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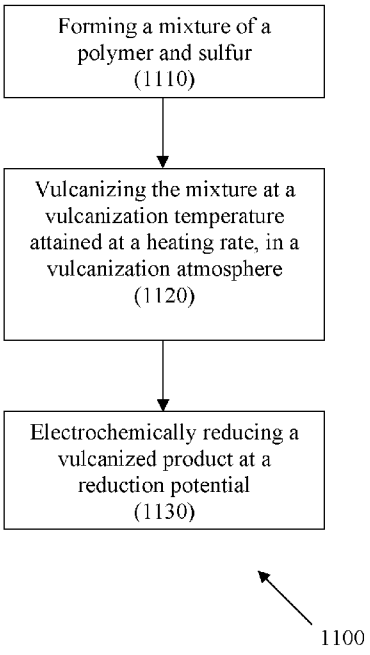
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(54) Title: METHOD OF PREPARING CATHODE MATERIAL FOR A BATTERY

FIGURE 1



(57) Abstract: Disclosed is a method for producing polymer-encapsulated Li_2S_x (where $1 \leq x \leq 2$) nanoparticles. The method comprises the step of forming a mixture of a polymer and sulfur. The method further comprises vulcanizing the mixture at a vulcanization temperature attained at a heating rate, in a vulcanization atmosphere, and electrochemically reducing a vulcanized product at a reduction potential. Also disclosed is a method for producing a battery component, the component comprising a cathode and a separator.

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Method of Preparing Cathode Material for a Battery

Technical Field

[0001] The present invention generally relates to polymer-encapsulated nanoparticles, and more specifically to a method or process of synthesizing or preparing a cathode including polymer-encapsulated nanoparticles. In further specific examples, polymer-encapsulated nanoparticles are formed or provided as the active material in a cathode for a battery.

Background

[0002] Lithium-sulfur (Li-S) batteries are an attractive alternative to lithium-ion cells, possessing higher energy density and reduced cost due to the use of sulfur.

[0003] A Li-S battery typically includes a lithium metal anode and a sulfur cathode. One of the major issues with this configuration is the poor stability of the sulfur cathode; discharge operation results in the formation of polysulfide ions which can permanently bond with the lithium anode. This in turn leads to a permanent loss of the sulfur material, greatly reducing the cycle life of the battery. A solution to this problem has been to confine the polysulfides by using porous carbon.

[0004] Another issue to using a sulfur cathode is related to large-scale manufacturing. The operation of a Li-S battery requires that one electrode, either anode or cathode, contains lithium. In traditional Li-S battery design, having a sulfur cathode means that the anode must contain metallic lithium, which constitutes a handling hazard during manufacturing.

[0005] A further issue with traditional Li-S batteries lies in their separators, such as polypropylene. These are typically designed to impede electron flow while allowing ions to freely migrate between the two electrodes. Despite their basic functionality, serving only to prevent short circuiting of the anode and cathode, such separators are expensive in general.

[0006] A further issue lies with polymer binders included in a Li-S battery electrode. In general, cathode polymer binders consist of polyvinylidene fluoride (PVDF) or other water insoluble compounds. The use of organic solvents in massive amounts during fabrication

of electrodes is hazardous and costly. One approach could be to use water as the solvent during battery fabrication. However, whether water-soluble binders can be beneficial to Li-S battery operation has not yet been demonstrated or fully understood.

[0007] There is a need for new or improved cathode materials and/or new or improved methods or processes of synthesizing or preparing cathode materials for Li-S batteries.

[0008] The reference in this specification to any prior publication (or information derived from the prior publication), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that the prior publication (or information derived from the prior publication) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

Summary

[0009] This Summary is provided to introduce a selection of concepts in a simplified form that are further described below in the Preferred Embodiments. This Summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter.

[0010] According to one example aspect, there is provided a method for producing polymer-encapsulated Li_2S_x (where $1 \leq x \leq 2$) nanoparticles. According to another example aspect, there is provided a method for producing a battery component, the component comprising a cathode and a separator.

[0011] According to another example aspect, there is provided a method for producing polymer-encapsulated Li_2S_x (where $1 \leq x \leq 2$) nanoparticles, comprising the steps of: forming a mixture of a polymer and sulfur; vulcanizing the mixture at a vulcanization temperature attained at a heating rate, in a vulcanization atmosphere; and electrochemically reducing a vulcanized product at a reduction potential.

[0012] According to another example aspect, there is provided a method for producing a battery component, the component comprising a cathode and a separator, the method

comprising the steps of: (a) producing the cathode by: forming a mixture of a polymer and elemental sulfur; vulcanizing the mixture at a vulcanization temperature attained at a heating rate, in a vulcanization atmosphere; and electrochemically reducing a vulcanized product at a reduction potential; and (b) producing the separator by: depositing cellulose filter paper on a surface of the cathode; and grafting graphene oxide onto the cellulose paper.

Brief Description of Figures

[0013] Example embodiments are apparent from the following description, which is given by way of example only, of at least one preferred but non-limiting embodiment, described in connection with the accompanying figures.

[0014] Figure 1 illustrates an example method for producing polymer-encapsulated Li_2S_x (where $1 \leq x \leq 2$) nanoparticles, demonstrated by vulcanization of a polymer with sulfur and electrochemical reduction of a vulcanized product.

[0015] Figure 2 illustrates an example method for preparing a cathode of an electrochemical cell to be used for electrochemical reduction.

[0016] Figure 3 illustrates cycle performance and capacity of an example polyacrylonitrile- (PAN) encapsulated Li_2S_x cathode produced using PVDF as a binder.

[0017] Figure 4 illustrates cycle performance and capacity of an example PAN-encapsulated Li_2S_x cathode produced using PAA as a binder.

[0018] Figure 5 illustrates cycle performance and capacity of an example PAN-encapsulated Li_2S_x cathode produced using PVA as a binder.

[0019] Figure 6 illustrates cycle performance and capacity of an example PAN-encapsulated Li_2S_x cathode produced using CMC as a binder.

[0020] Figure 7 illustrates cycle performance and capacity of an example PAN-encapsulated Li_2S_x cathode produced using alginate as a binder.

[0021] Figure 8 illustrates cycle performance and specific capacity of an example PAN-encapsulated Li_2S_x cathode produced using graphene oxide as a binder.

[0022] Figure 9 illustrates an example method for producing a battery component including a cathode and a separator. The cathode includes polymer-encapsulated Li_2S_x nanoparticles as the active cathode material. The separator includes graphene oxide grafted onto cellulose filter paper.

[0023] Figure 10 illustrates an example battery component including a cathode and a separator. The cathode includes polymer-encapsulated Li_2S_x nanoparticles as the active cathode material. The separator includes graphene oxide grafted onto cellulose filter paper.

[0024] Figure 11 illustrates a scanning electron microscope (SEM) image of an example cellulose separator.

[0025] Figure 12 illustrates an SEM image of an example graphene oxide coated cellulose separator.

[0026] Figure 13 illustrates cycle performance and specific capacity of example PAN-encapsulated Li_2S_x cathodes produced using different vulcanization temperatures.

[0027] Figure 14 illustrates a voltammogram depicting an electrochemical reduction profile applied to an example electrode including vulcanized PAN, using 1.0 V reduction potential.

[0028] Figure 15 illustrates a further voltammogram depicting an electrochemical reduction profile applied to an example electrode including vulcanized PAN, using 1.0 V reduction potential.

[0029] Figure 16 illustrates a voltammogram depicting an electrochemical reduction profile applied to an example electrode including vulcanized PAN, using 1.6 V reduction potential.

[0030] Figure 17 illustrates a further voltammogram depicting an electrochemical reduction profile applied to an example electrode including vulcanized PAN, using 1.6 V reduction potential.

[0031] Figure 18 illustrates a voltammogram depicting an electrochemical reduction profile applied to an example electrode including vulcanized PAN, using 1.8 V reduction potential.

[0032] Figure 19 illustrates a further voltammogram depicting an electrochemical reduction profile applied to an example electrode including vulcanized PAN, using 1.8 V reduction potential.

[0033] Figure 20 illustrates a plot of the voltage versus capacity of an example reduced (discharge), and oxidized (charge) cathode during the electrochemical reduction process.

[0034] Figure 21 illustrates a transmission electron microscope (TEM) image of an example PANS sample before electrochemical reduction.

[0035] Figure 22 illustrates a further TEM image of an example PANS sample before electrochemical reduction.

[0036] Figure 23 illustrates a TEM image of an example PANS sample after electrochemical reduction.

[0037] Figure 24 illustrates a TEM image of an example PANS sample after cycling.

[0038] Figure 25 illustrates X-ray diffraction profiles for the example pristine, reduced (discharge), and oxidized (charge) cathode.

[0039] Figure 26 illustrates Fourier transform infrared spectroscopy results for the example pristine, reduced (discharge), and oxidized (charge) cathode.

[0040] Figure 27 illustrates X-ray absorption spectroscopy results for the example pristine, reduced (discharge), and oxidized (charge) cathode.

[0041] Figure 28 illustrates X-ray photoelectron spectroscopy results for the example pristine, reduced (discharge), and oxidized (charge) cathode.

[0042] Figure 29 illustrates Raman spectroscopy results for the example pristine, reduced (discharge), and oxidized (charge) cathode.

[0043] Figure 30 illustrates cycle performance and capacity of example PAN-encapsulated Li_2S_x cathodes produced using different quantities of graphene oxide binder.

Preferred Embodiments

[0044] The following modes, given by way of example only, are described in order to provide a more precise understanding of the subject matter of a preferred embodiment or embodiments. In the figures, incorporated to illustrate features of an example embodiment, like reference numerals are used to identify like parts throughout the figures.

[0045] The Applicant has identified that the safety and performance of Li-S batteries can be improved by confining the lithium to the cathode as ions, rather than the traditional arrangement where the anode comprises metallic lithium. By using this modified design, it is possible to deploy lithium-free and safe anode materials, such as graphite or silicon. Advantageously, the modified design enables the realization of more durable Li-S batteries. To this end, the Applicant has developed a method for preparing polymer-encapsulated Li_2S_x (where $1 \leq x \leq 2$) nanoparticles as the active cathode material. This method is composed of two basic steps: vulcanization and electrochemical reduction. During the vulcanization process, sulfur molecules are homogeneously dispersed into a polymer substrate, resulting in the uniform encapsulation of sulfur. Subsequently, the inlayed sulfur molecules are electrochemically reduced using a potential lower than, or equal to, about 1.6 V. Electrochemical reduction may occur in the presence of a binder which may be a water-soluble oxygen-containing polymer or graphene oxide. This results in a polymer-encapsulated Li_2S_x nanoparticle cathode with strong confinement due to the ionic conducting polymer sheath.

[0046] Referring to Figure 1, there is provided a method 1100 for producing polymer-encapsulated, lithium-rich Li_2S_x (where $1 \leq x \leq 2$) nanoparticles. Method 1100 includes the step 1110 of forming a mixture of a polymer and sulfur. Then vulcanizing, at step 1120, the mixture at a vulcanization temperature attained at a heating rate, in a vulcanization atmosphere, to form a vulcanized product. The vulcanized product is then electrochemically reduced, at step 1130, at a reduction potential to produce polymer-encapsulated Li_2S_x nanoparticles.

[0047] According to a preferred example, the polymer used in method 1100 is polyacrylonitrile (PAN), and the weight ratio of PAN to sulfur in the mixture of step 1110 is selected to be between about PAN:S = 1:3 and 1:15, inclusively. PAN is used as a component in lithium ion conducting solid state polymer electrolytes. The interaction of lithium ions with the nitrile groups is responsible for the ionic conductivity. This characteristic allows the application of PAN as an ionic conducting sheathing material for Li_2S_x nanoparticles. To obtain a uniform encapsulation, it is important to disperse sulfur at a molecular level in the PAN matrix. Vulcanization of PAN offers a simple and direct method for this purpose. In other examples, other types of polymers, such as polyaniline or polypyrrole, may be used in method 1100.

[0048] In another example, the heating rate during vulcanization step 1120 is selected to be between about 1°C/min and about 10°C/min, inclusively. In another example, the atmosphere throughout vulcanization step 1120 is selected as one of argon gas, nitrogen gas, or vacuum. In another example, the vulcanization temperature during vulcanization step 1120 is selected to be between about 300°C and about 800°C, inclusively.

[0049] According to a further example, electrochemical reduction step 1130 occurs in an electrochemical cell comprising an anode, a cathode, and an electrolyte, wherein the cathode includes a nonzero percentage by weight of the vulcanized product, and wherein the reduction potential is lower than, or equal to, about 1.6 V. Preferably, though not necessarily, the reduction potential is about 1.0 V. In one example, the anode of the electrochemical cell used for electrochemical reduction may at least partially include lithium, for example the anode may be made of lithium, a lithium alloy, a lithium

compound, or a mixture including lithium. Additionally, or alternatively, the anode may at least partially include graphite, or any material with a standard electrode potential close to lithium, and the electrolyte may at least partially comprise lithium ions.

[0050] In an example, the cathode of the electrochemical cell is prepared via a slurry coating method. Figure 2 illustrates a method 1200 for preparing the cathode of the electrochemical cell. Method 1200 includes the step 1210 of slurry coating a surface. In one example, the surface is aluminium foil. The surface is then dried at step 1220. In an example, a slurry to slurry coat the surface is formed composed by about 70 wt% vulcanized product, about 15 wt% carbon black as a conducting agent, about 15 wt% binder, and an amount of a solvent determined by the respective binder. In another example, the composition of the slurry may include between about 5 wt% to 50 wt%, inclusively, of binder. The binder may be one of polyvinylidene fluoride (PVDF), sodium carboxymethyl cellulose (CMC), polyacrylic acid (PAA), polyvinyl alcohol (PVA), alginate, graphene oxide (GO), or any other water-soluble oxygen-containing polymer with varying polymerization degrees or with N, S groups, or mixtures thereof.

[0051] Figures 3 to 8 illustrate cycle performance (including coulombic efficiency) and specific capacity of example cathodes, including PAN-encapsulated Li_2S_x nanoparticles, using different binders. Figure 3 corresponds to PVDF; Figure 4 corresponds to PAA; Figure 5 corresponds to PVA; Figure 6 corresponds to CMC; Figure 7 corresponds to alginate; Figure 8 corresponds to GO. These results indicate that by using water-soluble polymers, the stability of the cathode material can be greatly improved (compared to conventional PVDF binders), with relatively minor capacity reductions over more than 500 cycles. Another advantage of using water-soluble polymers as binders is that they are environmentally friendly and they allow for a reduction of production costs. Most importantly, the presence of carboxyl, carbonyl, or hydroxyl groups is found to boost capacity, in some examples by about 50%. The boosted performance is attributed to the interaction between oxygen and sulfur atoms, and the affinity between oxygen and polysulfide anions. While GO is not a polymer, it contains abundant oxygen groups. As such, it is still capable of improving the stability and capacity of the cathode.

[0052] During electrochemical reduction 1130, the sulfur molecules intercalated in the polymer substrate are reduced to Li_2S_x. In this process, the properties of the electrode undergo a significant change, Li_2S_x being highly polar and ionic while sulfur is non-polar and covalent. It is for this reason that oxygen function groups in the binder (e.g. PAA or CMC), and the PAA's carbonyl group in particular, are able to boost the capacity of the cathode, in some examples by about 50%.

[0053] Referring to Figure 9, there is provided a method 1400 for producing a battery component including a cathode and a separator. Method 1400 includes the steps of producing 1480 the cathode and producing 1490 the separator. Producing 1480 the cathode includes the steps of producing polymer-encapsulated, lithium-rich Li_2S_x (where $1 \leq x \leq 2$) nanoparticles as the cathode material, according to method 1100. Producing the separator includes the step of depositing 1420 cellulose filter paper on a surface of the cathode, followed by grafting 1430 graphene oxide onto the cellulose filter paper.

[0054] Figure 10 illustrates an example battery component 1500 produced through method 1400. Battery component 1500 includes a cathode 1510 and a separator 1520. Cathode 1510 is composed of polymer-encapsulated Li_2S_x (where $1 \leq x \leq 2$) nanoparticles which act as electroactive components. In one example, cathode 1510 has a uniformly blended single layer structure integrated with electroactive components, protective components, and conducting components. Separator 1520 includes a graphene oxide membrane 1540 grafted onto a cellulose filter paper 1530, which is in turn deposited onto a surface of cathode 1510. Cellulose filter paper 1530 acts to support graphene oxide membrane 1540 and enhance its strength. Graphene oxide membrane 1540 functions to regulate ion conduction and is insulating, helping to prevent short circuiting of cathode 1510 with an anode when battery component 1500 is arranged in a battery.

[0055] Figure 11 illustrates a scanning electron microscope (SEM) image of a cellulose separator. Figure 12 illustrates an SEM image of a graphene oxide coated cellulose separator as described in Figure 10. This separator can be used to replace more expensive polypropylene separators, while delivering similar performance.

Further examples

[0056] The following examples provide more detailed discussion of particular embodiments. The examples are intended to be merely illustrative and not limiting to the scope of the present invention.

Example 1: Preparation of a cathode comprising PAN-encapsulated Li_2S_x nanoparticles

[0057] A mixture was formed by grinding commercialized PAN and elemental sulfur for thirty minutes. The weight ratio of PAN to sulfur in the grinded mixture was PAN:S = 1:3, selected as the optimized ratio from the perspective of production cost. The mixture was then transferred in a tube furnace for vulcanization. The vulcanization atmosphere and heating rate were selected as nitrogen and 10°C/min, respectively. These values were determined to be optimized from the perspective of production cost. Seven different vulcanization temperatures (300°C, 400°C, 500°C, 550°C, 600°C, 700°C, 800°C) were used throughout different trials, and the measured cycling performance for each trial is shown in Figure 13. Based on these measurements, a temperature of 550°C was selected as the optimized vulcanization temperature. After the temperature in the tube furnace dropped to 25°C, vulcanized PAN, namely PANS, was collected as a dark black powder with a yield of 95–105% (based on initial mass of PAN).

[0058] The vulcanized product, which in this example was PANS, included sulfur covalently bonded with the carbon in the PAN polymer matrix. This vulcanized product was then subjected to electrochemical reduction in order to reduce sulfur to Li_2S_x at a suitable potential. Because the reduction occurred in-situ, the newly formed Li_2S_x located preferentially at the original sites of the sulfur molecules. Thus, Li_2S_x nanoparticles were encapsulated in the PAN polymer matrix. The final sample contained lithium and sulfur elements, as well as nitrogen and carbon elements from the polymer backbone.

[0059] Electrochemical reduction was carried out in a 2032 battery cell, as part of a Land battery test system. Lithium metal was used as anode material while 1.0 M LiPF6 / ethylene carbonate (EC) / dimethyl carbonate (DMC) / ethylmethyl carbonate (EMC) was used as an electrolyte. A PANS composite cathode was prepared via a slurry coating method. The slurry was composed of: about 70 wt% PANS composites, about 15 wt% carbon black as conducting agent, about 15 wt% binder, and an appropriate amount of a particular solvent for the respective binder. The slurry was then coated onto aluminium foil

as the current collector and was dried in a vacuum oven at 60°C for twelve hours after which, the cell was assembled.

[0060] During electrochemical reduction, different binders and reduction potentials were trialled. Figures 3, 4, and 6 illustrate battery cycling performances measured when using three different binders. Figure 3 corresponds to polyvinylidene fluoride (PVDF); Figure 6 corresponds to sodium carboxymethyl cellulose (CMC); Figure 4 corresponds to polyacrylic acid (PAA). Based on these results, PAA was determined to be the optimized binder for the PANS composite. Figures 14 to 19 illustrate voltammograms for when different electrochemical reduction profiles were applied to the PANS electrode. Three reduction potentials were tested: 1.0 V vs. Li/Li^+ (Figures 14 and 15), 1.6 V vs. Li/Li^+ (Figures 16 and 17), and 1.8 V vs. Li/Li^+ (Figures 18 and 19). The lack of redox peaks in Figures 16 to 19 indicated that only when the reduction potential was lower than 1.6 V did the sulfur molecules in the PANS electrode start to be reduced, becoming electrochemically active to store energy reversibly. The reduction process completed at around 1.2 V, as suggested by the significant reduction peak in that region. Based on these results, 1.0 V vs. Li/Li^+ was determined to be the optimized reduction potential to guarantee a complete reduction.

[0061] Figure 20 illustrates a plot 3300 of the voltage versus capacity of the reduced (discharge), and oxidized (charge) cathode during the electrochemical reduction process. Figures 21 to 24 illustrate transmission electron microscope (TEM) images of the reduction process and phase separation in the electrode including vulcanized PAN. These images were used to demonstrate the existence and morphology of electrochemically active Li_2S_x nanoparticles encapsulated by PAN after electrochemical reduction. Figures 21 and 22 illustrate a PANS sample before reduction; Figure 23 illustrates the PANS sample after reduction, and Figure 24 after cycling. Figure 21 corresponds to stage 3310 in Figure 20. Figure 22 corresponds to stage 3320 in Figure 20. Figure 23 corresponds to stage 3330 in Figure 20. Figure 24 corresponds to stage 3340 in Figure 20. With reference to Figures 21 to 24, before electrochemical reduction it can be observed that PANS has a spherical outline and a uniform microscopic texture. No obvious contrast can be observed throughout the whole sample. Such even distribution of transmitted electron signals indicated that the dispersion of sulfur molecules within the PAN substrate was molecularly

homogeneous. After being reduced to 1.0 V, crystalline nanoparticles with size of around 2 nm started emerging on the surface or in the inner part of a bulk PANS spherical particle. Through characterization of its identical lattice (0.33 nm), it was confirmed that these nanoparticles were Li_2S generated by electrochemical reduction. Following formation, these nanoparticles remained present even after cycling.

[0062] TEM characterization was also conducted on samples reduced at 1.6 V and 1.8 V. Consistent with the electrochemical test results, no particles emerged in the sample reduced at 1.8 V, while only a few nanoparticles started emerging in the sample reduced at 1.6 V. These results confirmed successful electrochemical synthesis of PAN-encapsulated Li_2S_x nanoparticles.

[0063] The structural evolution of the vulcanized PAN before and after electrochemical reduction was further characterized by combining a number of different measurements. Figure 25 illustrates X-ray diffraction profiles for the pristine, reduced (discharge), and oxidized (charge) cathode. Figure 26 illustrates Fourier transform infrared spectroscopy results for the pristine, reduced (discharge), and oxidized (charge) cathode. Figure 27 illustrates X-ray absorption spectroscopy results for the pristine, reduced (discharge), and oxidized (charge) cathode. Figure 28 illustrates X-ray photoelectron spectroscopy results for the pristine, reduced (discharge), and oxidized (charge) cathode. Figure 29 illustrates Raman spectroscopy results for the pristine, reduced (discharge), and oxidized (charge) cathode. Figures 20 to 25 indicate that the formation of Li_2S_x nanoparticles is irreversible, i.e. oxidation of the Li_2S_x nanoparticles produces delithiated nanoparticles which differ from the pristine PANS. Therefore, PAN-encapsulated Li_2S_x nanoparticles are suitable as an active cathode material.

Example 2: Preparation of graphene oxide

[0064] Graphene oxide (GO) is a two-dimensional material which contains abundant oxygen function groups. GO was synthesized through the following procedure.

[0065] 6.0 g of $KMnO_4$ were slowly added to a dispersion of expandable graphite flakes (1.0 g) and 120 mL of concentrated H_2SO_4 under magnetic stirring in an ice bath (0°C).

After $KMnO_4$ was completely dissolved, the ice bath was removed and the resulting green-coloured solution was stirred at room temperature for four hours. To terminate the reaction, 10 mL of 30% H_2O_2 mixed with 100 mL of water were added. The resulting golden suspension was washed by repeat centrifugation (20,000 rpm for ten minutes) until the pH level reached 7. The residual colloidal graphite oxide was dried and re-dispersed in neutral water for long-term storage purposes.

[0066] To evaluate the effect of a GO binder, different amounts of GO were added to the PANS when preparing the cathode. Specifically, 1 mg and 5 mg were added into a slurry which contained 35 mg PANS during electrode preparation. Figure 30 illustrates the cycle performance and capacity of the resulting cathode.

[0067] Optional embodiments may also be said to broadly include the parts, elements, steps and/or features referred to or indicated herein, individually or in any combination of two or more of the parts, elements, steps and/or features, and wherein specific integers are mentioned which have known equivalents in the art to which the invention relates, such known equivalents are deemed to be incorporated herein as if individually set forth.

[0068] Although a preferred embodiment has been described in detail, it should be understood that many modifications, changes, substitutions or alterations will be apparent to those skilled in the art without departing from the scope of the present invention.

The claims:

1. A method for producing polymer-encapsulated Li_2S_x (where $1 \leq x \leq 2$) nanoparticles, comprising the steps of:

forming a mixture of a polymer and sulfur;

vulcanizing the mixture at a vulcanization temperature attained at a heating rate, in a vulcanization atmosphere; and

electrochemically reducing a vulcanized product at a reduction potential.

2. The method of claim 1, wherein the polymer is polyacrylonitrile (PAN).

3. The method of claim 2, wherein the mixture of PAN and sulfur has a weight ratio of PAN to sulfur between about 1:3 to about 1:15, inclusively.

4. The method of any one of the preceding claims, wherein the vulcanization temperature is between about 300°C to about 800°C, inclusively.

5. The method of any one of the preceding claims, wherein the heating rate is between about 1°C/min to about 10°C/min, inclusively.

6. The method of any one of the preceding claims, wherein the vulcanization atmosphere is argon gas, nitrogen gas, or vacuum.

7. The method of any one of the preceding claims, wherein the reduction potential is less than, or equal to, about 1.6 V.

8. The method of any one of the preceding claims, wherein the step of electrochemically reducing the vulcanized product occurs in a cell comprising:

an anode;

a cathode; and

an electrolyte.

9. The method of claim 8, wherein the anode at least partially comprises lithium and/or the electrolyte at least partially comprises lithium ions.

10. The method of claim 8 or 9, wherein the cathode comprises a nonzero percentage by weight of the vulcanized product.

11. The method of any one of claims 8 to 10, wherein the cathode is prepared via a method comprising the steps of:

slurry coating a surface; and

drying the surface.

12. The method of claim 11, wherein a slurry used for slurry coating comprises:

the vulcanized product;

a conducting agent;

a binder; and

a solvent.

13. The method of claim 12, wherein the binder comprises polyvinylidene fluoride (PVDF), sodium carboxymethyl cellulose (CMC), polyacrylic acid (PAA), polyvinyl alcohol (PVA), alginate, graphene oxide (GO), or any other water-soluble oxygen-containing polymer with varying polymerization degrees or with N, S groups, or mixtures thereof.

14. A method for producing a battery component, the component comprising a cathode and a separator, the method comprising the steps of:

producing the cathode by:

forming a mixture of a polymer and elemental sulfur;

vulcanizing the mixture at a vulcanization temperature attained at a heating rate, in a vulcanization atmosphere; and

electrochemically reducing a vulcanized product at a reduction potential;

and

producing the separator by:

depositing cellulose filter paper on a surface of the cathode; and

grafting graphene oxide onto the cellulose paper.

15. The method of claim 14, wherein the polymer is polyacrylonitrile (PAN).

16. The method of claim 15, wherein the mixture of PAN and sulfur has a weight ratio of PAN to sulfur between about 1:3 to about 1:15, inclusively.

17. The method of any one of claims 14 to 16, wherein the vulcanization temperature is between about 300°C to about 800°C, inclusively.

18. The method of any one of claims 14 to 17, wherein the heating rate is between about 1°C/min to about 10°C/min, inclusively.

19. The method of any one of claims 14 to 18, wherein the vulcanization atmosphere is argon gas, nitrogen gas, or vacuum.

20. The method of any one of claims 14 to 19, wherein the reduction potential is less than, or equal to, about 1.6 V.

21. The method of any one of claims 14 to 20, wherein the step of electrochemically reducing the vulcanized product occurs in a cell comprising:

an anode;

a cathode; and

an electrolyte.

22. The method of claim 21, wherein the anode at least partially comprises lithium and/or the electrolyte at least partially comprises lithium ions.

23. The method of claim 21 or 22, wherein the cathode comprises a nonzero percentage by weight of the vulcanized product.

24. The method of any one of claims 21 to 23, wherein the cathode is prepared via a method comprising the steps of:

slurry coating a surface; and

drying the surface.

25. The method of claim 24, wherein a slurry used for slurry coating comprises:

the vulcanized product;

a conducting agent;

a binder; and

a solvent.

26. The method of claim 25, wherein the binder comprises polyvinylidene fluoride (PVDF), sodium carboxymethyl cellulose (CMC), polyacrylic acid (PAA), polyvinyl alcohol (PVA), alginate, graphene oxide (GO), or any other water-soluble oxygen-containing polymer with varying polymerization degrees or with N, S groups, or mixtures thereof.

FIGURE 1

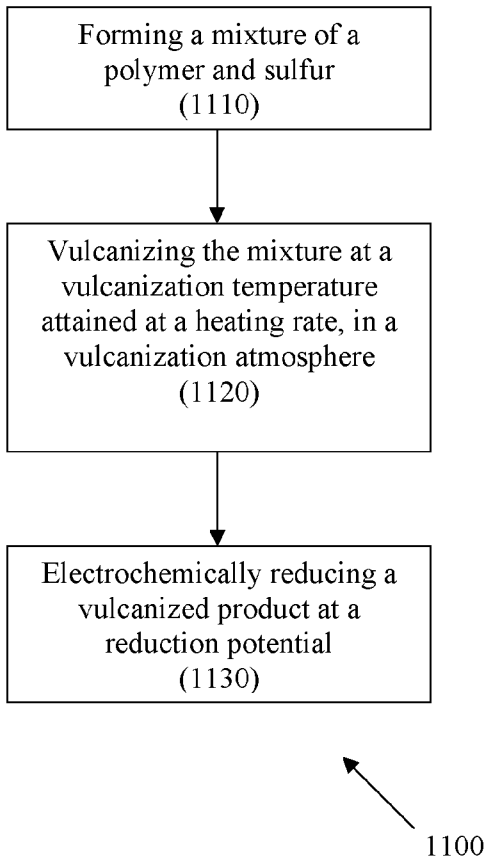

Forming a mixture of a polymer and sulfur (1110)
Vulcanizing the mixture at a vulcanization temperature attained at a heating rate, in a vulcanization atmosphere (1120)
Electrochemically reducing a vulcanized product at a reduction potential (1130)
1100

FIGURE 2

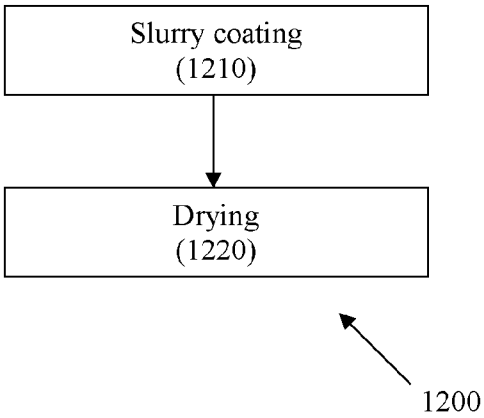


FIGURE 3

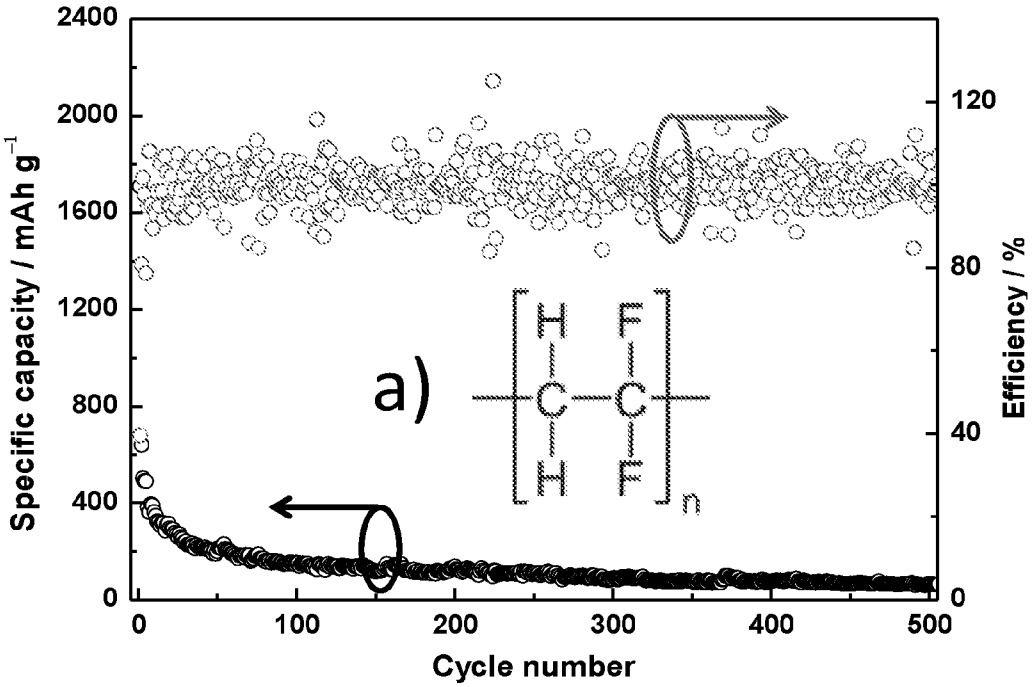

2400
2000
1600
1200
800
400
0
Specific capacity / mAh g^{-1}
120
80
40
0
Efficiency / %
0
100
200
300
400
500
Cycle number
a)
H
F
C
C
H
F
n

FIGURE 4

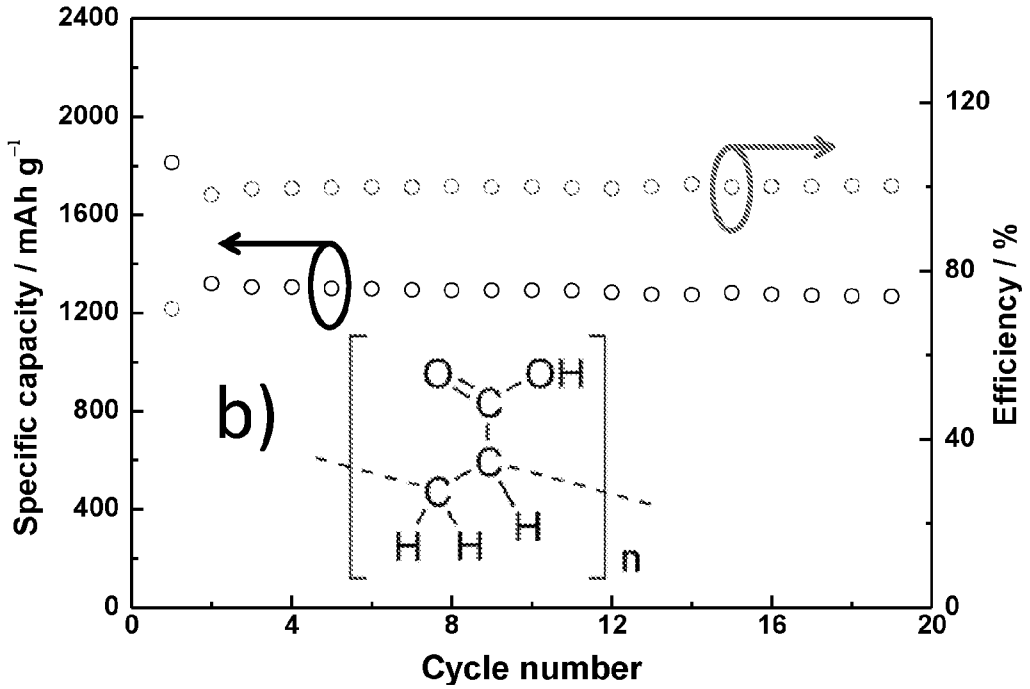


FIGURE 5

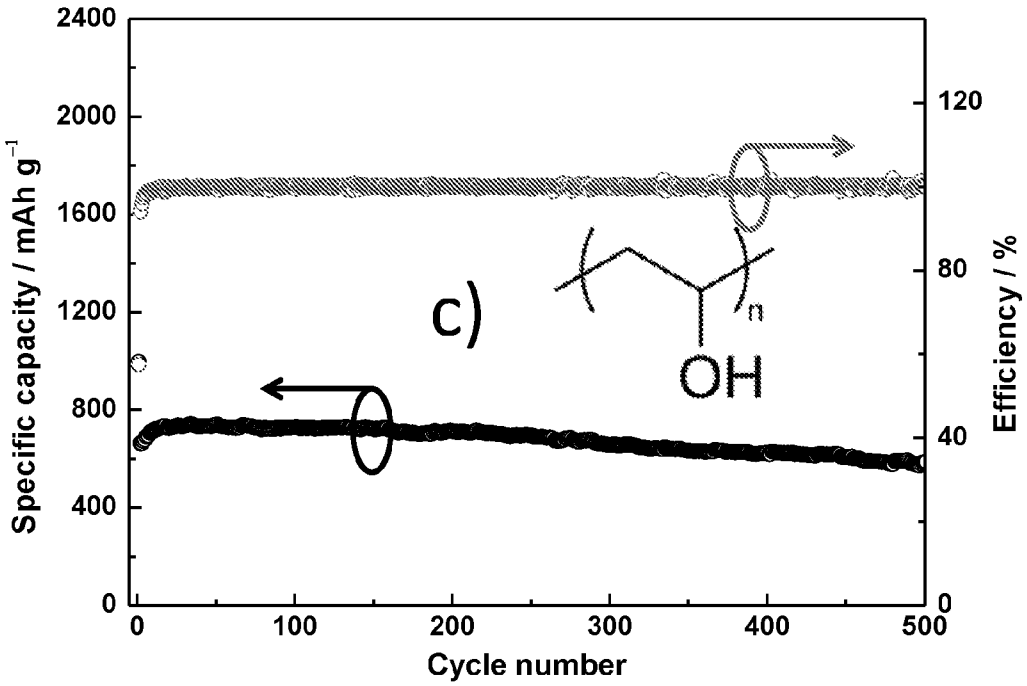

2400
2000
1600
1200
800
400
0
Specific capacity / mAh g^{-1}
120
80
40
0
Efficiency / %
0
100
200
300
400
500
Cycle number
c)
OH
n

FIGURE 6

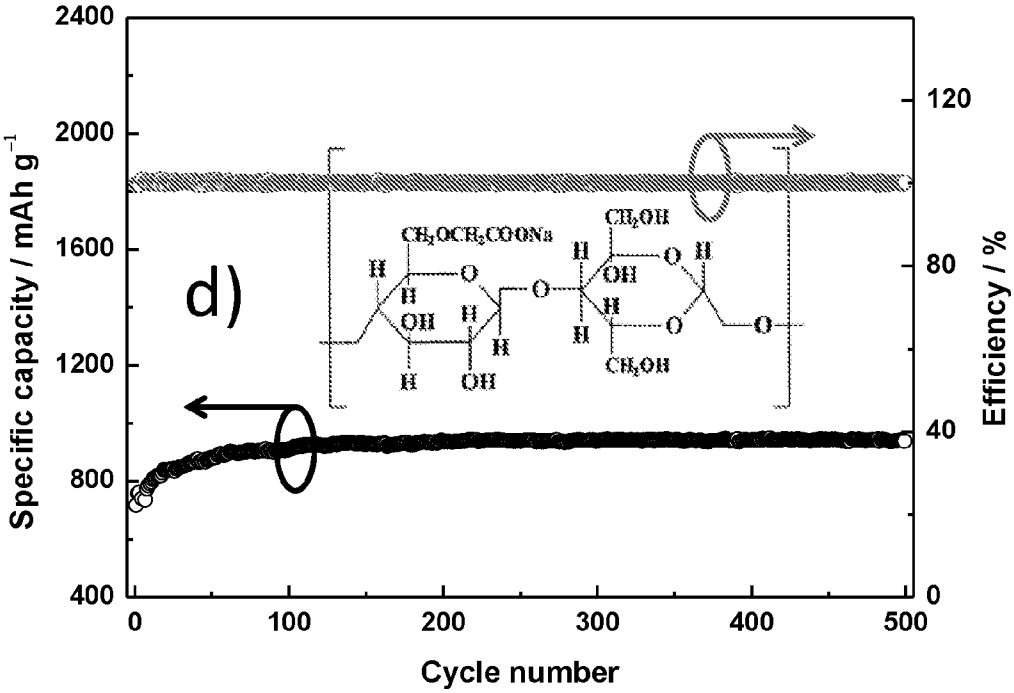

d)
Specific capacity / mAh g^{-1}
Efficiency / %
Cycle number
2400
2000
1600
1200
800
400
120
80
40
0
0
100
200
300
400
500

FIGURE 7

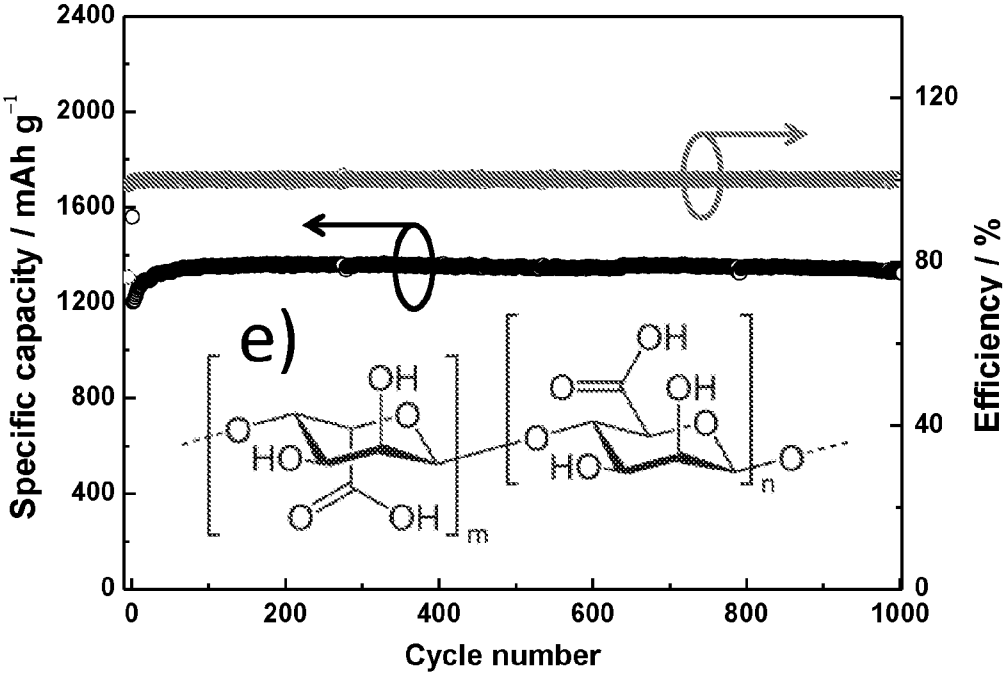

Specific capacity / mAh g^{-1}
Efficiency / %
Cycle number
2400
2000
1600
1200
800
400
0
120
80
40
0
200
400
600
800
1000
e)
OH
O
HO
O
OH
m
n

FIGURE 8

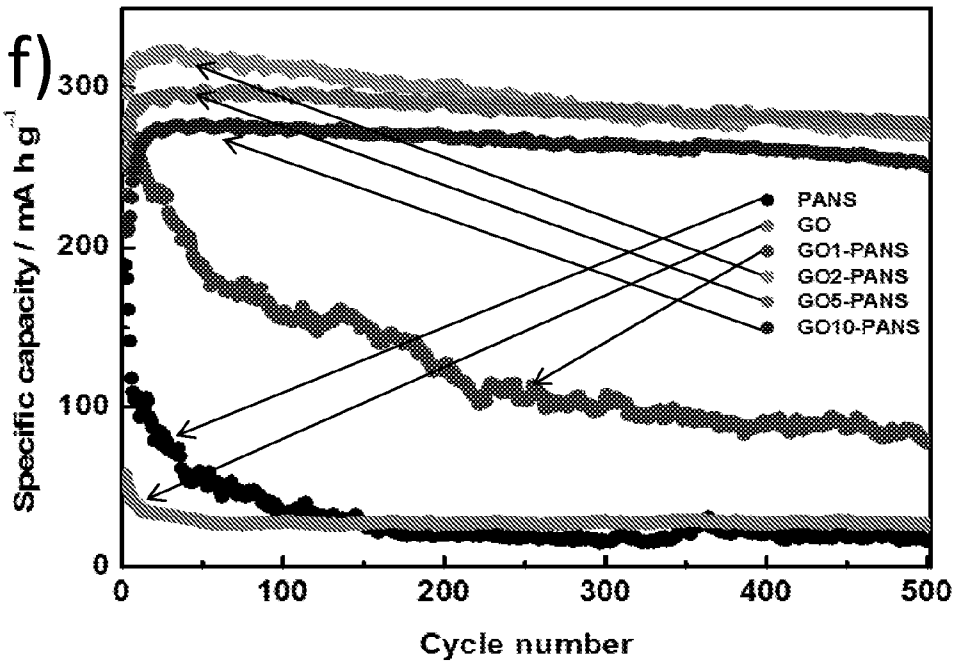

f)
Specific capacity / mA h g^{-1}
300
200
100
0
0
100
200
300
400
500
Cycle number
PANS
GO
GO1-PANS
GO2-PANS
GO5-PANS
GO10-PANS

FIGURE 9

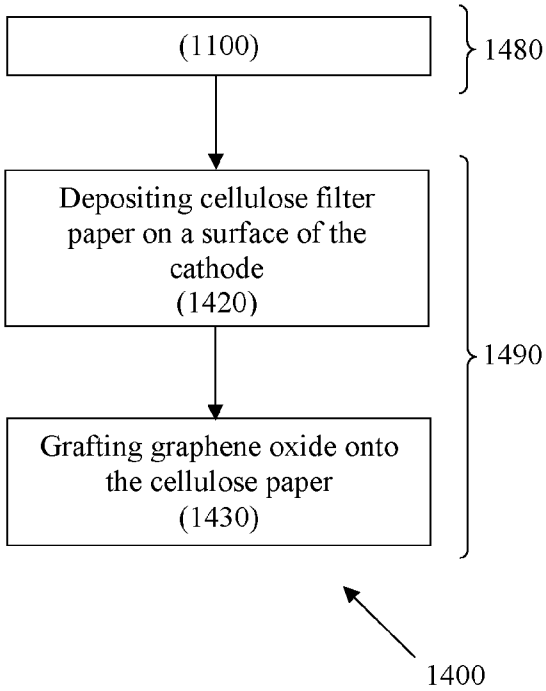

(1100)
1480
Depositing cellulose filter paper on a surface of the cathode (1420)
1490
Grafting graphene oxide onto the cellulose paper (1430)
1400

FIGURE 10

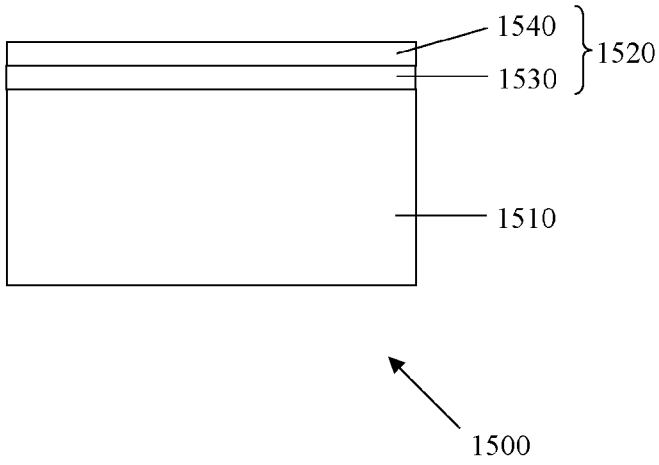


FIGURE 11

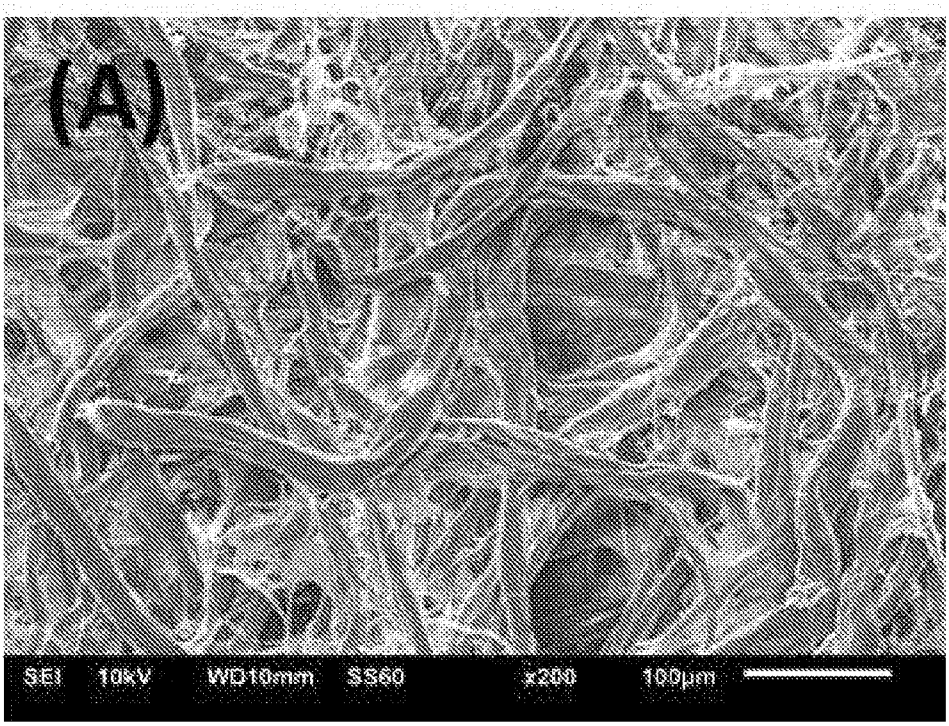


FIGURE 12

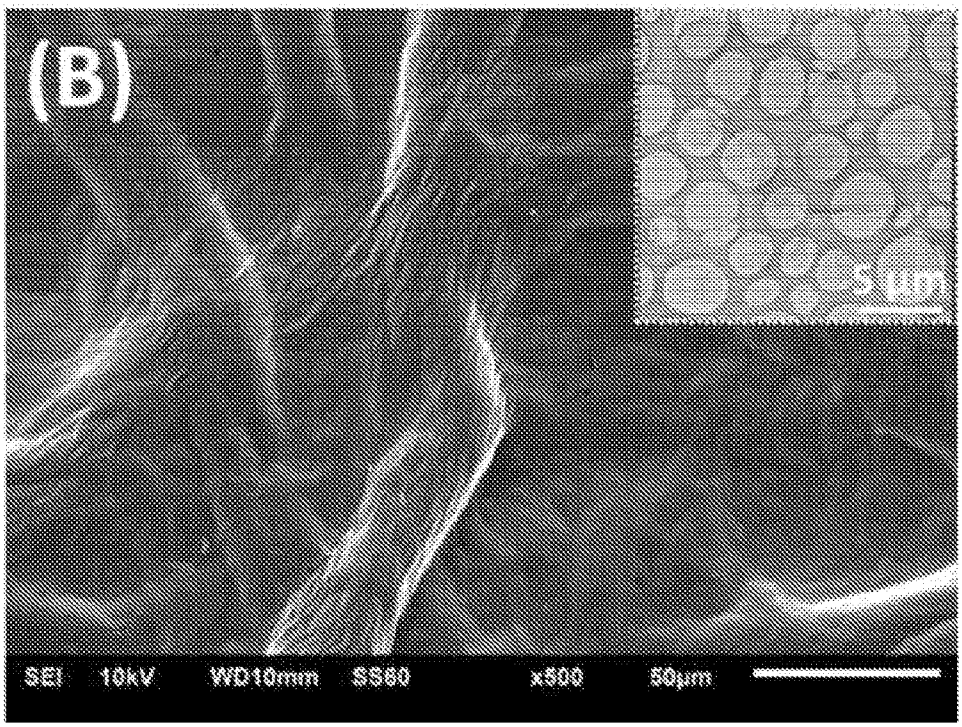


FIGURE 13

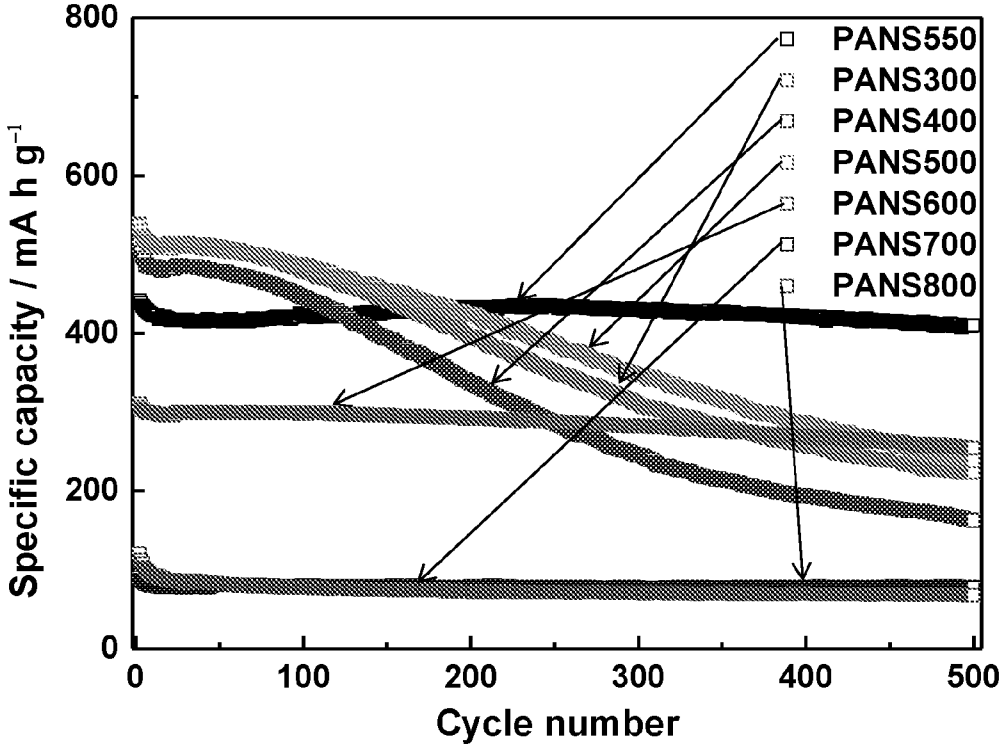

Specific capacity / mA h g^{-1}
Cycle number
0
200
400
600
800
0
100
200
300
400
500
PANS550
PANS300
PANS400
PANS500
PANS600
PANS700
PANS800

FIGURE 14

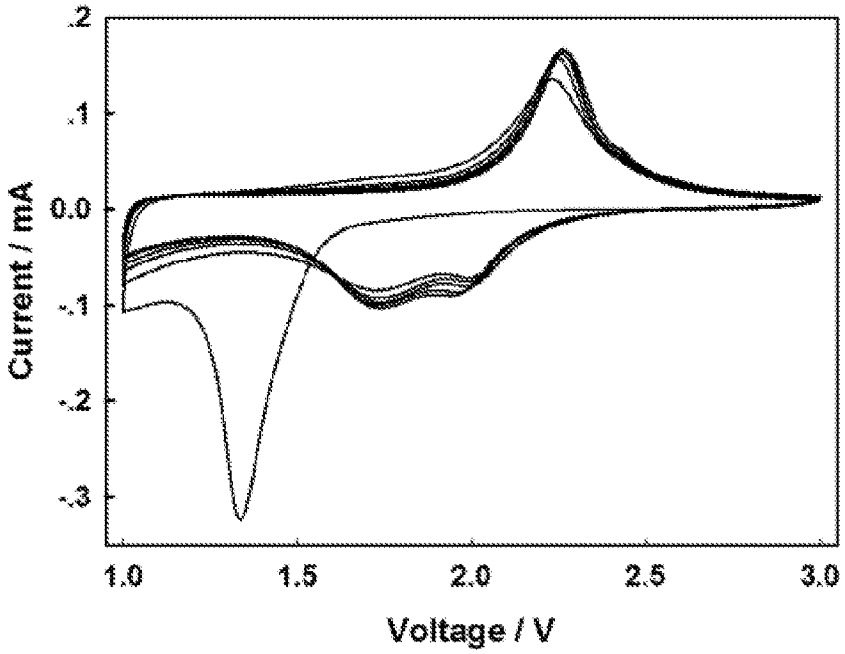


FIGURE 15

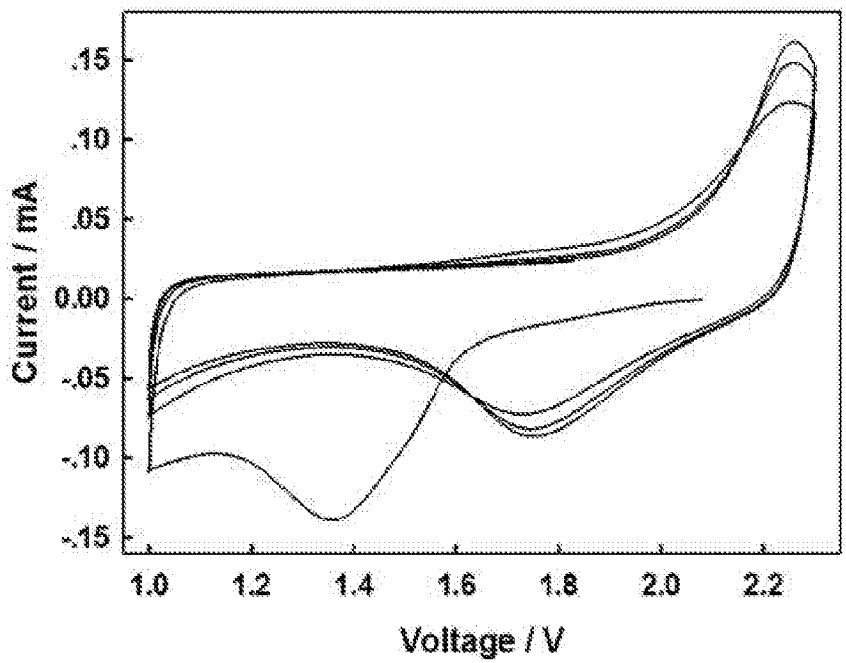


FIGURE 16

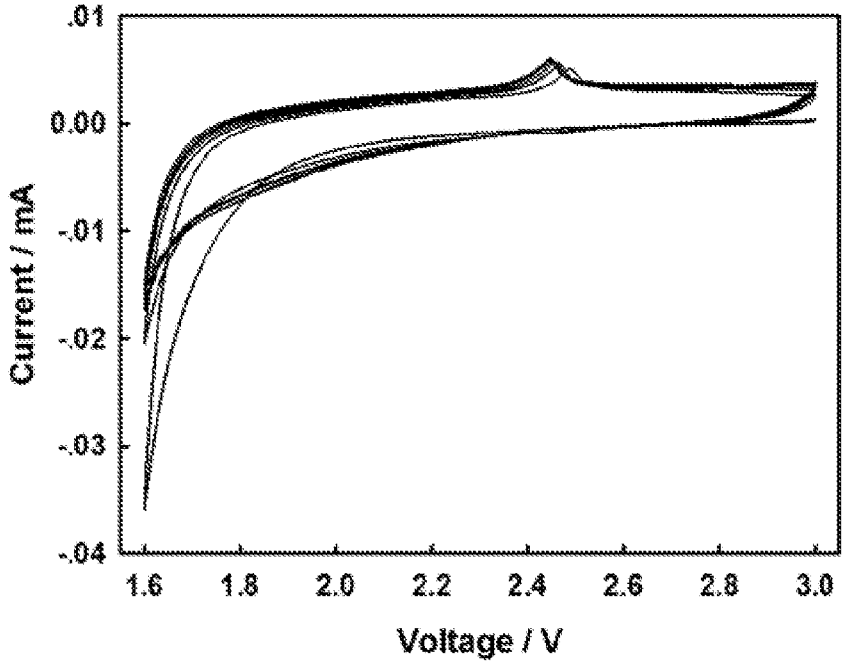


FIGURE 17

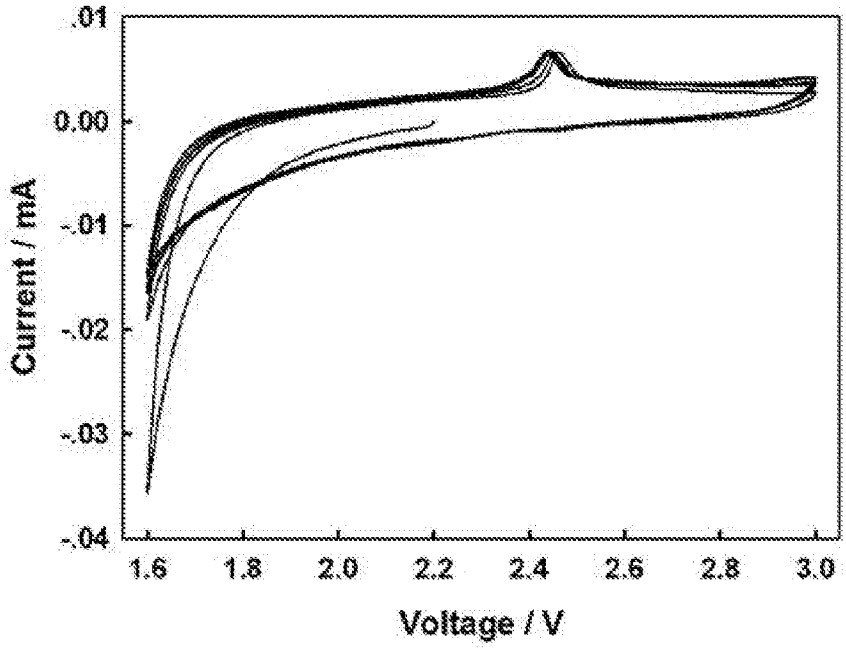


FIGURE 18

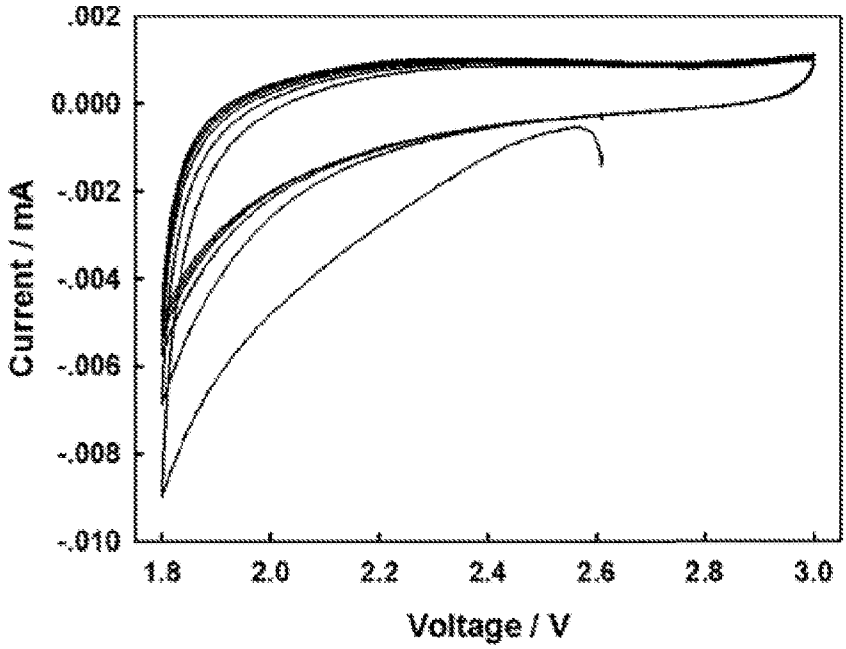


FIGURE 19

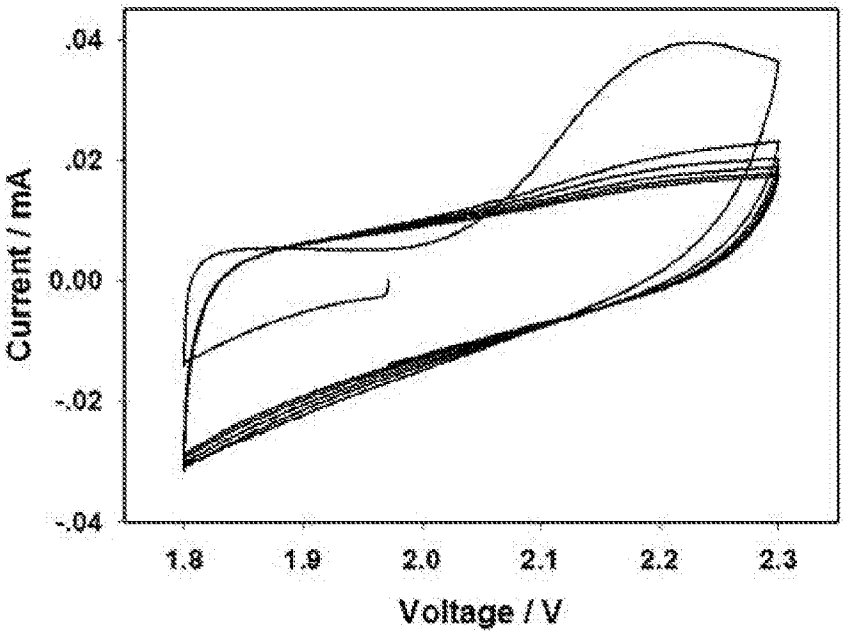


FIGURE 20

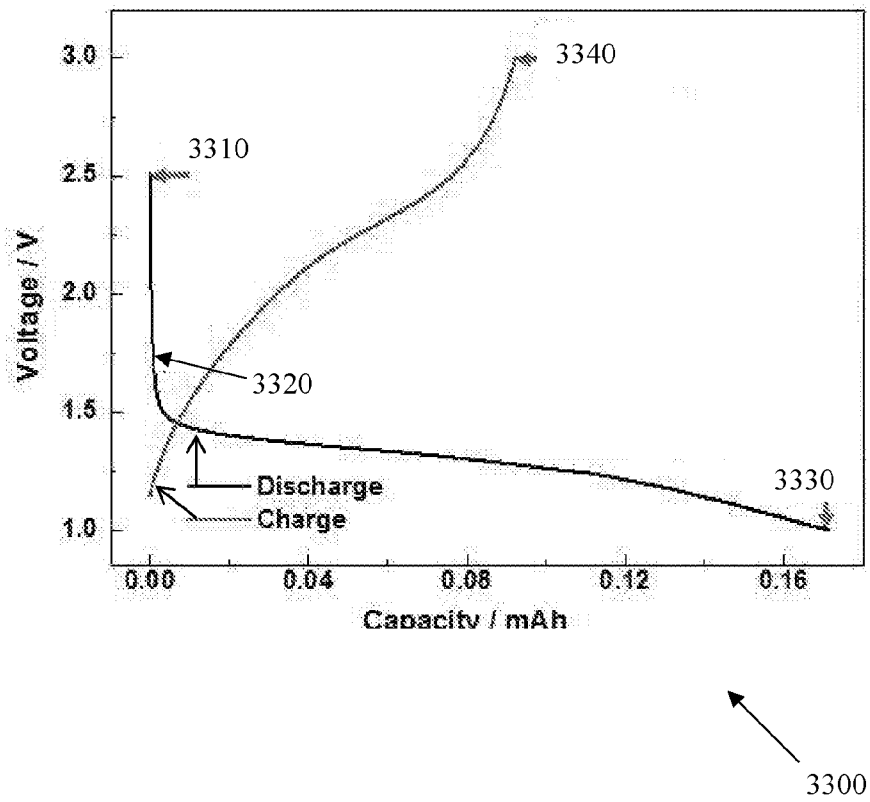

3.0
2.5
2.0
1.5
1.0
Voltage / V
0.00
0.04
0.08
0.12
0.16
Capacity / mAh
3310
3320
3330
3340
Discharge
Charge
3300

FIGURE 21

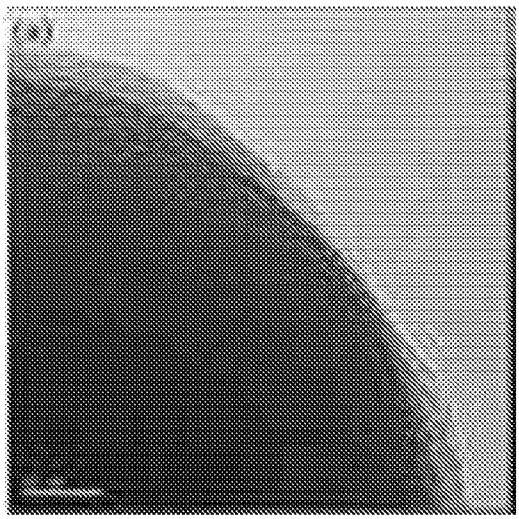


FIGURE 22

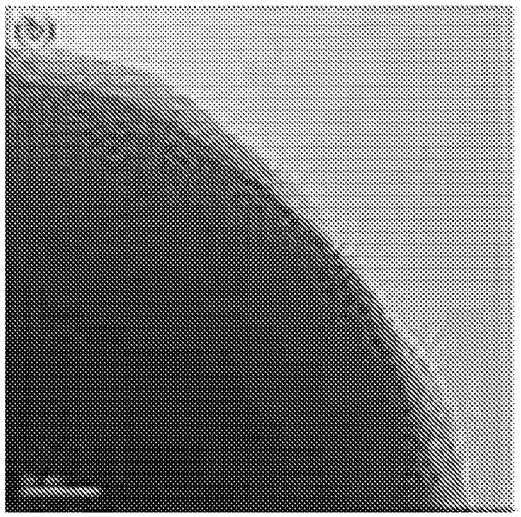


FIGURE 23

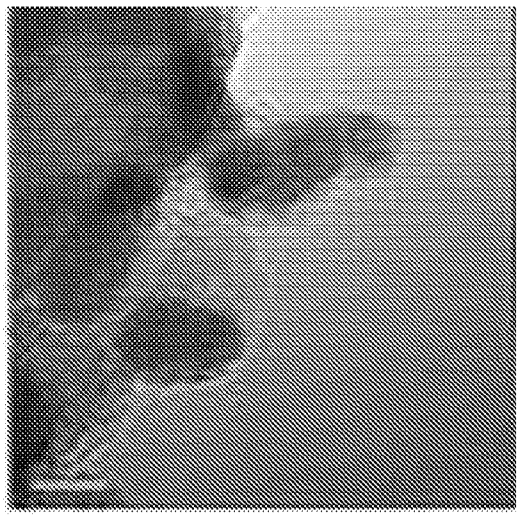


FIGURE 24

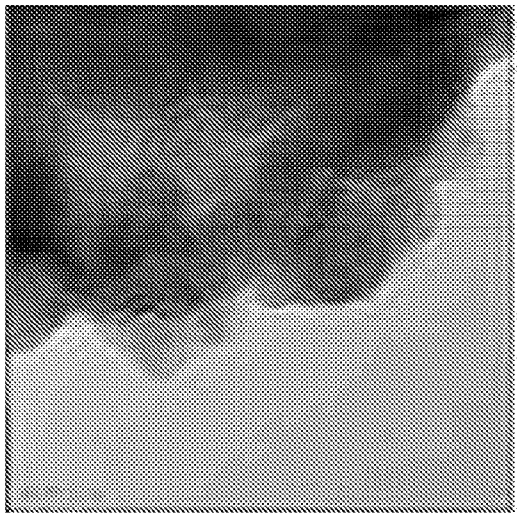


FIGURE 25

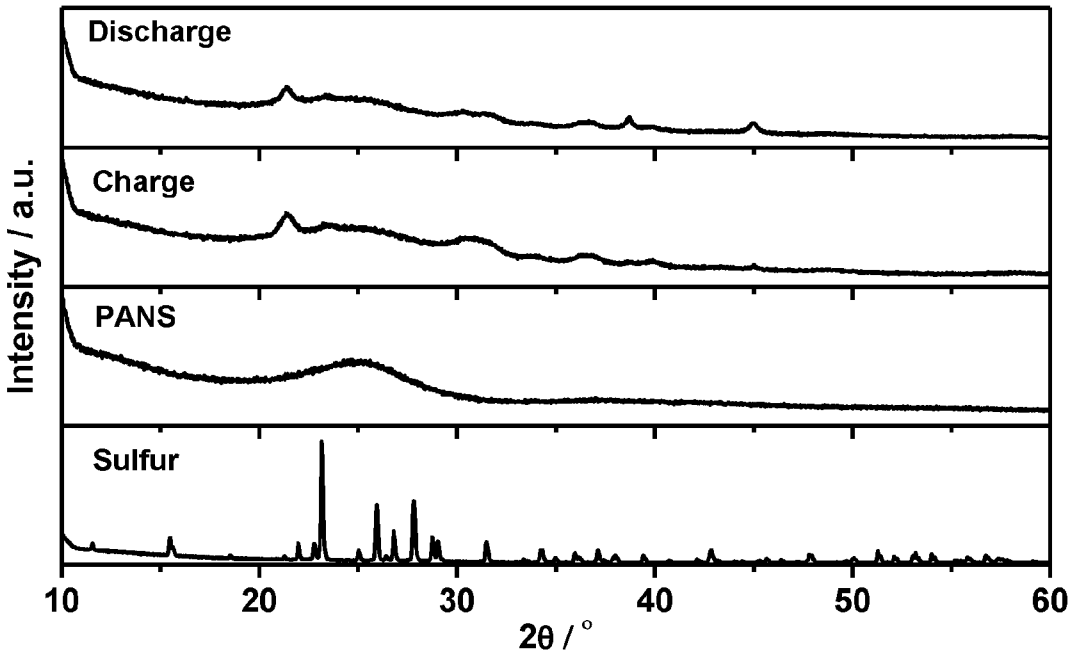

Discharge
Charge
PANS
Sulfur
Intensity / a.u.
10
20
30
40
50
60
2θ / °

FIGURE 26

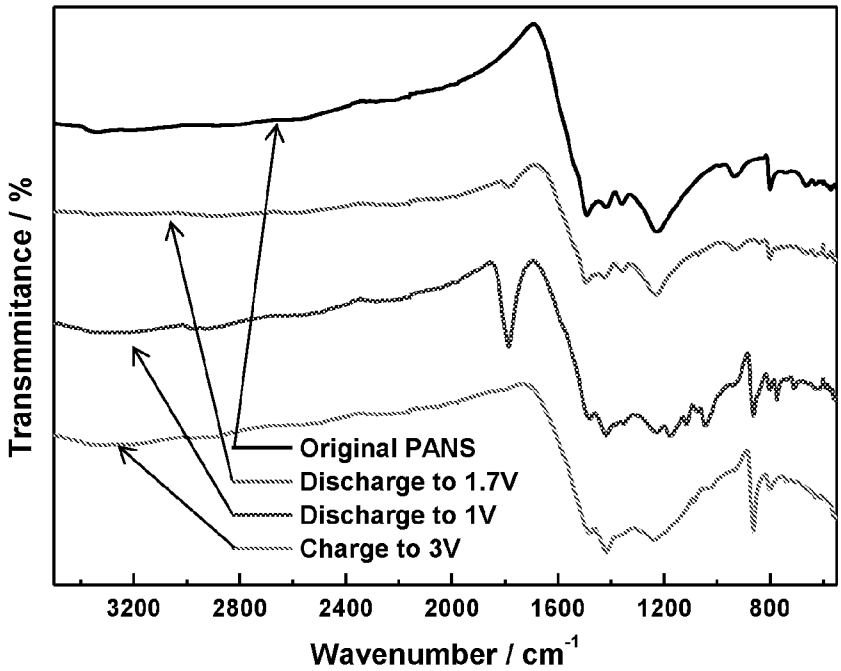

Transmmitance / %
Original PANS
Discharge to 1.7V
Discharge to 1V
Charge to 3V
3200
2800
2400
2000
1600
1200
800
Wavenumber / cm-1

FIGURE 27

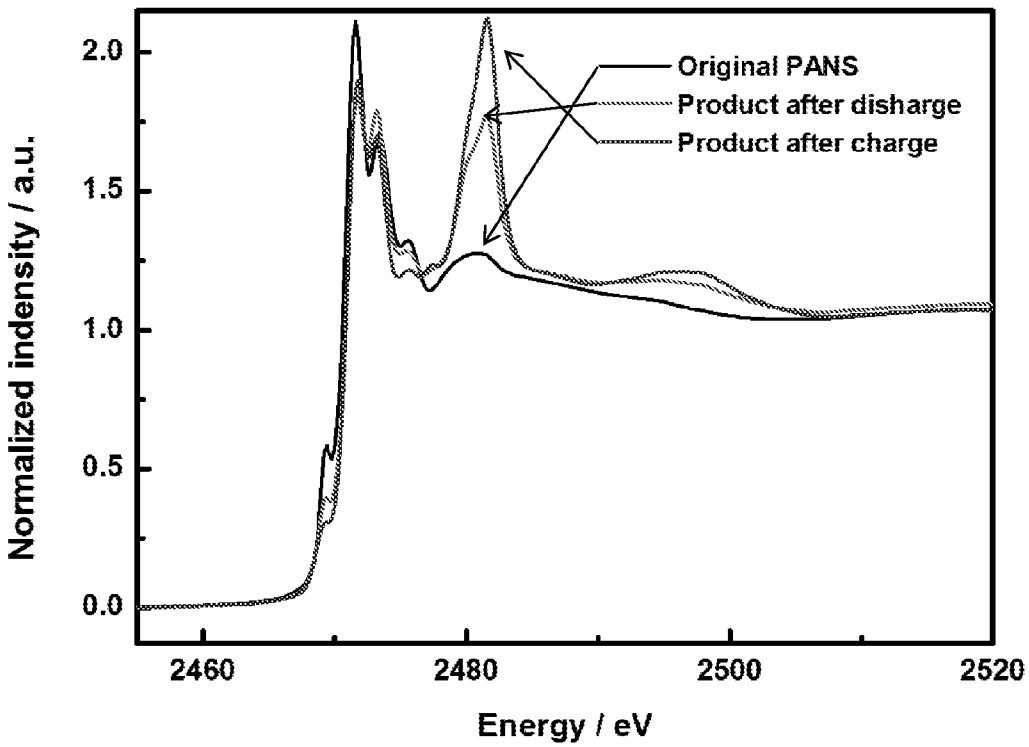

Original PANS
Product after disharge
Product after charge
Normalized indensity / a.u.
2.0
1.5
1.0
0.5
0.0
2460
2480
2500
2520
Energy / eV

FIGURE 28

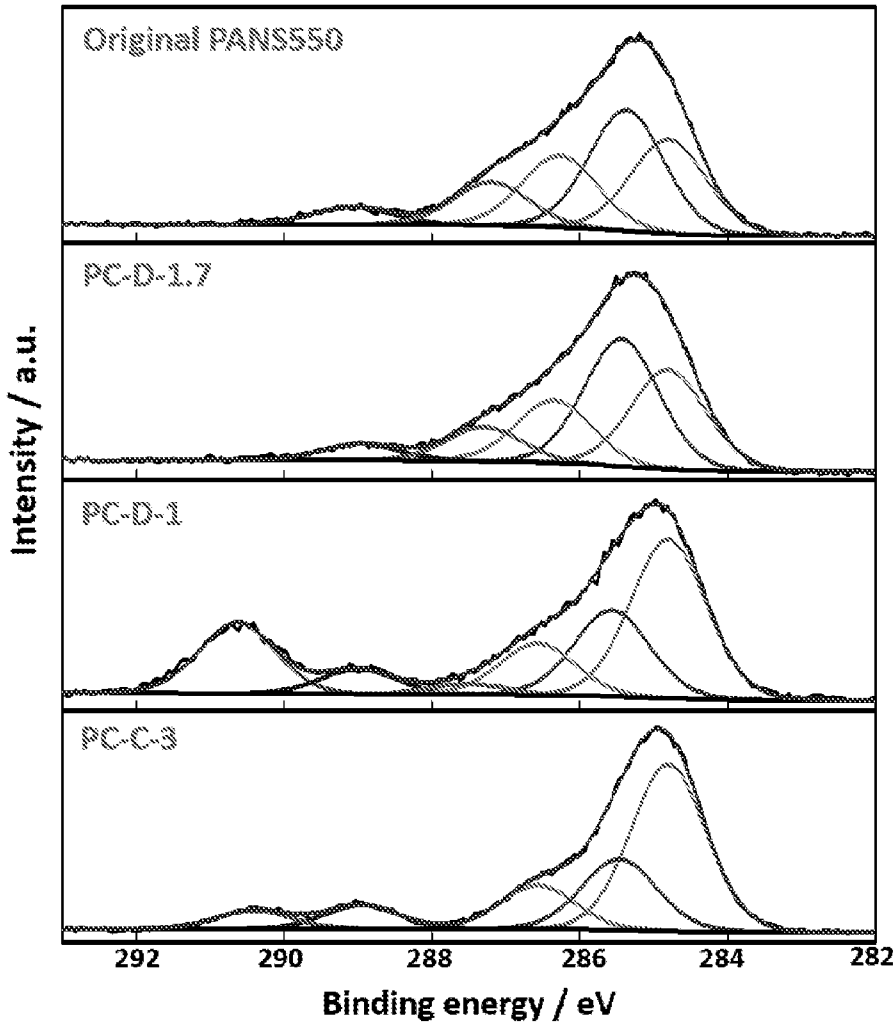

Original PANS550
PC-D-1.7
PC-D-1
PC-C-3
Intensity / a.u.
292
290
288
286
284
282
Binding energy / eV

FIGURE 29

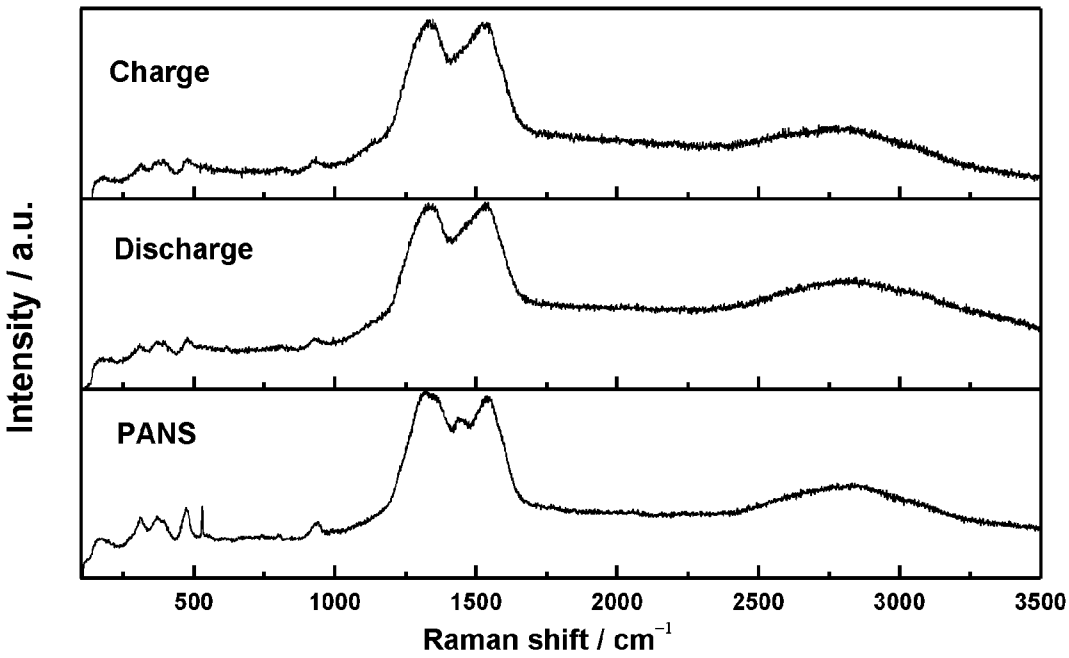
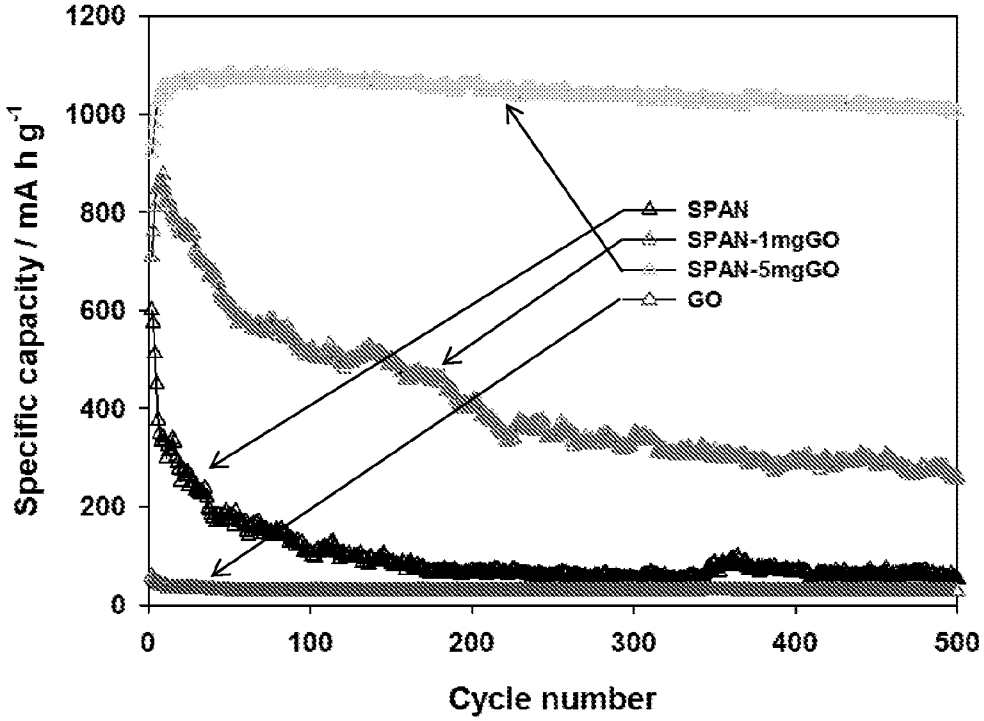

Charge
Discharge
PANS
Intensity / a.u.
500
1000
1500
2000
2500
3000
3500
Raman shift / cm^{-1}

FIGURE 30


Specific capacity / mA h g-1
Cycle number
SPAN
SPAN-1mgGO
SPAN-5mgGO
GO
0
200
400
600
800
1000
1200
0
100
200
300
400
500

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2015/098194

A. CLASSIFICATION OF SUBJECT MATTER

H01M 10/0525(2010.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS,CNKI, CNTXT, WPI, EPODOC: Li2Sx, nanoparticle, sulfur, atmosphere, electrochemically, reducing, potential, anode, cathode, polyacrylonitrile, PAN, lithium

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 103390767 A (UNIV. TSINGHUA ET AL.) 13 November 2013 (2013-11-13) paragraph [0034]	1-26
Y	CN 102593416 A (NINGDE AMPEREX TECHNOLOGY LTD. ET AL.) 18 July 2012 (2012-07-18) claim 3	1-26
A	CN 103456991 A (NINGDE CONTEMPORARY AMPEREX TECHNOLOGY LTD. ET AL.) 18 December 2013 (2013-12-18) the whole document	1-26
A	CN 1883064 A (GILLETTE CO.) 20 December 2006 (2006-12-20) the whole document	1-26
A	CN 103427125 A (UNIV. TSINGHUA ET AL.) 04 December 2013 (2013-12-04) the whole document	1-26
A	WO 0139302 A1 (MOLTECH CORP. ET AL.) 31 May 2001 (2001-05-31) the whole document	1-26

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 September 2016	**21 September 2016**

Name and mailing address of the ISA/CN	Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China**	**TANG,Tiantian**
Facsimile No. **(86-10)62019451**	Telephone No. **(86-10)010-62414120**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2015/098194

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	103390767	A	13 November 2013	US	2013302678	A1	14 November 2013
				TW	I464931	B	11 December 2014
				TW	201347268	A	16 November 2013
				CN	103390767	B	20 January 2016
				US	8889293	B2	18 November 2014
CN	102593416	A	18 July 2012	CN	102593416	B	27 August 2014
CN	103456991	A	18 December 2013	CN	103456991	B	15 July 2015
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				US	8048556	B2	01 November 2011
				US	7914920	B2	29 March 2011
				CN	100435387	C	19 November 2008
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				WO	2005038961	A2	28 April 2005
				US	2005079424	A1	14 April 2005
				US	8288034	B2	16 October 2012
				US	2012034508	A1	09 February 2012
				US	2011143182	A1	16 June 2011
				JP	2007507850	A	29 March 2007
				WO	2005038961	A8	15 June 2006
				BR	PI0415180	A	28 November 2006
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				AU	1796701	A	04 June 2001
				KR	20020059781	A	13 July 2002
				EP	1236231	B1	22 October 2014
				CN	1214476	C	10 August 2005
				JP	2003515893	A	07 May 2003
				EP	1234348	B1	22 October 2003
				CN	1415123	A	30 April 2003
				JP	5112584	B2	09 January 2013
				DE	60006150	D1	27 November 2003
				KR	100686948	B1	27 February 2007
				CN	1212682	C	27 July 2005
				CN	100344014	C	17 October 2007
				EP	1236231	A1	04 September 2002
				JP	2003515892	A	07 May 2003
				JP	5106732	B2	26 December 2012
				EP	1234348	A1	28 August 2002
				CN	1415122	A	30 April 2003