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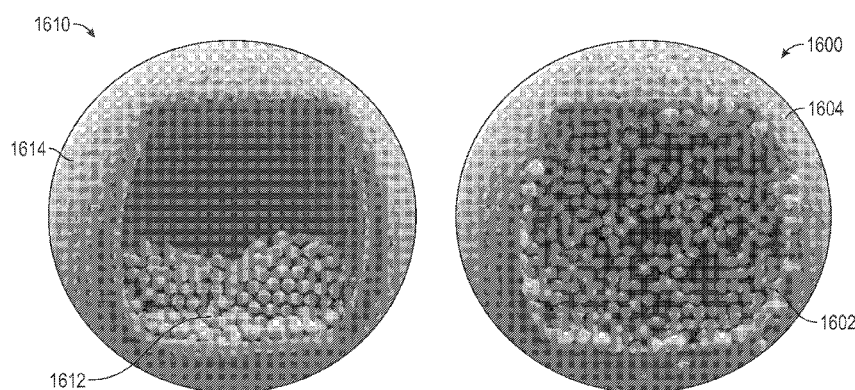


FIG. 16

(57) Abstract: A silicon-carbon composite particle based material is shown. In one example, the silicon-carbon composite particle based material is used as an electrode in a battery, such as a lithium ion battery.



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SILICON CARBON COMPOSITE ELECTRODE AND METHOD

Cross Reference to Related Applications

[001] This application claims the benefit of priority to U.S. Patent Provisional Application No. 62/517,161, filed on June 9, 2017, which is incorporated by reference herein in its entirety.

Technical Field

[002] This invention relates to silicon-carbon composite material microstructures and methods. In one example, this invention relates to silicon-carbon composite anodes for lithium ion batteries.

Background

[003] Improved electrical devices, such as lithium ion batteries are desired. One example of a battery structure that can be improved is an anode structure.

Brief Description of the Drawings

[004] FIG. 1 shows the cycle stability and coulombic efficiency (CE) of SiNPs@C_{PS} at lithiation-delithiation rates of 1/10 C, 1/3 C, 1 C, and 2 C according to an example of the invention.

[005] FIG. 2 shows the representative lithiation-delithiation curves at 1/10 C, demonstrating a stable potential profile according to an example of the invention.

[006] FIG. 3 shows cycling stability and CE of the graphite-SiNPs@C_{HD} anodes under 250 mA g⁻¹ and 500 mA g⁻¹ according to an example of the invention.

[007] FIG. 4 shows representative lithiation-delithiation voltage profiles of the graphite-SiNPs@C_{HD} anode at 250 mA g⁻¹ vs. Li⁺/Li according to an example of the invention.

[008] FIG. 5 shows TGA of C₁₂H₂₅-SiNPs (black), SiNPs@C_{PS} (red), and SiNP@C_{HD} (blue) in a dry-air environment. The Si content of C₁₂H₂₅-SiNPs was calculated to be 86.5 %, considering that the surface alkyl chain entirely decomposed at around 400 °C. The SiNPs@C composites were assumed to be fully

oxidized to SiO₂ after total oxidization of the carbon content in air at 800 °C. The Si content of SiNPs@CPS and SiNP@CHD were calculated to be 35 wt.% and 46 wt.%, respectively.

[009] FIG. 6 shows N₂ adsorption-desorption isotherms of SiNPs@CPS and SiNPs@CHD. Both SiNPs@CPS and SiNPs@CHD composites show type-IV curves, demonstrating the presence of mesopores. The H₂ hysteresis of the SiNPs@CPS composite indicates the particle-packing structure, while the H₄ hysteresis of SiNPs@CHD composite indicates the layer structure.

[0010] FIG. 7 shows Calculated BET specific surface area and pore volume of SiNPs@CPS and SiNPs@CHD according to an example of the invention.

[0011] FIG. 8 shows cycle stability and CE at 100 mAh g⁻¹ according to an example of the invention.

[0012] FIG. 9 shows CV at 0.1 mV s⁻¹ of the pure SiNPs according to an example of the invention.

[0013] FIG. 10 shows N₂ adsorption-desorption isotherms according to an example of the invention.

[0014] FIG. 11 shows TGA analysis of the SiNPs@CHD after CVD carbon coating according to an example of the invention. The Si content of the composite was calculated to be 44.5 wt.%, with a slight decrease compared to that of the uncoated SiNPs@CHD (46 wt.%).

[0015] FIG. 12 shows cycle stability of the graphite anode under 100 mA g⁻¹ current density according to an example of the invention.

[0016] FIG. 13 shows XRD patterns of SiNPs, SiNPs@CPS, and SiNPs@CHD according to an example of the invention.

[0017] FIG. 14 shows a battery according to an example of the invention.

[0018] FIG. 15 shows a method of forming a material according to an example of the invention.

[0019] FIG. 16 shows silicon-carbon composite particles according to an example of the invention.

Detailed Description

[0020] In the following detailed description, reference is made to the accompanying drawings which form a part hereof, and in which is shown, by way of illustration, specific embodiments in which the invention may be practiced. In the drawings, like numerals describe substantially similar components throughout the several views. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, or logical changes, etc. may be made without departing from the scope of the present invention.

[0021] Colloidal routes to synthesize silicon and carbon (silicon@carbon) composites are shown. Surface-functionalized Si nanoparticles (SiNPs) dissolved in styrene and hexadecane, respectively, are used as the dispersed phase in oil-in-water emulsions, from which yolk-shell and dual-shell hollow SiNPs@C composites are produced via polymerization and subsequent carbonization. Evaluated as anode materials for lithium-ion (Li-ion) batteries, the synthesized SiNPs@C composites demonstrate excellent cycling stability and rate performance, which is ascribed to the uniform distribution of SiNPs within the carbon hosts. The Li-ion anodes composed of 46 wt.% of dual-shell SiNPs@C, 46 wt.% of graphite, 5 wt.% of acetylene black, and 3 wt.% of carboxymethyl cellulose binder with $> 3 \text{ mg cm}^{-2}$ areal loading achieve an overall specific capacity of $> 600 \text{ mAh g}^{-1}$, which shows $> 100\%$ improvement from the pure graphite anode and additionally demonstrates high first cycle coulombic efficiency and stable cyclability. These new colloidal routes present a promising general method to produce viable Si-C composites for Li-ion batteries.

[0022] Silicon (Si) is recognized as the most promising anode material to replace or complement graphite in lithium-ion (Li-ion) batteries. However, the large volume change associated with lithiation-delithiation of Si causes significant challenges to practical Si-based anodes. Although particle pulverization may no longer be the primary problem attributed to the utilization of Si of nano-size or with nano-features, repeated volume change can degrade the electrical contact and destabilize the solid electrolyte interphase (SEI) in the electrodes. Therefore,

composite materials with Si primary particles incorporated into secondary structures, particularly Si-carbon composites, are one method to accommodate the impact of Si volume change. For Si-C composites, the Si particles are small with narrow size distribution to minimize the absolute dimensional change. The Si particles may be uniformly dispersed in the carbon structure to achieve homogeneous lithiation-delithiation. In addition, certain porosity of the carbon framework is desirable to maintain the overall dimensional stability during lithiation-delithiation.

[0023] Si-C composites with various nanostructures including yolk-shell Si-C, pomegranate-like Si-C¹⁴, sandwich-structured Si-graphene oxide, graphene or carbon coated silicon nanoparticles or nanowires, are demonstrated having excellent electrochemical performance. Incorporating Si into a carbon matrix does indeed improve the structural and electrical integrity of the Si-C composites. However, many synthetic methods face challenges in the uniform dispersal of the primary Si particles due to their poor solubility in any solvent. The present disclosure shows a unique colloidal method to synthesize Si@C composites using Si nanoparticles (SiNPs) that are soluble in organic solvents. Using a scalable non-thermal plasma synthetic method, we synthesized SiNPs with a hydrogen-terminated surface and an average particle size of ~10 nm with a narrow size distribution. Enabled by the surface -H, dodecyl chains (-C₁₂H₂₅) are tethered onto the SiNP surface upon reaction with dodecane. The obtained C₁₂H₂₅-SiNPs becomes readily soluble in many organic solvents. In one example, the Si content in C₁₂H₂₅-SiNPs is 86.5 wt.% as measured with thermogravimetric analysis (TGA, Figure 5). In one example, to synthesize the SiNPs@C composite, C₁₂H₂₅-SiNPs are first dissolved in styrene, and the obtained solution was dispersed in the aqueous solution of hexadecyltrimethylammonium bromide by sonication to form a stable emulsion. Free radical emulsion polymerization is then initiated to produce a colloid of SiNPs@polystyrene (SiNPs@PS) particles dispersed in water. The SiNPs@PS particles are subsequently coated with a layer of resorcinol-formaldehyde resin (RF) via a seeded sol-gel synthesis followed by carbonization to produce the SiNPs@C composite denoted as SiNPs@Cps.

[0024] In one example, SiNPs are enclosed in thin (~10 nm) carbon shells. A yolk-shell structure of the individual SiNPs@Cps particle 1602, are illustrated in a schematic composite particle 1610 as shown in Figure 16. The yolk-shell structure originated from the formation of SiNPs@PS particles in the emulsion polymerization: The droplets of styrene becomes more viscous during polymerization while the solubility of C₁₂H₂₅-SiNPs in the droplets decreased, leading to phase separation (i.e. SiNPs aggregated and separated from PS). As a result, the synthesized SiNPs@PS particle attained a Janus morphology with clear separation of the SiNPs aggregation on one side of the particle (1610 as illustrated schematically in Figure 16). The PS portion of the Janus particles underwent decomposition during the carbonization of SiNPs@PS@RF, thus resulting in the yolk-shell SiNPs@Cps. In one example, the specific surface area of the SiNPs@Cps composite was 437 m² g⁻¹ with a pore volume of 0.45 cm³ g⁻¹ from the N₂ adsorption-desorption isotherms analysis (Figure 6 and the Table in Figure 7); the Si content in the SiNPs@Cps composite was measured as 35 wt.% (Figure 5).

[0025] The Li-ion anode performance of the SiNPs@Cps composite was evaluated in a half-cell configuration with Li as the counter electrode. Figure 1 shows the cycle stability and coulombic efficiency (CE) of SiNPs@Cps at lithiation-delithiation rates of 1/10 C, 1/3 C, 1 C, and 2 C (1 C is defined as 1 A g⁻¹ with respect to the mass of SiNPs@Cps, which is 85 wt.% of the electrode). Despite the low CE in the first cycle (43% at 1/10 C, 41% at 1/3 C, 30% at 1 C, and 30% at 2 C), the reversible capacities were stabilized after the second cycle. After 200 cycles, the remaining lithiation capacities were 740 mAh g⁻¹ at 1/10 C, 678 mAh g⁻¹ at 1/3 C, 615 mAh g⁻¹ at 1 C, and 560 mAh g⁻¹ at 2 C, and the corresponding capacity retentions were 77% (vs. 2nd cycle at 1/10 C), 78% (vs. 2nd cycle at 1/3 C), 92% (vs. the highest capacity at 1 C), and 96% (vs. the highest capacity at 2 C). Figure 2 displays the representative lithiation-delithiation curves at 1/10 C, demonstrating a stable potential profile. The cycle stability of the SiNPs@Cps composite is significantly improved from that of pure SiNPs (Figure 8), which can be attributed to the yolk-shell structure accommodating the volume change of Si. However, the initial CE is low, likely due to the SEI formation promoted by the relatively high

specific surface area. The Si content is limited by the solubility of $C_{12}H_{25}$ -SiNPs in styrene. Furthermore, the aggregation of SiNPs inside the carbon shell is not the ideal particle distribution, which could be responsible for the capacity fading during the cycling.

[0026] To improve the performance of the SiNPs@C composite, a modified colloidal method was developed. Instead of styrene, hexadecane (HD) was used to dissolve $C_{12}H_{25}$ -SiNPs and as the dispersed phase in the oil-in-water emulsion. Resorcinol and formaldehyde were subsequently dissolved into the emulsion, followed by adding ammonium hydroxide to initiate the sol-gel formation of RF on the surface of the droplets of the HD solution of $C_{12}H_{25}$ -SiNPs. The synthesized SiNPs-in-HD@RF particles were extracted and carbonized to produce the SiNPs@C composite denoted as SiNPs@CHD. Schematic composite particle 1600 in Figure 16 shows the microstructure of SiNPs@CHD composed of fused hollow carbon spheres encapsulating SiNPs. Elemental mapping reveals a dual-shell hollow structure of the individual SiNPs@CHD particle with SiNPs uniformly coated on an inner wall of the carbon shell 1604, which is clearly different from the yolk-shell structure of SiNPs@CPS 1610. The formation of the dual-shell hollow structure is attributed to the use of SiNPs-in-HD droplets as the template for RF coating in the colloidal synthesis: each droplet remained as a homogenous solution of SiNPs without aggregation during the sol-gel RF coating process. Upon evaporation of HD, SiNPs were uniformly coated on the inner wall of the RF shell, which retained its structure after carbonization.

[0027] Not only is the morphology improved by the modified route, but the specific surface area and pore volume of SiNPs@CHD are also reduced to $317 \text{ m}^2 \text{ g}^{-1}$ and $0.23 \text{ cm}^3 \text{ g}^{-1}$ (Figure 7). Furthermore, the Si content is enhanced to 46 wt.% due to the higher solubility and stability of $C_{12}H_{25}$ -SiNPs in HD (Figure 5). The electrochemical performance of the SiNPs@CHD composite was evaluated under the same conditions as those used to test SiNPs@CPS. Figures 1 and 2 demonstrate the unambiguously improved performance of SiNPs@CHD compared to SiNPs@CPS in parameters including capacity, CE, and cycle stability. The CE in the first cycle is 49% at 1/10 C, 47% at 1/3 C, 44% at 1 C, and 36% at 2 C. Although these CEs are

still modest, it is a considerable improvement from those of SiNPs@Cps. It is worth noting that the CEs of SiNPs@CHD during prolonged cycling is also improved from those of SiNPs@Cps. The lithiation capacity at the second cycle are 1074 mAh g⁻¹ at 1/10 C, 786 mAh g⁻¹ at 1/3 C, 410 mAh g⁻¹ at 1 C, and 385 mAh g⁻¹ at 2 C, which are all higher than those of SiNPs@Cps. Finally, the capacity retention is significantly improved: the remaining lithiation capacities after 200 cycles are 980 mAh g⁻¹ at 1/10 C, 763 mAh g⁻¹ at 1/3 C, 512 mAh g⁻¹ at 1 C, and 511 mAh g⁻¹ at 2 C, corresponding to 92% (vs. 2nd cycle at 1/10 C), 97% (vs. 2nd cycle at 1/3 C), 95% (vs. highest at 1 C) and 93% (vs. highest at 2 C) retentions.

[0028] The most realistic application of Si-based composites is their use as additives to conventional graphite anodes to boost their capacities. Therefore, the SiNPs@CHD composite was further evaluated in an electrode composed of 46 wt.% of SiNPs@CHD, 46 wt.% of commercial graphite, 5 wt.% of acetylene black, and 3% of carboxymethyl cellulose binder, with the mass loading of the active materials (SiNPs@CHD + graphite) > 3 mg cm⁻². It is worth noting that a very thin carbon layer was coated on the SiNPs@CHD via chemical vapor deposition (CVD) prior to the electrode's fabrication. The CVD carbon coating significantly reduced the specific surface area of SiNPs@CHD to 13 m² g⁻¹ with a slight decrease of the Si content to 44.5 wt.% (Figure 10). In one example, the SiNPs@CHD composite has a flake-like secondary structure composed of fused SiNPs@CHD particles. In one example, the graphite-SiNPs@CHD anode includes the primary material and the secondary flake like structure that are uniformly stacked together with a total thickness of about 50-60 μm. The graphite-SiNPs@CHD anodes demonstrate reversible capacity of 600 mAh g⁻¹ (3.1 mg cm⁻² loading) under a current density of 250 mA g⁻¹ and 450 mAh g⁻¹ (4.5 mg cm⁻² loading) under a current density of 500 mA g⁻¹, with corresponding CEs of 74% and 72% in the first cycle. Compared to the specific capacity of 292 mAh g⁻¹ obtained from the pure graphite anode with comparable loading (Figure 12), the capacity shows an increase of over 100% with the addition of the SiNPs@CHD composite. The graphite-SiNPs@CHD anode under 250 mA g⁻¹ current density displays excellent capacity retention, demonstrated by the stable lithiation-delithiation voltage profile at various cycles in Figure 4.

[0029] In summary, we developed unique colloidal routes to synthesize SiNPs@C composite materials. The surface functionalization of the SiNPs' surface with long alkyl chains renders good solubility in organic solvents, thus enabling oil-in-water emulsions with SiNPs dissolved in the dispersed phase. Sol-gel polymerization of RF resin in the emulsions can encapsulate the dispersed phase containing the SiNPs, from which SiNPs@C composites can be obtained via carbonization. We studied PS (hard template) from *in situ* polymerization of styrene and HD (soft template) as the dispersed phase in the colloidal synthesis. The results clearly show that the SiNPs@C from the soft template route demonstrates superior performance as the anode material for Li-ion batteries due to the more uniform SiNPs distribution in the composite. As the additive to the conventional graphite anode, this SiNPs@C composite could significantly improve the overall specific capacity with relatively high areal loading of active materials. The promising performance of the SiNPs@C composites are strong evidence that the colloidal synthesis based on soluble SiNPs can be a viable method by which to produce practical Si-based anode materials for Li-ion batteries. However, the low CE remains the most significant challenge of the reported SiNPs@C composites, although CVD carbon coating appears a viable approach to reducing the high surface area. Future investigation will focus on optimizing the secondary carbon structure to minimize the surface area, and more emphasis will be put on the design and fabrication of graphite-SiNPs@C composite anodes.

Experimental Procedures

[0030] Synthesis of SiNPs and surface functionalization: The SiNPs were synthesized using a radio-frequency induced non-thermal plasma technique, and the dodecyl chains were grafted onto the surface of SiNPs via a reflux reaction. In brief, 300 mg SiNPs were transferred to a round-bottom flask within a glove box and then dispersed in a solution of 1-dodecane in mesitylene (1:4 volume ratio) under ultrasonication for 15 min. The grafting reaction took place through a reflux process with Ar protection at 165 °C for 4 h till the color of the solution changed to a

translucent dark brown. After that, the surface functionalized particles $C_{12}H_{25}$ -SiNPs were collected by rotary evaporation.

[0031] Synthesis of the SiNPs@Cps composite (hard-template route): In a typical experiment, 200 mg of the $C_{12}H_{25}$ -SiNPs, 200 μ L HD and 0.011 g azobisisobutyronitrile (AIBN) were co-dissolved in 1 mL styrene. The solution was then mixed into a 30 mL H_2O solution of 1 mM hexadecyltrimethylammonium bromide (CTAB) with probe sonication to form a stable emulsion. The emulsion was heated at 60 °C to initiate the free radical polymerization of polystyrene under agitation. The reaction was kept at 60 °C for 8 h to obtain the colloid containing SiNPs@PS Janus particles. To coat RF on SiNPs@PS, the as-prepared SiNPs@PS dispersion was diluted by adding 30 mL water, after which it was mixed with 0.1 mL ammonium hydroxide (28 wt.% NH_3 in H_2O), 0.2 g resorcinol, and 0.28 mL formaldehyde solution (37 wt.% in H_2O). The mixture was further stirred for 16 hours at room temperature. The SiNPs@PS@RF was extracted from the colloid via freeze-drying and was heated at 800 °C for 3 h in Ar to produce the SiNPs@Cps composite.

[0032] Synthesis of the SiNPs@CHD composite (soft-template route): In a typical experiment, 200 mg $C_{12}H_{25}$ -SiNPs was first dissolved in 600 μ L HD. The obtained HD solution was dispersed in a 30 mL water solution of 1 mM CTAB with sonication to form a uniform oil-in-water emulsion. 0.1 mL ammonium hydroxide (28 wt.% NH_3 in H_2O), 0.05 g resorcinol, and 0.07 mL formaldehyde (37 wt.% in H_2O) were dissolved into the obtained emulsion to coat the SiNPs-in-HD droplets with RF. The mixture was stirred for 16 hours at room temperature. The final product was collected via freeze-drying and carbonized at 800 °C for 3 h in Ar to produce the SiNPs@CHD composite.

[0033] Carbon coating SiNPs@CHD composite via CVD: CVD carbon coating was performed by flowing acetylene gas at 15 sccm through a 1-inch diameter, 20-inch long quartz reactor. The system was heated up to 650 °C and held at a pressure of ~380 Torr for 15 min. After that, the reactor was naturally cooled

down to room temperature, and the chamber was refilled with pure Ar in order to remove the sample without abruptly pressurizing the chamber.

[0034] Characterizations: The morphology and microstructures of the SiNPs@C composites and electrodes were characterized with scanning electron microscopy (Nova NanoSEM 450) and transmission electron microscopy (Tecnai 12 and Titan Themis 300 STEM). The crystallinity of the SiNPs in the obtained SiNPs@C composites were analyzed using X-ray diffraction (XRD, PANalytical EMPYREAN) with a CuK α source (Figure 13). TGA was conducted with a TA Instrument analyzer (Q 500) at a heating rate of 10 °C min⁻¹ from room temperature to 800 °C. The high temperature was held for 60 min in dry air. N₂ adsorption-desorption was performed with an ASAP 2020 instrument. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method.

[0035] Electrochemical Measurements: The SiNPs@C anode slurry was prepared by mixing the SiNPs@C composites, acetylene black, and CMC binder in a weight ratio of 85: 10: 5 in deionized water. The homogeneous slurry was pasted onto the carbon-coated copper foil and then vacuum dried at 110 °C overnight. The SiNPs@C composite load was approximately 1.0 mg cm⁻². Lithium foil was used as the counter electrode and a Celgard 2400 membrane was used as the separator. The electrolyte was 1.0 M LiPF₆ in ethylene carbonate/diethyl carbonate (1:1 volume ratio). The 2032 coin cells were assembled in an argon-filled glove box. The electrochemical lithiation-delithiation were carried on an Arbin battery test station, and CV was conducted on a Gamry Interface 1000 with a scan rate of 0.1 mV s⁻¹. To prepare the graphite-SiNPs@CHD anodes, aqueous slurry consisting of carbon-coated SiNPs@CHD composite, graphite (artificial graphite powder from MTI Inc.), acetylene black, and carboxymethyl cellulose binder with weight ratio of 46: 46: 5: 3 was pasted onto the copper current collector and then dried in a vacuum oven at 110 °C overnight. The mass loading of active materials (graphite+SiNPs@CHD) was > 3.0 mg cm⁻². The cycling performance of the anodes was evaluated using a protocol with constant-current-constant-voltage (CCCV) lithiation (charging in full battery) and constant-current delithiation (discharging in full battery). The CCCV lithiation was used to overcome the lithiation potential difference between graphite

and Si; a constant current was applied until the potential dropped to 0.02 V vs. the Li counter electrode, and the potential was subsequently maintained at 0.02 V for 3h.

[0036] Figure 14 shows an example of a battery 1400 according to an embodiment of the invention. The battery 1400 is shown including an anode 1410 and a cathode 1412. An electrolyte 1414 is shown between the anode 1410 and the cathode 1412. In one example, the battery 1400 is a lithium-ion battery. In one example, the anode 1410 is formed from one or more silicon-carbon composite particles as described in examples above. In one example, although the invention is not so limited, the battery 1400 is formed to comply with a 2032 coin type form factor.

[0037] Figure 15 shows an example method of forming according to an embodiment of the invention. In operation 1502, a hydrogen terminated surface is formed on a plurality of silicon nanoparticles. In operation 1504, a plurality of hydrocarbon chains are tethered onto the hydrogen terminated surface to form coated silicon nanoparticles. In operation 1506, the coated silicon nanoparticles are dissolved in a solvent. In operation 1508, the solvent and silicon nanoparticles are mixed with an aqueous medium and emulsifying to form silicon nanoparticle droplets. In operation 1510, the silicon nanoparticle droplets are carbonized to form a plurality of silicon-carbon composite particles.

[0038] To better illustrate the method and apparatuses disclosed herein, a non-limiting list of embodiments is provided here:

[0039] Example 1 includes a silicon-carbon composite material, including a number of hollow shell carbon particles, and a plurality of silicon nanoparticles within each of the hollow shell carbon particles and occupying less than a total volume within the each hollow shell carbon particle, wherein at least a portion of the plurality of silicon nanoparticles are located along an inside wall of each hollow shell carbon particle.

[0040] Example 2 includes the silicon-carbon composite material of example 1, wherein the plurality of silicon nanoparticles are uniformly distributed along the inside wall of each hollow shell carbon particle.

[0041] Example 3 includes any one of examples 1-2, wherein a specific surface area of the number of hollow shell carbon particles is approximately $317 \text{ m}^2 \text{ g}^{-1}$.

[0042] Example 4 includes any one of examples 1-3, wherein a specific volume of the number of hollow shell carbon particles is approximately $0.23 \text{ cm}^3 \text{ g}^{-1}$.

[0043] Example 5 includes a battery, comprising a first electrode. The first electrode includes a number of hollow shell carbon particles, and a plurality of silicon nanoparticles within each of the hollow shell carbon particles and occupying less than a total volume within the each hollow shell carbon particle, wherein at least a portion of the plurality of silicon nanoparticles are located along an inside wall of each hollow shell carbon particle. The battery also includes a second electrode, and an electrolyte in contact with both the first electrode and the second electrode.

[0044] Example 6 includes the battery of example 5, wherein the plurality of silicon nanoparticles are uniformly distributed along the inside wall of each hollow shell carbon particle.

[0045] Example 7 includes the battery of any one of examples 5-6, wherein the first electrode includes approximately 46 wt% hollow shell carbon particles.

[0046] Example 8 includes the battery of any one of examples 5-7, wherein the first electrode further includes approximately 46 wt% graphite.

[0047] Example 9 includes the battery of any one of examples 5-8, wherein the first electrode further includes approximately 5 wt% carbon black.

[0048] Example 10 includes the battery of any one of examples 5-9, wherein the first electrode further includes approximately 3 wt% carboxymethyl cellulose binder.

[0049] Example 11 includes a method of forming a battery electrode, comprising forming a hydrogen terminated surface on a plurality of silicon nanoparticles, tethering a plurality of hydrocarbon chains onto the hydrogen terminated surface to form coated silicon nanoparticles, dissolving the coated silicon nanoparticles in a solvent, mixing the solvent and silicon nanoparticles with

an aqueous medium and emulsifying to form silicon nanoparticle droplets, and carbonizing the silicon nanoparticle droplets to form a plurality of silicon-carbon composite particles. The silicon-carbon composite particles include a number of hollow shell carbon particles, and a plurality of silicon nanoparticles within each of the hollow shell carbon particles and occupying less than a total volume within the each hollow shell carbon particle, wherein at least a portion of the plurality of silicon nanoparticles are located along an inside wall of each hollow shell carbon particle.

[0050] Example 12 includes the method of example 11, further including coating the silicon nanoparticle droplets with resorcinol-formaldehyde prior to carbonization.

[0051] Example 13 includes the method of any one of examples 11-12, wherein dissolving the coated silicon nanoparticles in the solvent includes dissolving the coated silicon nanoparticles in styrene.

[0052] Example 14 includes the method of any one of examples 11-13, wherein dissolving the coated silicon nanoparticles in the solvent includes dissolving the coated silicon nanoparticles in hexadecane.

[0053] Example 15 includes the method of any one of examples 11-14, wherein carbonizing the silicon nanoparticle droplets includes carbonizing to form a plurality of silicon nanoparticles uniformly distributed along the inside wall of each hollow shell carbon particle.

[0054] Throughout this specification, plural instances may implement components, operations, or structures described as a single instance. Although individual operations of one or more methods are illustrated and described as separate operations, one or more of the individual operations may be performed concurrently, and nothing requires that the operations be performed in the order illustrated. Structures and functionality presented as separate components in example configurations may be implemented as a combined structure or component. Similarly, structures and functionality presented as a single component may be implemented as separate components. These and other variations, modifications, additions, and improvements fall within the scope of the subject matter herein.

[0055] Although an overview of the inventive subject matter has been described with reference to specific example embodiments, various modifications and changes may be made to these embodiments without departing from the broader scope of embodiments of the present disclosure. Such embodiments of the inventive subject matter may be referred to herein, individually or collectively, by the term “invention” merely for convenience and without intending to voluntarily limit the scope of this application to any single disclosure or inventive concept if more than one is, in fact, disclosed.

[0056] The embodiments illustrated herein are described in sufficient detail to enable those skilled in the art to practice the teachings disclosed. Other embodiments may be used and derived therefrom, such that structural and logical substitutions and changes may be made without departing from the scope of this disclosure. The Detailed Description, therefore, is not to be taken in a limiting sense, and the scope of various embodiments is defined only by the appended claims, along with the full range of equivalents to which such claims are entitled.

[0057] As used herein, the term “or” may be construed in either an inclusive or exclusive sense. Moreover, plural instances may be provided for resources, operations, or structures described herein as a single instance. Additionally, boundaries between various resources, operations, modules, engines, and data stores are somewhat arbitrary, and particular operations are illustrated in a context of specific illustrative configurations. Other allocations of functionality are envisioned and may fall within a scope of various embodiments of the present disclosure. In general, structures and functionality presented as separate resources in the example configurations may be implemented as a combined structure or resource. Similarly, structures and functionality presented as a single resource may be implemented as separate resources. These and other variations, modifications, additions, and improvements fall within a scope of embodiments of the present disclosure as represented by the appended claims. The specification and drawings are, accordingly, to be regarded in an illustrative rather than a restrictive sense.

[0058] The foregoing description, for the purpose of explanation, has been described with reference to specific example embodiments. However, the

illustrative discussions above are not intended to be exhaustive or to limit the possible example embodiments to the precise forms disclosed. Many modifications and variations are possible in view of the above teachings. The example embodiments were chosen and described in order to best explain the principles involved and their practical applications, to thereby enable others skilled in the art to best utilize the various example embodiments with various modifications as are suited to the particular use contemplated.

[0059] It will also be understood that, although the terms “first,” “second,” and so forth may be used herein to describe various elements, these elements should not be limited by these terms. These terms are only used to distinguish one element from another. For example, a first contact could be termed a second contact, and, similarly, a second contact could be termed a first contact, without departing from the scope of the present example embodiments. The first contact and the second contact are both contacts, but they are not the same contact.

[0060] The terminology used in the description of the example embodiments herein is for the purpose of describing particular example embodiments only and is not intended to be limiting. As used in the description of the example embodiments and the appended examples, the singular forms “a,” “an,” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will also be understood that the term “and/or” as used herein refers to and encompasses any and all possible combinations of one or more of the associated listed items. It will be further understood that the terms “comprises” and/or “comprising,” when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

[0061] As used herein, the term “if” may be construed to mean “when” or “upon” or “in response to determining” or “in response to detecting,” depending on the context. Similarly, the phrase “if it is determined” or “if [a stated condition or event] is detected” may be construed to mean “upon determining” or “in response to

determining” or “upon detecting [the stated condition or event]” or “in response to detecting [the stated condition or event],” depending on the context.

What is claimed is:

1. A silicon-carbon composite material, comprising:
a number of hollow shell carbon particles; and
a plurality of silicon nanoparticles within each of the hollow shell carbon particles and occupying less than a total volume within the each hollow shell carbon particle;
wherein at least a portion of the plurality of silicon nanoparticles are located along an inside wall of each hollow shell carbon particle.
2. The silicon-carbon composite material of claim 1, wherein the plurality of silicon nanoparticles are uniformly distributed along the inside wall of each hollow shell carbon particle.
3. The silicon-carbon composite material of claim 1, wherein a specific surface area of the number of hollow shell carbon particles is approximately $317 \text{ m}^2 \text{ g}^{-1}$.
4. The silicon-carbon composite material of claim 1, wherein a specific volume of the number of hollow shell carbon particles is approximately $0.23 \text{ cm}^3 \text{ g}^{-1}$.
5. A battery, comprising:
a first electrode, including:
a number of hollow shell carbon particles; and
a plurality of silicon nanoparticles within each of the hollow shell carbon particles and occupying less than a total volume within the each hollow shell carbon particle;
wherein at least a portion of the plurality of silicon nanoparticles are located along an inside wall of each hollow shell carbon particle;
a second electrode; and
an electrolyte in contact with both the first electrode and the second electrode.

6. The battery of claim 5, wherein the plurality of silicon nanoparticles are uniformly distributed along the inside wall of each hollow shell carbon particle.
7. The battery of claim 5, wherein the first electrode includes approximately 46 wt% hollow shell carbon particles.
8. The battery of claim 7, wherein the first electrode further includes approximately 46 wt% graphite.
9. The battery of claim 8, wherein the first electrode further includes approximately 5 wt% carbon black.
10. The battery of claim 9, wherein the first electrode further includes approximately 3 wt% carboxymethyl cellulose binder.
11. A method of forming a battery electrode, comprising:
 - forming a hydrogen terminated surface on a plurality of silicon nanoparticles;
 - tethering a plurality of hydrocarbon chains onto the hydrogen terminated surface to form coated silicon nanoparticles;
 - dissolving the coated silicon nanoparticles in a solvent;
 - mixing the solvent and silicon nanoparticles with an aqueous medium and emulsifying to form silicon nanoparticle droplets;
 - carbonizing the silicon nanoparticle droplets to form a plurality of silicon-carbon composite particles having:
 - a number of hollow shell carbon particles;
 - a plurality of silicon nanoparticles within each of the hollow shell carbon particles and occupying less than a total volume within the each hollow shell carbon particle;

wherein at least a portion of the plurality of silicon nanoparticles are located along an inside wall of each hollow shell carbon particle.

12. The method of claim 11, further including coating the silicon nanoparticle droplets with resorcinol-formaldehyde prior to carbonization.

13. The method of claim 11, wherein dissolving the coated silicon nanoparticles in the solvent includes dissolving the coated silicon nanoparticles in styrene.

14. The method of claim 11, wherein dissolving the coated silicon nanoparticles in the solvent includes dissolving the coated silicon nanoparticles in hexadecane.

15. The method of claim 11, wherein carbonizing the silicon nanoparticle droplets includes carbonizing to form a plurality of silicon nanoparticles uniformly distributed along the inside wall of each hollow shell carbon particle.

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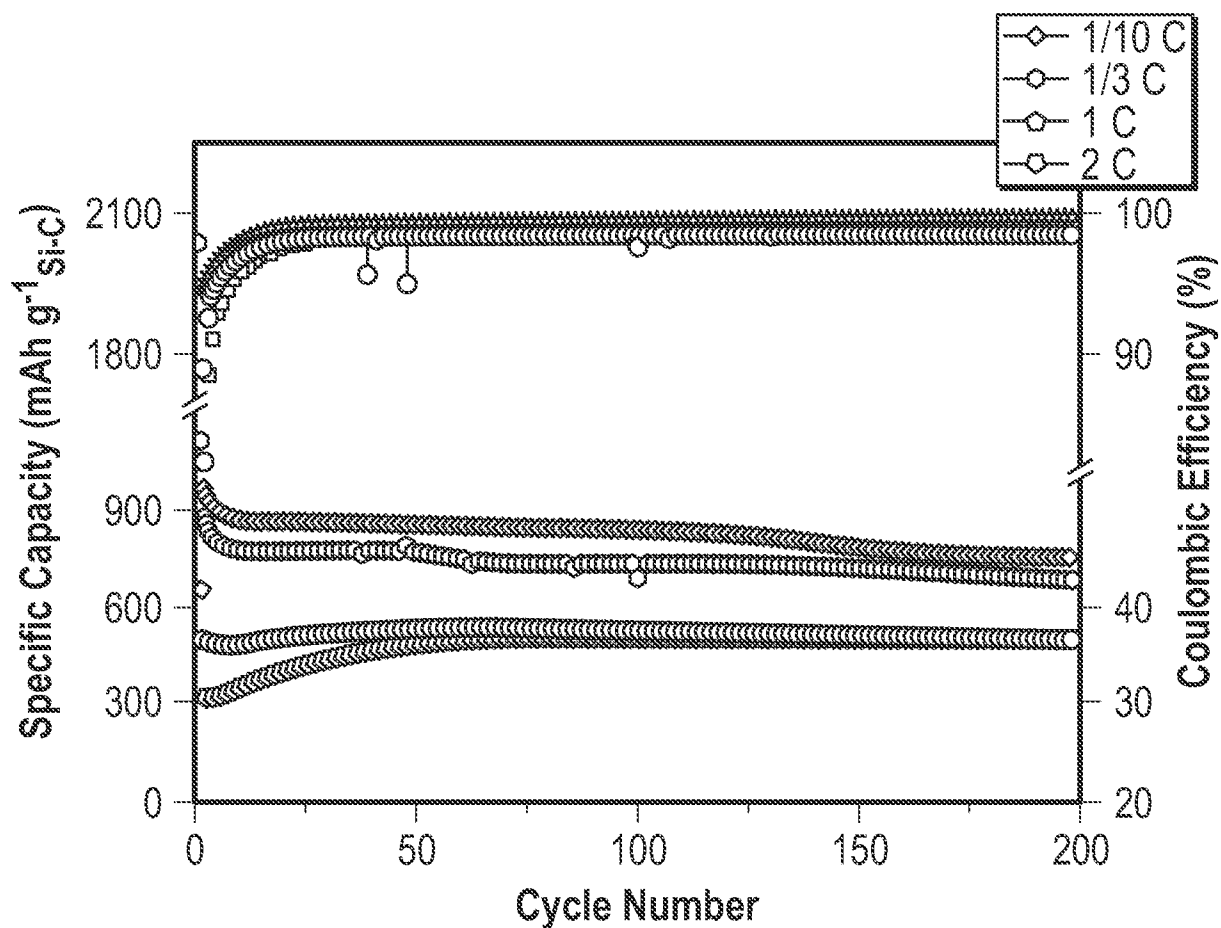


FIG. 1

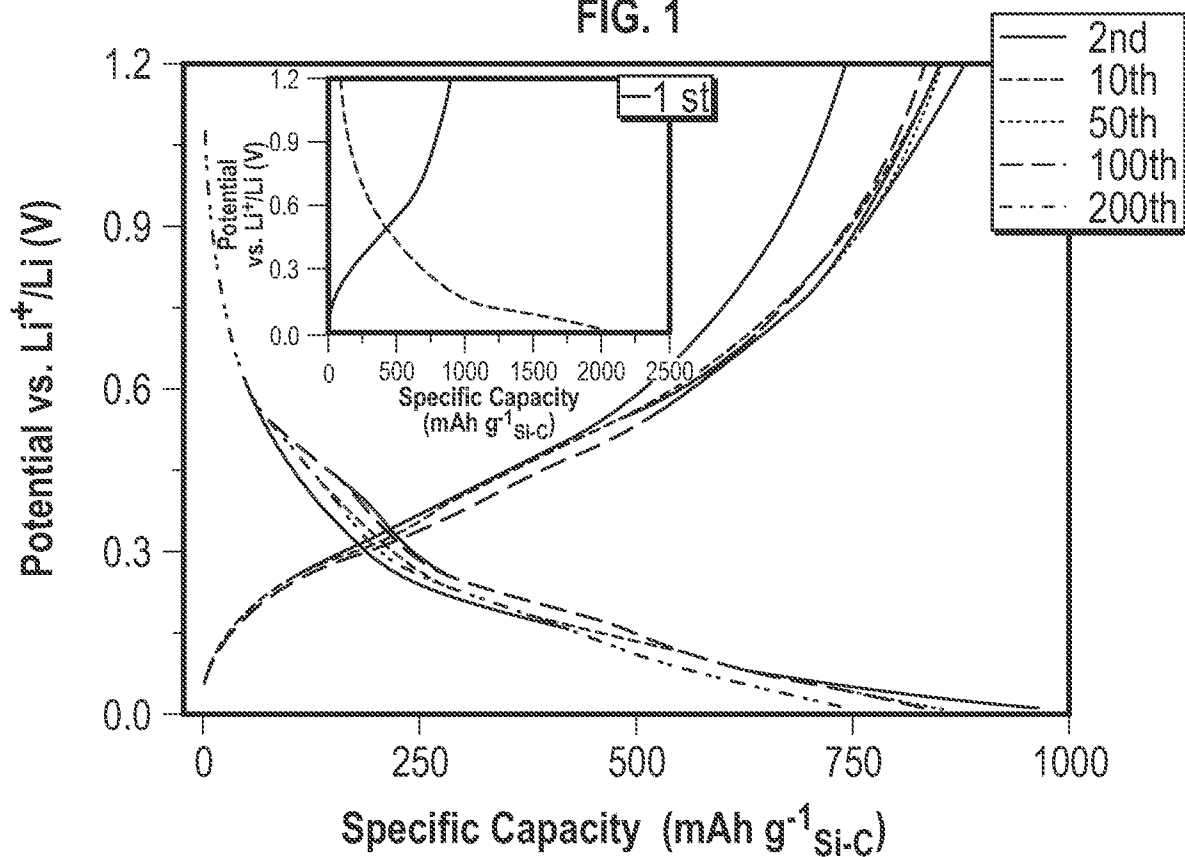


FIG. 2

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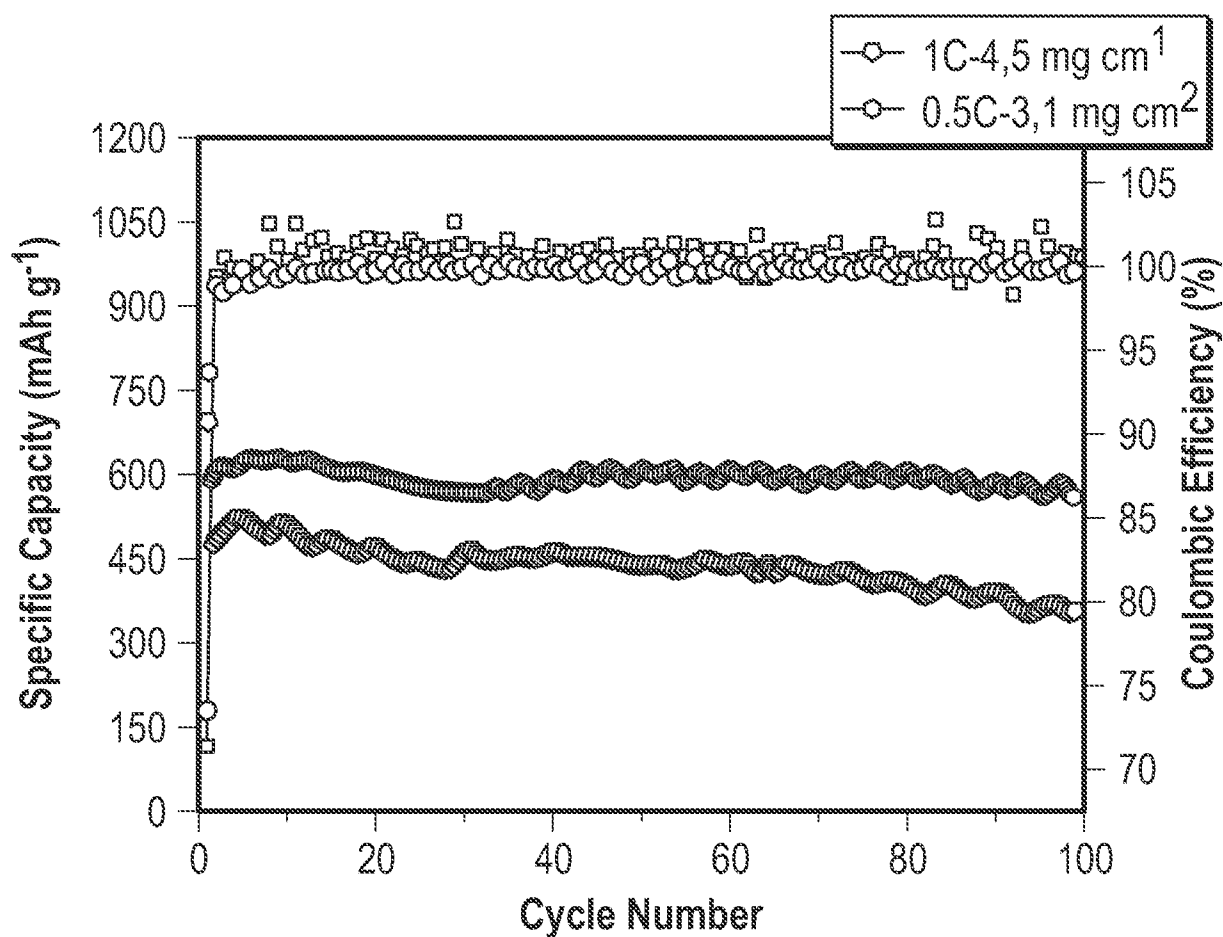


FIG. 3

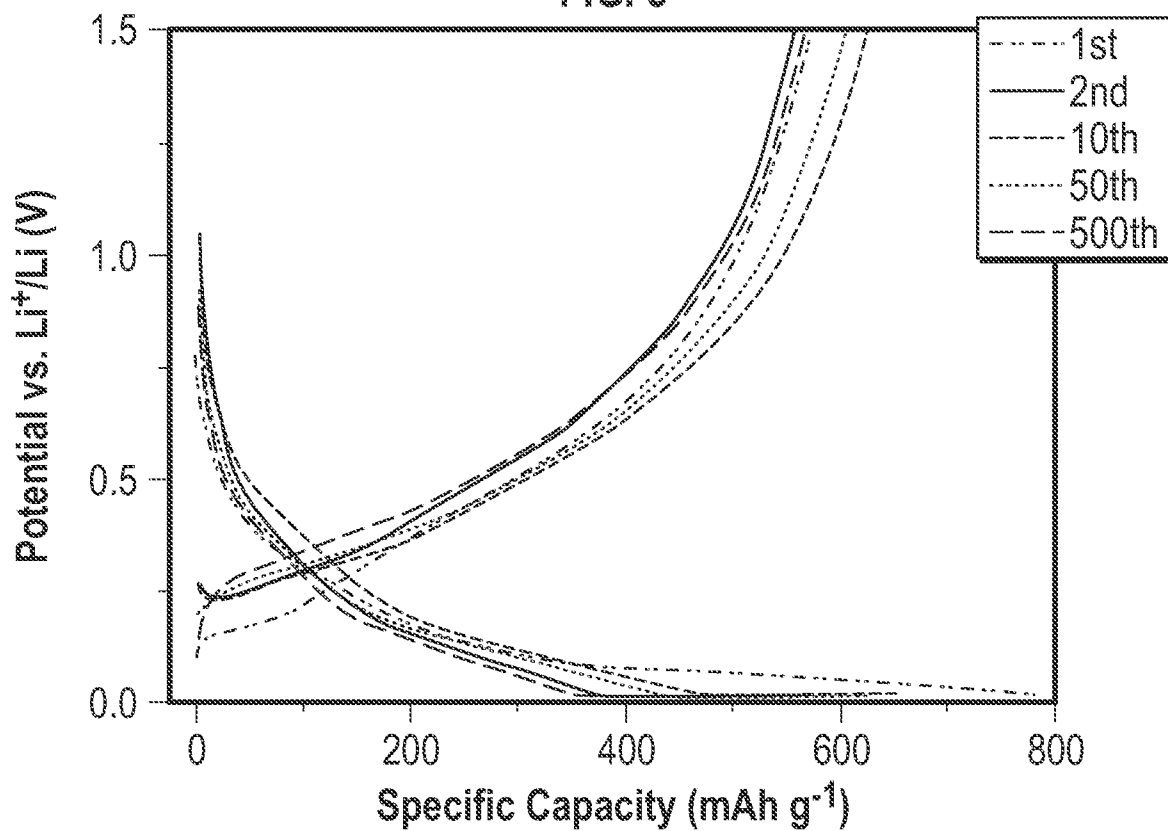


FIG. 4

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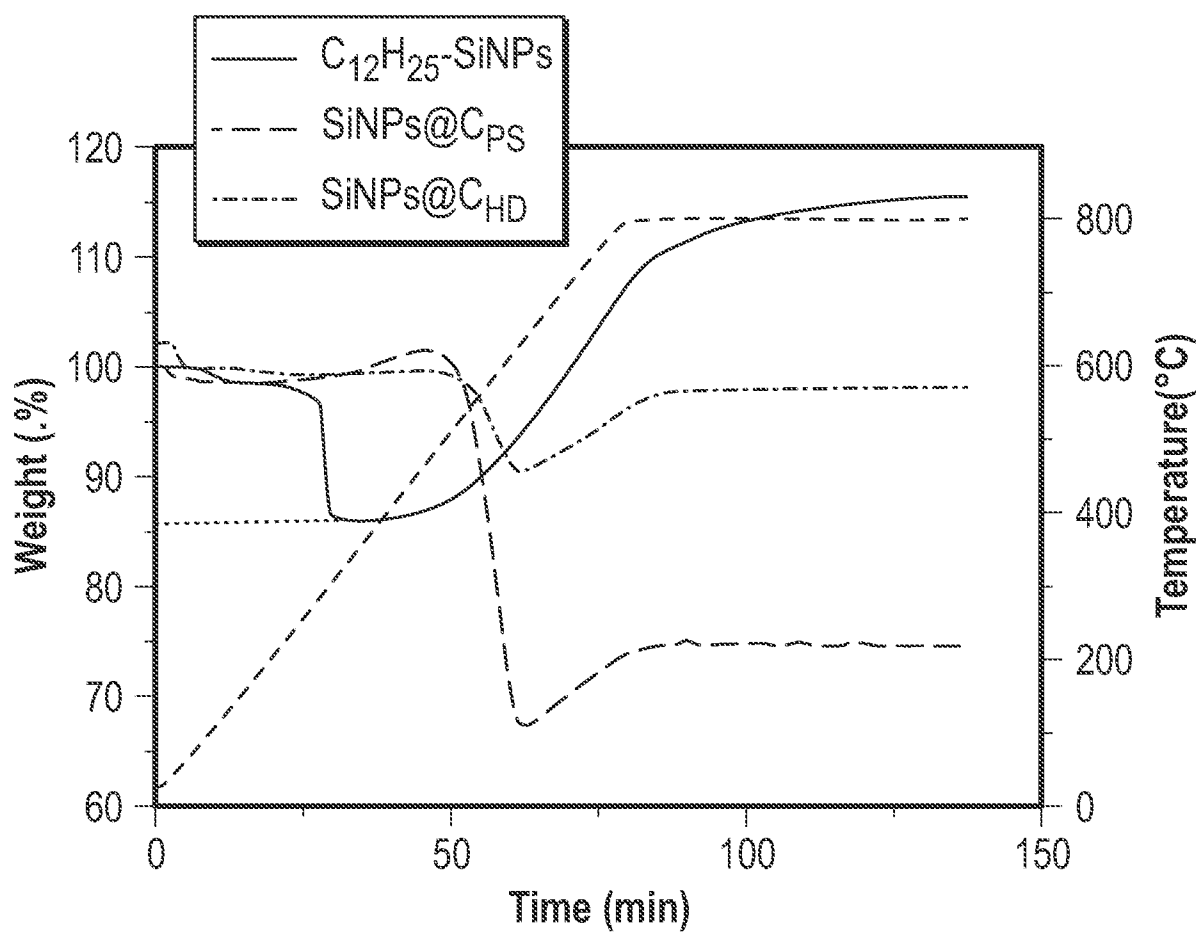


FIG. 5

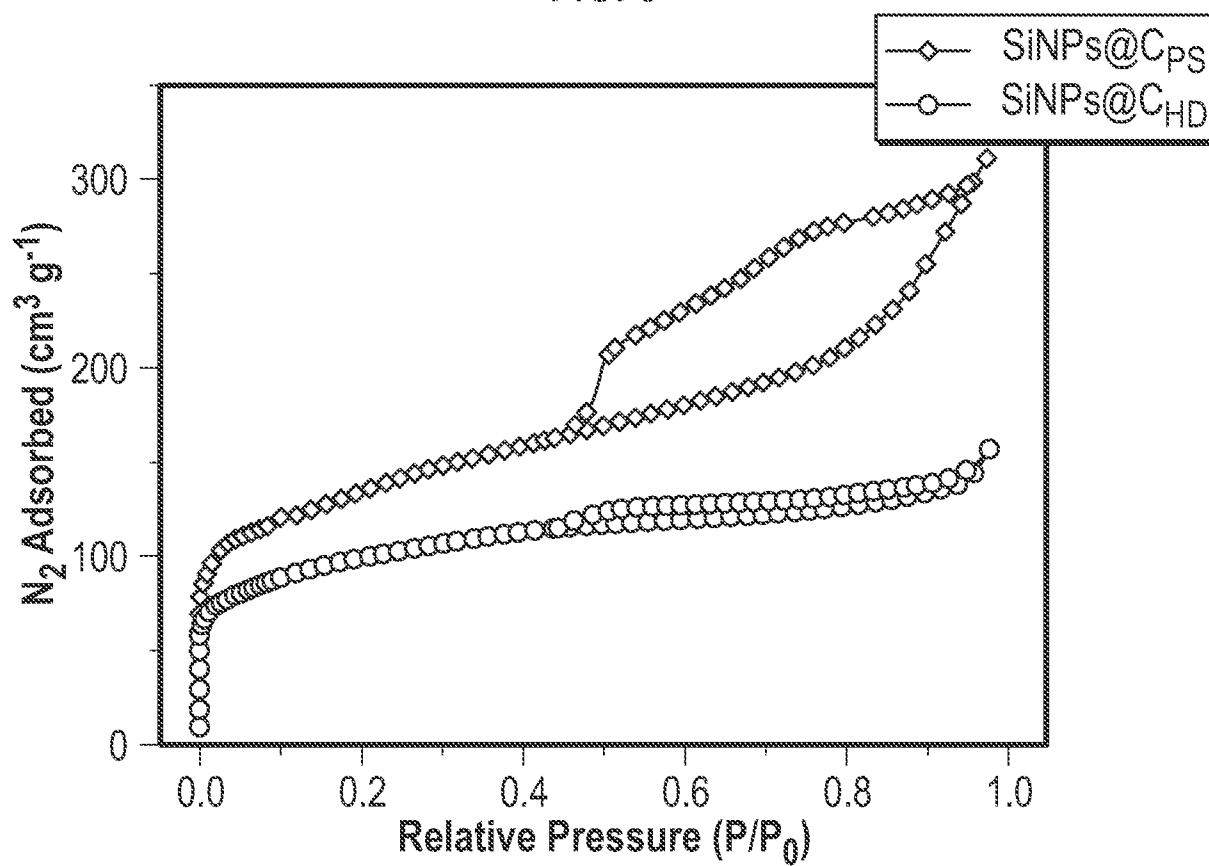


FIG. 6

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	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_t ($\text{cm}^3 \text{g}^{-1}$)
SINPs@C _{PS}	437	0.45
SINPs@C _{HD}	317	0.23

FIG. 7

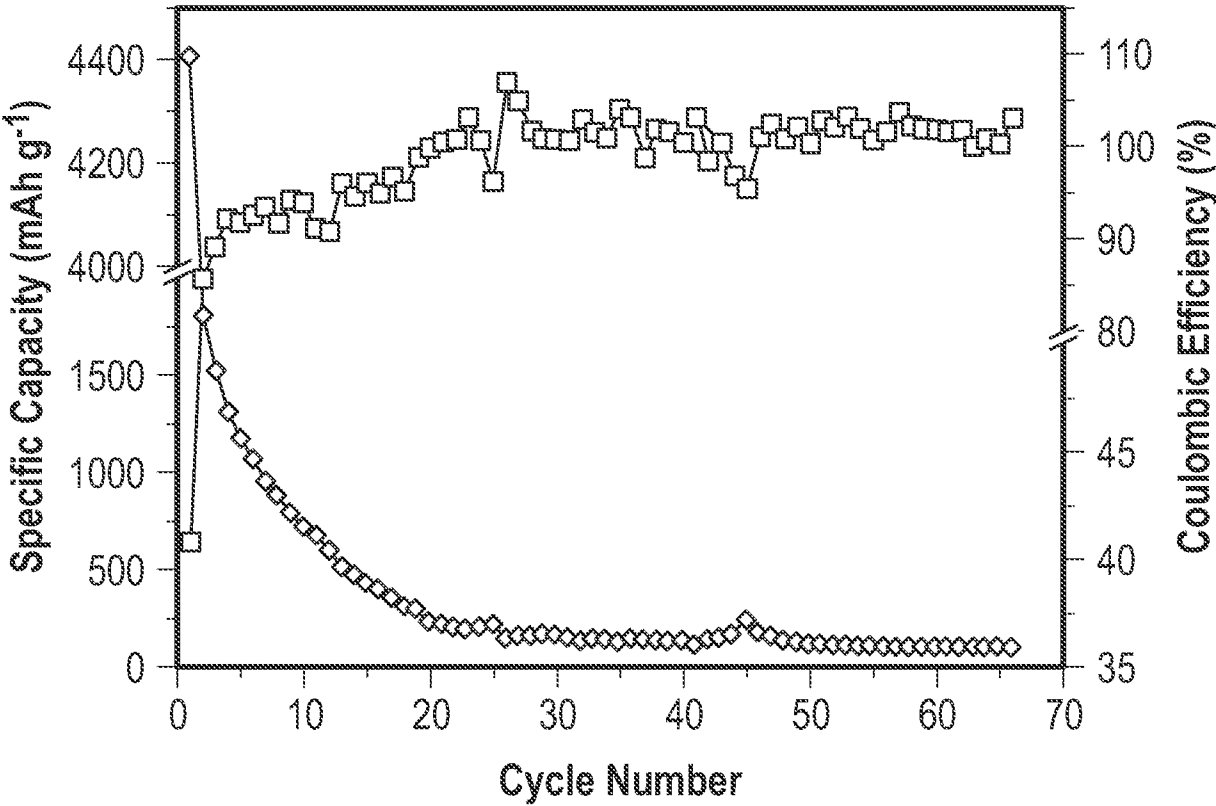


FIG. 8

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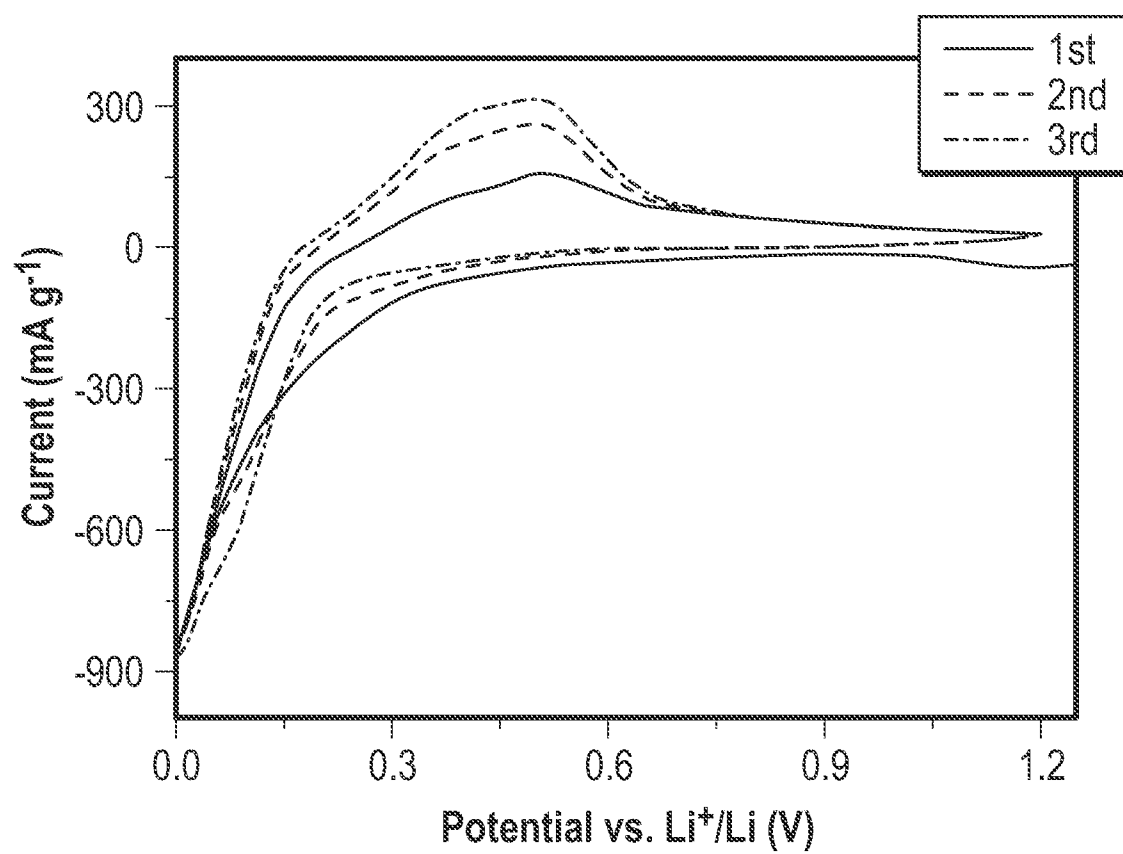


FIG. 9

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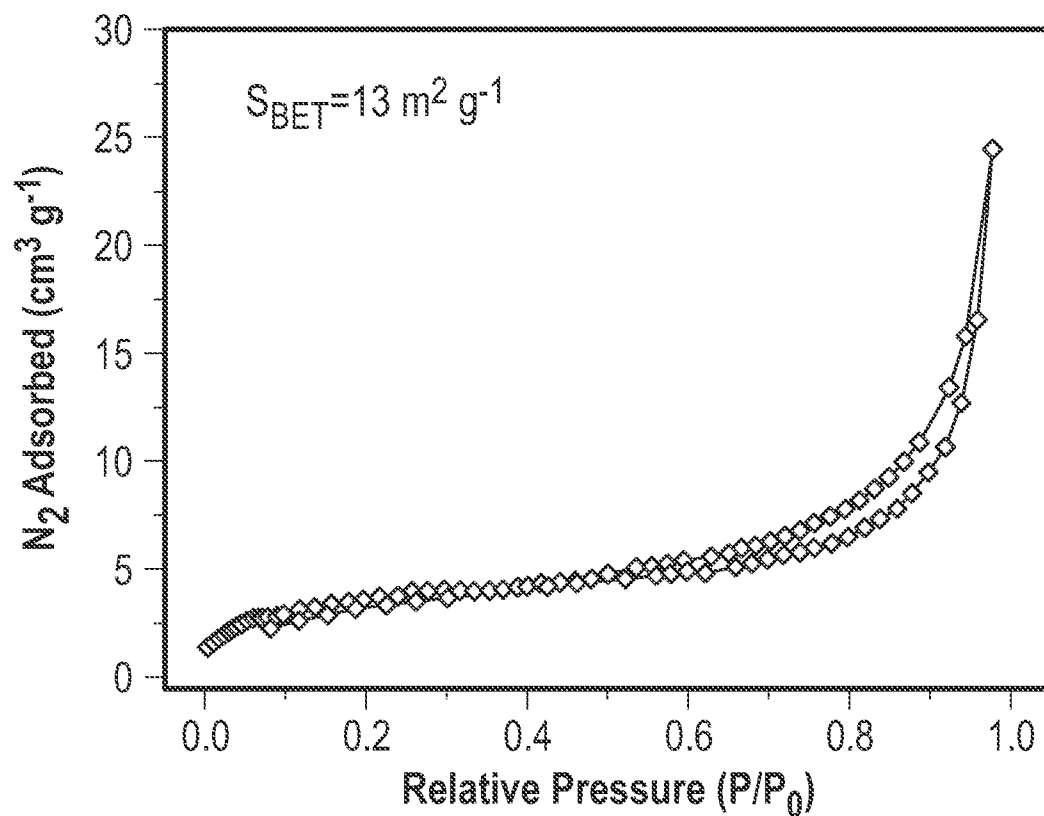


FIG. 10

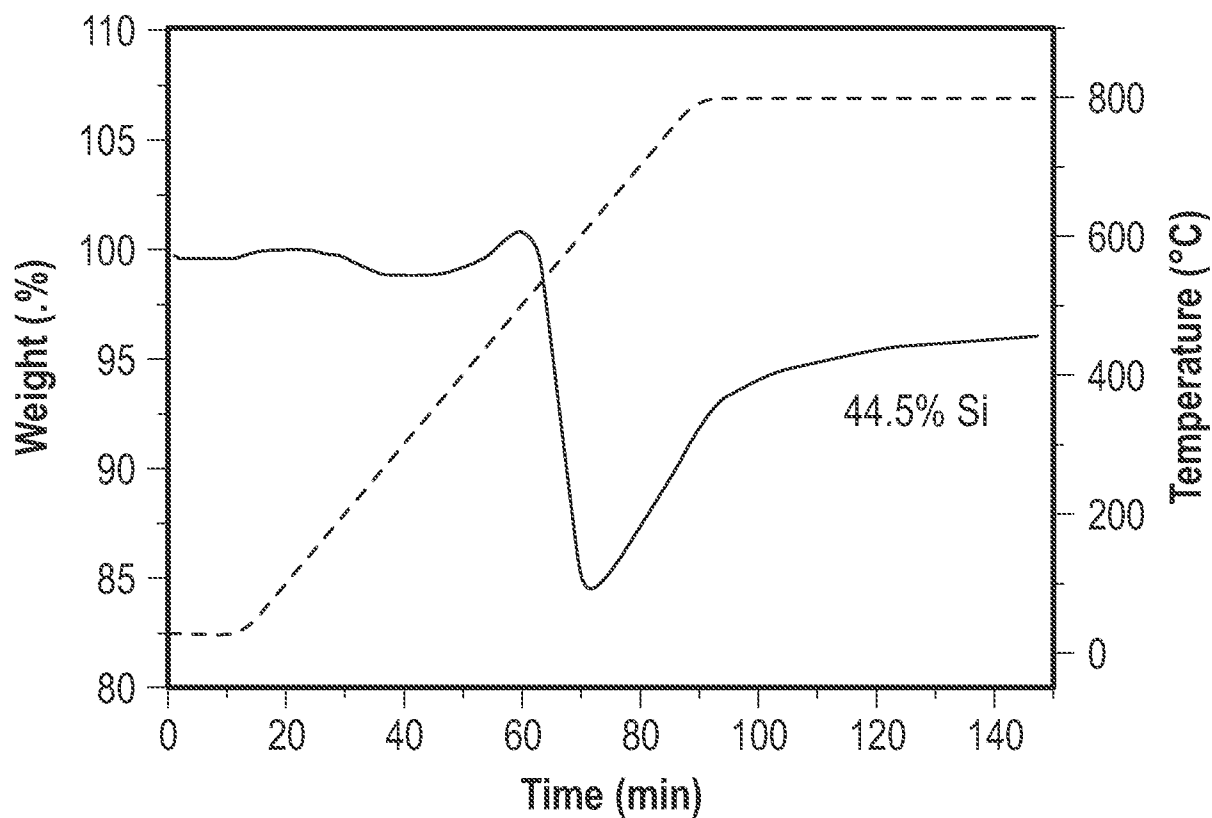


FIG. 11

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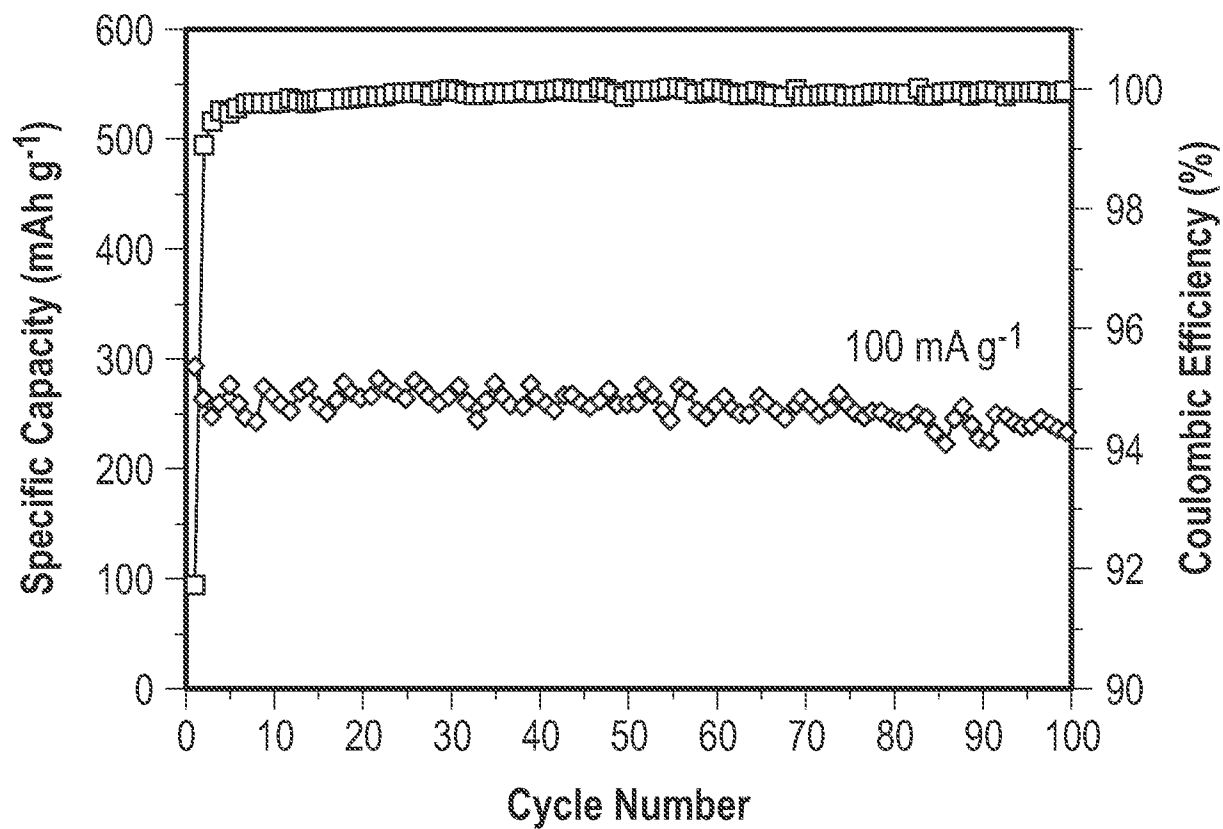


FIG. 12

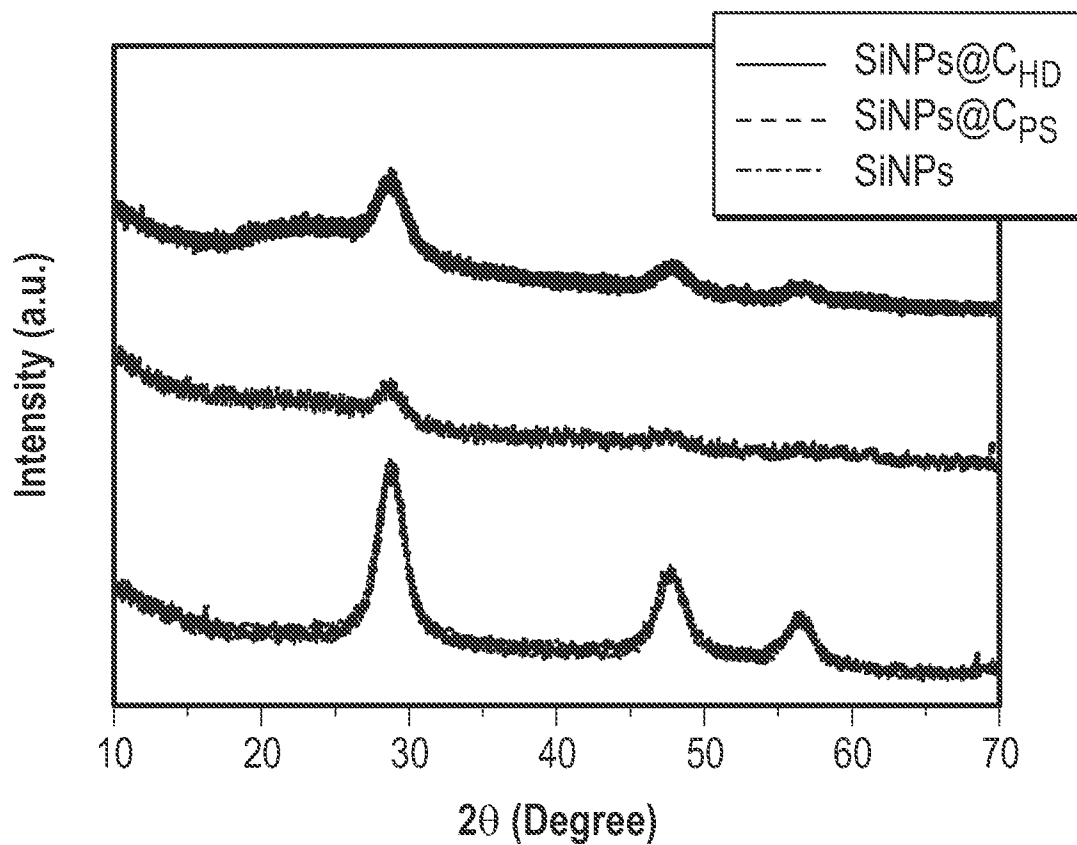


FIG. 13

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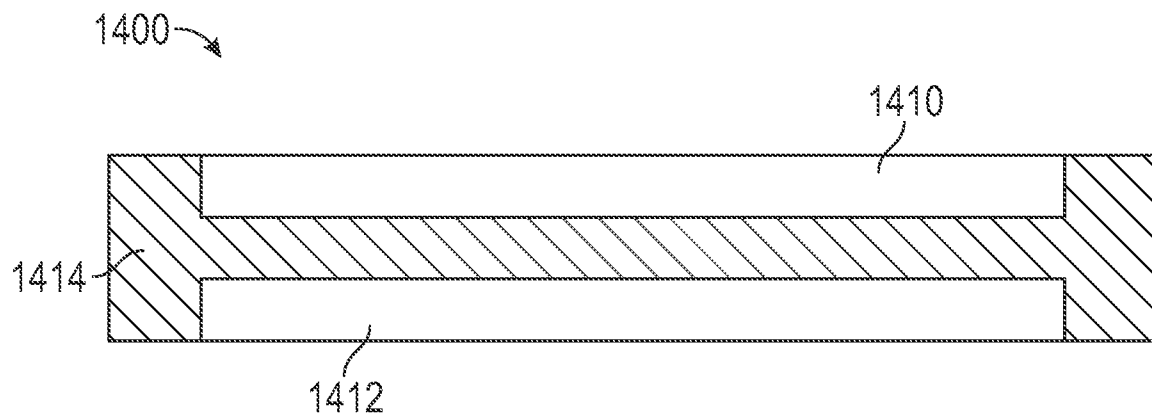


FIG. 14

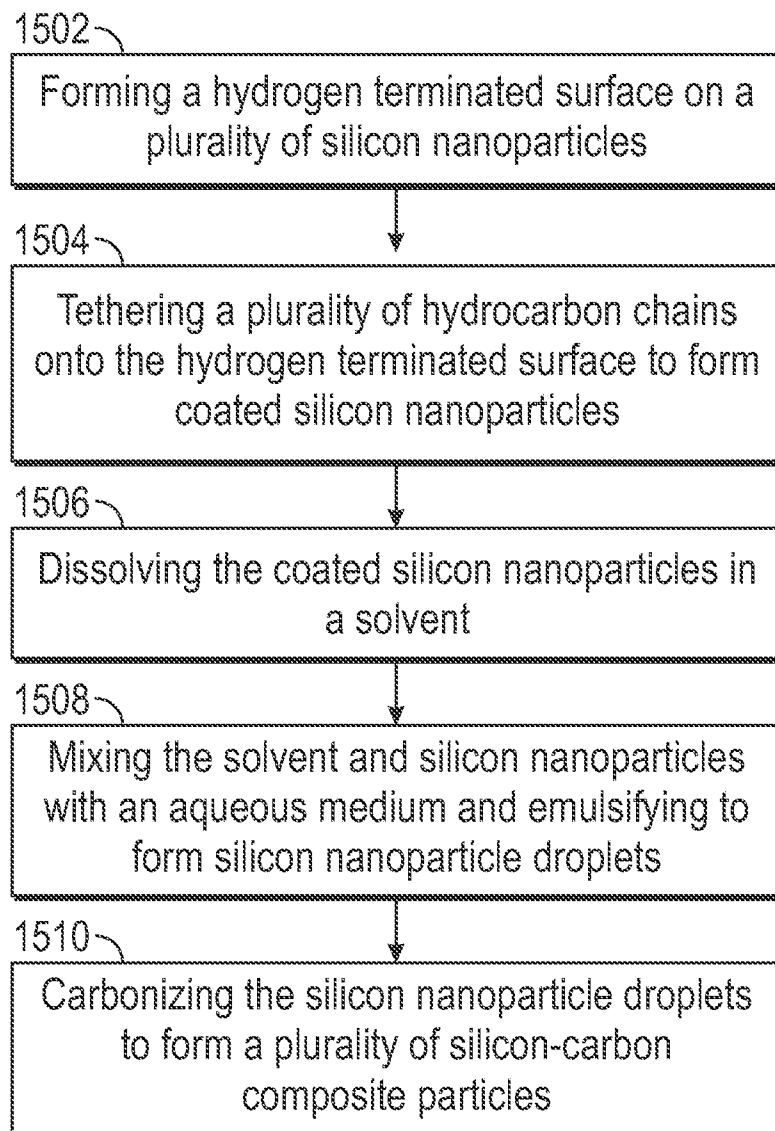


FIG. 15

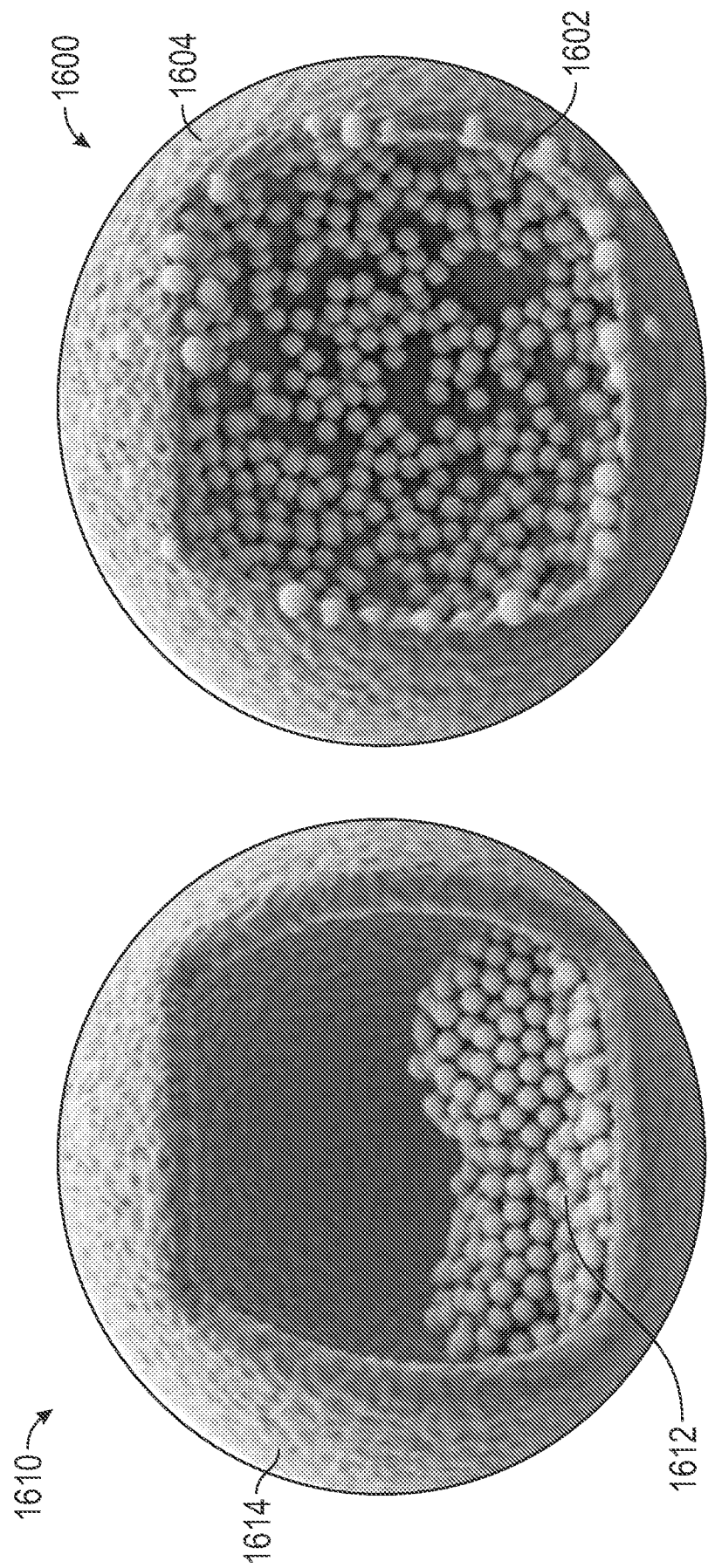


FIG. 16

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/36756

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(8) - H01M 4/04, H01M 4/133, H01M 4/134 (2018.01)
 CPC - C01B 33/02, H01M 10/0525, H01M 2004/021

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)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y -- A	US 2013/0344392 A1 (NORTHWESTERN UNIVERSITY), 26 December 2013 (26.12.2013), para [0006]-[0007], [0034], [0042].	1, 5 ----- 2-3, 6-10 ----- 4
Y	US 2013/0344391 A1 (SILA NANOTECHNOLOGIES) 26 December 2013 (26.12.2013), figures 18-22; para [0008], [0030], [0046], [0059], [0083].	2, 6
Y	US 2014/0287315 A1 (WACKER CHEMIE) 25 September 2014 (25.09.2014), para [0017]-[0018], [0173]-[0175].	3
Y	US 2017/0012282 A1 (KABUSHIKI KAISHA TOYOTA JIDOSHOKKI) 12 January 2017 (12.01.2017), para [0023]-[0024], [0233], [0238]-[0239], [0280].	7-10
A	US 2015/0162617 A1 (NANO AND ADVANCED MATERIALS INSTITUTE), 11 June 2015 (11.06.2015), figures 1, 5, 7; para [0002], [0011], [0027]-[0028].	4
A	'Density of the Elements', periodictable.com, 1 June 2017 (01.06.2017), [retrieved 14 August 2018 (14.08.2018) via the internet at < https://web.archive.org/web/20170601085937/http://periodictable.com/Properties/A/Density.al.html >].	4

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"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

15 August 2018

Date of mailing of the international search report

24 OCT 2018

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
 P.O. Box 1450, Alexandria, Virginia 22313-1450
 Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/36756

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-10, directed to a composite material comprising a number of hollow shell carbon particles and a plurality of silicon nanoparticles within each of the hollow shell carbon particles; and a battery comprising the same.

Group II: Claims 11-15, directed to a method of forming a battery electrode comprising forming an aqueous emulsion of hydrocarbon-functionalized silicon nanoparticles.

The inventions listed as Groups I-II do not relate to a single inventive concept under PCT Rule 13.1 because under PCT Rule 13.2 they lack the same or corresponding technical features for the following reasons:

***** Continued in the Supplemental Sheet below *****

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-10

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Special Technical Features

Group II includes the special technical features of forming a hydrogen terminated surface on a plurality of silicon nanoparticles; tethering a plurality of hydrocarbon chains onto the hydrogen terminated surface to form coated silicon nanoparticles; dissolving the coated silicon nanoparticles in a solvent; mixing the solvent and silicon nanoparticles with an aqueous medium and emulsifying to form silicon nanoparticle droplets; and carbonizing the silicon nanoparticle droplets; not required by Group I.

Shared Technical Features

Groups I-II share the common technical features of silicon-carbon composite material, comprising: a number of hollow shell carbon particles; and a plurality of silicon nanoparticles within each of the hollow shell carbon particles and occupying less than a total volume within the each hollow shell carbon particle; wherein at least a portion of the plurality of silicon nanoparticles are located along an inside wall of each hollow shell carbon particle. However, these shared technical features do not represent a contribution over prior art as being anticipated by US 2013/0344392 A1 to Northwestern University (hereinafter 'Northwestern'), which teaches a silicon-carbon composite material (para [0006], 'capsules comprising: a crumpled graphene shell ... and silicon nanostructures encapsulated within the crumpled graphene shell'), comprising: a number of hollow shell carbon particles (para [0006], 'capsules comprising: a crumpled graphene shell comprising graphene sheets having a crumpled morphology'); and a plurality of silicon nanoparticles within each of the hollow shell carbon particles (para [0006], 'and silicon nanostructures encapsulated within the crumpled graphene shell') and occupying less than a total volume within the each hollow shell carbon particle (para [0034], 'Voids inside the crumpled graphene ... allow the nanostructures to expand and contract freely, without rupturing the crumpled shell'); wherein at least a portion of the plurality of silicon nanoparticles are located along an inside wall of each hollow shell carbon particle (para [0034], 'the crumpled structure can clasp the nanostructures within its folds'; para [0042], 'No unwrapped Si nanoparticles were observed suggesting high encapsulation yield... Si nanoparticles were wrapped in the crumpled graphene').

Therefore, Groups I-II lack unity under PCT Rule 13 because they do not share a same or corresponding technical feature.