



(51) International Patent Classification:

H01M 4/02 (2006.01) *B82Y 30/00* (2011.01)
H01M 4/04 (2006.01) *B82Y 40/00* (2011.01)
H01M 4/134 (2010.01)

(21) International Application Number:

PCT/US2024/060234

(22) International Filing Date:

13 December 2024 (13.12.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/611,003 15 December 2023 (15.12.2023) US

(71) Applicants: **THE REGENTS OF THE UNIVERSITY OF CALIFORNIA** [US/US]; 1111 Franklin Street, Twelfth Floor, Oakland, California 94607 (US). **SILI-ION INC.** [US/US]; 17224 Coriander Court, Yorba Linda, California 92886 (US).

(72) Inventors; and

(71) Applicants: **GHILDIYAL, Pankaj** [US/US]; c/o SiLi-ion Inc., 17224 Coriander Court, Yorba Linda, California 92886 (US). **MANGOLINI, Lorenzo**; c/o The Regents of the Uni-

versity of California, 1111 Franklin Street, Twelfth Floor, Oakland, California 94607 (US).

(74) Agent: **SATHE, Vinay P.**; c/o Perkins Coie LLP, PO Box 1247, Seattle, Washington 98111 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE,

(54) Title: SUPER-ASSEMBLED MICRON-SIZED SILICON PARTICLES

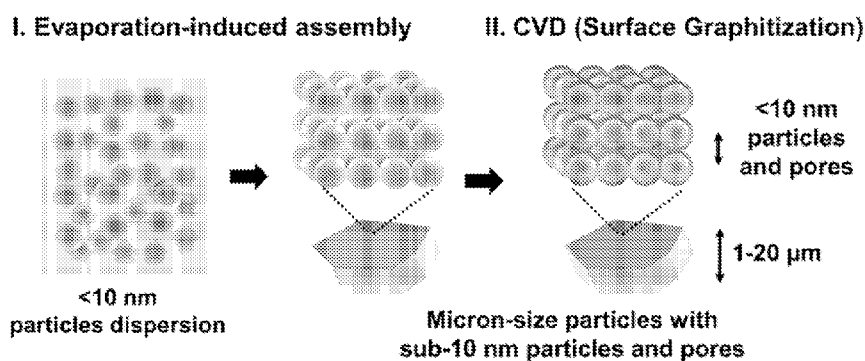


FIG.1

(57) Abstract: A composition of matter includes silicon nanoparticles having nanopores disperse among the silicon nanoparticles, wherein the silicon nanoparticles have an average particle size of less than about 12 nm, and the nanopores have an average size of less than about 10 nm. An anode material includes a micron-sized assembly of silicon nanoparticles having an average particle size of less than about 12 nm, wherein the silicon nanoparticles are spaced by nanopores having average pore size of less than about 10 nm, and wherein the anode material is made by: dispersing the silicon nanoparticles in a solvent; and evaporating the solvent from the silicon nanoparticles to provide an evaporation-induced assembly of the silicon nanoparticles.

SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))*

SUPER-ASSEMBLED MICRON-SIZED SILICON PARTICLES

TECHNICAL FIELD

[0001] This patent document relates to silicon particles, assemblies, preparation methods, and applications thereof.

BACKGROUND

[0002] Silicon is widely considered the best candidate anode material for next-generation lithium-ion batteries because its specific capacity exceeds that of the current anode material, graphite, both on a gravimetric and a volumetric basis (3579 mAh/g and 2194 mAh/cm³). While promising, silicon-dominant anodes have yet to be broadly utilized on a commercial scale. The primary issue with this material is its low cycling stability. While graphite retains its capacity over thousands of charge-discharge cycles, silicon degrades much faster. This behavior is not rooted in a single cause but is due to many failure mechanisms. Lithium does not intercalate in silicon, rather, it forms a silicide resulting in large volume change (roughly 400% upon lithiation). This results in mechanical failure, pulverization, and loss of electrical contact. Further, a solid electrolyte interphase (SEI) layer is typically developed on the surface of the active material (e.g., graphite). For silicon-based active material, the significant volume change upon lithiation degrades the SEI, which then partially reforms every cycle, leading to the irreversible loss of lithium. For these reasons, the design of a silicon-based anode that achieves sufficient stability for real-life applications has proved to be a significant challenge.

SUMMARY

[0003] Compositions, materials, and preparation methods are described for ultrasmall silicon particle-pore assemblies.

[0004] In one example aspect, a composition of matter includes silicon nanoparticles having nanopores disperse among the silicon nanoparticles, wherein the silicon nanoparticles have an average particle size of less than about 12 nm, and the nanopores have an average size of less than about 10 nm.

[0005] In another example aspect, an anode material includes a micron-sized assembly of silicon nanoparticles having an average particle size of less than about 12 nm, wherein the

silicon nanoparticles are spaced by nanopores having an average pore size of less than about 10 nm, and wherein the anode material is made by: dispersing the silicon nanoparticles in a solvent; and evaporating the solvent from the silicon nanoparticles to provide an evaporation-induced assembly of the silicon nanoparticles.

[0006] In another example aspect, an anode material includes a micron-sized assembly of silicon nanoparticles, wherein the micron-sized assembly comprises nanopores having an average pore size of less than about 10 nm, and the silicon nanoparticles have an average particle size ranging from about 8 nm to about 12 nm.

[0007] In yet another example aspect, a method of preparing an anode material described herein includes dispersing silicon nanoparticles in a solvent; and evaporating the solvent from the silicon nanoparticles to provide an evaporation-induced assembly of the silicon nanoparticles, wherein the evaporation-induced assembly of silicon nanoparticles comprises silicon nanoparticles having an average particle size of less than about 12 nm spaced by nanopores having an average pore size of less than 10 nm.

[0008] These and other aspects and associated implementations and benefits of the disclosed technology are described in greater detail in the drawings, the description, and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] This application contains at least one drawing executed in color. Copies of this application with color drawing(s) will be provided by the Office upon request and payment of the necessary fees.

[0010] FIG. 1 depicts the preparation of hierarchically structured ultrasmall silicon particle-pore assemblies in accordance with the present technology.

[0011] FIG. 2 shows scanning electron microscope (SEM) images of super-assembled micron-sized particles in accordance with the present technology.

[0012] FIG. 3 is a graph showing x-ray diffraction (XRD) patterns and calculated crystallite size of super-assembled micron-sized particles in accordance with the present technology.

[0013] FIG. 4A is a graph showing the pore diameter of silicon nanoparticle assemblies in accordance with the present technology.

[0014] FIG. 4B is a graph showing the tap density of silicon nanoparticle assemblies in accordance with the present technology.

[0015] FIG. 4C is a graph showing the specific area of silicon nanoparticle assemblies in accordance with the present technology.

[0016] FIG. 4D is a graph showing the estimated bulk porosity of silicon nanoparticle assemblies and commercial silicon samples in accordance with the present technology.

[0017] FIG. 4E is a graph showing the pore diameter of silicon nanoparticle assemblies and in accordance with the present technology.

[0018] FIG. 5A is a graph showing the capacity over charge cycle of silicon nanoparticle assemblies in accordance with the present technology.

[0019] FIG. 5B is a graph showing the coulombic efficiency over charge cycle of silicon nanoparticle assemblies in accordance with the present technology.

[0020] FIG. 6 is a graph showing the capacity retention of a super-assembled silicon nanoparticle assembly in accordance with the present technology.

[0021] FIG. 7A shows scanning transmission electron microscopy dispersive X-ray spectroscopy (STEM-EDS) images of a solid electrolyte interphase (SEI) layer on the outer surface of a cycled super-assembled silicon nanoparticle assembly in accordance with the present technology.

[0022] FIG. 7B is a schematic showing configurations of a C/O-rich layer on super-assembled nanoparticle assemblies and comparative silicon materials in accordance with the present technology.

[0023] FIG. 7C is a graph showing the coulombic efficiency of a cycled super-assembled silicon nanoparticle assembly in accordance with the present technology.

[0024] FIG. 8 shows high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of silicon nanoparticle super-assemblies in accordance with the present technology.

[0025] FIG. 9A is a graph comparing initial and stabilized coulombic efficiencies at C/10 rate of silicon nanoparticle super-assemblies in accordance with the present technology.

[0026] FIG. 9B is a graph of the areal capacity cycling data at C/10 of silicon nanoparticle super-assemblies in accordance with the present technology.

[0027] FIG. 9C is a graph of long-term cycling data of silicon nanoparticle super-assemblies in accordance with the present technology.

[0028] FIG. 10 is a graph of full cell performance of silicon nanoparticle super-assemblies in accordance with the present technology.

DETAILED DESCRIPTION

[0029] Silicon possesses high lithium storage capacity, although it is also marred by many problems including volume swelling, pulverization, poor electrical conductivity, and poor compatibility with standard electrolytes. These result in poor cycle life when incorporated into lithium-ion batteries. Many solutions have been proposed to alleviate these issues, including the design and synthesis of nanowires, yolk-shell nanoparticles etc. Another common approach is to use micron-sized silicon particles with void space dispersed within them to accommodate for the volume changes occurring during lithiation. This can be achieved by etching in strong acids in the presence of the appropriate catalyst particles. Alternatively, micron-sized silicon suboxide (SiO) particles can be annealed to give a uniform mixture of silicon and silicon oxide (SiO₂). After removal of the SiO₂ in hydrofluoric acid, a porous micron-sized particle is achieved. Unfortunately, these are top-down approaches that do not enable tight control of both pore and silicon domain size, and that generate large amount of highly reactive waste.

[0030] This document describes the bottom-up assembly of ultra-small silicon nanoparticles to give micron-sized particles with excellent energy density and cycle life. A relatively straightforward three-step method to utilize ultrasmall silicon particles (sub-10 nm diameter) produced from a plasma-based process has been developed. The ultrasmall silicon particles may be used as building blocks to form micron-scale superstructures with precisely designed porosity, void fraction, and surface features to stabilizing the SEI formation and achieving high charge-discharge stability. By assembling ultrasmall silicon nanoparticles (<12 nm), it is possible to achieve ultrasmall pore sizes (<10 nm). The combination of these two is necessary to stabilize the material during charge-discharge cycling. Anodes realized with these nanoparticle assemblies show excellent charge-discharge stability, with capacities ranging from 900-1400 mAh g⁻¹, while approaching 99.9% coulombic efficiencies.

[0031] In some embodiments, micron-scale silicon particles with ultrasmall grain and pore sizes are prepared by (1) dispersing freestanding ultrasmall nanoparticles into a solvent and (2) drying the dispersion so that the capillary forces pull the particles close together to give a dense assembly of particles. The assembled particles can then be infilled with carbon to lock the structure into place.

[0032] Ultrasmall silicon nanoparticles may be conveniently produced using a low-temperature plasma process described in Mangolini, L., et al. (2005). High-yield plasma synthesis of luminescent silicon nanocrystals. *Nano letters*, 5(4), 655-659. Other approaches

that produce comparable material are laser pyrolysis of silane followed by size reduction in an acid bath (Li, X., et al. (2003). Process for preparing macroscopic quantities of brightly photoluminescent silicon nanoparticles with emission spanning the visible spectrum. *Langmuir*, 19(20), 8490-8496) or annealing of hydrogen silsesquioxane (HSQ) followed by acid treatment to release the silicon particles from the oxide matrix (Hessel, C. M., Henderson, E. J., & Veinot, J. G. (2006). Hydrogen silsesquioxane: a molecular precursor for nanocrystalline Si-SiO₂ composites and freestanding hydride-surface-terminated silicon nanoparticles. *Chemistry of materials*, 18(26), 6139-6146). All these approaches give <12 nm silicon particles.

[0033] In some embodiments, the ultrasmall nanoparticles have an average particle size of less than about 15 nm. For example, the ultrasmall nanoparticles may have an average particle size of less than about 15 nm, less than about 12 nm, less than about 10 nm, less than about 8 nm, less than about 6 nm, less than about 4 nm, or less than about 2 nm. In some embodiments, the ultrasmall silicon nanoparticles have an average particle size of about 2 nm to about 12 nm, about 4 nm to about 12 nm, about 6 nm to about 12 nm, about 8 nm to about 12 nm, or about 10 nm to about 12 nm. In some embodiments, the ultrasmall silicon nanoparticles have an average particle size ranging about 2 nm to about 10 nm, about 4 nm to about 10 nm, about 6 nm to about 10 nm, about 8 nm to about 10 nm, about 2 nm to about 8 nm, about 4 nm to about 8 nm, about 6 nm to about 8 nm, about 2 nm to about 6 nm, or about 4 to about 6 nm, or about 7 nm.

[0034] The silicon nanoparticles may have an average particle size of 1 nm, 2 nm, 3 nm, 4 nm, 5 nm, 6 nm, 7 nm, 8 nm, 9 nm, or 10 nm. In some embodiments, the silicon nanoparticles have an average particle size of 5 nm, 7 nm, or 9 nm.

[0035] The silicon nanoparticles may have a narrow size distribution. For example, silicon nanoparticles may have a size distribution of about ± 1 nm to about ± 10 nm. In some embodiments, the silicon nanoparticles have a size distribution of about ± 1 nm, about ± 2 nm, about ± 3 nm, about ± 4 nm, about ± 5 nm, about ± 6 nm, about ± 7 nm, about ± 8 nm, about ± 9 nm, or about ± 10 nm. In some embodiments, the silicon nanoparticles have a size distribution of about ± 2 nm to about ± 8 nm, about ± 3 nm to about ± 7 nm, or about ± 4 nm to about ± 6 nm. The narrow size distribution achieved in the silicon nanoparticles of the present technology prevents swelling and cracking of silicon nanoparticles during charge and discharge.

[0036] Specifically, the silicon nanoparticles may range in size from about 1 nm to about 20 nm. In stark contrast, commercial silicon powders typically include particles ranging in size from about 20 nm to about 300 nm. In some embodiments, the silicon nanoparticles described herein may range in size from about 1 nm to about 15 nm, about 2 nm to about 18 nm, about 2 nm to about 16 nm, about 2 nm to about 15 nm, about 2 nm to about 12 nm, about 2 nm to about 10 nm, about 5 nm to about 15 nm, about 5 nm to about 12 nm, or about 5 nm to about 10 nm.

[0037] In the dense assembly of particles, the ultrasmall silicon nanoparticles may be spaced by nanopores. In some embodiments, the nanopores have an average pore size of less than about 10 nm. For example, the nanopores may have an average pore size of less than about 10 nm, less than about 9 nm, less than about 8 nm, less than about 7 nm, less than about 6 nm, less than about 5 nm, less than about 4 nm, less than about 3 nm, less than about 2 nm, or less than about 1 nm. In some embodiments, the nanopores have an average pore size of about 2 nm to about 10 nm, about 4 nm to about 10 nm, about 6 nm to about 10 nm, about 8 nm to about 10 nm, about 2 nm to about 8 nm, about 2 nm to about 6 nm, about 2 nm to about 4 nm, about 4 nm to about 10 nm, about 4 nm to about 8 nm, or about 4 nm to about 6 nm.

[0038] A typically procedure for the fabrication of micron-scale graphite-like assemblies composed of ultrasmall grain and pore size is shown in FIG. 1. First, ultrasmall silicon particles are dispersed in a solvent. The ultrasmall particles may be prepared by radiofrequency (RF) plasma synthesis. RF plasma synthesis produces ultrasmall particles with a narrow size distribution, because the plasma stabilizes the particles and prevents them from fusing into larger particles during preparation, which is common in commercial silicon powders. The solvent used to disperse the ultrasmall particles is not particularly limited. In some embodiments, the solvent is a non-polar solvent. The solvent may be a cosolvent. In some embodiments, the solvent comprises a volatile solvent. In some embodiments, the solvent comprises a non-volatile solvent. In some embodiments, the solvent is a co-solvent that comprises a volatile solvent and a non-volatile solvent. In some embodiments, the solvent comprises one or more of chloroform, dichloromethane, toluene, xylene, mesitylene, methanol, ethanol, and dichlorobenzene.

[0039] Dispersant agents such as polymers (polystyrene, polyvinylpyrrolidone, etc.) can be used to (1) improve the dispersion of the nanoparticles to give a more densely packed assembly and (2) build up a buffer space between the particles. In some embodiments a polymer

dispersant is included in the dispersion of ultrasmall silicon nanoparticles. In embodiments in which a polymer dispersant is included in the nanoparticle dispersion, the polymer may simply be burned off the material by gentle annealing to tune the void volume fraction and length scale.

[0040] After the silicon particles are dispersed in the solvent, the dispersion may be sonicated in a sonicating bath for ~30 minutes. Other feasible approaches to disperse the particles include utilization of a high-shear mixer or a sonicating horn. The dispersion is then poured in a large container such as a cooking pan to give a shallow (few millimeters deep) pool of the dispersion, and the dispersion is dried. In some embodiments, the dispersion is dried by leaving the dispersion at room temperature for an amount of time sufficient to evaporate the solvent. The dispersion may be left at room temperature for about 12 hours, about 18 hours, about 24 hours, about 36 hours, or about 24 hours to evaporate the solvent.

[0041] Upon drying, the material may appear as a thin crust which can then be scraped from the cooking pan and collected for further processing. Micron-sized particles comprising super-assembled silicon nanoparticles may be acquired from the thin crust. As used herein, the term “micron-sized particle” or “microparticle” is meant to include spherical and non-spherical micron-sized structures such as, for example, micro-rods and micro-flakes.

[0042] In some embodiments, the micron-sized particles have an average particle size of about 1 micrometer to about 20 micrometers. For example, micron-sized particles may have an average particle size of about 1 micrometer, about 2 micrometers, about 4 micrometers, about 6 micrometers, about 8 micrometers, about 10 micrometers, about 12 micrometers, about 14 micrometers, about 16 micrometers, about 18 micrometers, or about 20 micrometers. In some embodiments, the micron-sized particles have an average particle size of about 2 micrometers to about 20 micrometers, about 2 micrometers to about 18 micrometers, about 4 micrometers to about 16 micrometers, about 6 micrometers to about 14 micrometers, or about 8 micrometers to about 12 micrometers.

[0043] A carbon coating may be applied to the crust and/or micron-sized particles via chemical vapor deposition (CVD) using a process described in Nava, et al. (2019). Silicon-core–carbon-shell nanoparticles for lithium-ion batteries: rational comparison between amorphous and graphitic carbon coatings. *Nano letters*, 19(10), 7236-7245.

[0044] FIG. 2 shows the SEM of a super-assembled micron-sized particle in accordance with the present technology. TEM confirms the presence of very small crystalline silicon domains.

Elemental analysis also confirms that the CVD procedure uniformly infills the assembled silicon particles with carbon, resulting in the uniform mixture of silicon, carbon and void space. It is important to stress that this mixture is uniform on a sub 10 nm length scale. The small particles alleviate swelling and cracking issues associated with silicon. The void space is necessary in this application to accommodate the volume changes occurring during lithiation.

[0045] FIG. 3 shows x-ray diffraction (XRD) patterns of super-assembled silicon nanoparticle materials at different synthesis, assembly, and graphitization stages. As can be seen, the material shows characteristic peaks of crystalline silicon with peak broadening typically associated for sub-10 nm crystallites, with about 6 nm as the average particle size based on Scherrer analysis of the prominent Si (111) peak. The particles retained ultrasmall crystallite sizes (about 6 nm) throughout the assembly and graphitization steps, as estimated from Scherrer analysis shown in FIG. 3.

[0046] For comparison to the dense assembly of silicon nanoparticles prepared according to the present technology, control samples were prepared by (1) using the freestanding <10 nm particles without assembly and (2) assembling larger (~100 nm) nanoparticles. When tested as anodes for lithium-ion batteries, the control samples showed clearly inferior performance compared to the material which is realized by assembling <10 nm particles.

[0047] Nitrogen sorption porosimetry and tap density measurements, as well as Brunauer-Emmett-Teller (BET) analysis, of each of the control samples and a super-assembled sample are shown in FIGS. 4A-4E. As shown in FIGS. 4A-4E, a random assembly of the ultra-small (uSi) silicon particles, without the evaporation-induced assembly, had large pore size (20 nm) and very low tap density (<0.1 g/cm³). These values do not change significantly after application of a carbon layer via CVD (uSi-Gr). On the other hand, evaporation induced assembly reduced the pore size to ~5 nm (uSi-a). Additionally, as shown in FIGS. 4A and 4E, the pore size distribution in assembled samples is significantly narrowed, ranging from less than 10 nm, compared to the previous 5–100 nm. Consequently, the tap density increased by more than a factor of 10 to ~0.6 g/cm³. Application of the carbon coating (uSi-a-Gr) did not affect the pore size significantly but further increased the tap density to ~1.4 g/cm³. Importantly, this tap density value is on par with currently used commercial graphite powders, as shown in FIG. 4B. The high tap density ensures compatibility with high solid-loading slurries and roll-to-roll. As an additional control, the same measurements were also performed on commercially available ~100 nm silicon particles (from Nanostructured and Amorphous

Materials). The commercial nanoparticles gave, as expected, much larger pore sizes (>80 nm) and a tap density of $\sim 1 \text{ g/cm}^3$. Based on the measured tap density values, a reasonable estimate of the porosity (i.e., the fraction of empty volume or void space) can be obtained for each sample. The ultrasmall silicon nanoparticles (uSi), without assembly, have 97.8% porosity. After assembly, before CVD, the porosity decreased to 74%. After CVD, the porosity decreased further to 39%.

[0048] Testing in half cell, i.e., using lithium foil as a counter-electrode, indicated that the ultrasmall particles had superior performance after assembly, as shown in FIGS. 5A and 5B. FIGS. 5A and 5B show the capacity and coulombic efficiency of the control and experimental samples. The uSi-a-Gr particles had a capacity of roughly 1200 mAh/g, with good capacity retention over 100 charge-discharge cycles. The first cycle coulombic efficiency (first-CE) was 84.9%, and quickly rose to nearly 100% within 10 cycles and stabilizing at 99.9%. Without assembly, the same small particles (uSi-Gr) have a capacity of roughly 900 mAh/gram, with poor first-CE (51.8%) and lower stabilized CE (99.1%). Finally, the commercial particles, after assembly and coating with carbon, had a high capacity ($\sim 2400 \text{ mAh/gram}$) with a 92% first-CE. Unfortunately, they experienced a rapid capacity fade, dropping by a factor of 2 within 50 cycles. This data confirms that the combination of small particles, small pore size, and uniform carbon coating of the presently described super-assemblies enables outstanding electrochemical performance in a lithium-ion battery.

[0049] FIG. 6 shows the performance of the best material (ultra-fine, assembled silicon particles after carbon coating) when tested by an independent facility (Spectra Power) in a pouch cell, which used a real-life cathode material (NMC 811). The tests were conducted under standard conditions used for testing graphite-based cells and the full volt ranges (2.8V to 4.2V for NMC) were used. A standard cycling protocol, similar to that recommended by the U.S. Advanced Battery Consortium was employed to test the battery performance. Cells underwent one formation charge-discharge cycle at C/20, followed by three cycles at C/10 rate, before using a steady-state C/3 charge-discharge cycling rate for the remaining cycles. The areal capacity of the pouch cells ranged from about 1.5 mAh/cm^2 to about 2.0 mAh/cm^2 , and the first-cycle Coulombic efficiency (CE) for the pouch cells was about 70% to about 80%, rapidly climbing to over 99.5% within 4 cycles and stabilizing above 99.9%. Without intending to be limited by theory, the rapid CE improvement and high stabilized value achieved in these tests indicate that the super-assembled silicon nanoparticles of the present technology achieve fast

stabilization and minimal inventory loss, enabling high capacity and long cycle life. The pouch cell showed excellent capacity retention of about 84% at cycle 180 and maintained greater than 80% capacity retention for more than 400 cycles without any pre-lithiation, pre-cycling, or graphite blends.

[0050] In addition to electrochemical cycling stability, calendar life evaluations are critical for assessing the long-term viability of silicon anodes in commercial batteries. These tests measure the stability of materials during storage periods when the battery is not in use, which is particularly critical for silicon due to its high reactivity. The target calendar life for silicon anodes is greater than 10 years, which remains an unsolved challenge in the industry. Continuous interactions between silicon and the electrolyte over prolonged periods can lead to ongoing side reactions, resulting in capacity fade and potential safety issues.

[0051] Calendar aging in silicon anodes is primarily driven by chemical processes, and particularly by adverse reactions between the electrolyte and the inherently reactive silicon surface, which occur even during storage periods. The silicon super-assemblies of the present technology may prevent these common adverse electrolyte interactions and maintain a stable solid electrolyte interphase (SEI) layer. Specifically, the compact packing of ultra-small particles (less than 10 nm) in the silicon nanoparticle assemblies, as well as the ultra-small pores (some well below 5 nm), and the encapsulation of the particles into a graphitic matrix via the CVD step, may stabilize the SEI layer on the surface of the assembly, and thereby hinder adverse reactions with the electrolyte during storage as well as use.

[0052] To explore this theory, the cells were analyzed and tested for electrolyte after cycling. As shown in the scanning transmission electron microscopy-dispersive X-ray spectroscopy (STEM-EDS) images in FIG. 7A, a distinct C/O-rich layer about 40 nm to 50 nm thick formed on the outer surface of the cycled silicon nanoparticle assembly of the present technology. In contrast, the uncycled particles did not exhibit this distinct layer. Without intending to be limited by theory, this observation suggests that electrolyte interactions and subsequent SEI formation are limited to the exterior of the super-assemblies, with minimal penetration into the internal structure. This is also supported by the fact that the thickness of the SEI layer (about 40 nm to about 50 nm) was significantly larger than the size of the pores in the microstructure (less than 5 nm). FIG. 7B illustrates the effective clogging of the micron-sized pores of the super-assemblies described herein by the SEI layer, thereby preventing the electrolyte from penetrating and adversely reacting with the internal silicon surfaces, compared to the numerous

accessible surfaces in materials that have small particles and large pores or large particles and small pores.

[0053] The C/O-rich layer formed on the super-assemblies was further investigated by cycling the cells in half cells against lithium metal using a 1.0M LiPF₆ (lithium hexafluorophosphate) electrolyte, with and without fluoroethylene carbonate (FEC). FEC is an electrolyte additive typically added to enhance the performance and longevity of silicon anodes in lithium-ion batteries by promoting the formation of a stable and robust SEI layer. As shown in FIG. 7C, the Coulombic efficiency (CE) of the anodes comprising the super-assembled silicon nanoparticles of the present technology demonstrated negligible differences with or without FEC addition. This is in stark contrast with studies that show very low stabilized CE values in the absence of FEC additive (about 97% without FEC vs. about 99% with FEC). These data demonstrate that the micron-scale assemblies with sub-10 nm particles and pores achieve unexpectedly high SEI stabilization, independent of critical electrolyte additives like FEC. This finding further supports the theory that electrolyte penetration into the super-assembly is limited. Moreover, these results are also consistent with the excellent cycling stability and very fast CE stabilization. Collectively, these results strongly suggest that the super-assembled silicon nanoparticle material may have significant calendar life benefits in addition to cycle life improvements.

[0054] Overall, the super-assembled silicon particles described herein compete directly with the materials produced by commercial manufacturers such as, for example, Sila Nano and Group 14, in terms of functionality (i.e. drop-in replacement or additive to current anodes, with compatibility with roll-to-roll manufacturing). Moreover, the material described in this disclosure is significantly easier to achieve (i.e. faster and easier to manufacture). Feedstock ultrasmall silicon particles are simply dispersed in the appropriate solvent, which is then dried to produce dense assemblies with well-distributed nano-pores. Subsequent CVD of a carbon precursor locks the structure in place. Thus, the easier manufacturability of the material provides a competitive advantage in terms of cost.

Examples

Example 1. High-Performance Silicon-Dominant Lithium-Ion Anodes

[0055] Silicon is widely considered the best candidate anode material for next-generation lithium-ion batteries. Its specific capacity exceeds that of the current anode material, graphite,

both on a gravimetric and a volumetric basis (3579 mAh/g and 2194 mAh/cm³). Substituting graphite with silicon would enable a maximum theoretical capacity gain of roughly 25% at the cell level, i.e., when incorporating the silicon anode with real-life components (cathode, separator, current collectors, and packaging). While promising, silicon-dominant anodes have yet to be broadly utilized on a commercial scale. The primary issue with this material is its low cycling stability. While graphite retains its capacity over thousands of charge-discharge cycles, silicon degrades much faster. Moreover, this behavior is not rooted in a single cause, but due to many failure mechanisms. Lithium does not intercalate in silicon, but rather it forms a silicide resulting in large volume change (roughly 400% upon lithiation). This results in mechanical failure, pulverization, and loss of electrical contact. The community has accepted the use of nanoscale silicon as one viable approach to avoid pulverization of the active material. Still, this introduces additional challenges. While the single particle may not fracture, the use of small particles inevitably increases the number of particle-to-particle contact, requiring the need for specialized binders and conductive additives. Finally, a solid electrolyte interphase (SEI) layer is well-known to develop on the surface of the active material. For the case of graphite, this is highly stable due to the negligible volume change. For the case of silicon, the significant volume change upon lithiation degrades the SEI, which then partially reforms every cycle, leading to the irreversible loss of lithium.

[0056] Because of these reasons, the design of a silicon-based anode that achieves sufficient stability for real-life applications has proved to be a significant challenge. This has attracted the attention of several research groups. Many different approaches have been proposed to solve the many issues, ranging from using nanowires to careful engineering of void spaces around silicon particles.

[0057] This work describes the top-down assembly of ultra-small silicon nanoparticles to give micron-sized particles with excellent energy density and cycle life. The inventors have developed a relatively straightforward three-step method to utilize ultrasmall silicon particles (sub-10 nm diameter) produced from a plasma-based process and use them as building blocks to form micron-scale superstructures with precisely designed porosity, void fraction, and surface features to stabilizing the SEI formation and achieving high charge-discharge stability. The inventors found that by assembling ultrasmall silicon nanoparticles (<10 nm) it is possible to also achieve ultrasmall pore sizes, and that the combination of these two is necessary to stabilize the material during charge-discharge cycling. Anodes realized with

these nanoparticle assemblies showed excellent charge-discharge stability, with capacities ranging from 900-1400 mAh g⁻¹, while approaching 99.9% coulombic efficiencies.

[0058] Micron-scale silicon particles with <10 nm grain and pore sizes are prepared by (1) dispersing <10 nm freestanding nanoparticles into a solvent and (2) drying the dispersion so that the capillary forces pull the particles close together to give a dense assembly of particles. The assembled particles can then be infilled with carbon to lock the structure into place. Control samples were prepared by (1) using the freestanding <10 nm particles without assembly and (2) assembling larger (~100 nm) nanoparticles. When tested as anodes for lithium-ion batteries, the control samples showed clearly inferior performance compared to the material realized by assembling <10 nm particles. The inventors have found that it is the combination of (1) small size (<10 nm) and (2) small pore (<10 nm as well) that enables preparation of a material with excellent cycle life. As a result, in a full cell (pouch type format) paired with NMC532 cathode, this material achieved >250 cycle life with 80% capacity retention. These metrics were achieved without any pre-lithiation of the anode.

[0059] Additionally, the dense particle assemblies morphologically resembled graphite with a high tap density (~1 g cm⁻³), thus making them amenable to incorporation in slurries with high solid loadings (>30 wt.%). Therefore, this material is fully compatible with water-based slurries for application in roll-to-roll coating of the anode onto the copper foil. This is by far the most widespread approach towards anode manufacturing, with the industry having already invested significant capital in this manufacturing strategy. Hence, this work highlights the significance of both pore and particle size in a narrow sub-10 nm regime, which ultimately enables high-performance silicon-dominant anodes.

Material design and structural characterization

[0060] FIG. 1 illustrates the three-step bottom-up assembly to fabricate micron-scale graphite-like assemblies composed of ultrasmall (sub-10 nm) grain and pore size. First, a radiofrequency (RF) plasma is employed to nucleate and grow ultrasmall silicon nanoparticles (uSi) in the gas-phase using SiH₄ as the precursor. The plasma induced-surface charging results in electrostatic stabilization of the primary particles, which slows down particle aggregation, coalescence, and growth. As a result, the particles generated exhibit a highly narrow size distribution, as shown in FIG. 1. The lognormally fit particle size distributions of plasma-produced particles show a geometric standard deviation (σ_g) of 1.15, which is significantly lower than that of the coagulation-dominated, self-preserving size

distribution ($\sigma_g = 1.44$) typically encountered in aerosolized particles (supporting information). The synthesized particles were then used as building blocks to assemble micron-scale assemblies (uSi-a) using a simple solvent evaporation-driven approach, whereby capillary forces are used to densify the particle assembly. In the final step, the silicon surfaces in the assemblies are uniformly coated with highly graphitic shells via a two-step chemical vapor deposition (CVD) approach using C_2H_2 as the precursor. In the first step, the precursor (C_2H_2) is thermally cracked at low temperatures (590°C , 35 min) at a slightly positive C_2H_2 pressure of ~ 1.05 atm. The high gas pressure along with the high accessible surface area of the silicon assemblies ($\sim 400 \text{ m}^2 \text{ g}^{-1}$) ensures complete infiltration of carbon and uniform particle coating throughout the porous structure. The second step involved high-temperature annealing (750°C , 35 min) of the carbon-coated assemblies in argon to enable surface graphitization. Previous studies have shown that graphitization is necessary to improve conductivity and cycle life of silicon-based anodes.

[0061] As shown in FIG. 2, the resulting material (uSi-a-Gr) is a micron-scale structure with a morphology resembling graphite, composed of a tightly packed assembly of sub-10 nm silicon grains and sub-10 nm pores. This micro-nano material architecture represents a hierarchically porous assembly that has been explored by previous studies on silicon-based anode materials, albeit with limited control over particle size and pore structure. FIG. 3 shows the XRD patterns of uSi-based materials at different synthesis, assembly, and graphitization stages. As expected, the material shows characteristic peaks of crystalline silicon with peak broadening typically associated for sub-10 nm crystallites, with ~ 6 nm as the average particle size based on Scherrer analysis of the prominent Si (111) peak. Notably, the particles retain ultrasmall crystallite sizes (~ 6 nm) throughout the assembly and graphitization steps, as estimated from Scherrer analysis shown in FIG. 3. On the other hand, the assemblies exhibit a marked increase in particle size from ~ 6.6 nm to ~ 7.5 nm and ~ 9.7 nm when annealed at 500°C and 700°C , respectively, for 1 hour in argon, as evidenced by the increased XRD peak intensities (supporting information). These two temperatures represent the coating and graphitization steps involved during the carbon infiltration step. This indicates that carbon inclusion into the particle-pore assembly not only graphitizes and protects the silicon surface, but also prevents the sintering of ultrasmall silicon domains, thereby preserving the sub-10 nm crystallite and pore architecture throughout the process.

[0062] The morphology, particle arrangement, and elemental composition of the particle assemblies was investigated using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), along with energy dispersive spectroscopy (EDS). FIG. 8 shows HAADF-STEM images of two different ultrasmall silicon-based architectures explored in this work along with their respective EDS maps. Evidently, both assemblies comprise sub-10 nm silicon particles enveloped in a graphitic shell, while displaying markedly distinct morphologies. In the first case (uSi-Gr), sub-10 nm particles produced from the plasma are immediately coated with a graphitic shell using the previously described two-step protocol without any assembly or exposure to air. The resulting material, shown in FIG. 8, shows highly porous aggregates with an open-network morphology, as commonly observed with aerosol-based particles. On the other hand, the assembled particles (uSi-a-Gr) show densely packed structure with significantly diminished pore structure relative to the unassembled particles. Elemental analysis shown in FIG. 2 also confirms that the CVD procedure uniformly infills the assembled silicon particles with carbon, resulting in a uniform dispersion of silicon, carbon, and void space in the sub-10 nm length scale.

[0063] The inventors further investigated the nanoscale and bulk pores structure of different ultrasmall and commercial silicon-based materials using nitrogen sorption porosimetry and tap density measurements, respectively as shown in FIGs. 4A-4D. FIG. 4A shows the pore size distributions for different Si-based materials obtained from the desorption isotherm using Barrett–Joyner–Halenda (BJH) analysis. A random assembly of the ultrasmall silicon particles (uSi), without the evaporation-induced assembly, exhibits a large pore size (average about 12 nm) with a wide range of pore sizes (5 nm to 50 nm). As a result, the unassembled particles also showed a very low tap density (0.04 g cm^{-3}), reflecting its highly porous structure. These values do not change significantly after the application of a carbon layer via CVD (uSi-Gr). On the other hand, evaporation-induced assembly significantly reduces the average pore size from about 12 nm to about 3 nm (uSi-a), while also narrowing the pore size distribution (2-10 nm). Notably, the variation in nanoscale pore structure is also reflected on the bulk scale, as estimated by tap density measurements. FIG. 4B shows specific surface area as obtained from BET analysis. FIG. 4C shows that the tap density of the particles increases by more than a factor of 10 after assembly from about 0.04 g cm^{-3} to about 0.6 g cm^{-3} , with a corresponding reduction in bulk porosity from ~98% to ~75%. Application of the carbon coating onto the assemblies (uSi-a-Gr) further increases the tap density to about 1.0

g/cm³, while maintaining the sub-10 nm (about 3 nm) pore size. As a control, similar measurements were performed on assembled and carbon-coated equivalents obtained from commercially available about 100 nm silicon particles (cSi-a-Gr). As expected, the commercial silicon counterparts show much larger pore sizes (>50 nm) with negligible pore fraction in the sub-10 nm range, with a relatively low tap density of ~0.3 g cm⁻³, as well as the material's capacity to accommodate these changes. Most importantly, the surface graphitized and assembled ultrasmall silicon particles (uSi-a-Gr) exhibit a distinct structure, exhibiting highest tap density and low specific surface area while being composed of tight distributions of sub-10 nm particles and pores. Structurally, this material can be viewed as a graphite analog of silicon, featuring a microscale graphitic matrix with embedded ultrasmall silicon spheres and tailored pores, enabling large volumetric shifts during lithiation-delithiation cycles. As discussed later, this unique combination of the three sub-10 nm components (silicon, graphitic coating, and void space) enables highly stable lithium-ion batteries without any pre-lithiation.

Electrochemical Performance Characterization

[0064] Constituting a stable silicon-dominant anode is challenging primarily due to the complex interplay between the particle size and available pore volume which play a deciding role in long-term stability. While particle size distributions dictate the overall volumetric changes occurring in the anode during charge-discharge cycles, pore size distributions ultimately decide the ability of the anode to accommodate these changes. Although various stable porous materials have been studied, the impact of pore and particle sizes on electrochemical performance is unclear because of the limited precision in controlling each. The assembled and surface-graphitized materials described in this study span a range of pore and particle size distributions in the sub-100 nm regime, making them ideal materials to investigate how pore and particle dimensions affect their performance as anode materials. To investigate the electrochemical performance of these materials, we tested their cell performance as an active anode material against lithium metal as the counter electrode. The silicon-dominant anodes were prepared by mixing 75 wt.% of the active material (graphitized silicon), 10 wt. % Super P carbon black, 7.5 wt.% each of carboxymethylcellulose (CMC) and polyacrylic acid (PAA).

[0065] FIG. 5A shows the comparison of half-cell gravimetric capacities of different anodes based on the total weight of the active material (75 wt.%). As can be seen, the anodes based

on ultrasmall (<10 nm) silicon particle-pore assemblies (uSi-a-Gr) outperform their commercial and unassembled counterparts (cSi-a-Gr and uSi-Gr, respectively). The uSi-a-Gr sample shows a first-cycle discharge and charge capacity of 1540 mAh g⁻¹ and 1300 mAh g⁻¹, respectively at a 0.1C cycling rate (0.13 A g⁻¹). Considering the composite consists of about 54 wt.% silicon (obtained from SEM-EDS), the first cycle discharge capacity is estimated to be 2850 mAh g⁻¹, which represents about 80% of the total silicon contributes to the total material capacity. Despite the relatively high silicon utilization, the uSi-a-Gr anode shows good capacity retention (about 94%) over 60 charge-discharge cycles. FIG. 5B shows that uSi-a-Gr anodes also demonstrate high initial-cycle coulombic efficiency (ICE=84.9%), quickly rising to nearly 100% within 10 cycles and stabilizing at >99.8% (SCE). The rapid stabilization of the CE values can be attributed to compact structure and low specific surface area, which results in rapid SEI stabilization, reduced continued loss of lithium inventory, and high cycling stability. On the other hand, without any assembly, the same ultrasmall particles (uSi-Gr) have a charge capacity of roughly 1100 mAh g⁻¹, albeit with a poor ICE (51.8%) and lower stabilized CE (SCE=98.3%) than the assembled sample. As discussed earlier, the unassembled samples exhibit highly porous morphology with a wide range of pore size distributions (FIGs. 8 and 4A), which leads to a considerable irreversible loss of lithium ions during the first lithiation cycle. While the ultrasmall particle size minimizes the overall extreme volumetric changes during charge-discharge cycles, the associated high porosity (>98%) and large surface area accessible to the electrolyte and lithium ions exacerbates lithium inventory depletion. This continuous loss is compounded by the formation of a fresh SEI formation with each subsequent cycle, culminating in a low stabilized CE due to the irreversible lithium consumption in forming the new interphase layers. As a result, although the ultrasmall particles show decent capacity retention (82% in 60 cycles) in half cells, they are not amenable to forming high-stability full cells due to limited lithium inventory available. Finally, the commercial particles, after assembly and coating with carbon, display a high first-cycle capacity (about 2200 mAh g⁻¹) with a 92% ICE. However, they experience a rapid capacity fade, dropping by a factor of two within 50 cycles, while also showing low SCE value of about 98.9% (FIG. 9A). This is expected since in this case the relatively large particles in the wide particle size distribution (100-300 nm) result in extreme and catastrophic volumetric changes, resulting in fracture and side reactions despite the available pore space.

[0066] FIG. 9B shows that the areal capacity shows an almost linear relationship with the mass loading of the active material in the anode, with good capacity retention even under deep charge-discharge cycles at areal capacities as high as 3 mAh cm^{-2} . This suggests that the material can be coated at practically relevant areal loadings without significantly compromising the cycling stability. Additionally, as shown in FIG. 9C, the uSi-a-Gr samples show remarkable capacity (stabilized $\sim 900 \text{ mAh g}^{-1}$) and outstanding cycle life with $<1\%$ capacity loss over 500 cycles. Expectedly, these metrics are considerably superior when compared to the anodes composed of commercial (1300 mAh , $>50\%$ loss, 500 cycles) as well as unassembled samples (600 mAh g^{-1} , $<1\%$ loss, 500 cycles). Considering a composite made up of 1:1 silicon:graphite by volume, we can estimate that a minimum 50% pore volume fraction is necessary to allow for a 3x expansion of silicon in the composite. As shown in FIG. 4D, all three materials contain sufficient bulk porosities to accommodate silicon expansion (uSi-a-Gr: 54%, uSi-Gr: 98%, and cSi-a-Gr: 90%). However, as discussed above, the uSi-a-Gr sample with the lowest porosity value (54%) shows remarkably superior performance than others. This reflects a more intricate interplay between particle size, volumetric expansion, as well as the size of the void space accommodating that expansion. The uSi-a-Gr assemblies possess sufficient pore fraction ($\sim 54\%$), however, the small pores are highly localized and evenly distributed within a dense matrix of small silicon spheres, all on a similar sub-10 nm length scale (FIG. 2). As a result, the volumetric changes within each sub-10 nm particle are localized within the assembly, potentially alleviating large-scale stresses and cracking. Therefore, these observations confirm that the combination of narrowly distributed ultrasmall particles, pore size, and uniform carbon coating enables the outstanding electrochemical performance of silicon-based anodes in a lithium-ion battery.

[0067] Moreover, uSi-a-Gr-based anodes also showed excellent performance in pouch-type full cells when tested against Li ($\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}$) O_2 (NMC532) cathode, as shown in FIG. 10. The pouch cell shows a first-cycle discharge cell capacity of $\sim 9.9 \text{ mAh}$ with an areal capacity value of about 2 mAh cm^{-2} . Notably, due to the compact microstructure of the small silicon particles, the cells show a reasonably high first-cycle coulombic efficiency (about 78.6%) without any prelithiation. After the first four formation cycles (1 cycle at C/20, 3 cycles at C/10), the cells were cycled at a C/3 charge-discharge rate (0.2 A g^{-1}). The anode capacity in the full cell, based on the active anode material (75 wt.%), is estimated to be about 920 mAh g^{-1} , representing about 3x enhancement in energy density over graphite-based

materials. This value agrees well with the capacity obtained for these composites in a half-cell configuration at similar charge-discharge rates ($\sim 900 \text{ mAh g}^{-1}$, FIG. 9B), suggesting that the material's superior performance in half-cells replicates well in a full-cell as well. Most remarkably, the anode retains 84% of its capacity for 200 cycles at C/3 cycling rate, while maintaining a $>99.0\%$ coulombic efficiency. The anode achieves this stability without any pre-lithiation and is already among the most stable silicon-dominant anodes reported to date. The pre-lithiation step is well-known to extend cycle life significantly. For instance, a previous study on porous silicon-carbon nanotube structures showed a 76% retention over 120 cycles for pristine anodes; upon prelithiation, the capacity retention was significantly enhanced to $>92\%$ over 500 cycles. The ultrasmall silicon particle-pore assemblies demonstrated in this study can achieve >300 cycles with $\sim 76\%$ retention, therefore, upon pre-lithiation is expected to significantly prolong the cycle life to commercially relevant 1000 cycle range.

Material synthesis

[0068] The fabrication of ultrasmall silicon-pore assemblies (uSi-a-Gr) involved three key steps: a. particle synthesis, b. assembly, and c. surface graphitization. First, the ultrasmall silicon particles (uSi) were synthesized in a custom-built plasma reactor. A mixture of silane and argon (1.36% SiH_4 in Ar) was fed to a tubular quartz reactor with a 100 mm diameter, with the reactor pressure in the range of 2.5 Torr to 3 Torr. A radiofrequency electrode was used to sustain the plasma, with a typical power of 100W. The precursor was fed continuously to the reactor volume, and silicon particles were continuously nucleated, grown, and collected downstream of the plasma on a stainless-steel metal cloth. After particle synthesis, the reactor is evacuated and filled with argon and the particles are transferred to a glovebox to prevent ignition. The particles then undergo a simple assembly process, whereby they are first dispersed in a non-polar solvent (chloroform) at solid loadings of about 25-50 mg mL^{-1} and ultrasonicated for about 1 hour. This results in a relatively stable and homogeneous dispersion of particles in the solvent. The dispersion is then dried on a clean, smooth surface, whereby capillary forces driven by solvent evaporation induce particles to assemble into dense agglomerates which are then gently crushed to give micron-sized flakes (uSi-a). Finally, the micron-sized particles were locked into place by a carbon layer which is applied via modified CVD approach. The assembled sample was placed in an alumina crucible enclosed in a 100 mm diameter tubular quartz reactor. The reactor was then

evacuated and purged with argon, followed by introduction of acetylene gas (C_2H_2) at a flow rate of about 200 sccm till a slightly positive pressure of about 1.05 atm was achieved. The sample was then heated to $\sim 590^\circ C$ at a heating rate of $20^\circ C\ min^{-1}$, followed by a 35 min hold at $590^\circ C$. After this, the reactor was evacuated, and argon was introduced again at a flow rate of 400 sccm to purge out any residual C_2H_2 . The samples were then heated at $750^\circ C$ for 10 minutes to induce graphitization of the carbon shells formed during the first step. The final material was assembled, surface graphitized micron size structure with uniformly dispersed sub-10 nm particles and pores (uSi-a-Gr).

Characterization

[0069] Particle morphology on the micron-scale was analyzed with a ThermoFisher Scientific NNS450 scanning electron microscope at a 15 kV accelerating voltage. An FEI Titan Themis 300 transmission electron microscope was used to perform STEM-HAADF, HRTEM, and elemental analysis on the particle assemblies on the nanoscale. Powder X-ray diffraction was obtained using a PANalytical Empyrean Series 2 Cu with $K\alpha$ radiation. A Micrometrics ASAP 2020 Plus physisorption instrument was used to obtain nitrogen sorption porosimetry data (surface area, pore size) for different samples. Tap density measurements were performed by loading a certain mass of powders into a 5 mL graduated cylinder, followed by which the cylinder was gently tapped onto a padded surface until no change in volume was observed (typically >500 times). A set of triplicates was performed for each sample, and an average was obtained.

Electrochemical Analysis

[0070] All anodes explored in the study were composed of 75 wt.% active material, 10 wt.% Super P carbon black, and 15 wt.% of CMC and PAA with a 1:1 weight ratio. The active material and the carbon black were first crushed with a mortar and pestle, after which the appropriate water-based solutions of the binders (CMC-PAA) was added to prepare the slurry. The electrode slurries was then cast into electrodes on a copper current collector with typical loadings ranging from 1-3 mg cm^{-2} . Anode disks (12 mm) were then punched from the coated foils, which were then assembled into half cells against lithium metal (1 mm thickness) in a coin format (2032) in an argon glove box (O_2 , $H_2O < 1$ ppm). The electrolyte used in half cells was a 1M $LiPF_6$ solution in 1:1 v/v ethylene carbonate:diethyl carbonate (EC:DEC) with a 10 wt. % fluoroethylene carbonate (FEC) as an additive. Charge-discharge cycling measurements was performed on the coin cells between 0.05 and 1.5 V in a Neware

Instruments battery tester with a 0.1C as the deep-cycling current, and a stepwise accelerated ramp for long-term C/3 cycling experiments (1@C/20, 3@C/10, 3@C/5; 1000@C/3). Full cells were assembled at SpectraPower LLC using NMC532 as the cathode. 1.2 M LiPF₆ solution in 3:5 v/v ethylene carbonate:diethyl carbonate with a 10 wt. % FEC was used as the electrolyte for full cells. The formation cycles were performed in a sequential manner with 1 cycle at 0.05C, 3 cycles at 0.1C, followed by continued cycling at 0.3C.

Conclusion

[0071] In Example 1, the inventors demonstrate a simple three-step protocol to form microstructures composed of sub-10 nm particle and pore sizes. These assemblies show significantly superior performance compared to their unassembled and commercial counterparts. As a result, in a full cell, without pre-lithiation, a highly stable silicon-dominant anode is realized.

Example 2. Highly Stable Silicon Anodes

[0072] Silicon is widely recognized as a promising anode material for next-generation lithium-ion batteries. Its specific capacity largely exceeds that of graphite, both on a gravimetric and a volumetric basis (3579 mAh/g and 2194 mAh/cm³). While promising, silicon-dominant anodes typically show low cycle life because of multiple failure mechanisms. Lithiation results in a large volume change, leading to mechanical failure, pulverization, and loss of electrical contact. Nanostructuring is a viable approach to mitigate this problem. However, a stable solid electrolyte interphase (SEI) is also required for stable cycling. This is difficult to achieve when the material undergoes significant volume changes during cycling. The continuous reaction between the active material surface and the electrolyte leads to irreversible loss of lithium and capacity fade.⁷ As a consequence, achieving a silicon-based anode with sufficient stability for real-life applications has proven to be a significant challenge. Many approaches have been proposed to solve the many issues, ranging from using nanowires to carefully engineering void spaces around silicon particles, among many others. Despite these advances, there is still a need for novel anode materials that can leverage the potential of silicon, all while being simple to produce. This is needed to enable the successful commercialization of these novel technologies.

[0073] The inventors found a novel solution to this problem that has advantageous properties in terms of simplicity and scalability. Their approach relies on the bottom-up assembly of extra-small (<10 nm) silicon particles (uSi particles) into larger, micron-sized agglomerates.

The use of uSi particles, in combination with their careful assembly and encasing in a carbon matrix, allows realizing anode materials with 80% capacity retention after 400 cycles in pouch cell format, without the need for pre-lithiation, pre-cycling, or any other special cycling protocol.

[0074] FIG. 1 illustrates the protocol developed by the inventors to prepare the micro-sized material. In the first step (not shown), a radio frequency (RF) plasma is used to nucleate and grow the x-SiNPs using silane (SiH_4) as the precursor. This approach is characterized by an inherent non-thermal equilibrium between the free electrons and the background gas. This results in the rapid conversion of silane into solid particles, with sub-10 millisecond reaction time and near 100% silane utilization. It also results in the electrostatic stabilization of the primary particles in the gas phase, which slows down particle aggregation, coalescence, and growth. Plasma-produced particles generally exhibit a narrow size distribution. The lognormally fit of particle size distributions shows a geometric standard deviation (σ_g) of 1.15, significantly lower than that of the coagulation-dominated, self-preserving size distribution ($\sigma_g = 1.44$) typically encountered in aerosolized particles. This synthesis approach has already been successfully employed for a broad range of applications, including for the production of silicon quantum dots and energetic materials. Recently, the Neale group has published multiple reports on plasma-produced silicon particles for lithium-ion battery anodes, confirming that they enable excellent cycle life. In these reports, the silicon surface is carefully engineered with molecular groups to passivate the surface and provide good ionic conductivity. The inventors have previously investigated the use of plasma-produced silicon quantum dots as anode materials by embedding them into carbon matrixes derived by annealing various polymers and found that the resulting anodes are indeed highly stable. However, they typically show low initial Coulombic efficiency (ICE) because of their high surface area. The inventors have found that a simple assembly step solves this issue. In this second step, the ultrasmall Si particles are sonicated in chloroform, which is then evaporated so that capillary forces densify the particle agglomerates. In the third and final step, the assembled particles are coated with carbon via chemical vapor deposition (CVD) using acetylene (C_2H_2) as the precursor. Acetylene is first thermally cracked at low 590°C at a pressure of about 1.05 atm. The combination of relatively high pressure and moderate temperature ensures the infiltration of carbon into the porous structure. The particles are then annealed at 650-750°C to increase the degree of graphitization of the carbon coating. This

approach has been demonstrated to enhance the quality of the carbon shell, improving its electrical conductivity and the performance of the resulting anode.

[0075] As shown in FIGS. 2 and 3, the resulting material is composed of micron-sized particles with morphology resembling that of graphite flakes. FIG. 3 shows the XRD patterns of the material at different synthesis, assembly, and carbon coating stages. Scherrer analysis suggests that the particle size is about 6 nm. The particles retain a small crystallite size throughout the assembly and CVD steps. Without carbon coating, annealing for 1 hour in argon at the same CVD temperature leads to particle growth to about 10 nm, based on XRD analysis (not shown for brevity). This indicates that the carbon coating not only protects the silicon surface but also prevents the sintering of silicon domains. It also confirms the uniform infilling of carbon into the particle assembly.

[0076] The morphology and elemental composition of the assemblies were investigated using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), along with energy dispersive spectroscopy (EDS). FIGS. 2 and 8 shows HAADF-STEM images of uSi particles with and without assembly, respectively. Both cases show sub-10 nm silicon particles coated with carbon, but their morphology is very different. Without the evaporative assembly, the particles form highly porous aggregates with an open-network morphology. On the other hand, the assembled particles show a densely packed structure. The elemental mapping confirms that the CVD procedure uniformly infills the assembled silicon particles with carbon.

[0077] FIGS. 4A-4D summarize the results of nitrogen sorption porosimetry and tap density measurements. FIG. 4A shows the pore size distributions for different materials obtained from the desorption isotherm using Barrett–Joyner–Halenda (BJH) analysis. A random assembly of plasma-produced silicon particles, without the evaporation-induced assembly, exhibits a large pore size (average ~12 nm) with a wide range of pore sizes (5->50 nm). As a result, the unassembled particles also show a very low tap density (0.04 g cm^{-3}), consistent with a highly porous structure. These values do not change significantly after applying a carbon layer via CVD (coated uSi particles). On the other hand, the evaporation-induced assembly significantly reduces the average pore size from ~12 nm to ~3 nm (assembled uSi particles, uSi-a), and also narrows the pore size distribution (2-10 nm). FIG. 4B shows that the tap density of the particles increases by more than a factor of 10 after assembly from ~0.04 g cm^{-3} to ~0.6 g cm^{-3} , with a corresponding reduction in bulk porosity from ~98% to

~75%. Application of the carbon coating onto the assemblies (uSi-a-Gr) further increases the tap density to $\sim 1.0 \text{ g cm}^{-3}$ while maintaining the sub-10 nm ($\sim 3 \text{ nm}$) pore size. As a control, similar measurements were performed on assembled and carbon-coated equivalents obtained from commercially available $\sim 100 \text{ nm}$ silicon particles (c-SiNPs) obtained from Nanostructured & Amorphous Materials. As expected, the commercial silicon counterparts show much larger pore sizes ($>50 \text{ nm}$) with negligible pore fraction in the sub-10 nm range and a relatively low tap density of $\sim 0.3 \text{ g cm}^{-3}$. To summarize, the carbon-coated, assembled uSi particles (uSi-a-Gr), exhibit the highest tap density and low specific surface area. Their size distribution is small ($<15 \text{ nm}$) and narrow (all $<15 \text{ nm}$), both in terms of primary particle and pore sizes.

[0078] The inventors tested these materials first in half cells, against lithium metal as the counter electrode. The silicon-dominant anodes were prepared by mixing 75 wt.% of the active material (carbon coated, assembled uSi particles, uSi-a-Gr), 10 wt. % Super P carbon black, 7.5 wt.% each of carboxymethylcellulose (CMC) and polyacrylic acid (PAA). FIG. 5A shows the comparison of half-cell gravimetric capacities of different anodes based on the total weight of the active material. The anodes based on the uSi particles (uSi-a-Gr) outperform their commercial counterparts. The assembled uSi particles sample shows a first-cycle discharge and charge capacity of 1540 mAh g^{-1} and 1300 mAh g^{-1} , respectively at a 0.1C cycling rate (0.13 A g^{-1}). These capacities are calculated based on the active material, which constitutes 75 wt.% of the total anode weight. Considering the composite consists of about 54 wt.% silicon (obtained from SEM-EDS), the first cycle discharge capacity is estimated to be 2850 mAh g^{-1} , which represents about 80% of the theoretical silicon capacity. The anode shows good capacity retention ($\sim 94\%$) over 60 deep charge-discharge cycles (0.1C cycling rate). FIGS. 5B and 9A show that the same anodes also demonstrate high initial CE (ICE = 84.9%), quickly rising to nearly 100% within 10 cycles and stabilizing at $>99.8\%$ (stabilized Coulombic efficiency, or SCE). We attribute this rapid stabilization to the compact material structure and low specific surface area, which results in rapid SEI stabilization, reduced loss of lithium inventory, and high cycling stability. Without any assembly, the uSi particles (uSi-Gr) have a first-cycle charge capacity of roughly 1100 mAh g^{-1} , albeit with a poor ICE (51.8%) and lower stabilized CE (SCE=98.3%) than the assembled sample. As discussed earlier, the non-assembled samples have a highly porous morphology with a wide range of pore size distributions (FIG. 4A and 8), which leads to a considerable irreversible

loss of lithium ions during the first lithiation cycle. The high porosity (>98%) and large surface area accessible to the electrolyte exacerbates the lithium inventory depletion. The formation of fresh SEI with each cycle leads to low SCE. As a result, although the ultrasmall particles show decent capacity retention (82% in 60 cycles) in half cells, they are not compatible with full cells due to the limited lithium inventory available. For comparison, we also coated and assembled commercial silicon nanoparticles using the same procedure used for the uSi particles. These particles have broader particle and pore size distributions than the material derived from the plasma-produced particles. As shown in FIG. 9A, the commercial nanoparticle-based assemblies display a high first-cycle capacity ($\sim 2200 \text{ mAh g}^{-1}$) with a 92% ICE. However, they experience a rapid capacity fade, dropping by a factor of 2 within 50 cycles while also showing a low SCE value of $\sim 98.9\%$. FIG. 9B shows that the areal capacity has an almost linear relationship with the mass loading, with good capacity retention even under deep charge-discharge cycles at areal capacities as high as 3 mAh cm^{-2} . This confirms that the material can be coated at practically relevant areal loadings.

[0079] The assembled uSi particle anodes also show excellent performance in pouch-type full cells when tested against $\text{Li}(\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Ni}_{0.1})\text{O}_2$ (NMC 811) cathode, as shown in FIG. 6. Most remarkably, the anode retains more than 80% of its capacity for over 400 cycles at a C/3 cycling rate while maintaining a >99.0% coulombic efficiency. The anode achieves this stability without any special measure to counter the loss of lithium ions in the first few cycles. Techniques such as pre-lithiation or pre-cycling are effective at countering the lithium inventory loss typically encountered in the first few cycles and at extending the cycle life of full cells. The inventors avoid such approaches as they make cell manufacturing more complex, introducing an obstacle to real-life implementation.

[0080] The high stability of the material described here can be attributed to two factors. First, as already pointed out by Nava et al. and Schwan et al., commercially available silicon particles may have an average particle size below the broadly accepted critical size of 150 nm, but inevitably a fraction of particles is above this size. Even if this fraction is small, the larger particles occupy a significant fraction of the overall volume (with volume scaling as d_p^3 , with d_p being particle size). High cycle life can only be achieved if all the particles are below the critical size, and the uSi particles used in this study satisfy this condition. In addition, the porosity length scale of the assembled uSi particles is crucial for enabling both a reasonably high ICE and rapid stabilization of SCE to high values. This is because the pore

size is smaller than the typical thickness of the solid-electrolyte interphase, which is several tens of nanometers on graphite and has been reported below 50 nm for silicon anodes with FEC-containing electrolytes, but still significantly thicker than the characteristic pore size of our material (less than 10 nm). One common problem in the silicon anode field is the material high surface area (a consequence of nanostructuring) and the poor stability of the SEI (a result of the volume change during the charge-discharge cycle). This translates into excessive SEI formation, leading to low values of both ICE and SCE. The structure we developed bypasses this problem by volumetrically constraining the SEI growth, achieving high CE values despite its high surface area. The pore size is just too small to allow the growth of a thick SEI. Consistent with this, we observe a rapid stabilization of CE values in our materials, as shown in the inset of FIG. 5B.

[0081] To summarize, our work demonstrates that highly stable silicon-carbon composites are achievable by (1) using small silicon particles with a narrow size distribution as building blocks and (2) achieving a uniform distribution of small pores within the composite. The combination of these two characteristics enables high Coulombic efficiency and excellent cycle life when tested in pouch cells. Importantly, small particle sizes are readily achievable via the non-thermal plasma process described herein, which converts silane to ultra-small particles on a millisecond time scale. Moreover, the evaporation-induced assembly process is simple, as it involves simple sonication of the powder followed by evaporation of the solvent. Finally, the CVD process used herein to infiltrate the assembly with carbon utilizes a commodity precursor and readily available equipment. Overall, the simplicity of the preparation procedure makes this technology promising for scale-up and large-scale implementation.

Experimental Methods

[0082] The extra-small silicon particles were produced using a large version of the flow-through plasma reactor first introduced by Mangolini et al., High-yield plasma synthesis of luminescent silicon nanocrystals. *Nano Letters* **2005**, 5 (4), 655-659, which is incorporated herein by reference in its entirety. A mixture of silane and argon (1.36% SiH₄ in Ar) was fed to a tubular quartz reactor with a 2" mm diameter, with the reactor pressure in the range of 2.5-3 Torr. A radiofrequency electrode was used to sustain the plasma, with a typical power of 100W. The precursor was fed continuously to the reactor volume, and silicon particles were continuously nucleated, grown, and collected downstream of the plasma on a stainless-

steel metal cloth. After particle synthesis, the reactor is evacuated and filled with argon and the particles are transferred to a glovebox to minimize oxidation. The particles are then dispersed in a non-polar solvent (chloroform) at solid loadings of $\sim 25\text{-}50\text{ mg mL}^{-1}$ and ultrasonicated for ~ 1 hour. This results in a relatively stable and homogeneous dispersion of particles. The dispersion is then dried on a clean, smooth surface, whereby capillary forces driven by solvent evaporation induce particles to assemble into dense agglomerates, which are then gently crushed to give micron-sized flakes. Finally, the micron-sized particles are locked into place by a carbon layer applied via CVD. The assembled powders are placed in an alumina crucible enclosed in a 2-inch diameter tubular quartz reactor. The reactor is evacuated and purged with argon, followed by the introduction of acetylene (C_2H_2) at a flow rate of ~ 200 sccm till a slightly positive pressure of about 1.05 atm is achieved. The sample is then heated to $\sim 590^\circ\text{C}$ at a heating rate of $20^\circ\text{C min}^{-1}$, followed by a 35 min hold at 590°C . After this, the reactor is evacuated, and argon is introduced again at a flow rate of 400 sccm to purge out any residual C_2H_2 . The samples are then heated at $650\text{-}750^\circ\text{C}$ for 10 minutes to improve the quality of the carbon coating.

[0083] Particle morphology on the micron scale was analyzed with a ThermoFisher Scientific NNS450 scanning electron microscope at a 15 kV accelerating voltage. An FEI Titan Themis 300 transmission electron microscope was used to perform STEM-HAADF, HRTEM, and elemental analysis on the particle assemblies on the nanoscale. Powder X-ray diffraction was obtained using a PANalytical Empyrean Series 2 Cu with $\text{K}\alpha$ radiation. A Micrometrics ASAP 2020 Plus physisorption instrument was used to obtain nitrogen sorption porosimetry data (surface area, pore size) for different samples. Tap density measurements were performed by loading a known mass of powders into a 5 mL graduated cylinder, followed by which the cylinder was gently tapped onto a padded surface until no change in volume was observed (typically >500 times). A set of triplicates was performed for each sample, and an average was obtained.

[0084] All anodes explored in the study were composed of 75 wt.% active material, 10 wt.% Super P carbon black, and 15 wt.% of CMC and PAA with a 1:1 weight ratio. The active material and the carbon black were first crushed with a mortar and pestle, after which the appropriate water-based solutions of the binders (CMC-PAA) were added to prepare the slurry. The electrode slurries were then cast into electrodes on a copper current collector with typical loadings ranging from $1\text{-}3\text{ mg cm}^{-2}$. Anode disks (12 mm) were then punched from

the coated foils, which were then assembled into half cells against lithium metal (1 mm thickness) in a coin format (2032) in an argon glove box (O_2 , $H_2O < 1$ ppm). The electrolyte used in half cells was a 1M $LiPF_6$ solution in 1:1 v/v ethylene carbonate: diethyl carbonate (EC:DEC) with a 10 wt. % fluoroethylene carbonate (FEC) as an additive. Charge-discharge cycling measurements were performed on the coin cells between 0.05 and 1.5 V in a Neware Instruments battery tester with 0.1C as the deep-cycling current and a stepwise accelerated ramp for long-term C/3 cycling experiments (1@C/20, 3@C/10, 3@C/5, 1000@C/3). Full cells were assembled at SpectraPower LLC using NMC532 as the cathode. 1.2 M $LiPF_6$ solution in 3:5 v/v ethylene carbonate: diethyl carbonate with a 10 wt. % FEC was used as the electrolyte for full cells. The formation cycles were performed sequentially with 1 cycle at 0.05C, 3 cycles at 0.1C, and continued cycling at 0.3C.

[0085] Various exemplary embodiments of the present technology are set forth herein below in paragraphs [0086]-[0099]:

[0086] 1. A composition of matter, comprising: silicon nanoparticles having nanopores disperse among the silicon nanoparticles, wherein the silicon nanoparticles have an average particle size of less than about 12 nm, and the nanopores have an average size of less than about 10 nm.

[0087] 2. The composition of matter of example 1, wherein the silicon nanoparticles have a narrow size distribution.

[0088] 3. The composition of matter of example 1 or example 2, wherein the silicon nanoparticles have a size ranging from about 1 nm to about 15 nm.

[0089] 4. The composition of matter of any one of examples 1-3, wherein the nanoparticles have an average particle size of less than about 10 nm.

[0090] 5. The composition of matter of any one of examples 1-4, wherein the nanopores have an average pore size of about 5 nm.

[0091] 6. The composition of matter of any one of example 1-5, wherein the composition of matter is in the form of micron-sized particles having an average particle size ranging from about 1 to about 20 micrometers.

[0092] 7. An anode material, comprising: a micron-sized assembly of silicon nanoparticles having an average particle size of less than about 12 nm, wherein the silicon nanoparticles are spaced by nanopores having average pore size of less than about 10 nm, and wherein the anode material is made by: dispersing the silicon nanoparticles in a solvent; and evaporating the

solvent from the silicon nanoparticles to provide an evaporation-induced assembly of the silicon nanoparticles.

[0093] 8. The anode material of example 7, wherein the solvent comprises a volatile solvent.

[0094] 9. The anode material of example 7 or 8, wherein the solvent comprises a non-volatile solvent.

[0095] 10. The anode material of any one of examples 7-9, wherein the solvent comprises one or more of chloroform, dichloromethane, toluene, xylene, mesitylene, methanol, ethanol, and dichlorobenzene.

[0096] 11. The anode material of any one of examples 7-10, wherein evaporating the solvent from the silicon nanoparticles comprises leaving the dispersion of silicon nanoparticles at room temperature for an amount of time sufficient to evaporate the solvent.

[0097] 12. An anode material comprising: a micron-sized assembly of silicon nanoparticles, wherein the micron-sized assembly comprises nanopores having an average pore size of less than about 10 nm, and the silicon nanoparticles have an average particle size ranging from about 8 nm to about 12 nm.

[0098] 13. A method of preparing an anode material, comprising: dispersing silicon nanoparticles in a solvent; and evaporating the solvent from the silicon nanoparticles to provide an evaporation-induced assembly of the silicon nanoparticles, wherein the evaporation-induced assembly of silicon nanoparticles comprises silicon nanoparticles having an average particle size of less than about 12 nm spaced by nanopores having an average pore size of less than 10 nm.

[0099] 14. The method of example 13, wherein evaporating the solvent from the silicon nanoparticles comprises leaving the dispersion of silicon nanoparticles at room temperature for an amount of time sufficient to evaporate the solvent.

Conclusion

[00100] While this specification contains many specifics, these should not be construed as limitations on the scope of an invention or of what may be exemplified, but rather as descriptions of features specific to particular embodiments of the invention. Certain features that are described in this specification in the context of separate embodiments can also be implemented in combination in a single embodiment. Conversely, various features that are described in the context of a single embodiment can also be implemented in multiple

embodiments separately or in any suitable subcombination. Moreover, although features may be described above as acting in certain combinations and even initially claimed as such, one or more features from a claimed combination can in some cases be excised from the combination, and the claimed combination may be directed to a subcombination or a variation of a subcombination.

[00101] Only a few implementations are disclosed. However, variations and enhancements of the disclosed implementations and other implementations can be made based on what is described and illustrated in this specification.

CLAIMS

We claim:

1. A composition of matter, comprising:

silicon nanoparticles having nanopores disperse among the silicon nanoparticles, wherein the silicon nanoparticles have an average particle size of less than about 12 nm, and the nanopores have an average size of less than about 10 nm.

2. The composition of matter of claim 1, wherein the silicon nanoparticles have a narrow size distribution.

3. The composition of matter of claim 1 or 2, wherein the silicon nanoparticles have a size ranging from about 1 nm to about 15 nm.

4. The composition of matter of claim 1 or claim 2, wherein the nanoparticles have an average particle size of less than about 10 nm.

5. The composition of matter of claim 1 or claim 2, wherein the nanopores have an average pore size of about 5 nm.

6. The composition of matter of claim 5, wherein the composition of matter is in the form of micron-sized particles having an average particle size ranging from about 1 to about 20 micrometers.

7. An anode material, comprising:

a micron-sized assembly of silicon nanoparticles having an average particle size of less than about 12 nm,

wherein the silicon nanoparticles are spaced by nanopores having average pore size of less than about 10 nm, and wherein the anode material is made by:

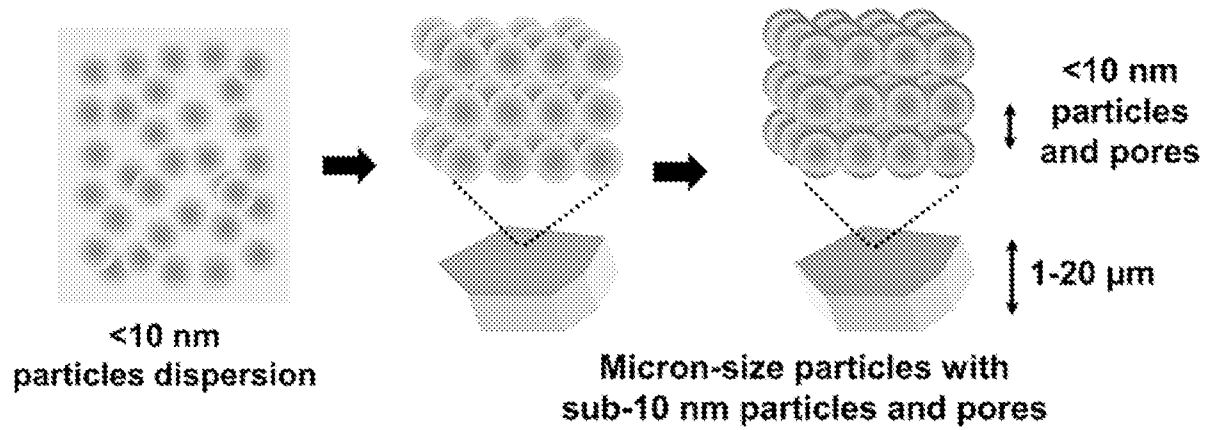
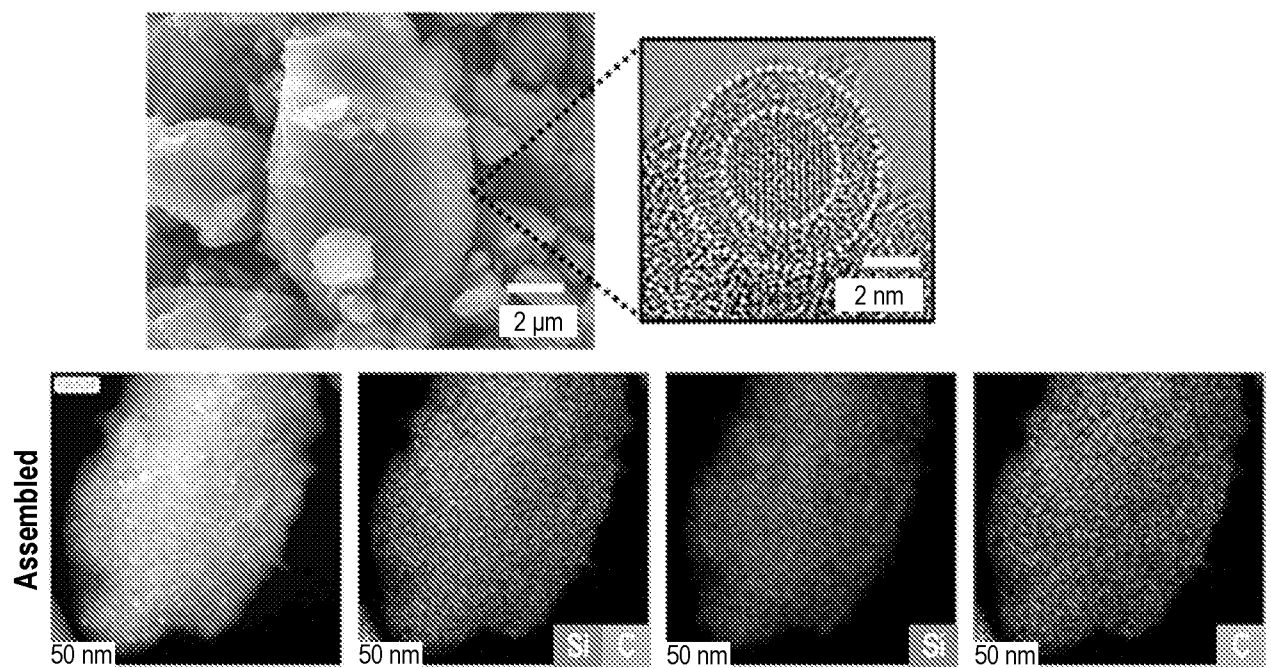
dispersing the silicon nanoparticles in a solvent; and

evaporating the solvent from the silicon nanoparticles to provide an evaporation-induced assembly of the silicon nanoparticles.

8. The anode material of claim 7, wherein the solvent comprises a volatile solvent.
9. The anode material of claim 7 or 8, wherein the solvent comprises a non-volatile solvent.
10. The anode material of claim 7, wherein the solvent comprises one or more of chloroform, dichloromethane, toluene, xylene, mesitylene, methanol, ethanol and dichlorobenzene.
11. The anode material of claim 7, wherein evaporating the solvent from the silicon nanoparticles comprises leaving the dispersion of silicon nanoparticles at room temperature for an amount of time sufficient to evaporate the solvent.
12. An anode material comprising:
 - a micron-sized assembly of silicon nanoparticles,
 - wherein the micron-sized assembly comprises nanopores having an average pore size of less than about 10 nm, and the silicon nanoparticles have an average particle size ranging from about 8 nm to about 12 nm.
13. A method of preparing an anode material, comprising:
 - dispersing silicon nanoparticles in a solvent; and
 - evaporating the solvent from the silicon nanoparticles to provide an evaporation-induced assembly of the silicon nanoparticles,
 - wherein the evaporation-induced assembly of silicon nanoparticles comprises silicon nanoparticles having an average particle size of less than about 12 nm spaced by nanopores having an average pore size of less than 10 nm.
14. The method of claim 13, wherein evaporating the solvent from the silicon nanoparticles comprises leaving the dispersion of silicon nanoparticles at room temperature for an amount of time sufficient to evaporate the solvent.

I. Evaporation-induced assembly

II. CVD (Surface Graphitization)

**FIG. 1****FIG. 2**

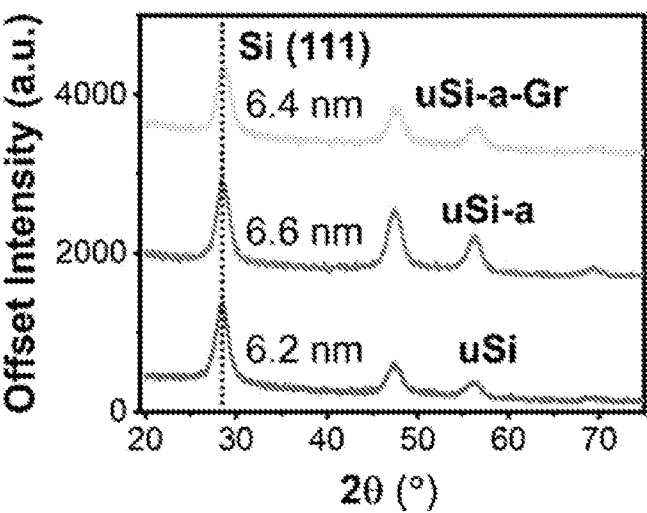


FIG. 3

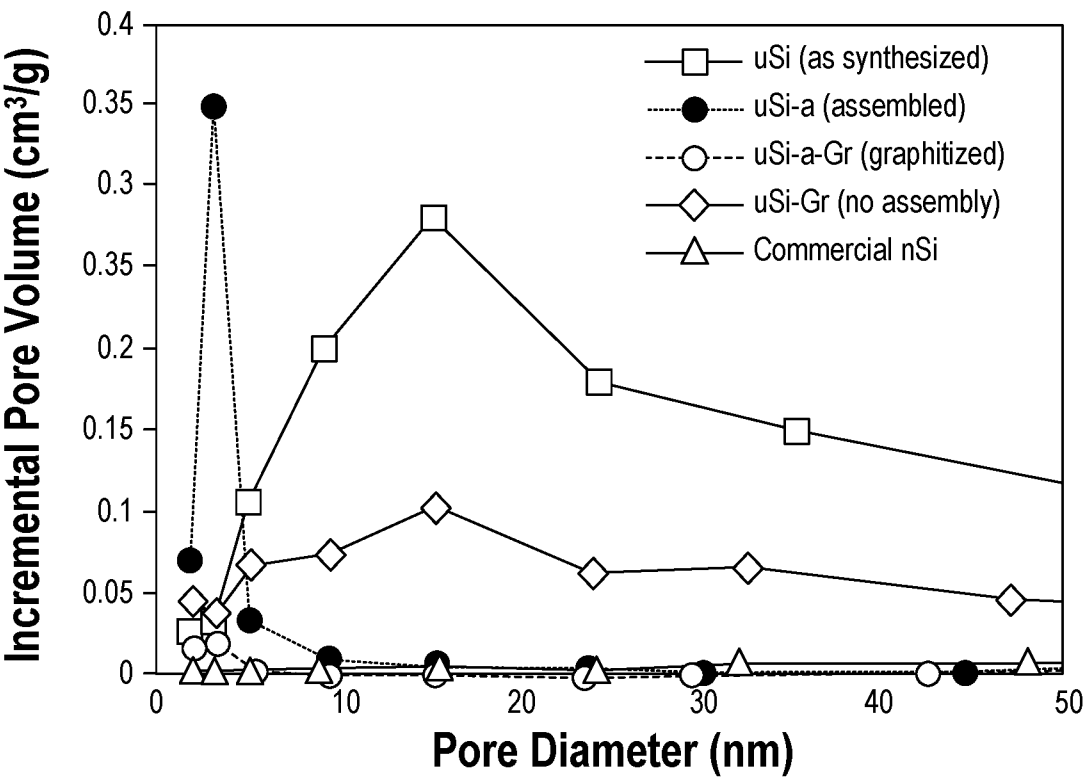


FIG. 4A

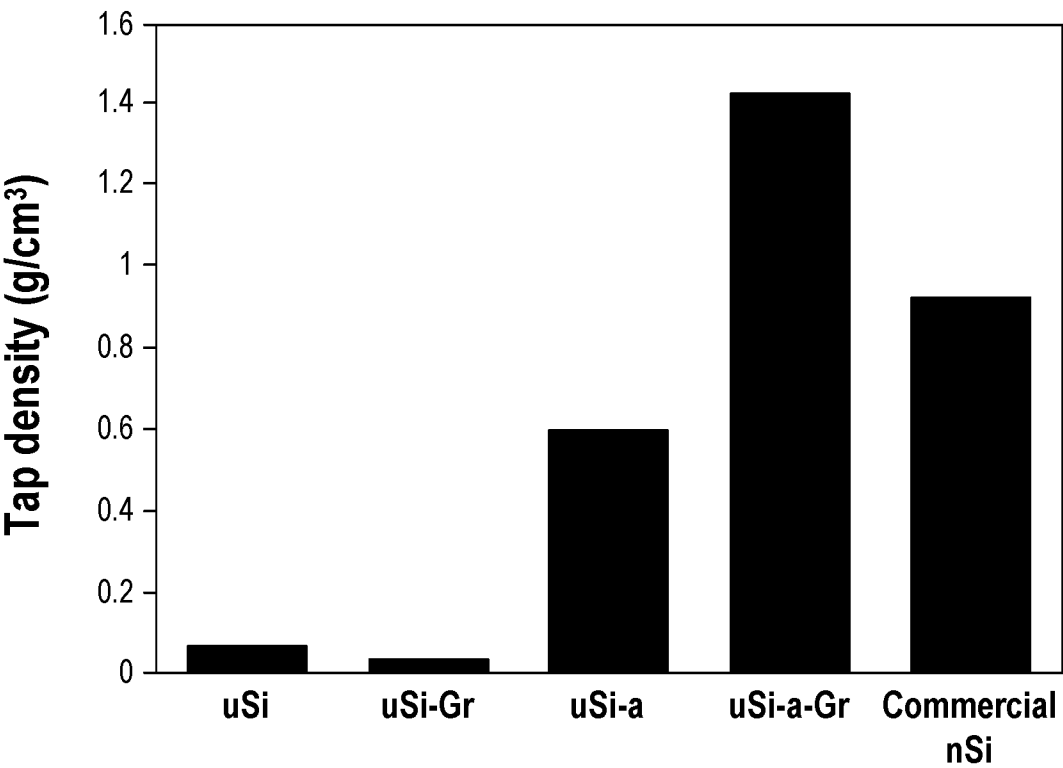


FIG. 4B

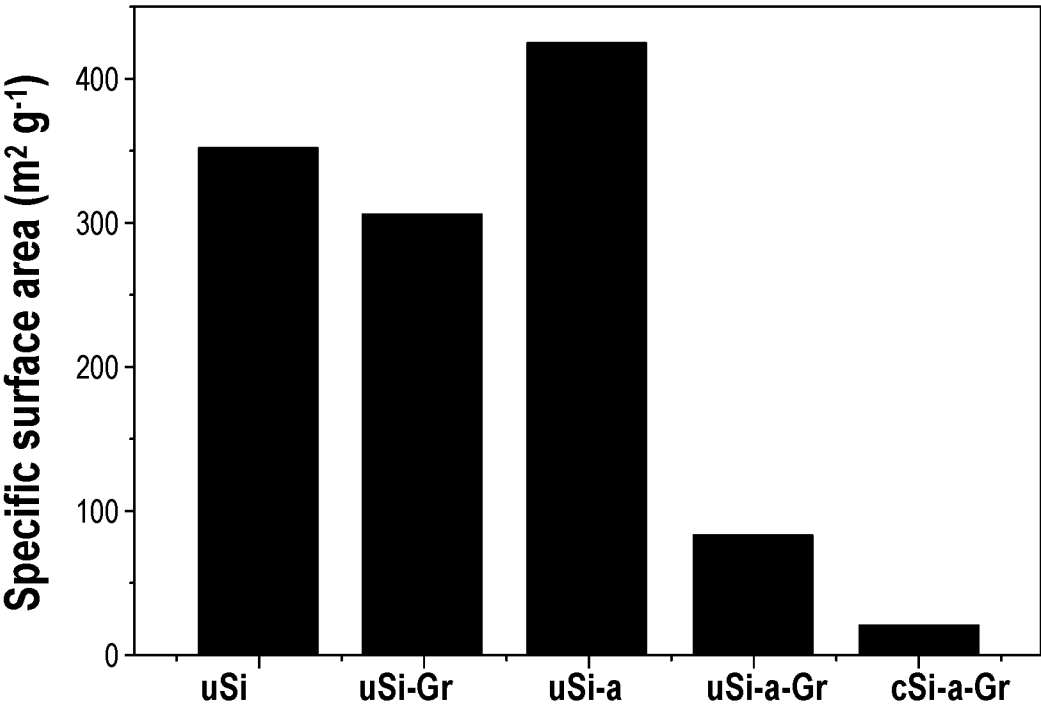


FIG. 4C

4/10

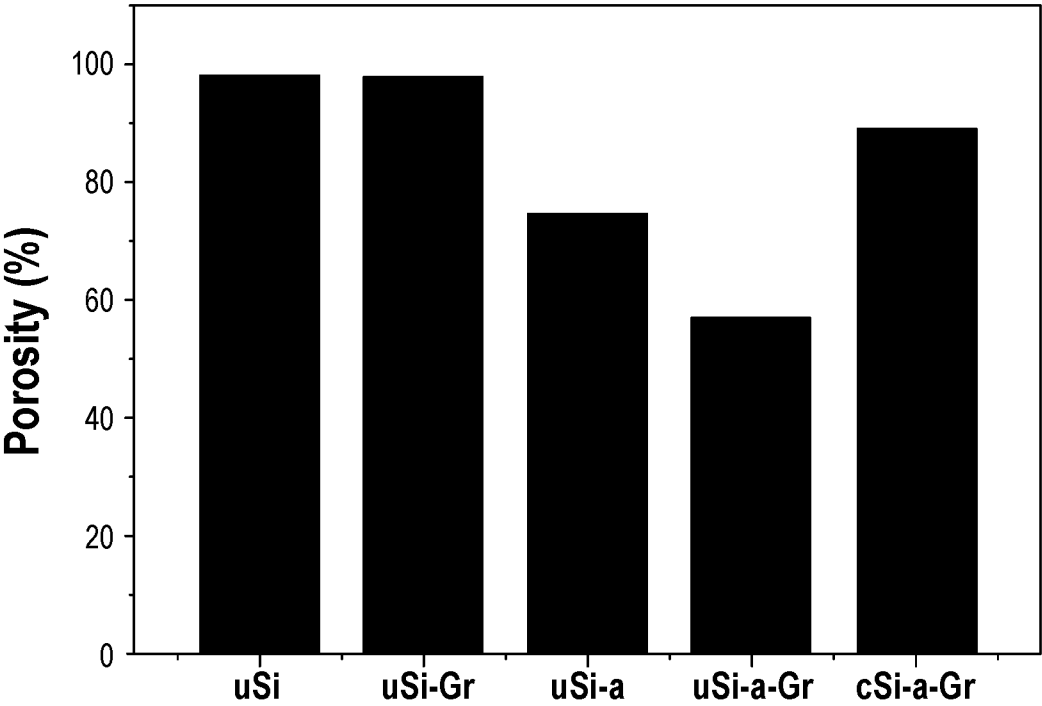


FIG. 4D

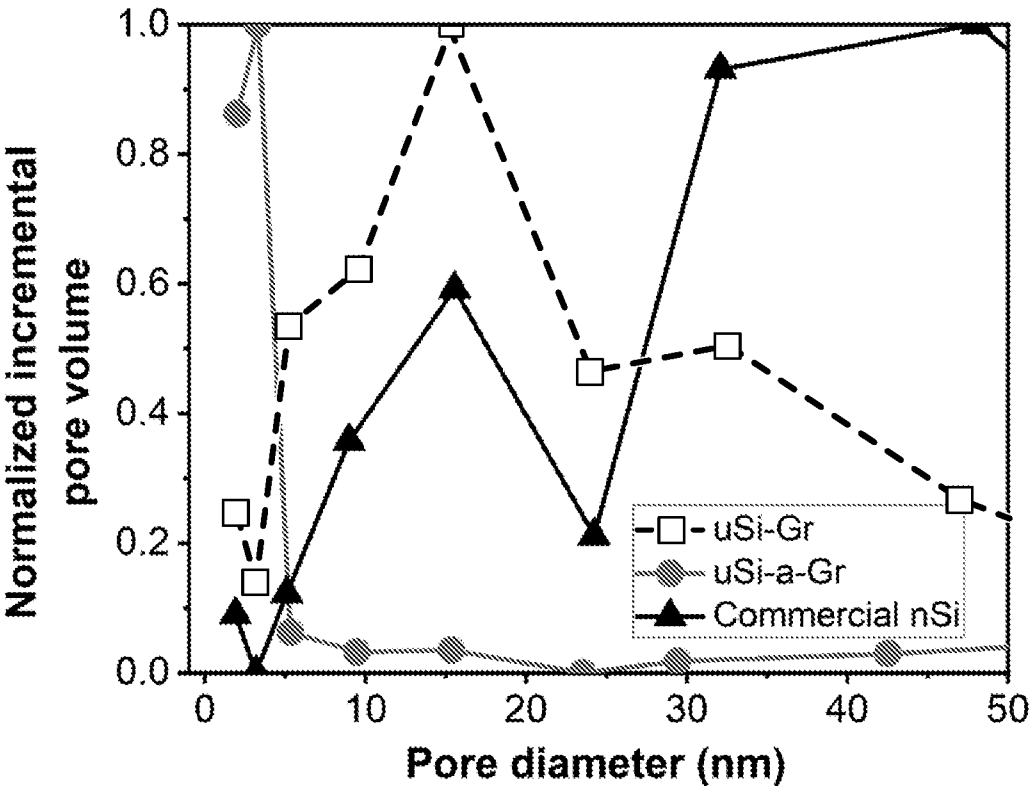


FIG. 4E

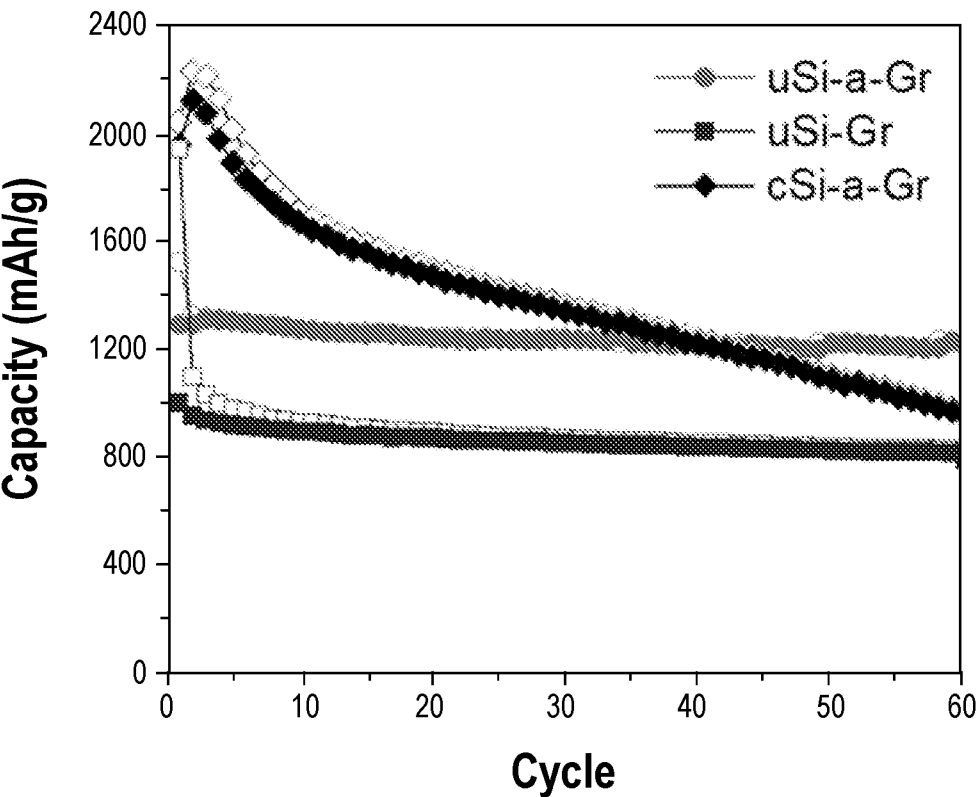


FIG. 5A

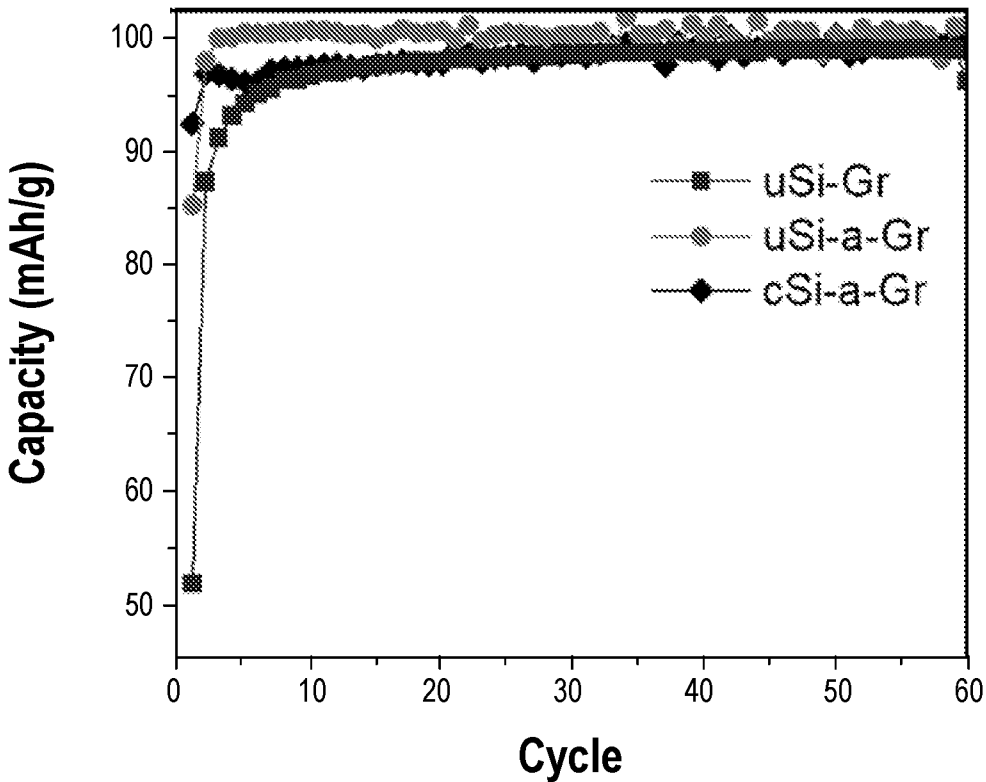
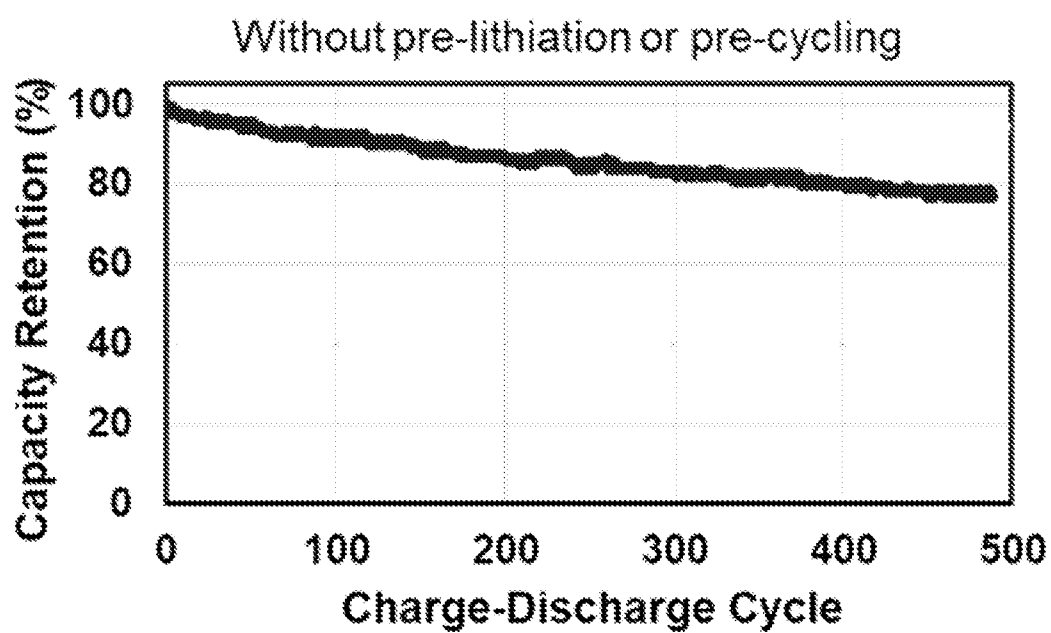
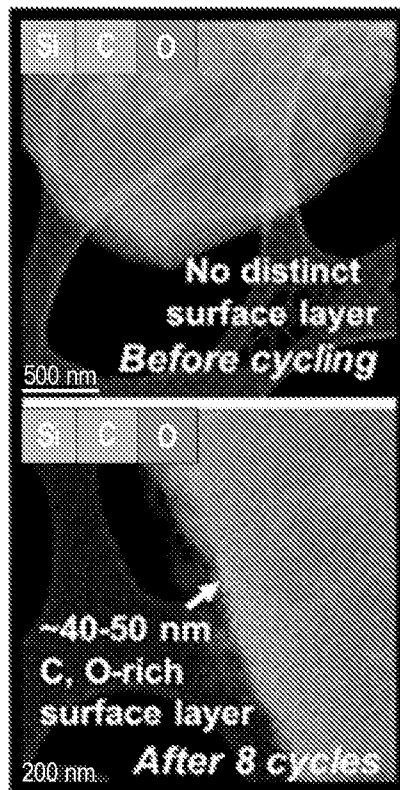
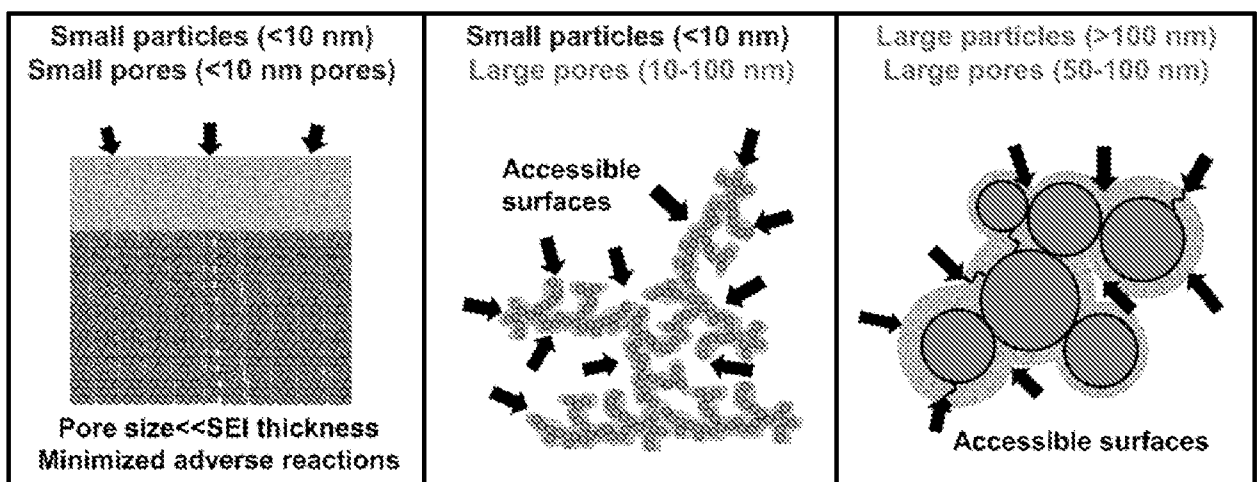


FIG. 5B

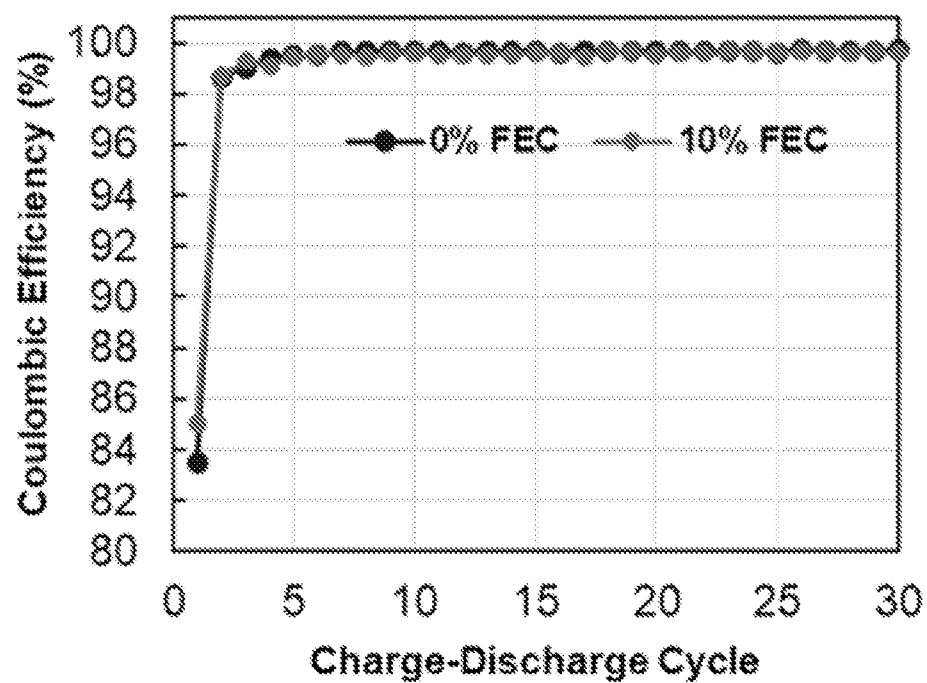
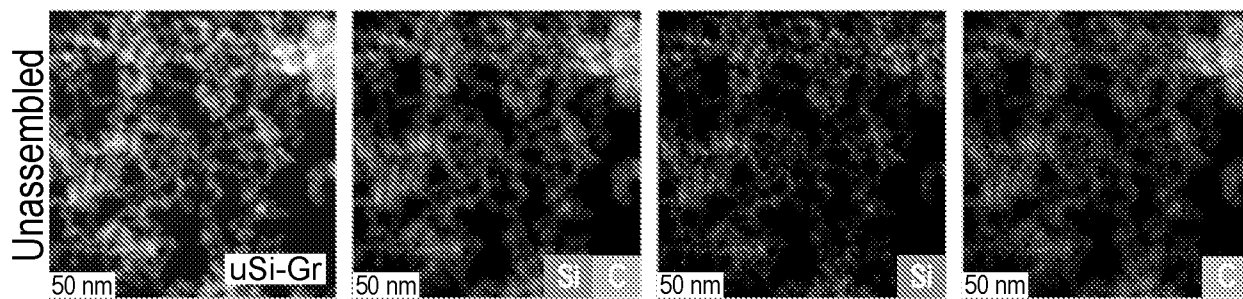
6/10

**FIG. 6**

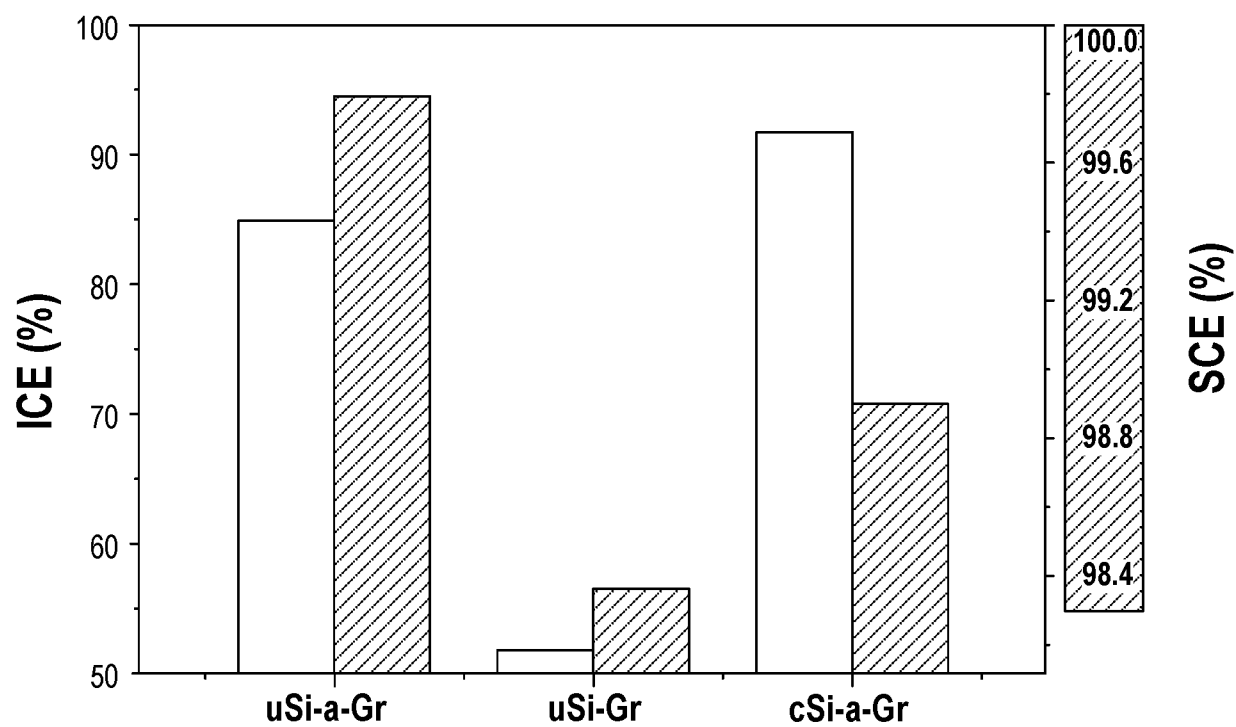
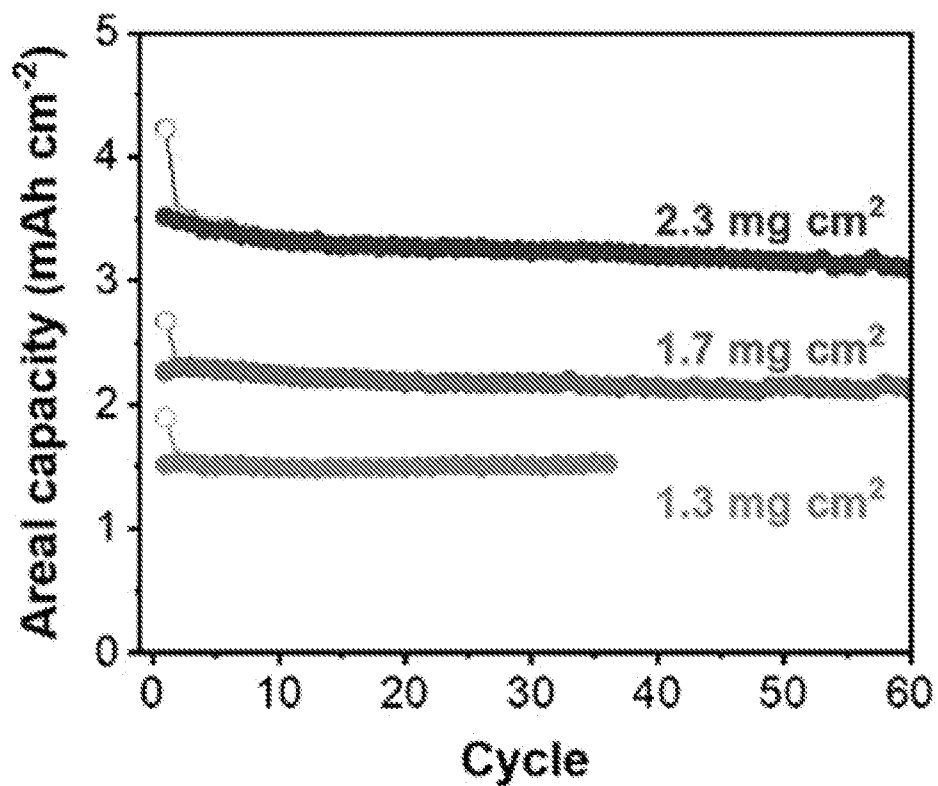
7/10

**FIG. 7A****FIG. 7B**

8/10

**FIG. 7C****FIG. 8**

9/10

**FIG. 9A****FIG. 9B**

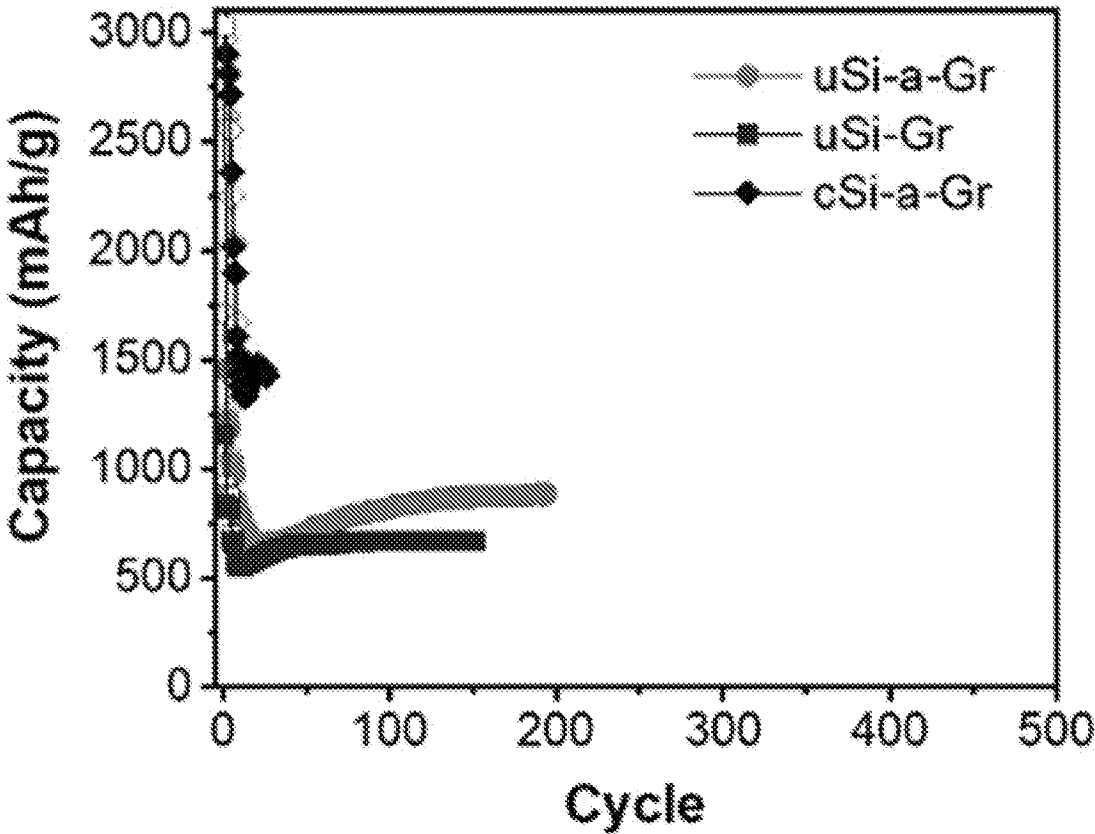


FIG. 9C

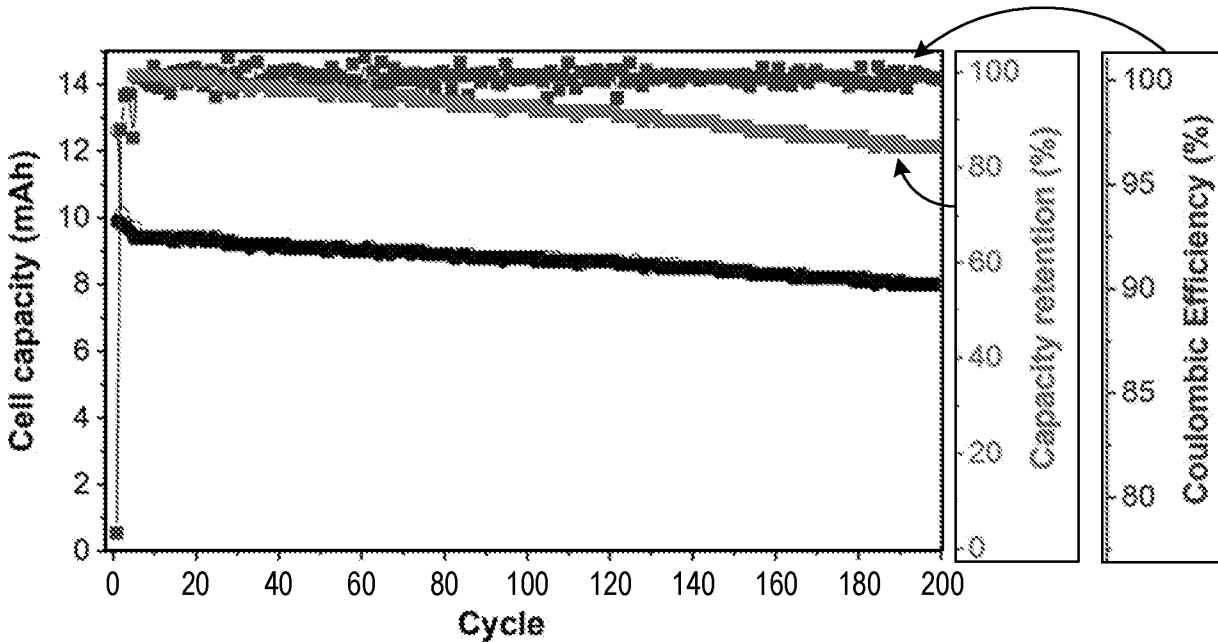


FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/060234

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.

Group I: Claims 1-6, 12 drawn to a composition of matter for an anode material.

Group II: Claims 7-11, 13, 14, drawn to a method of preparing an anode material.

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.: **1-6, 12**

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.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/060234

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **H01M 4/02** (2025.01); **H01M 4/04** (2025.01); **H01M 4/134** (2025.01); **B82Y 30/00** (2025.01); **B82Y 40/00** (2025.01)
CPC: **H01M 4/02**; **H01M 4/04**; **H01M 4/134**; **H01M 10/0525**; **H01M 4/386**; **H01M 2004/027**; **B82Y 30/00**; **B82Y 40/00**;
Y02E 60/10

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	US 2020/0161635 A1 (APPLE INC.) 21 May 2020 (21.05.2020) Fig 1; abstract; para [0038]-[0043]	1-6, 12

☐ 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

“D” document cited by the applicant in the international application

“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

31 March 2025 (31.03.2025)

Date of mailing of the international search report

08 April 2025 (08.04.2025)

Name and mailing address of the ISA/US

COMMISSIONER FOR PATENTS
MAIL STOP PCT, ATTN: ISA/US
P.O. Box 1450
Alexandria, VA 22313-1450
UNITED STATES OF AMERICA

Facsimile No. 571-273-8300

Authorized officer

KARI RODRIQUEZ

Telephone No. PCT Help Desk: 571-272-4300