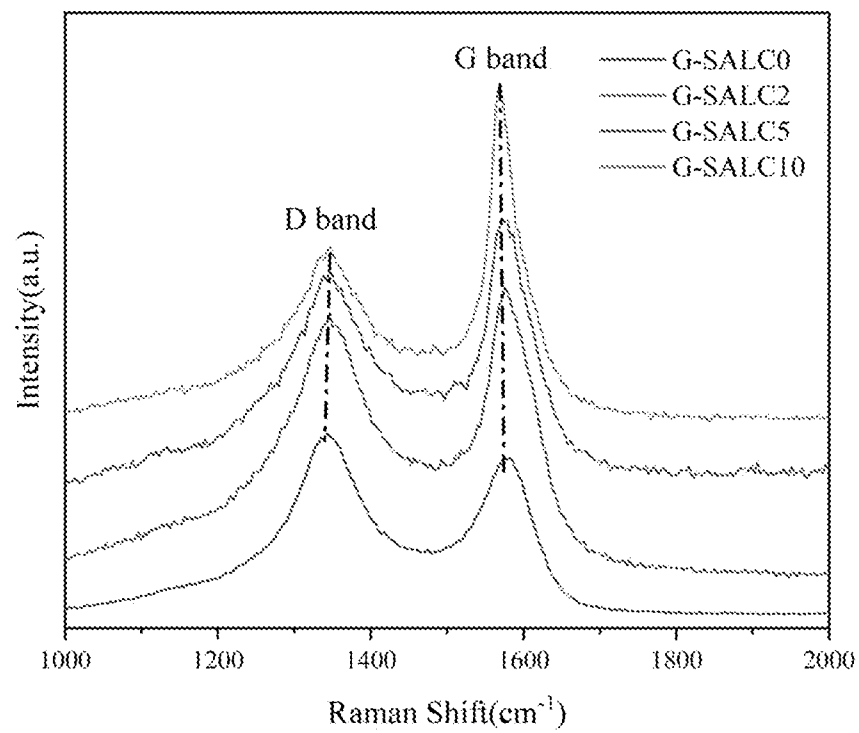


FIG. 6(b)

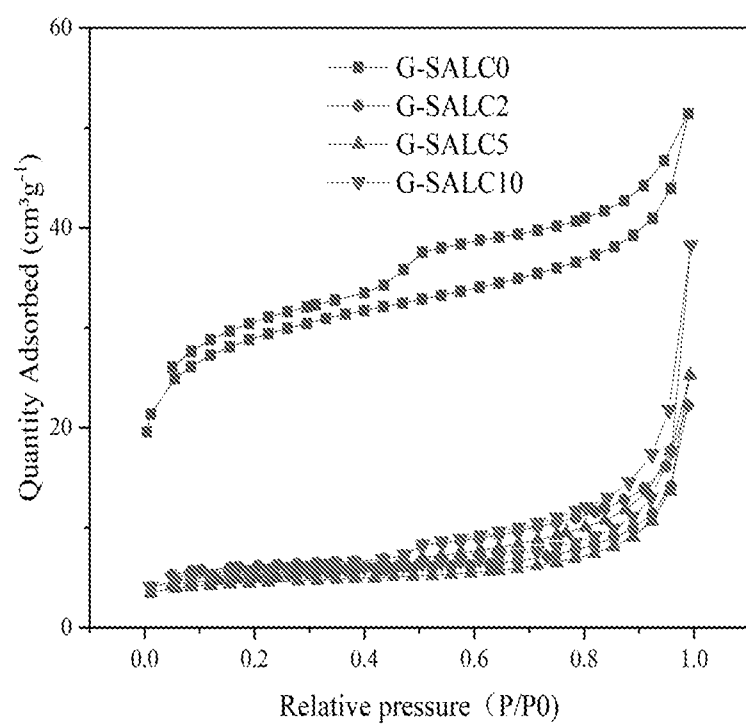


FIG. 6(c)

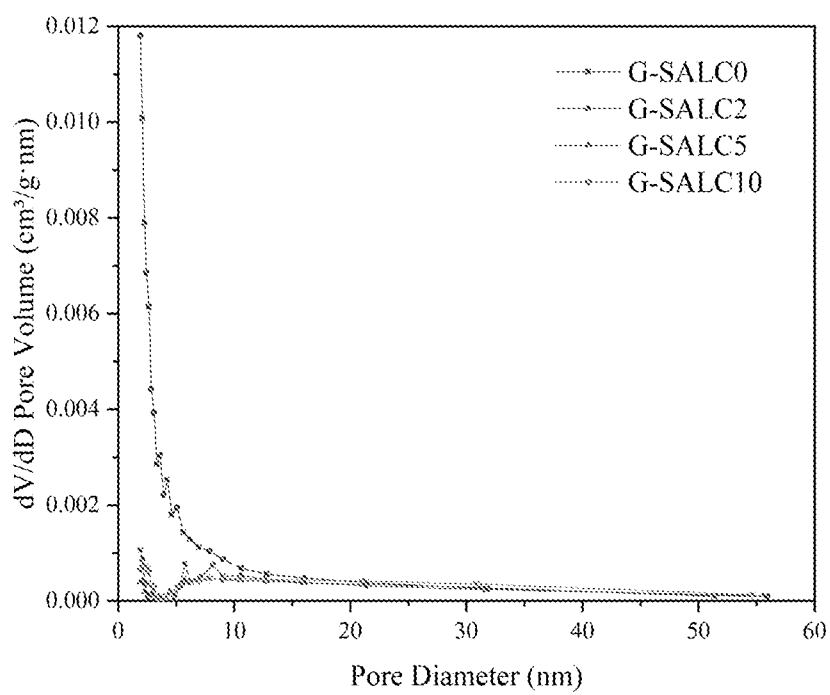


FIG. 6(d)

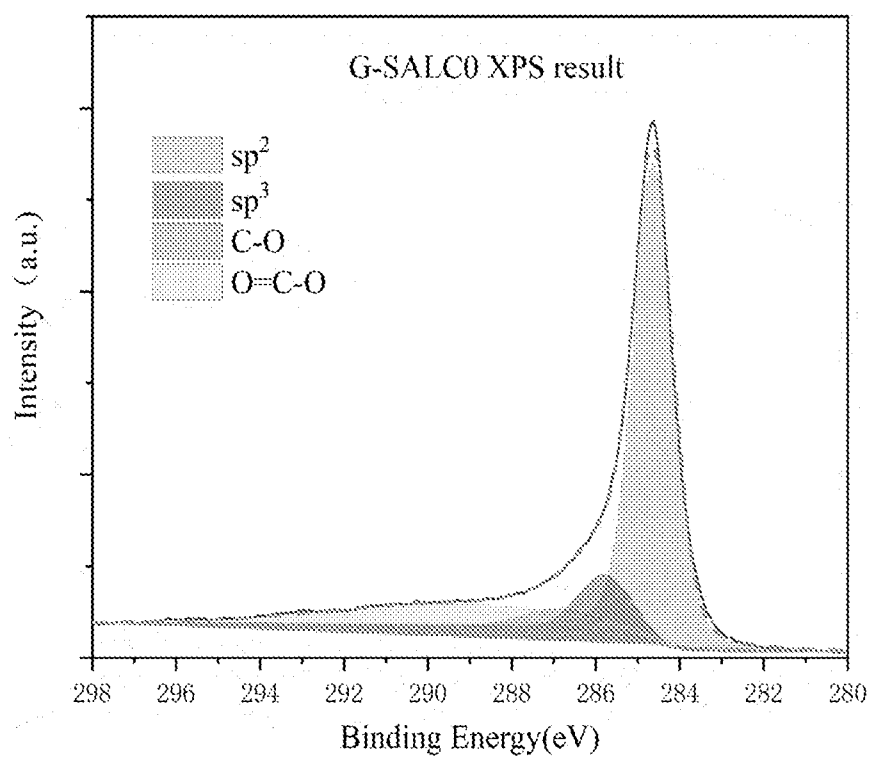


FIG. 7(a)

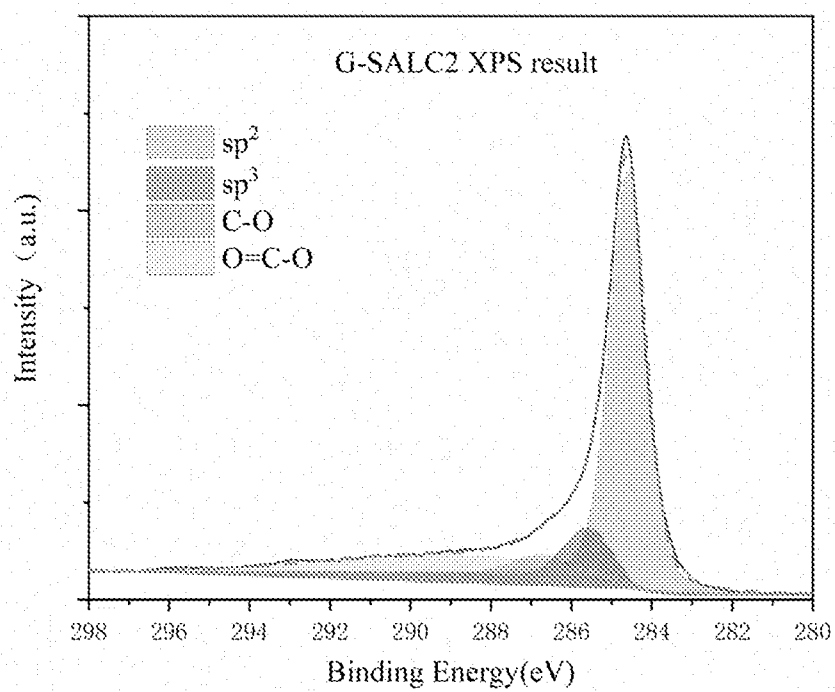


FIG. 7(b)

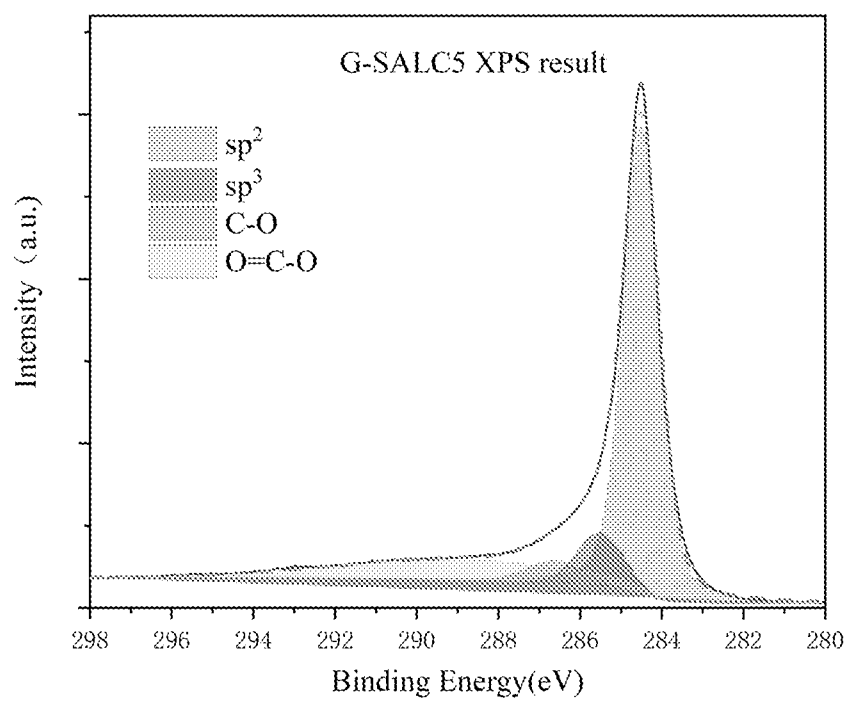


FIG. 7(c)

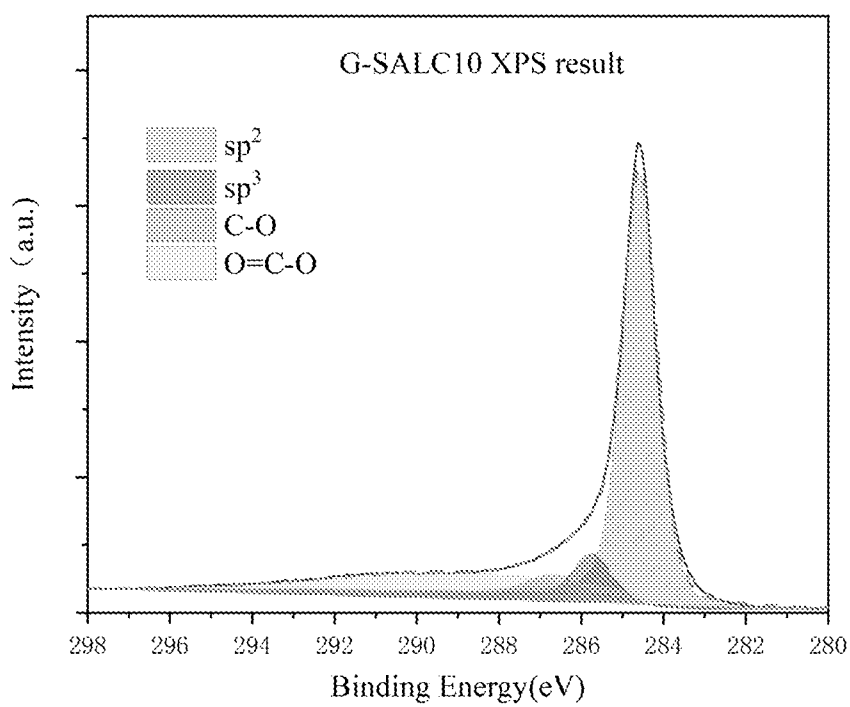


FIG. 7(d)

FIG. 7

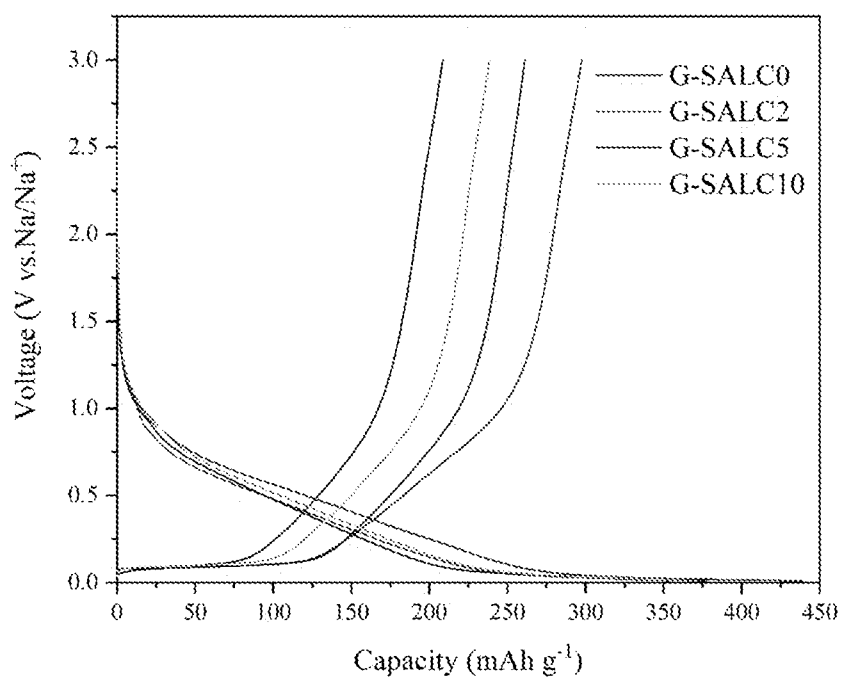


FIG. 8(a)

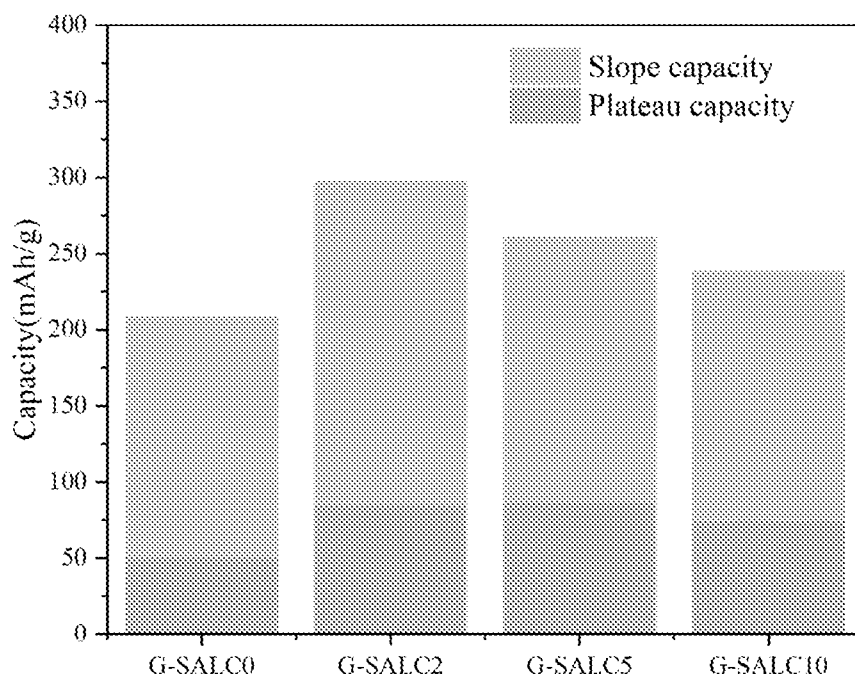


FIG. 8(b)

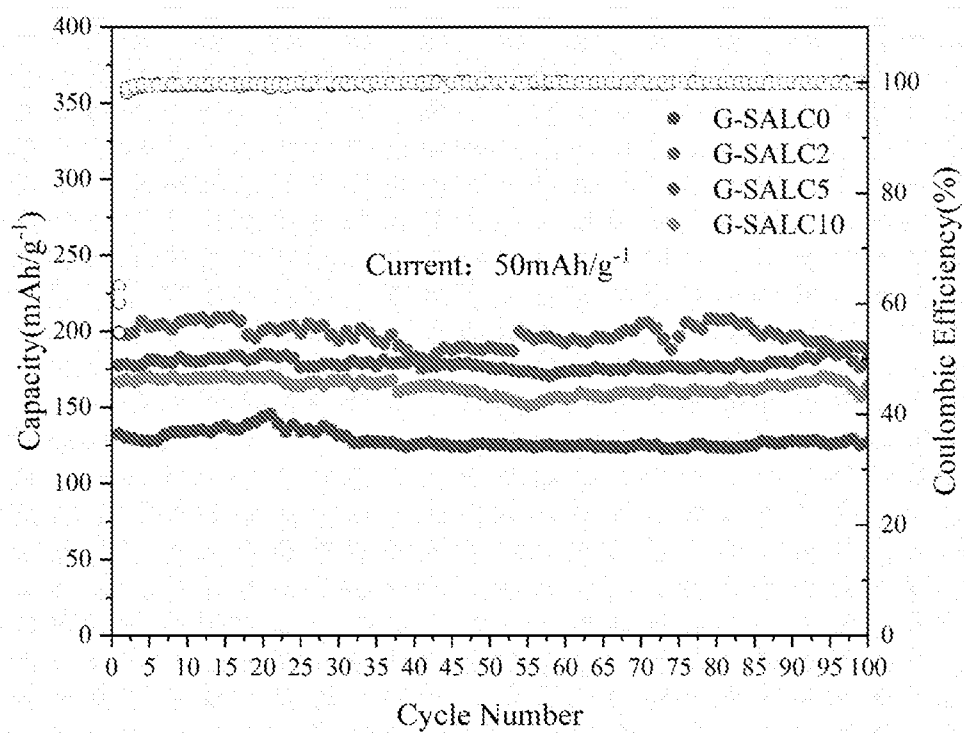


FIG. 8(c)

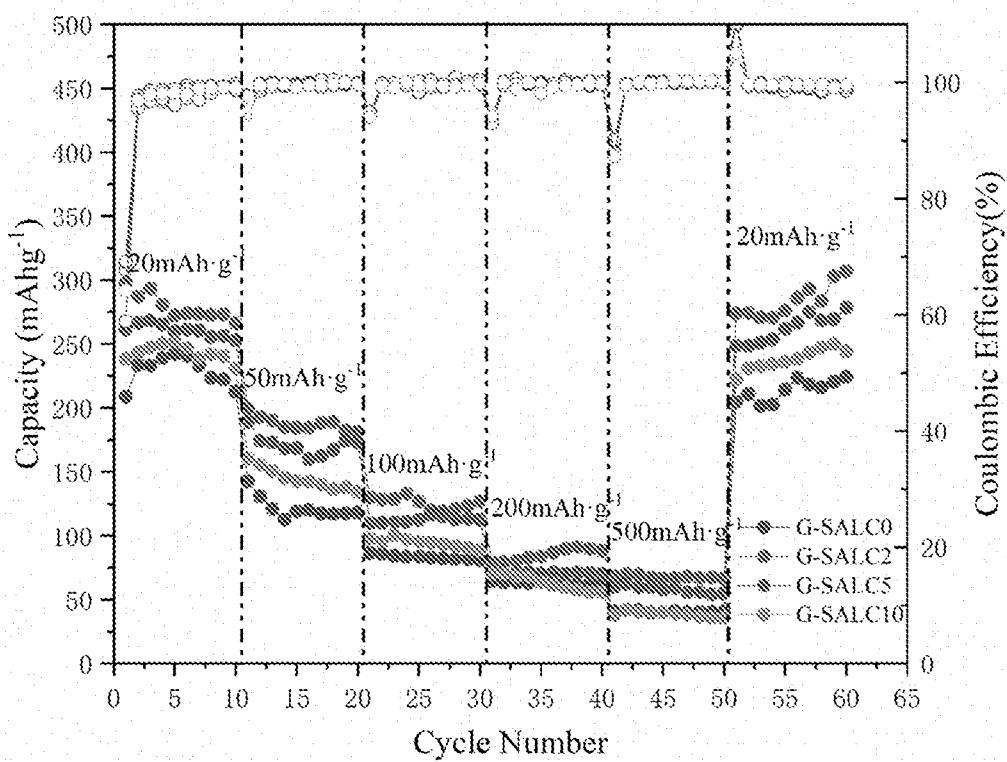


FIG. 8(d)

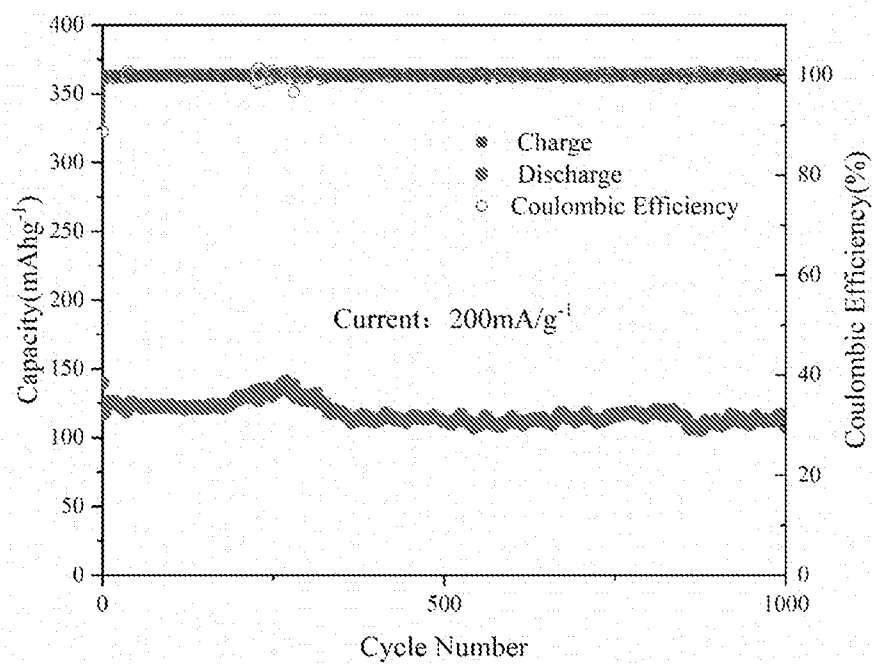


FIG. 8(e)

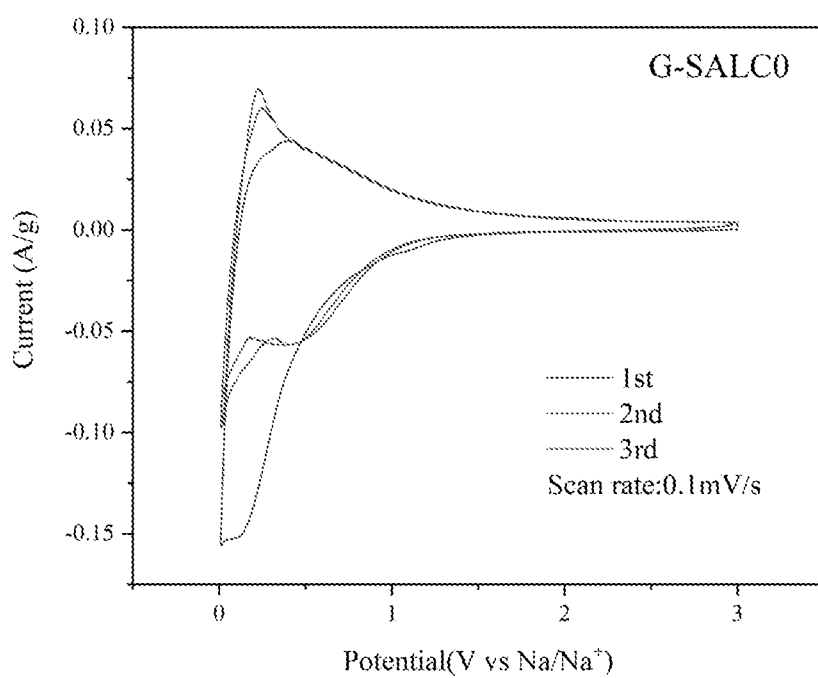


FIG. 9(a)

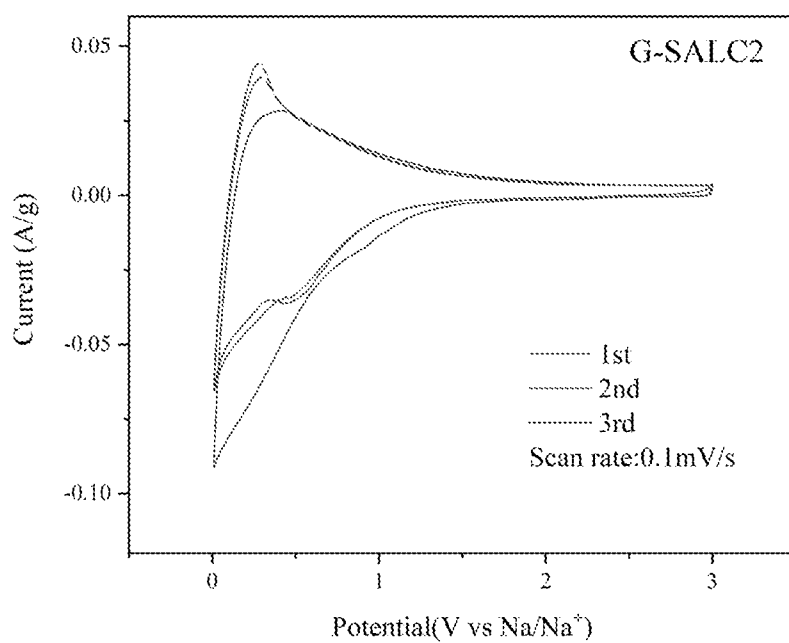


FIG. 9(b)

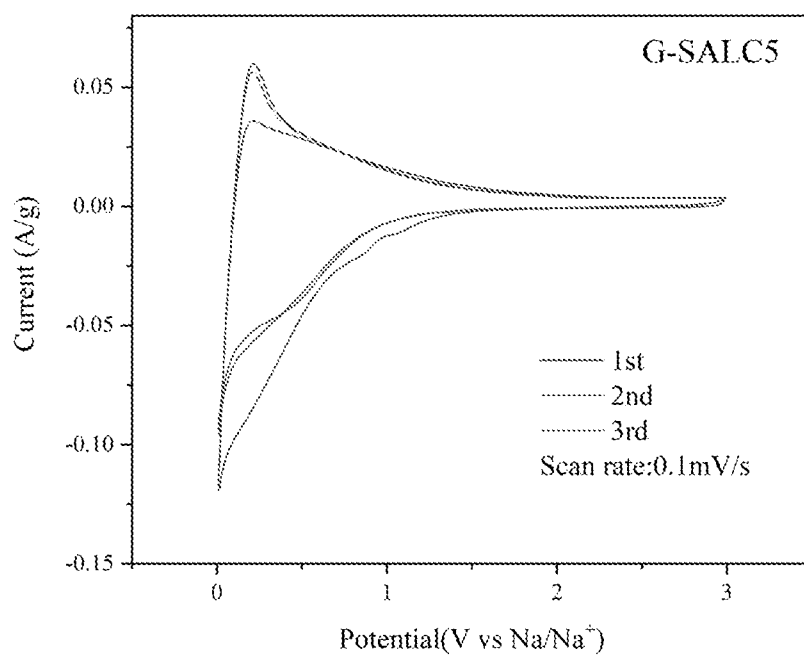


FIG. 9(c)

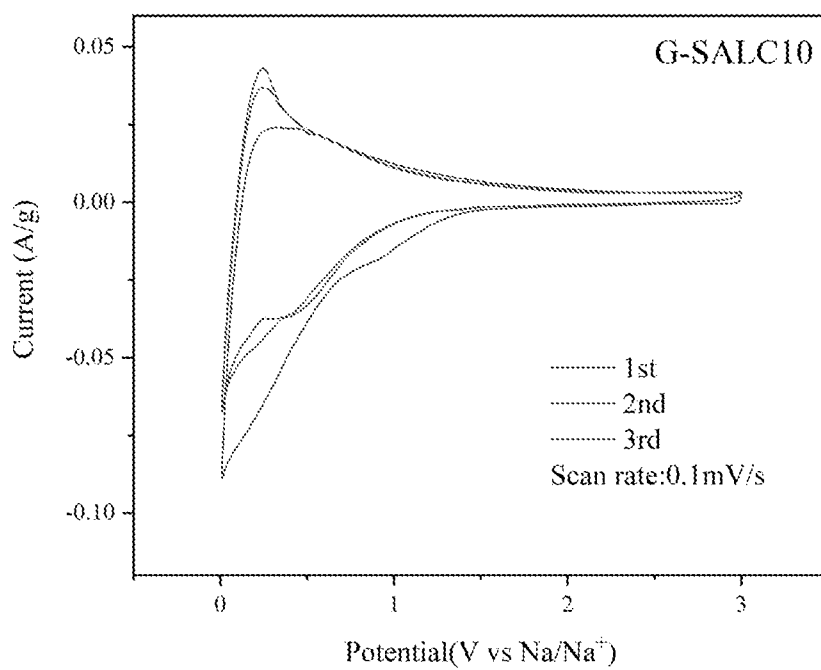


FIG. 9(d)

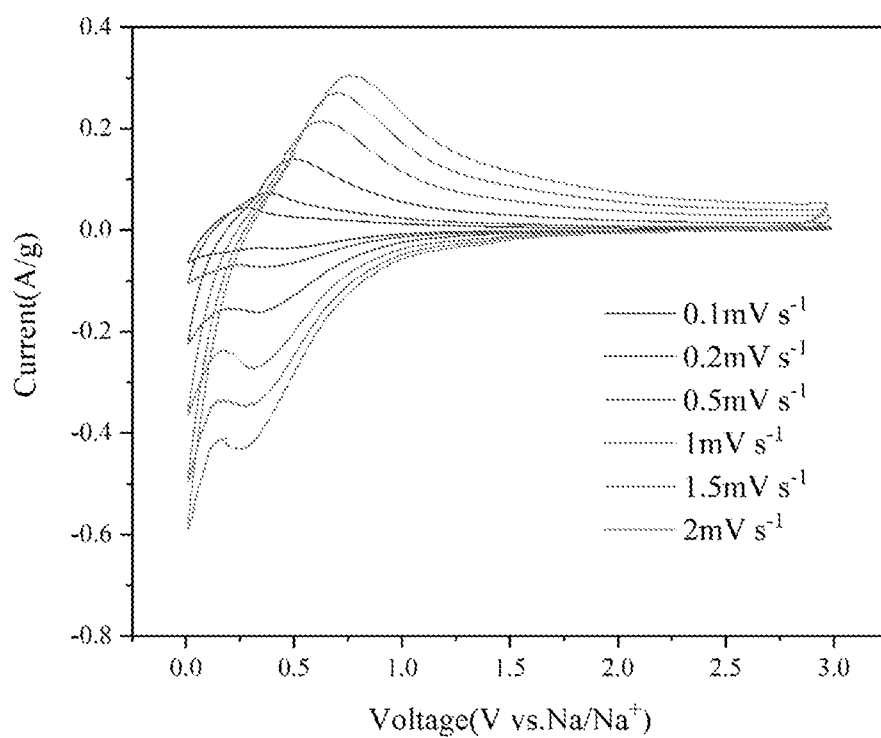


FIG. 10(a)

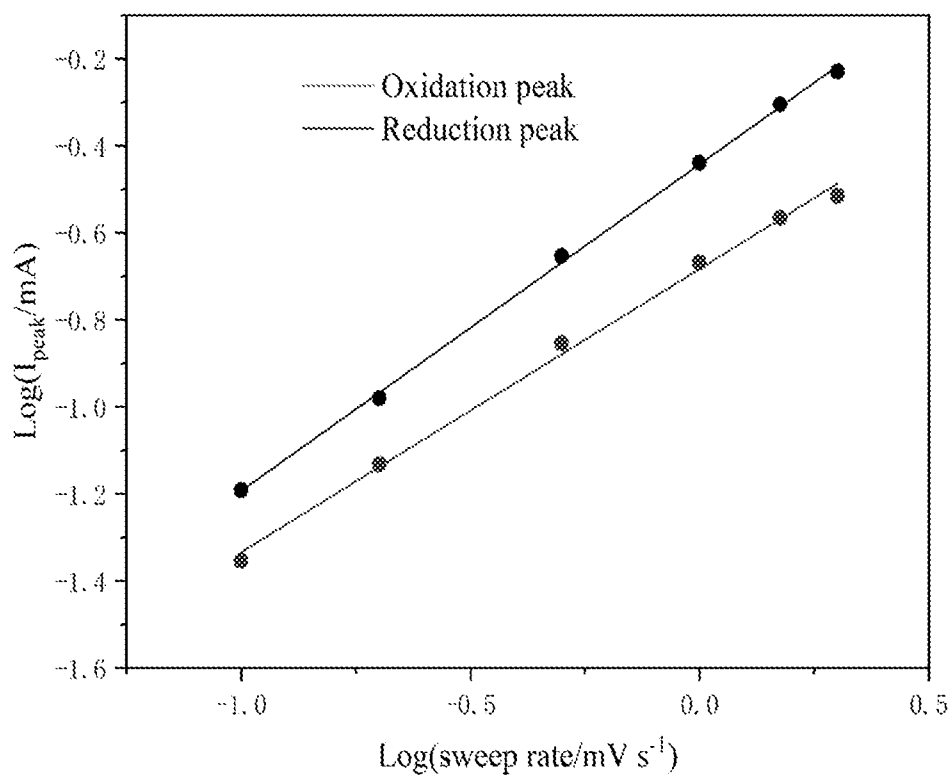


FIG. 10(b)

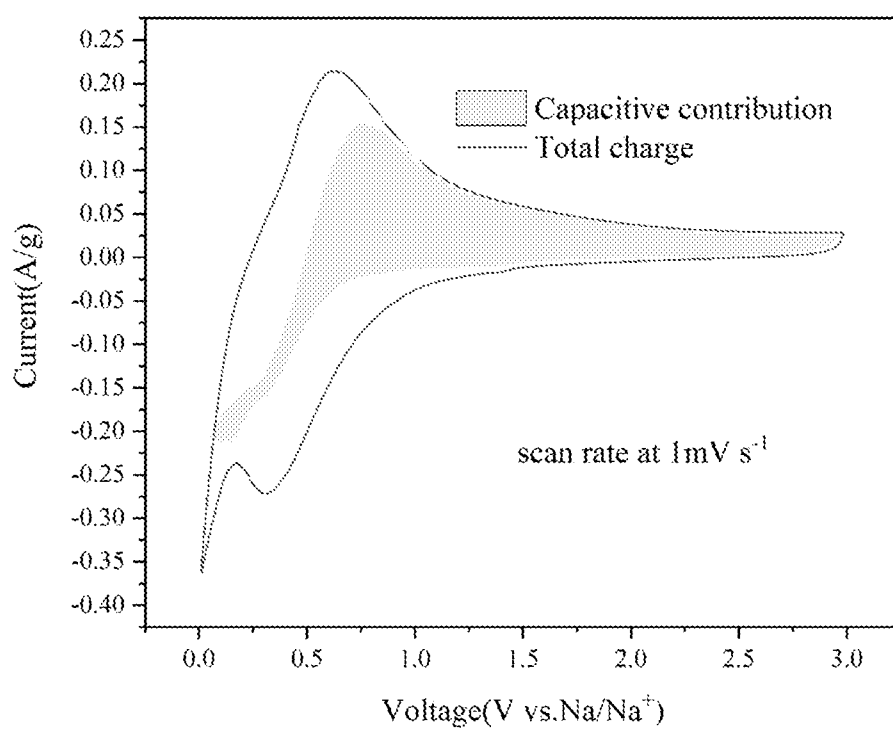


FIG. 10(c)

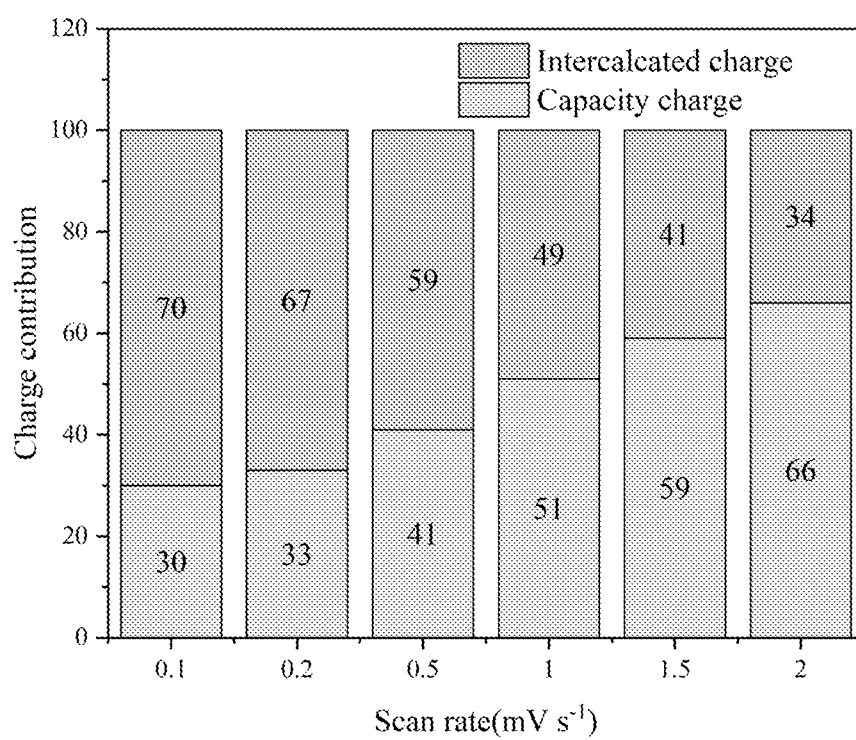


FIG. 10(d)

FIG. 10

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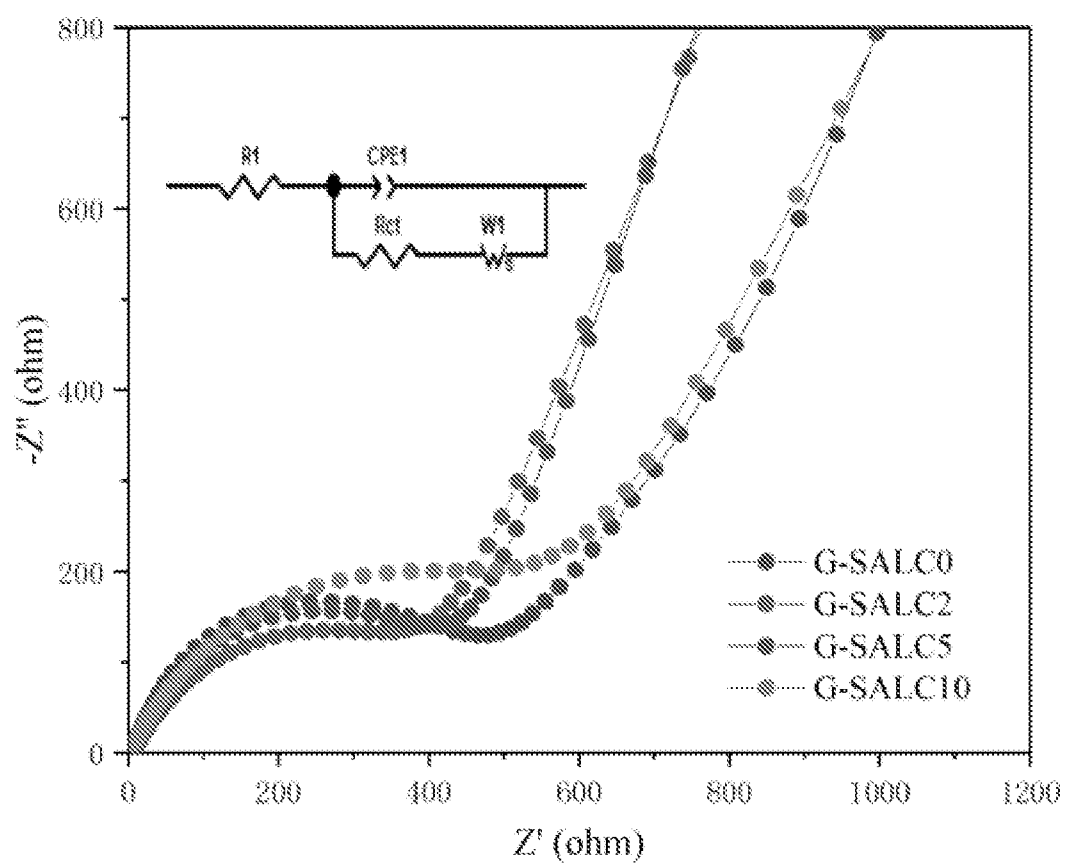


FIG. 11