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(54) **PROCESS FOR THE PREPARATION OF A POROUS CARBON STRUCTURE**

VERFAHREN ZUR HERSTELLUNG EINER PORÖSEN KOHLENSTOFFSTRUKTUR

PROCÉDÉ DE PRÉPARATION D'UNE STRUCTURE CARBONÉE POREUSE

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EP 3 233 757 B1

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Description

Object of the invention

[0001] It is the object of the present invention to provide a process for the preparation of porous carbon structures.

Background of the invention

[0002] Development of methods for storage of electrical energy has become highly important in recent time. Two main general approaches for reversible storage of electric energy are commonly used. The first one is supercapacitors, where energy is stored in the form of an electric double layer. In the second approach, the energy is stored in the form of chemical energy in rechargeable batteries. While the supercapacitors allow higher power density, the rechargeable batteries are able to provide higher energy density. Among all variety of rechargeable batteries, ones based on lithium deserve particular attention. In fact, lithium is the lightest metal and has the highest oxidation potential among the metals that allows much higher energy density comparing, for example, to Ni-Cd rechargeable batteries. Currently, Li-ion batteries based on LiMnO_2 and LiCoO_2 cathodes are practically used. These Li-ion batteries provide good cycling and very high Coulombic efficiency. On the other hand, they suffer from insufficient energy density. For example, the distance which can be traveled by a car equipped with a Li-ion battery is about 50-160 km, which in many cases is insufficient for everyday use. Li-S batteries are the emerging class of rechargeable batteries, which potentially can provide much higher energy density. Although the lithium-sulfur system operates at a comparably low average potential of 2.1 V against Li^+/Li , it shows a high theoretic specific energy of 2600 Wh/kg due to the extraordinary theoretical specific capacity of 1675 mAh/g_s (g_s stands for per gram of sulfur).

[0003] The essential element of Li-S batteries is the sulfur cathode. Sulfur itself is electrically insulating and therefore composite cathodes, which consist of sulfur and porous conductive materials such as carbon, are used. Different carbon materials including acetylene black, carbon nanotubes, graphene, CMK-3 and microporous activated carbon fibers were used as conductive component. Typically, these carbon materials are powders, which consist of grains with certain size. The porosity of these materials is controlled by the size of the grains and internal porosity of the grains. Very recently, polymers were introduced as precursors for design of porous carbon cathodes. Due to their flexibility, polymers may be used for fabrication of carbon materials with various micro and nano-morphologies. For example, carbonization of polyacrylonitrile (PAN) mixed with Na_2CO_3 , poly(methyl methacrylate) (PMMA) - PAN blends, polymer; fibers prepared by electrospinning, polypyrrole, sucrose, formaldehyde-phenol resin mixed with tetraethyl orthosilicate were used to prepare porous carbon cath-

odes. Due to interconnectivity of pores and carbon phase as well as large surface area, opal and inverse-opal-structures deserve particular interest as candidate for possible carbon structures. For example, Schuster, J.; He, G.; Mandlmeier, B.; Yim, T.; Lee, K. T.; Bein, T.; Nazar, L. F., Spherical Ordered Mesoporous Carbon Nanoparticles with High Porosity for Lithium-Sulfur Batteries, *Angewandte Chemie, International Edition* 2012; 51, (15), 3591-3595 disclose fabrication of opal-like porous carbon structure using PMMA particles as template, which was filled with SiO_2 and PMMA was replaced by CMK-3 carbon. Inverse-opal like carbon structures were also prepared by carbonization of poly(furfuryl alcohol) and demonstrated very good cycling properties

[0004] US 2005/260118 A1 discloses a method of preparing a mesoporous carbon film having a hierarchical, bimodal pore structure.

Detailed description

[0005] It is one purpose of the present invention to provide new method for preparation of porous carbon structure, which are suitable for design of cathodes for Li-S batteries.

[0006] The present invention concerns a process for the preparation of a porous carbon structure comprising the following steps:

- a) providing a template comprising voids,
- b) filling of at least part of the voids with a precursor for the formation of the porous carbon structure,
- c) carbonizing the precursor for the formation of the porous carbon structure and
- d) removing at least part of the template,

wherein the template comprises a mixture of inorganic oxide particles with a bimodal particle size distribution which are at least partially removed in step d) by etching with a suitable acid or base, preferably comprising hydrofluoric acid (HF), and wherein the template comprises voids between the particles, wherein the inorganic oxide particles have a diameter of 100 nm or less and a diameter of 500 nm or more, wherein the partial removal of bimodal particles in step d) removes the particles of a smaller size and only partially etches the particles of a larger size to create adsorption sites for polysulfides.

[0007] This procedure allows the use of material for the template that will provide a porous carbon structure for use as sulfur-carbon cathodes with an optimized microstructure, while it allows at the same time to choose a precursor for the porous carbon structure, which provides porous carbon with improved electrochemical properties for use in sulfur-carbon cathodes. This procedure provides well defined carbon structures with regular micro structures and disordered nanostructures that result in a high conductivity and a high initial capacity in sulfur-carbon cathodes. Preferred is the aforementioned

process wherein the precursor for the formation of the porous carbon structure is a formaldehyde-phenol resin. It can be easily prepared in the template by soaking the template in a mixture of the starting materials for the preparation of the precursor. The soaked template is subsequently heated mildly to provide the cross-linked polymer, which is the precursor for the formation of the porous carbon structure. More preferable the precursor for the formation of the porous carbon structure is a resorcinol-formaldehyde resin. Resorcinol-formaldehyde resins provide carbon that is disordered in the nano scale and partially graphitized and has a high conductivity and a high capacity.

[0008] A preferred process of the present invention is a process as described above comprising the following steps:

- a) providing a solution comprising a solvent or a mixture of solvents, a block copolymer and an amphiphilic molecule,
- b) producing a body by evaporation of the solvent,
- c) removal of the amphiphilic molecules to produce a template comprising voids,
- d) filling of at least part of the voids with a precursor for the formation of the porous carbon structure,
- e) carbonization of the precursor for the formation of the porous carbon structure and removal of the block copolymer by heating,

wherein the block copolymer comprises polymeric units of at least one lipophilic monomer and polymeric units of at least one hydrophilic monomer.

[0009] In such a process, the polymeric units of the at least one lipophilic monomeric unit tend to attach themselves to the lipophilic parts of the amphiphilic molecules and the polymeric units of the at least one hydrophilic monomer tend to attach themselves to the hydrophilic parts of the amphiphilic molecules, resulting in an ordered structure. The ordered structure has been found to have bicontinuous gyroid morphology. A bicontinuous gyroid morphology means infinitely connected ordered or periodic three dimensional structures. When the amphiphilic molecules are removed, they leave voids that have the form of channels in the ordered structure. These voids in the form of channels are connected with each other and allow the precursor solution of the precursor for the formation of the porous carbon structure to easily penetrate the voids in the template by capillary force. They also provide the resulting carbon cathode with a highly porous ordered structure with a high surface area.

[0010] According to one preferred embodiment of the present invention, the voids of the template comprising voids do not comprise a precursor for the formation of the porous carbon structure before filling of at least part of the voids with a precursor for the formation of the porous carbon structure, more preferably the voids do not comprise a resorcinol resin before filling at least part of the voids with a precursor for the formation of the porous

carbon structure.

[0011] According to another preferred embodiment of the present invention, the template comprising voids is formed in the absence of a precursor for the formation of the porous carbon structure, more preferably it is formed in the absence of a resorcinol resin.

[0012] According to a preferred embodiment of the present invention, voids of the template comprising voids are free of any organic material. According to another preferred embodiment of the present invention, voids of the template comprising voids are free of any inorganic material. According to a particularly preferred embodiment of the present invention, voids of the template comprising voids are free of any organic material and free of any inorganic material.

[0013] Further preferred is such a process as directly aforementioned wherein in step c) the amphiphilic molecules are removed by soaking the body produced in step b) in a solvent, preferably in ethanol and more preferably in an ethanol/water mixture. This procedure allows a very easy and simple removal of the amphiphilic molecules without disturbing the structure of the remaining block copolymer which forms the template.

[0014] In one preferred embodiment the at least one hydrophilic monomer and the amphiphilic molecule comprise groups that allow the formation of hydrogen bonds between the part of the block copolymer comprising the hydrophilic monomer and the amphiphilic molecule. Preferably the aforementioned at least one hydrophilic monomer comprises at least one functional group selected from the group consisting of a nitrogen atom with one lone electron pair, an oxygen atom with two lone electron pairs and a fluorine atom and the amphiphilic molecule comprises at least one functional group selected from the group consisting of N-H and -O-H or the amphiphilic molecule comprises at least one functional group selected from the group consisting of a nitrogen atom with one lone electron pair, an oxygen atom with two lone electron pairs and a fluorine atom and the hydrophilic monomer comprises at least one functional group selected from the group consisting of N-H and -O-H. Preferably the at least functional group selected from the group consisting of N-H and -O-H are selected from the group consisting of a primary amine group a secondary amine group, an amide group, a carboxyl group or a hydroxyl group. These functional groups allow the formation of hydrogen bonds between the block copolymer and the amphiphilic molecule, which supports the formation of ordered structures with tunnel shaped elements.

[0015] Most preferably the block copolymer used in a process according to the present invention is a polystyrene - poly(4-vinylpyridine) block copolymer (P4VP). Further preferably the aforementioned amphiphilic molecule is selected from the group consisting of 3-pentadecylphenol (PDP) and 2-(4'-hydroxyphenylazo)benzoic acid (HABA). Most preferably the aforementioned amphiphilic molecule is 3-pentadecylphenol. Further preferably, the solvent mentioned in steps a) and b) of the above process

is chloroform.

[0016] A preferred combination of the aforementioned block copolymer and the aforementioned amphiphilic molecule is the combination of a polystyrene - poly(4-vinylpyridine) block copolymer in combination with 3-pentadecylphenol as the amphiphilic molecule. Preferred is therefore a process as aforementioned wherein the solution in step a) comprises polystyrene - poly(4-vinylpyridine) block copolymer and 3-pentadecylphenol. Most preferably the solution in step a) consists of one or more solvents, polystyrene - poly(4-vinylpyridine) block copolymer and 3-pentadecylphenol. Such solutions form upon evaporation of the solvent in step b) of the aforementioned process complexes of the polystyrene - poly(4-vinylpyridine) block copolymer with 3-pentadecylphenol that have a gyroid morphology. According to one preferred embodiment, the solution in step a) does not comprise a precursor for the formation of the porous carbon structure, preferably the solution in step a) does not comprise a starting material for the preparation of a crosslinked formaldehyde-phenol resin.

[0017] A preferred process of the present invention is therefore a process as described above comprising the following steps:

- a) providing a solution comprising chloroform, polystyrene - poly(4-vinylpyridine) block copolymer and 3-pentadecylphenol,
- b) producing a body by evaporation of chloroform,
- c) removal of the amphiphilic molecules by selective washing with an ethanol/water mixture to produce a template comprising voids,
- d) filling of at least part of the voids with a starting material for the preparation of a cross-linked resorcinol-formaldehyde resin, and subsequent heating of the starting material to form a cross-linked resorcinol-formaldehyde resin
- e) and carbonization of the precursor for the formation of the porous carbon structure and removal of the block copolymer by heating.

[0018] Figure 1 describes the directly aforementioned process where a template is formed by evaporation of the solvent of a solution comprising a solvent (chloroform), polystyrene - poly(4-vinylpyridine) block copolymer and 3-pentadecylphenol. The complex of the polystyrene - poly(4-vinylpyridine) block copolymer with 3-pentadecylphenol having gyroid morphology is depicted in the first drawing. It has a bicontinuous gyroid morphology. The dark parts depict the space occupied by the polystyrene - poly(4-vinylpyridine) block copolymer and the white parts depict the space that was occupied by the 3-pentadecylphenol and now it is free space giving porous template to be filled with carbon precursor (Figure 1, drawing 2). Owing to the hydrogen bonding interaction between hydroxyl groups and nitrogen atoms of pyridine rings, 3-pentadecylphenol prefers to assemble into the poly(4-vinylpyridine) phase. A selective washing of 3-

pentadecylphenol molecules from block copolymer films in ethanol, which was confirmed by FTIR spectroscopy, resulted in the formation of a nanoporous template with gyroid morphology exhibiting the polystyrene struts coated with poly(4-vinylpyridine) chains (Figure 1, drawing 2). The resulting nanoporous gyroid template is depicted in Figure 1, Drawing 2, wherein the dark part depicts the space occupied by the block copolymer and the white parts depict the void channels.

[0019] Subsequently the nanoporous gyroid template was impregnated with starting material (carbon precursor) for the preparation of resorcinol-formaldehyde resin (dotted dark part in Figure 1 drawing 3) which will be crosslinked after complete filling of the void spaces to provide the resin filled gyroid nanoporous template (Figure 1, Drawing 3). As visualized in microscopic analysis (scanning electron microscopy, transmission electron microscopy), template films have nano-scaled interconnected channels, therefore capillary forces can also be expected to facilitate the penetration of starting materials into the film. In a subsequent step, the sample is heated, which results in the formation of cross-linked resorcinol-formaldehyde resin inside the gyroid template. Finally, the resin filled sample is pyrolyzed at elevated temperature in an inert media to obtain highly porous gyroid carbon replicas. Pyrolysis not only converts the cross-linked resin into the carbon but also removes the block copolymer phase leaving behind the interconnected porous carbon network (Figure 1, drawing 4) with high surface area, which is around 885 m²/g. The porous carbon was characterized by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The obtained results suggest that the carbon material of the fabricated sample is a mixture of disordered and graphitized carbon structures.

[0020] Figure 2a further shows a SEM image of the obtained porous carbon. The regular structure deriving from the gyroid structure of the template is clearly visible.

[0021] A further preferred combination of the aforementioned block copolymer and the aforementioned amphiphilic molecule is the use of a polystyrene - poly(4-vinylpyridine) block copolymer in combination with 2-(4'-hydroxyphenylazo)benzoic acid as the amphiphilic molecule. Preferred is therefore a process as aforementioned wherein the solution in step a) comprises polystyrene - poly(4-vinylpyridine) block copolymer and 2-(4'-hydroxyphenylazo)benzoic acid. Most preferably the solution in step a) consists of one or more solvents, polystyrene - poly(4-vinylpyridine) block copolymer and 2-(4'-hydroxyphenylazo)benzoic acid. Such solutions form upon evaporation of the solvent in step b) of the aforementioned process complexes of the polystyrene - poly(4-vinylpyridine) block copolymer with 2-(4'-hydroxyphenylazo)benzoic acid that have a gyroid morphology.

[0022] A further preferred process of the present invention as defined above is therefore a process as described above comprising the following steps:

- a) providing a 20 wt % solution of polystyrene - poly(4-vinylpyridine) block copolymer with 2-(4'-hydroxyphenylazo)benzoic acid in *N,N*-dimethylformamide-tetrahydrofuran mixed solvent,
- b) producing a body by partial evaporation of the solvent followed by phase inversion,
- c) removal of the amphiphilic molecules by selective washing with ethanol to produce a template comprising voids,
- d) filling of at least part of the voids with a starting material for the preparation of a cross-linked resorcinol-formaldehyde resin, and subsequent heating of the starting material to form a cross-linked resorcinol-formaldehyde resin
- e) and carbonization of the precursor for the formation of the porous carbon structure and removal of the block copolymer by heating.

[0023] The process is analogous to that described in Figure 1. The product of this process has a very high conductivity which is around 222.4 mS/cm.

[0024] The present method allows for the preparation of a wide variation of the properties of the prepared carbon structures, by variation of the block copolymer and the amphiphilic molecules.

[0025] Further preferred is a process as described herein, wherein the template comprising the precursor for the formation of the porous carbon structure is heated to more than 600 °C, more preferably to 900 °C to carbonize the precursor for the formation of the porous carbon structure and to remove the template.

[0026] According to the present invention the template comprises inorganic oxide particles, in particular a mixture of inorganic oxide particles with a bimodal particle size distribution, which are removed from the template by etching with a suitable acid or base and wherein the template comprises voids between the particles. More preferred is such a process wherein the template consists of inorganic oxide particles with a bimodal particle size distribution. The inorganic oxides forming the template should be chosen in such a way that they should not react or should not be soluble in the void filling material or any of its components.

[0027] The present invention defined in the appended claims 1-11.

[0028] In a preferred embodiment, the inorganic oxide particles with a bimodal particle size distribution are selected from the group comprising silicon dioxide, titanium dioxide, aluminium oxide, vanadium(V) oxide and zinc oxide. In a more preferred embodiment, the inorganic oxide particles are silicon dioxide particles.

[0029] According to the invention, the suitable etchant is an acid or a base, preferably the suitable etchant is hydrofluoric acid (HF). The other etchant for preferred embodiment can be buffered hydrofluoric acid (mixture of NH₄F (40 wt. %) and HF (49 wt %) in 6:1 v/v ratio, hot concentrated potassium hydroxide/sodium hydroxide etc. The etchants can be chosen depending on their abil-

ity to solubilize or wash away the template but keeping the porous carbon unaltered. Such a process is exemplarily depicted in Figure 5 for the case of silicon dioxide particles as inorganic oxide particles.

[0030] The template comprises inorganic oxide particles with a diameter of 100 nm or less and particles with a diameter of 500 nm or more, more preferably the template comprises inorganic oxide particles with a diameter of 60 nm or less and particles with a diameter of 1 μm or more. Further, the particles preferably have a spherical shape. In the present invention, the partial removal of bimodal particles in step d) of the above process removes the particles of a smaller size and only partially etches the particles of a larger size to create adsorption sites for polysulfides.

[0031] The cyclic voltammetry curves of cathodes prepared by such a process demonstrate typical charge/discharge behavior of Li-S batteries. They have large charge/discharge capacities of around 800 mAh/g_s after the second discharge, which corresponds to ca. 50% of the theoretical specific capacity of a sulfur electrode.

[0032] It is very interesting that this cathode material, demonstrates relatively slow decay of the charge/discharge capacity which remains around 600 mAh/g_s after 50 cycles. The most probable reason of improved cycling behavior is adsorption of polysulfides on material from the SiO₂ particles which remains in the porous carbon. As result polysulfides remain entrapped within the cathode and do not diffuse to the anode to form Li₂S and Li₂S₂. In other words, the use of SiO₂ particles allows the suppression of the polysulfide shuttle. This effect is also possible with other inorganic oxide particles already mentioned.

[0033] In fact, the effect of inorganic oxide particles e.g. silica can also be loaded into the porous network of carbon (particle size should be well below the pore diameter of the carbon to accommodate the silica particle inside) and an improvement of capacity decay minimizing the polysulfide shuttle can be expected. This additional loading may be advantageously combined with any process for the preparation of a porous carbon structure as described herein. The loading of the inorganic oxide particles that are promising candidates for polysulfide shuttle inhibitor can be loaded by dipping the porous carbon in a suspension of the inorganic oxide particles (particle loading 1- 20 wt % in water) for a while (5-30 min) and heating further at 100 °C followed by drying at 80 °C under vacuum. Preferably, the inorganic oxide particles loaded into the porous carbon network have a diameter of 200 nm or less, preferably of 100 nm or less, more preferably of 60 nm or less. Also preferably, the inorganic oxide particles loaded into the porous carbon network have a diameter of 10 nm or more, preferably of 30 nm or more, more preferably of 50 nm or more.

[0034] Therefore, according to a preferred embodiment, any process as described herein may include a step of loading inorganic oxide particles into the porous carbon structure, more preferably these inorganic oxide

particles are selected from the group comprising silicon dioxide, titanium dioxide, aluminium oxide, vanadium(V) oxide and zinc oxide, even more preferably the inorganic oxide particles are silicon dioxide particles. The present disclosure further includes the use of inorganic oxide particles, in particular of silica particles, within a porous carbon structure for the preparation of a battery.

[0035] A process as described herein is preferred wherein the precursor for the formation of the porous carbon structure is a crosslinked formaldehyde-phenol resin, which is formed by filling of at least part of the voids of the template with starting material for the preparation of the crosslinked formaldehyde-phenol resin and crosslinking the starting material for the preparation of the crosslinked formaldehyde-phenol resin. Thereby preferably the template is heated to 60 to 110 °C to form the crosslinked formaldehyde-phenol resin from the starting material for the preparation of the crosslinked formaldehyde-phenol resin.

[0036] Further disclosed is a non-claimed porous carbon structure prepared according to a process as described herein, a cathode prepared therefrom and a battery comprising such a porous carbon structure.

[0037] Finally, a further disclosure is the non-claimed use of a template comprising voids for the preparation of a porous carbon structure, wherein the template comprises a block copolymer and an amphiphilic molecule and wherein the block copolymer comprises polymeric units of at least one lipophilic monomer and polymeric units of at least one hydrophilic monomer. In this embodiment the block copolymer and the amphiphilic molecule may be any block copolymer and the amphiphilic molecule described herein. Preferably the block copolymer and the amphiphilic molecule are those described as herein preferred.

[0038] The present disclosure encompasses the non-claimed use of the porous carbon structure obtained by any of the processes described herein as sulfur-carbon cathodes. The use of the porous carbon structure obtained by any of the processes described herein for lithium-sulfur batteries is envisaged. In particular, the aforementioned porous carbon structure is used as sulfur-carbon cathodes in lithium-sulfur batteries.

[0039] All embodiments of the present invention as described herein are deemed to be combinable in any combination, unless the skilled person considers such a combination to not make any technical sense.

Brief description of the figures

[0040]

Figure 1: Figure 1 describes the process of Example 1.

Figure 2: Figure 2a shows an SEM image of the product of the porous carbon obtained in Example 1, Figure 2b shows the cyclovoltametric

measurement of the cathode produced in Example 1 and Figure 2c shows its charge/discharge measurements.

5 Figure 3: Figure 3 shows the scheme of fabrication of porous carbon using block copolymer via phase inversion route as described in Example 2.

10 Figure 4: Figure 4 shows the SEM image of (a) block copolymer template, (b) after filling the template with resorcinol-formaldehyde resin and (c) porous carbon after pyrolysis of the template obtained in Example 2. Figure 4d shows the cyclovoltametric measurement of the cathode produced in Example 2 and Figure 4e shows its charge/discharge measurements.

20 Figure 5: Figure 5 depicts the process of the present invention according to Example 3, wherein silicon dioxide particles are comprised in the template.

25 Figure 6: Figure 6 depicts (a) the cyclovoltametric measurements and (b) charge/discharge measurements.

30 Figure 7: Figure 7 shows SEM images of the final carbon structure according to Example 3 at different magnifications at the stage of (a, c) resin-silica after carbonization and (b, d) after etching of silica with HF.

35 Examples:

Measurement methods:

40 **[0041]** Cyclovoltametric measurements: The cyclic voltammetry measurements of the lithium-sulfur batteries with different cathodes have been performed in between 1 V -3 V at a scanning rate of 0.05 mV/s. The details of the method is described in Agrawal, M.; Choudhury, S.; Gruber, K.; Simon, F.; Fischer, D.; Albrecht, V.; Göbel, M.; Koller, S.; Stamm, M.; Ionov, L, Porous carbon materials for Li-S batteries based on resorcinol-formaldehyde resin with inverse opal structure, Journal of Power Sources 2014; 261, 363-370.

45 **[0042]** Charge/discharge measurements: The galvanostatic charge/discharge measurement was done following the method described in Agrawal, M.; Choudhury, S.; Gruber, K.; Simon, F.; Fischer, D.; Albrecht, V.; Göbel, M.; Koller, S.; Stamm, M.; Ionov, L, Porous carbon materials for Li-S batteries based on resorcinol-formaldehyde resin with inverse opal structure, Journal of Power Sources 2014; 261, 363-370.

50 **[0043]** XPS: X-ray photoelectron spectroscopy of all carbon samples were done using the protocol described

in Agrawal, M.; Choudhury, S.; Gruber, K.; Simon, F.; Fischer, D.; Albrecht, V.; Göbel, M.; Koller, S.; Stamm, M.; Ionov, L, Porous carbon materials for Li-S batteries based on resorcinol-formaldehyde resin with inverse opal structure, *Journal of Power Sources* 2014; 261, 363-370. Raman spectroscopy: Raman spectroscopy of the carbon samples were done in the way described in Agrawal, M.; Choudhury, S.; Gruber, K.; Simon, F.; Fischer, D.; Albrecht, V.; Göbel, M.; Koller, S.; Stamm, M.; Ionov, L, Porous carbon materials for Li-S batteries based on resorcinol-formaldehyde resin with inverse opal structure, *Journal of Power Sources* 2014; 261, 363-370.

[0044] The XPS and Raman spectra of the carbon material are indicative of the conducting nature (extent of graphitic nature). In all three of the examples the carbon precursor were kept the same to keep the nature of the carbon, so the XPS and Raman spectra are very similar in all cases.

Example 1: Polystyrene-poly(4-vinylpyridine) block copolymer and of 3-pentadecylphenol

[0045] 44.3 mg of polystyrene - poly(4-vinylpyridine) block copolymer (obtained from Polymer Source Inc.) and 30,7mg of 3-pentadecylphenol where dissolved in 5 ml chloroform . The solution was placed in a small bottle in a closed chamber together with six small bottles filled with chloroform for 11 days. During this period the block copolymer attains the stable gyroid morphology. Afterwards, the solvent was slowly evaporated for 5 more days and a 100 μm thick film resulted. The obtained block copolymer 3-pentadecylphenol complex film was inserted into 10 ml of ethanol for a time of 24 hours to obtain the template. FTIR spectroscopy was used to confirm the supramolecular association of the nitrogen atom of the pyridine group with the hydroxyl group of 3-pentadecylphenol. Subsequently, the template was immersed in a solution of 5 ml resorcinol-formaldehyde resin (prepared by mixing resorcinol and formalin solution in 1:1.8 molar ratio catalyzed by 0.1 ml of 1 % Na_2CO_3 solution, all chemicals obtained from Sigma Aldrich, Germany), which was used as starting material for impregnation. Then the sample is heated, resulting in the formation of cross-linked resorcinol-formaldehyde resin inside the template. Finally, the resin-filled template is pyrolyzed at 800 °C for a time of 2 hours in the flow of argon to obtain a highly porous gyroid carbon replica. Pyrolysis of the samples not only converts the cross-linked resin into carbon but also removes the block copolymer phase leaving behind the interconnected porous carbon network with high surface area, which is 885 m^2/g . Porous carbon material was pre-mixed with sulfur powder in a mortar in 1:2 w/w ratio in a mortar followed by mixing in a ball mill for even intensive mixing and subsequently heat treated at 155 °C for 5 h in an oven operated under argon. Heat treatment at 155 °C was done to facilitate the pore coverage by sulfur in to the entire available surface area of

carbon.

[0046] A cathode was produced via the following route. Cathode slurry of desired viscosity was prepared by adding carbon-sulfur composite material (82 wt%), blended with, Super P® Li (10 wt%) conducting additive (carbon black) in a solution of PVdF in N-Methyl-2-pyrrolidone (8 wt% with respect to 82 wt% of carbon-sulfur composite). A thin layer of the as prepared slurry was coated on nickel foil (60-80 μm wet thickness) and disc shaped cathodes were cut out from the whole piece after proper drying in a vacuum oven for 2 days. Cyclic voltametric measurements of this cathode performed as described above show two reduction peaks at 2.4 V and 2 V. The result of the measurements is shown in Figure 2b. A lithium sulfur battery was assembled in the following way. Resulting electrodes had a mass load of 0.40 mg cm^{-2} in dry state and a sulfur content of 55 wt%. A Swagelok® T-cell was used as testing device. Carbon-sulfur composite electrode served as working electrode, lithium metal served as counter and reference electrode respectively. 1 M solution of lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in a mixture of 1,2-Dimethoxyethane/1,3-Dioxolane (1/1, v/v) was used as electrolyte, which was used to soak the nonwoven polypropylene separator during cell assembly. The charging curve of the battery is represented by a typical single peak at 2.4V. It was found that cathode demonstrate moderate capacity in the first charge/discharge cycle, which is about 1600 mAh/g_s. The charge/discharge curve for the first 50 cycles is depicted in Figure 2c. The capacity rapidly decreases during cycling and reaches the value of around 300 mAh/g_s after 50 cycles. The rapid capacity degradation may be due to the well-known problems occurring in lithium sulfur batteries, like the dissolution of long chain polysulfides in the polar electrolyte solvent and the subsequent migration to and direct reduction at the lithium anode during cycling (polysulfide shuttle).

Example 2: Polystyrene-poly(4-vinylpyridine) block copolymer and of 2-(4'-hydroxyphenylazo) benzoic acid

[0047] Example 2 is performed as Example 1, however instead of 30.7 mg of 3-pentadecylphenol, 202.8 mg of 2-(4'-hydroxyphenylazo)benzoic acid is used. A 5 ml 20 wt. percent solution of the block copolymer and 2-(4'-hydroxyphenylazo)benzoic acid in 1:1 molar ratio of 2-(4'-hydroxyphenylazo)benzoic acid to 4-vinylpyridine unit is prepared in 56:24 w/w ratio of N,N-dimethylformamide/tetrahydrofuran solvent mixture and casted on a substrate to form 100 μm thick films. After 30seconds the film formed is immersed in a water/methanol mixture, resulting in the phase inversion. The phase inverted membrane was washed to get rid of 2-(4'-hydroxyphenylazo)benzoic acid and to get template comprising void spaces. This template is a block copolymer mat consisting of cylindrical micelles where polystyrene forms the core and poly(4-vinylpyridine) part pointing outward (Figure 3). Subsequently, the nanoporous carbon was pre-

pared with the help of the template by following the same procedure described in claim 1.

[0048] The obtained carbon has very high conductivity 222.4 mS/cm. The carbon was mixed with elemental sulfur in molten state to get carbon-sulfur composite as cathode powder in the same way as described in claim 1. The cyclic voltammetry curves look like typical ones characteristic to Li-S batteries (Figure 4d). It was found that cathode demonstrate moderate capacity in first charge-discharge cycle, which is in the range 600-800 mAh/g_s. The capacity however rapidly decreases during cycling and reaches the value of around 100 mAh/g_s after 50 cycles that is due to polysulfide shuttle (Figure 4e).

Example 3: Bimodal silicon dioxide particles

[0049] Example 3 is also performed as Example 1 and 2 but differs only in the template. In Example 3, inorganic template was used instead of using polymeric template but the carbon precursor is the same in all three claims which is resorcinol-formaldehyde resin. 40 nm SiO₂ particles were prepared in the following way. 455 mg of L-Arginin dissolved in 345 ml of water then 25 ml of cyclohexane was added. Then it was heated to 60 °C. After this 27.5 ml of Tetraethyl orthosilicate (TEOS) was added and stirred for 48 hours yielding 70% of SiO₂. Then cyclohexane was separated by separating funnel and solution was concentrated up to ~ conc. 450 mg/ml in a rotary evaporator.

[0050] A mixture of 4 ml of dispersion of as synthesized 40 nm of silica particles that corresponds to 1.8 g and 200 mg of 1 μm amine functionalized silica microparticles (obtained from Kisker Biotech GmbH & Co.) were ultrasonicated for 1 hour until a nice dispersion of particles were achieved. 0.2 g of resorcinol was added to the dispersion and stirred for complete dissolution followed by addition of sodium carbonate solution (20 mg in 0.5 ml of water) which acts as catalyst. Afterwards, 0.25 ml of formaldehyde was added. The total mixture formed a gel immediately upon addition of formaldehyde. In order to obtain dispersion again ~1 ml of water was added and kept stirring over the weekend, drying the residual water in a water bath. Then the gelled material was kept in a close vessel and crosslinked at 80 °C for 4 days to avoid any changes in the nanostructure arising out of the flow of polymer. Finally, resulting dark brown colored material were carbonized at 800 °C at a heating rate of 4 °C/min for 2h in an argon atmosphere. Thereafter, a nanoporous carbon was prepared by etching silica particles by dilute hydrofluoric acid. The removal of silica particles was done by dipping the pyrolyzed carbon-silica mixture in 400 ml of 1 wt% dilute hydrofluoric acid. It was followed by washing with water several times and drying in a vacuum oven.

[0051] The obtained carbon has poor conductivity relative to two other systems studied so far of 13 mS/cm. The poor conductivity was due to leftover 20 wt% of silica particles which was washed only from the periphery and

stayed inside the system like loose spheres. During etching out of silica particles it was controlled considering the reaction of silica with hydrofluoric acid ($\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2 \text{H}_2\text{O}$) so that all the 40nm sized silica particles could be washed away and the 1 μm silica particles could be washed partially from the periphery and residing in the carbon matrix creating adsorption sites for polysulfides. The washing with hydrofluoric acid leads to the formation of bimodal porous carbon with polysulfide reservoir inside. These silica particles have advantages to retain the cycle stability by creating adsorption sites on the surface of such inorganic particle surfaces. The carbon was mixed with elemental sulfur in molten state to get carbon-sulfur composite as cathode powder in the same way as described in claim 1 and electrochemistry was also performed keeping the same parameter.

[0052] The cyclic voltammetry curves look like typical ones intrinsic to Li-S batteries (Figure 6a). Interestingly, from the charge-discharge experiment (Figure 6b) it was found that the initial specific capacity started a bit low (800 mAh/g_s in the second discharge cycle) which is nearly 50 % of the theoretical specific capacity of sulfur electrode. Very interesting that contrary to other two cathode systems this one demonstrate quite good cycle stability reached to 600 mAh/g_s up to 50 charging/discharging cycles. The stable cycle performance was due to the polysulfide adsorption on the surfaces of silica particles reside as loose spheres and polysulfides remain entrapped within cathode and do not diffuse to anode and avoid passivation of lithium anode by formation of Li₂S and Li₂S₂ as well. This effect altogether helps in minimizing the active material loss per charging/discharging cycles.

Claims

1. Process for the preparation of a porous carbon structure comprising the following steps:
 - a) providing a template comprising voids,
 - b) filling of at least part of the voids with a precursor for the formation of the porous carbon structure,
 - c) carbonizing the precursor for the formation of the porous carbon structure and
 - d) removing at least part of the template,

wherein the template comprises a mixture of inorganic oxide particles with a bimodal particle size distribution which are at least partially removed in step d) by etching with a suitable acid or base, preferably comprising hydrofluoric acid (HF), and wherein the template comprises voids between the particles, wherein the inorganic oxide particles have a diameter of 100 nm or less and a diameter of 500 nm or more, wherein the partial removal of bimodal particles in

step d) removes the particles of a smaller size and only partially etches the particles of a larger size to create adsorption sites for polysulfides.

2. Process according to claim 1 comprising the following steps:

- a) providing a solution comprising a solvent, a block copolymer and an amphiphilic molecule,
- b) producing a body by evaporation of the solvent,
- c) removal of the amphiphilic molecules to produce a template comprising voids,
- d) filling of at least part of the voids with a precursor for the formation of the porous carbon structure,
- e) carbonization of the precursor for the formation of the porous carbon structure and removal of the block copolymer by heating,

wherein the block copolymer comprises polymeric units of at least one lipophilic monomer and polymeric units of at least one hydrophilic monomer.

3. Process according to claim 2 wherein in step c) the amphiphilic molecules are removed by soaking the body produced in step b) in a solvent, preferably in an ethanol/water or methanol/water mixture.

4. Process according to claim 2 or 3 wherein

- the hydrophilic monomer comprises at least one functional group selected from the group consisting of a nitrogen atom with one lone electron pair, an oxygen atom with two lone electron pairs and a fluorine atom and the amphiphilic molecule comprises at least one functional group selected from the group consisting of N-H and -O-H

or

- the amphiphilic molecule comprises at least one functional group selected from the group consisting of a nitrogen atom with one lone electron pair, an oxygen atom with two lone electron pairs and a fluorine atom and the hydrophilic monomer comprises at least one functional group selected from the group consisting of N-H and -O-H.

5. Process according to any of claims 2 to 4 wherein the block copolymer is a polystyrene - poly(4-vinylpyridine) block copolymer.

6. Process according to any of claims 2 to 5 wherein the amphiphilic molecule is selected from the group consisting of 3-pentadecylphenol and 2-(4'-hydroxyphenylazo)benzoic acid.

7. Process according to any of the preceding claims wherein the template comprising the precursor for the formation of the porous carbon structure is heated to more than 600 °C, preferably to 900 °C to carbonize the precursor for the formation of the porous carbon structure and to remove the template.

8. Process according to claim 1 wherein the inorganic oxide particles with a bimodal particle size distribution are silicon dioxide, titanium dioxide, aluminum oxide, vanadium(V) oxide or zinc oxide, in particular wherein the inorganic oxide particles with a bimodal particle distribution are silicon dioxide particles.

9. Process according to any of claims 1 or 8 wherein the template comprises particles with a size of 100 nm or less and particles with a size of 500 nm or more, preferably wherein the template comprises inorganic oxide particles with a size of 60 nm or less and particles with a size of 1 μm or more.

10. Process according to any of the preceding claims wherein the precursor for the formation of the porous carbon structure is a cross-linked formaldehyde-phenol resin, which is formed by filling of at least part of the voids of the template with a starting material for the preparation of the cross-linked formaldehyde-phenol resin and crosslinking the starting material for the preparation of the cross-linked formaldehyde-phenol resin.

11. Process according to claim 10 wherein the template is heated to 60 to 110 °C to form the cross-linked formaldehyde-phenol resin from the starting material for the preparation of the cross-linked formaldehyde-phenol resin.

Patentansprüche

1. Verfahren zur Herstellung einer porösen Kohlenstoffstruktur umfassend die folgenden Schritte:

- a) Bereitstellen eines Templats umfassend Hohlräume,
- b) Füllen von mindestens einem Teil der Hohlräume mit einem Vorläufer zur Bildung der porösen Kohlenstoffstruktur,
- c) Karbonisieren des Vorläufers zur Bildung der porösen Kohlenstoffstruktur und
- d) Entfernen von mindestens einem Teil des Templats,

wobei das Templat ein Gemisch von anorganischen Oxidteilchen mit einer bimodalen Teilchengrößenverteilung, welche mindestens teilweise in Schritt d) durch Ätzen mit einer geeigneten Säure oder Base, bevorzugt umfassend Fluorwasserstoffsäure (HF),

entfernt werden, umfasst und wobei das Templat Hohlräume zwischen den Teilchen umfasst, wobei die anorganischen Oxidteilchen einen Durchmesser von 100 nm oder weniger und einen Durchmesser von 500 nm oder mehr aufweisen, wobei die teilweise Entfernung von bimodalen Teilchen in Schritt d) die Teilchen einer kleineren Größe entfernt und nur teilweise die Teilchen einer größeren Größe ätzt, um Adsorptionsstellen für Polysulfide zu erzeugen.

2. Verfahren gemäß Anspruch 1 umfassend die folgenden Schritte:

- a) Bereitstellen einer Lösung umfassend ein Lösungsmittel, ein Blockcopolymer und ein amphiphiles Molekül,
- b) Herstellen eines Körpers durch Verdampfen des Lösungsmittels,
- c) Entfernen der amphiphilen Moleküle, wobei ein Templat umfassend Hohlräume hergestellt wird,
- d) Füllen von mindestens einem Teil der Hohlräume mit einem Vorläufer zur Bildung der porösen Kohlenstoffstruktur,
- e) Karbonisieren des Vorläufers zur Bildung der porösen Kohlenstoffstruktur und Entfernen des Blockcopolymers durch Erwärmen,

wobei das Blockcopolymer polymere Einheiten von mindestens einem lipophilen Monomer und polymere Einheiten von mindestens einem hydrophilen Monomer umfasst.

3. Verfahren gemäß Anspruch 2, wobei in Schritt c) die amphiphilen Moleküle durch Einweichen des in Schritt b) hergestellten Körpers in einem Lösungsmittel, bevorzugt in einem Ethanol/Wasser- oder Methanol/WasserGemisch, entfernt werden.

4. Verfahren gemäß Anspruch 2 oder 3, wobei

- das hydrophile Monomer mindestens eine funktionelle Gruppe umfasst, die aus der Gruppe ausgewählt ist, welche aus einem Stickstoffatom mit einem freien Elektronenpaar, einem Sauerstoffatom mit zwei freien Elektronenpaaren und einem Fluoratom besteht, und das amphiphile Molekül mindestens eine funktionelle Gruppe umfasst, die aus der Gruppe ausgewählt ist, welche aus N-H und -O-H besteht, oder
- das amphiphile Molekül mindestens eine funktionelle Gruppe umfasst, die aus der Gruppe ausgewählt ist, welche aus einem Stickstoffatom mit einem freien Elektronenpaar, einem Sauerstoffatom mit zwei freien Elektronenpaaren und einem Fluoratom besteht, und das hy-

drophile Monomer mindestens eine funktionelle Gruppe umfasst, die aus der Gruppe ausgewählt ist, welche aus N-H und -O-H besteht.

5. Verfahren gemäß einem der Ansprüche 2 bis 4, wobei das Blockcopolymer ein Polystyrol/Poly(4-vinylpyridin)-Blockcopolymer ist.

6. Verfahren gemäß einem der Ansprüche 2 bis 5, wobei das amphiphile Molekül aus der Gruppe ausgewählt ist, welche aus 3-Pentadecylphenol und 2-(4'-Hydroxyphenylazo)benzoesäure besteht.

7. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei das Templat umfassend den Vorläufer zur Bildung der porösen Kohlenstoffstruktur auf mehr als 600 °C, bevorzugt auf 900 °C erwärmt wird, um den Vorläufer zur Bildung der porösen Kohlenstoffstruktur zu karbonisieren und um das Templat zu entfernen.

8. Verfahren gemäß Anspruch 1, wobei die anorganischen Oxidteilchen mit einer bimodalen Teilchengrößenverteilung Siliciumdioxid, Titandioxid, Aluminiumoxid, Vanadium(V)-oxid oder Zinkoxid sind, wobei insbesondere die anorganischen Oxidteilchen mit einer bimodalen Teilchenverteilung Siliciumdioxidteilchen sind.

9. Verfahren gemäß einem der Ansprüche 1 oder 8, wobei das Templat Teilchen mit einer Größe von 100 nm oder weniger und Teilchen mit einer Größe von 500 nm oder mehr umfasst, wobei bevorzugt das Templat anorganische Oxidteilchen mit einer Größe von 60 nm oder weniger und Teilchen mit einer Größe von 1 µm oder mehr umfasst.

10. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei der Vorläufer zur Bildung der porösen Kohlenstoffstruktur ein vernetztes Formaldehyd-Phenol-Harz ist, das durch Füllen von mindestens einem Teil der Hohlräume des Templats mit einem Ausgangsmaterial zur Herstellung des vernetzten Formaldehyd-Phenol-Harzes und Vernetzen des Ausgangsmaterials zur Herstellung des vernetzten Formaldehyd-Phenol-Harzes gebildet wird.

11. Verfahren gemäß Anspruch 10, wobei das Templat auf 60 bis 110 °C erwärmt wird, um das vernetzte Formaldehyd-Phenol-Harz aus dem Ausgangsmaterial zur Herstellung des vernetzten Formaldehyd-Phenol-Harzes zu bilden.

55 Revendications

1. Procédé de préparation d'une structure de carbone poreuse comprenant les étapes suivantes consis-

tant à :

- a) fournir une matrice comprenant des vides,
- b) remplir au moins certains des vides d'un précurseur pour la formation de la structure de carbone poreuse,
- c) carboniser le précurseur pour la formation de la structure de carbone poreuse et
- d) retirer au moins une partie de la matrice,

dans lequel la matrice comprend un mélange de particules d'oxyde inorganique ayant une distribution granulométrique bimodale qui sont au moins partiellement retirées à l'étape d) par gravure avec un acide ou une base convenable, comprenant de préférence de l'acide fluorhydrique (HF), et où la matrice comprend des vides entre les particules, où les particules d'oxyde inorganique ont un diamètre inférieur ou égal à 100 nm et un diamètre supérieur ou égal à 500 nm, où le retrait partiel de particules bimodales à l'étape d) retire les particules de plus petite taille et ne grave que partiellement les particules de plus grande taille pour créer des sites d'adsorption pour les polysulfures.

2. Procédé selon la revendication 1 comprenant les étapes suivantes consistant à :

- a) fournir une solution comprenant un solvant, un copolymère à blocs et une molécule amphiphile,
- b) produire un corps par évaporation du solvant,
- c) retirer des molécules amphiphiles pour produire une matrice comprenant des vides,
- d) remplir au moins certains des vides d'un précurseur pour la formation de la structure de carbone poreuse,
- e) carboniser le précurseur pour la formation de la structure de carbone poreuse et retirer le copolymère à blocs par chauffage,

où le copolymère à blocs comprend des motifs polymères d'au moins un monomère lipophile et des motifs polymères d'au moins un monomère hydrophile.

3. Procédé selon la revendication 2 dans lequel à l'étape c) les molécules amphiphiles sont retirées par trempage du corps produit à l'étape b) dans un solvant, de préférence dans un mélange éthanol/eau ou méthanol/eau.

4. Procédé selon la revendication 2 ou 3 dans lequel

- le monomère hydrophile comprend au moins un groupe fonctionnel choisi dans le groupe constitué d'un atome d'azote avec une paire

d'électrons célibataires, d'un atome d'oxygène avec deux paires d'électrons célibataires et d'un atome de fluor et la molécule amphiphile comprend au moins un groupe fonctionnel choisi dans le groupe constitué de N-H et -O-H

ou
- la molécule amphiphile comprend au moins un groupe fonctionnel choisi dans le groupe constitué d'un atome d'azote avec une paire d'électrons célibataires, d'un atome d'oxygène avec deux paires d'électrons célibataires et d'un atome de fluor et le monomère hydrophile comprend au moins un groupe fonctionnel choisi dans le groupe constitué de N-H et -O-H.

- 5. Procédé selon l'une des revendications 2 à 4, dans lequel le copolymère à blocs est un copolymère à blocs polystyrène-poly(4-vinylpyridine).
- 6. Procédé selon l'une des revendications 2 à 5, dans lequel la molécule amphiphile est choisie dans le groupe constitué par le 3-pentadécylphénol et l'acide 2-(4'-hydroxyphénylazo) benzoïque.
- 7. Procédé selon l'une des revendications précédentes, dans lequel la matrice comprenant le précurseur pour la formation de la structure de carbone poreuse est chauffé à une température supérieure à 600°C, de préférence à 900°C pour carboniser le précurseur pour la formation de la structure de carbone poreuse et pour retirer la matrice.
- 8. Procédé selon la revendication 1 dans lequel les particules d'oxyde inorganique ayant une distribution granulométrique bimodale sont le dioxyde de silicium, le dioxyde de titane, l'oxyde d'aluminium, l'oxyde de vanadium (V) ou l'oxyde de zinc, en particulier dans lequel les particules d'oxyde inorganique ayant une distribution de particules bimodale sont des particules de dioxyde de silicium.
- 9. Procédé selon l'une des revendications 1 ou 8, dans lequel la matrice comprend des particules d'une taille inférieure ou égale à 100 nm et des particules d'une taille supérieure ou égale à 500 nm, de préférence dans lequel la matrice comprend des particules d'oxyde inorganique d'une taille inférieure ou égale à 60 nm et des particules d'une taille supérieure ou égale à 1 µm.
- 10. Procédé selon l'une des revendications précédentes, dans lequel le précurseur pour la formation de la structure de carbone poreuse est une résine formaldéhyde-phénol réticulée, qui est formée en remplissant au moins certains des vides de la matrice d'une matière première pour la préparation de la résine formaldéhyde-phénol réticulée et en réticulant la matière première pour la préparation de la résine

formaldéhyde-phénol réticulée.

11. Procédé selon la revendication 10, dans lequel la matrice est chauffée à une température de 60 à 110°C pour former la résine formaldéhyde-phénol réticulée à partir de la matière première pour la préparation de la résine formaldéhyde-phénol réticulée.

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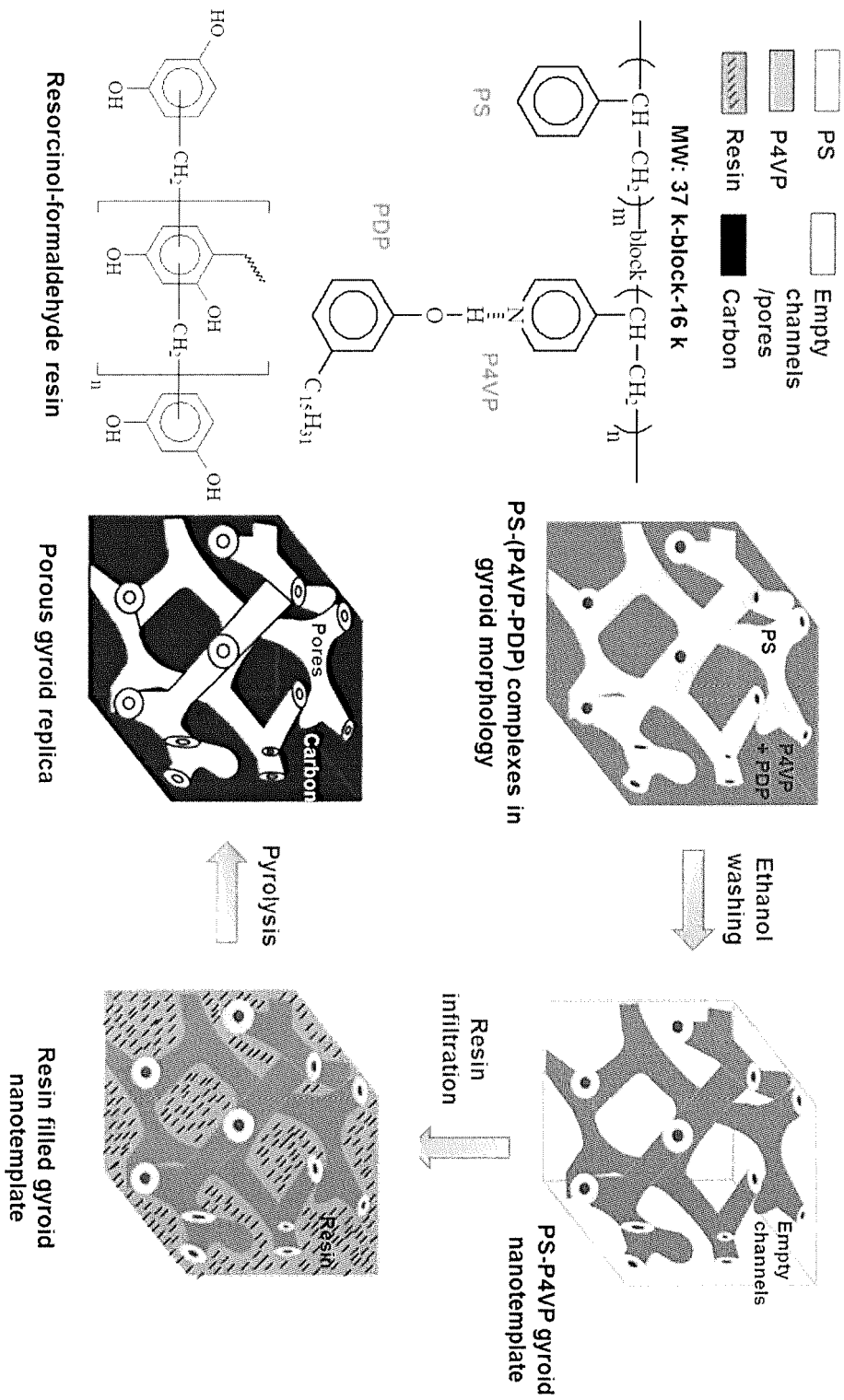


Figure 1

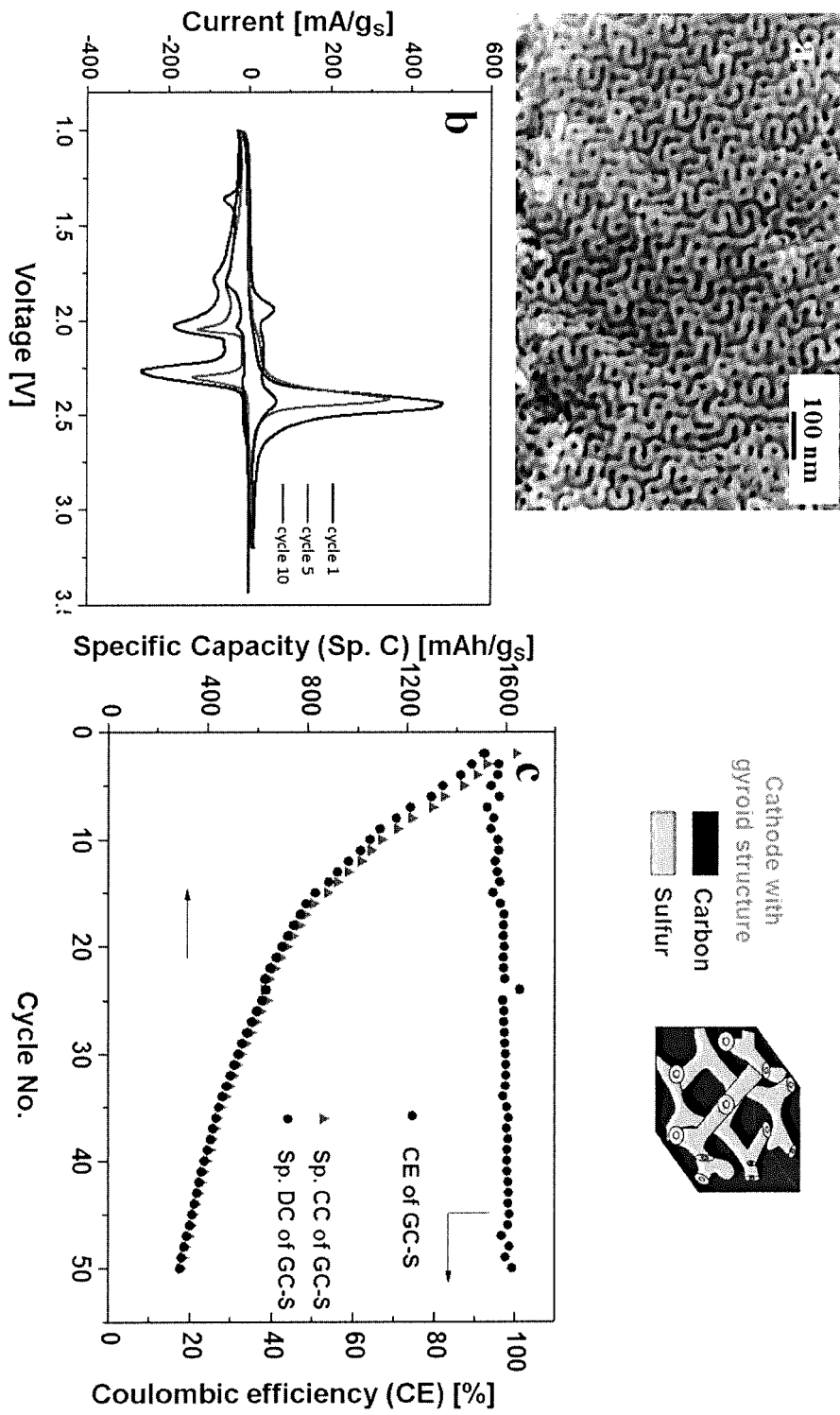


Figure 2

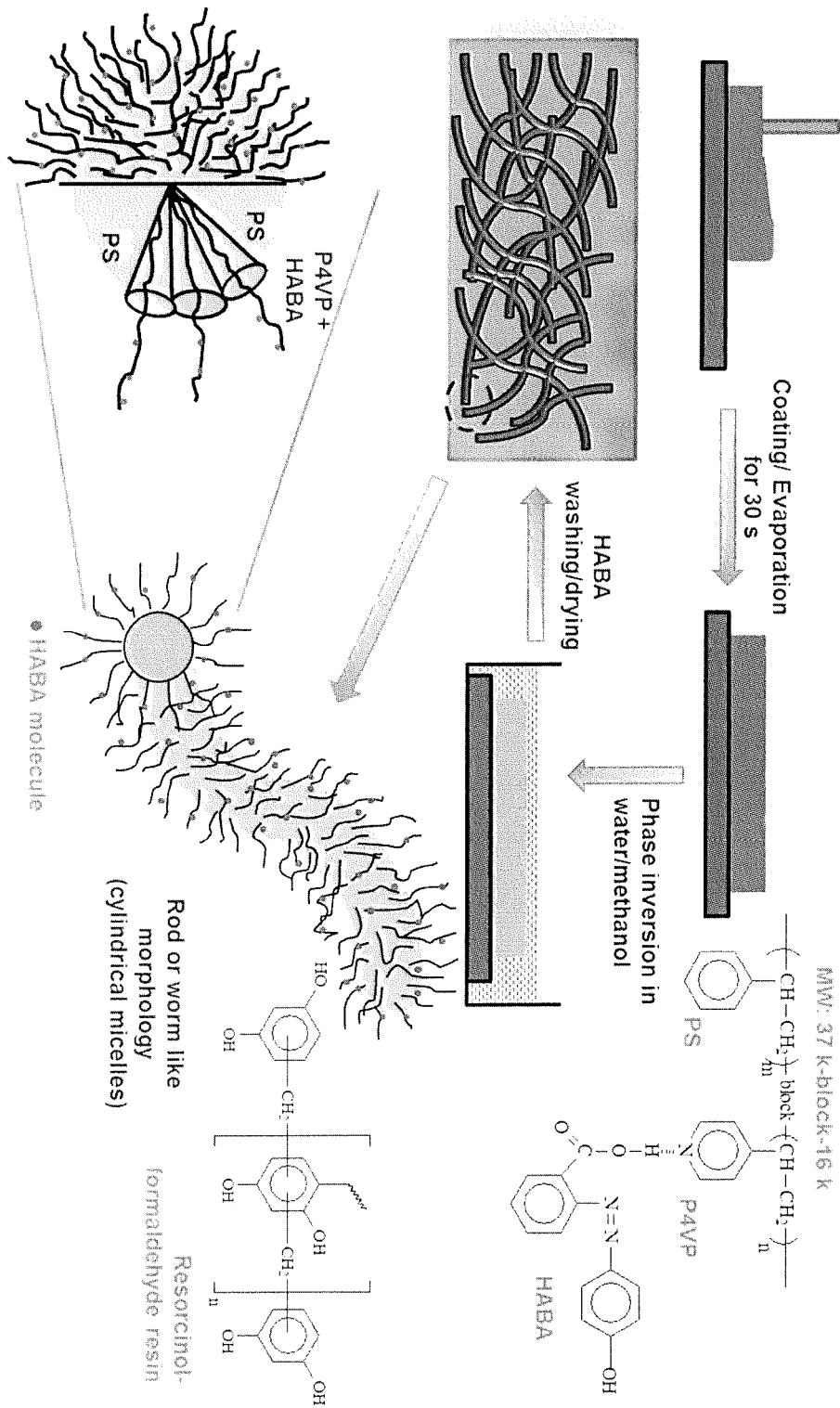


Figure 3

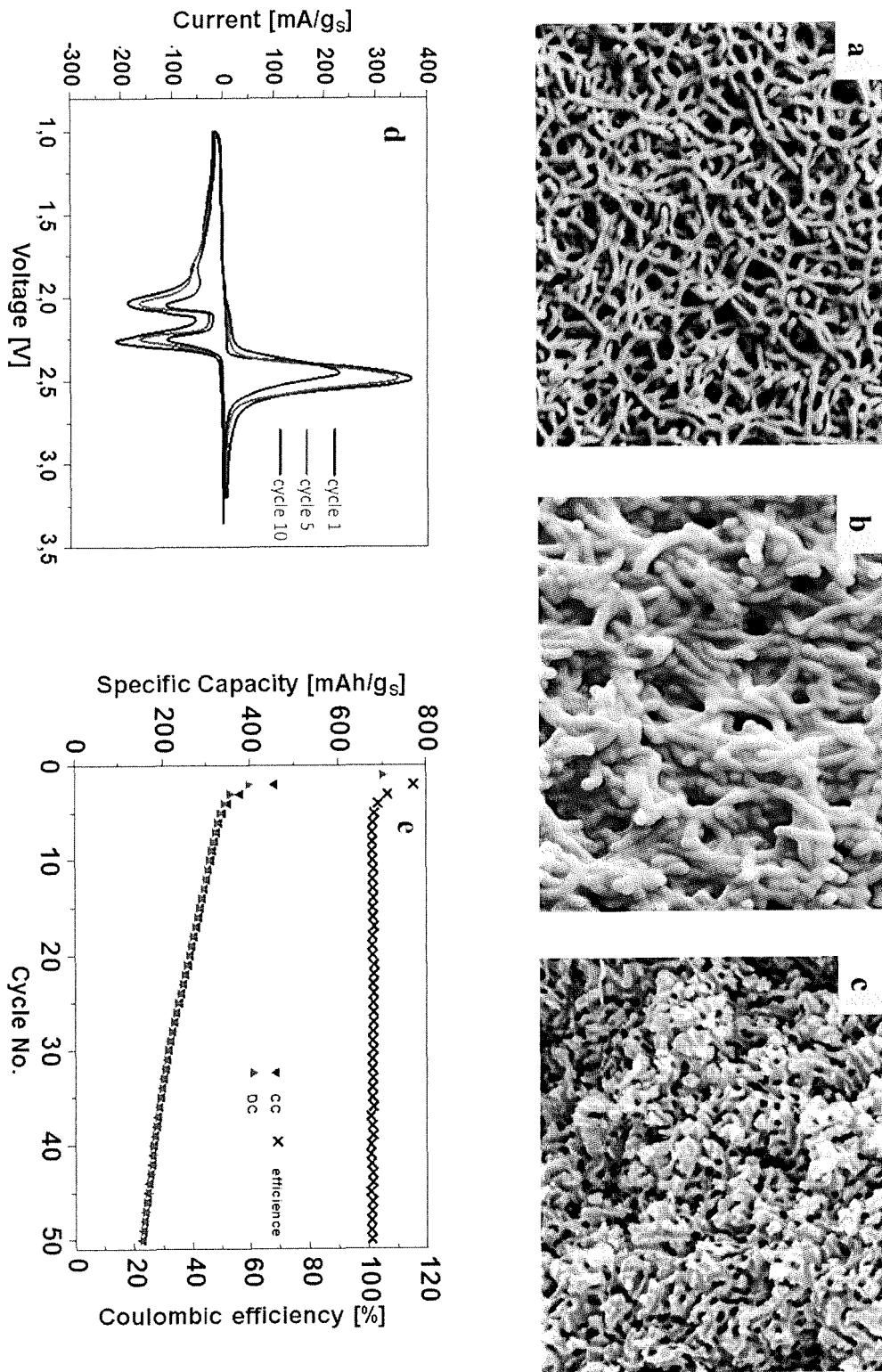


Figure 4

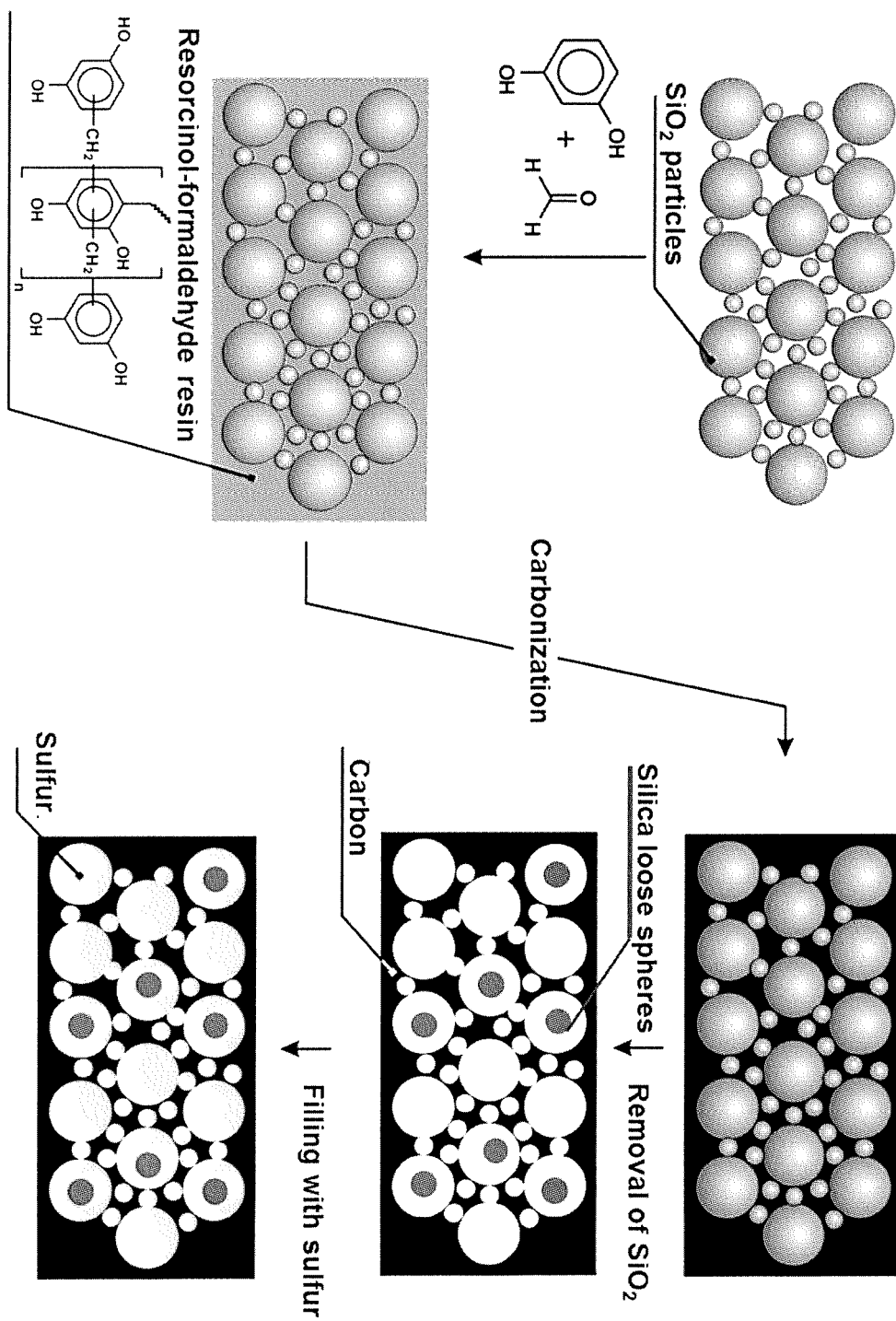


Figure 5

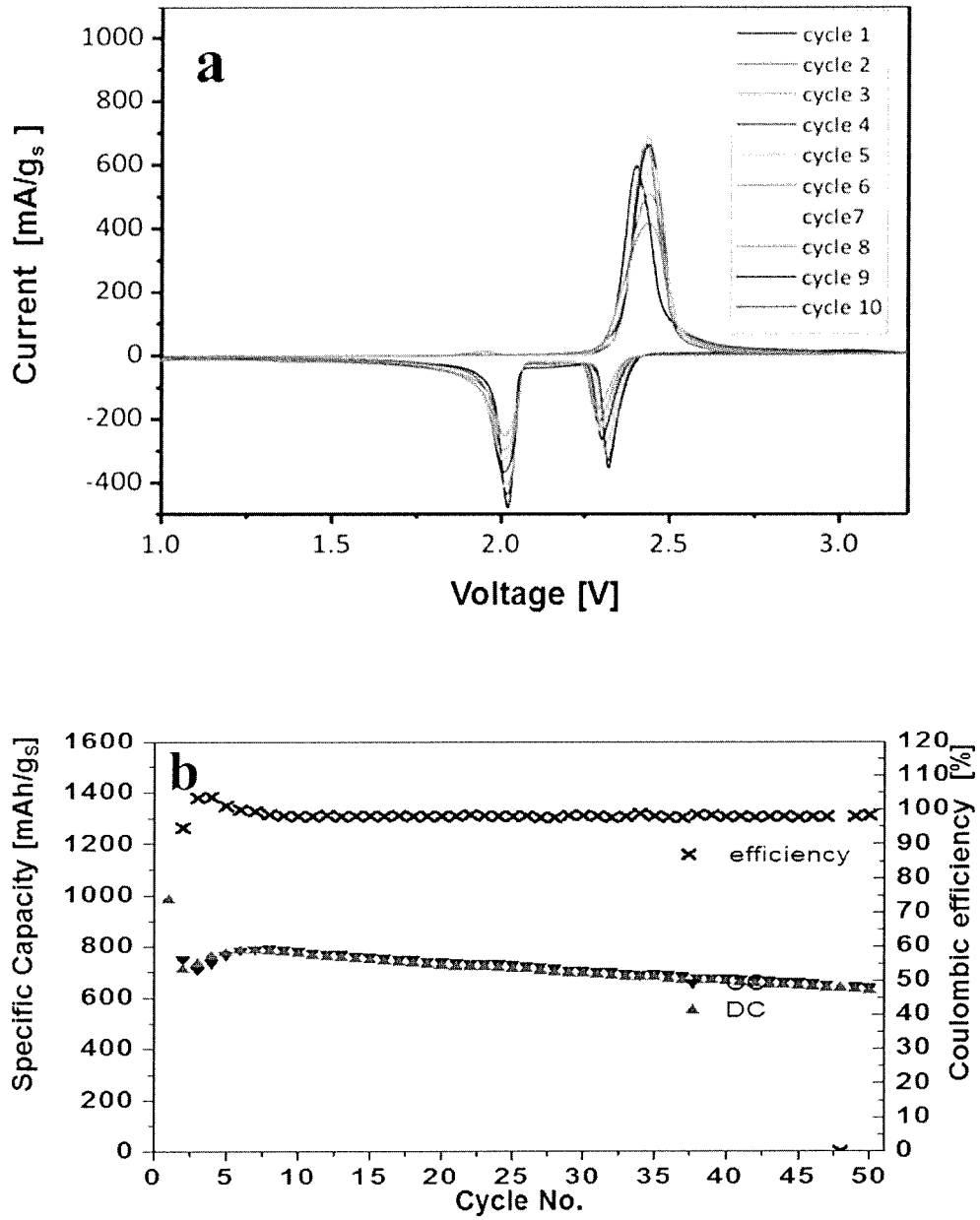


Figure 6

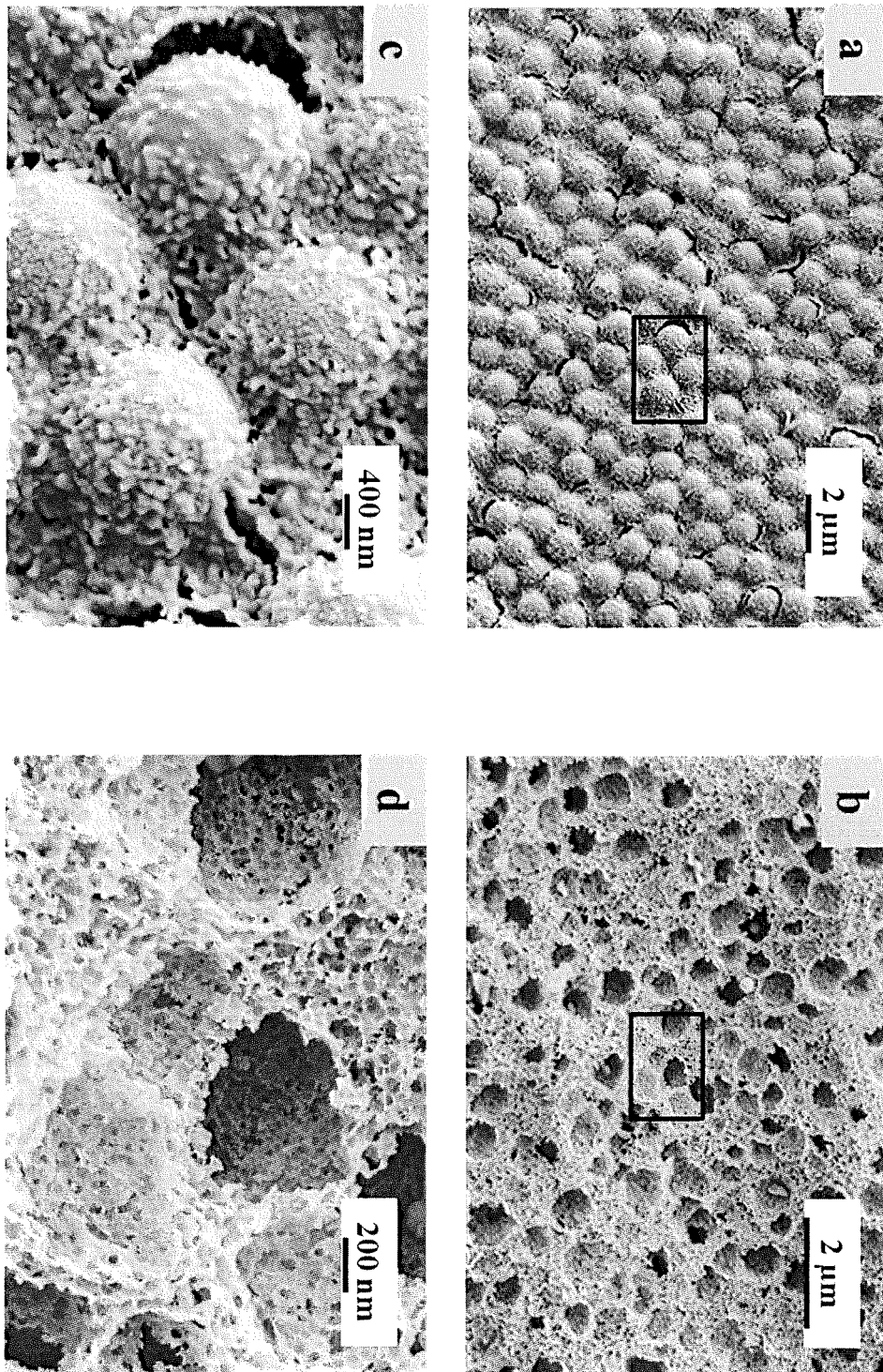


Figure 7

REFERENCES CITED IN THE DESCRIPTION

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