Enhanced Secondary Battery Anodes Based on Si and Fe₃O₄ Nanoparticle Infilled Monodisperse Carbon Starburst Colloidal Crystals

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Secondary batteries, due to the ever-increasing demand for energy storage, are receiving considerable attention,[1–3] with a focus on systems that offer long-term stabilities,[4] reasonable rate capacities,[5,11] and high energy densities.[6–9] The demand for high energy densities has led to research in new high energy density anode and cathode materials. Current Li-ion batteries typically utilize carbon-based anodes, which have a theoretical capacity of about 370 mAh g⁻¹[2,10] with most of the higher capacity anode materials, e.g., Si,[11–13] Sn,[7,14] and metal oxides,[15–17] still in the research stage. Si, with a theoretical capacity of ≈4200 mAh g⁻¹, has been of particular interest. However, during lithium insertion, Si expands up to 400%, resulting in large stresses which can cause cracking and pulverization, leading to rapid capacity decay.[11] To alleviate the induced strain and provide sufficient electrical conductivity, various electrode designs based on nanostructured Si in conjunction with a conductive matrix have been considered.[16,13,18–24] To stabilize the solid–electrolyte interface (SEI) during volume changes, mechanical clamping via an SiO₂ protective layer,[25] Cui’s yolk–shell structures,[18,26] and various electrolyte additives (e.g., vinylene carbonate (VC))[27,28] have been investigated. Interestingly, while some reports indicate VC improves the performance of Si-based anodes,[27,28] others indicate optimal cyclability with a VC-free electrolyte.[29] Fe₃O₄ and other metal oxide based anodes are also considered promising due to their generally high theoretical capacity (~1000 mAh g⁻¹ for Fe₃O₄), low cost, and low toxicity.[1,30] Fe₃O₄ is believed to store energy primarily through the conversion reaction of Fe₃O₄ → 8Li⁺ + 8e⁻ → 3Fe + 4Li₂O.[31] Challenges, however, include Li₂O’s low electrical conductivity, the observed capacity fade, the poor calendar life, and a large hysteresis during cycling.[1] Strategies currently utilized to improve conductivity include addition of carbon,[32] use of a conductive scaffold,[15,16] and carbon nanotubes[30] and “coating” by graphene encapsulation.[17,33] However, even after conductivity is improved, the charge–discharge hysteresis remains significant. Some of the hysteresis is likely due to activation barriers for the reduction and oxidation reactions, which may be a function of the size and uniformity of the Fe₃O₄ active materials formed after the first discharge.[1] Fe₃O₄ nanoparticle-based anodes have been investigated as a route to decrease this barrier; however, particle aggregation is a problem.[15,17,30,33] Interestingly, when Fe₃O₄ nanoparticles were decorated on graphene sheets, the hysteresis was reduced to 0.7 V, as compared to that of 0.9 V for a graphene-free Fe₃O₄ anode.[34]

Reported here is a novel anode system utilizing monodisperse starburst carbon spheres (MSCS)[35] as a scaffold for the active materials Si and Fe₃O₄ to form anodes with remarkably high gravimetric energy densities. The MSCS can be assembled into a colloidal crystal,[36] maximizing the MSCS packing fraction, and providing good pathways for both electron transport and ion diffusion in the electrolyte. The internal mesopores of the MSCS host the electrolytically active materials, which were deposited into the mesopores via static chemical vapor deposition (sCVD). The MSCS used here have a diameter of 480 nm, a polydispersity index (PDI) of 1.039, a pore volume of 1.47 mL g⁻¹, and a specific surface area of 1190 m² g⁻¹. The average pore size, as determined via nitrogen isotherms (Figure S1, Supporting Information), was 4.29 nm, with a distribution between 2 and 8 nm (the MSCS synthesis was tuned to provide large pores.[37] The mesoporous carbon structure acts as a confining layer and high surface area current collector. The Si anodes exhibited Coulombic efficiencies exceeding 99%, and specific capacities of over 1500 mAh g⁻¹ (1200 mAh g⁻¹ on an electrode basis), after 85 cycles at a cycling rate of 0.33 C. The Fe₃O₄-based anodes were synthesized via the sCVD of Fe, followed by Fe oxidation to Fe₃O₄. These anodes exhibited a specific capacity of ≈700 mAh g⁻¹ (550 mAh g⁻¹ on an electrode basis), after 40 cycles, ≈600 mAh g⁻¹ after 100 cycles, and high Coulombic efficiencies. When the Fe₃O₄ was confined to the mesopores, the charge–discharge hysteresis was only 0.60 V; when it was both in the mesopores and on the surface of the colloids the hysteresis increased to 0.75 V. As discussed in the Supporting Information, the capacity due to the carbon in the MSCS does not contribute sufficiently to the overall electrode capacity.
sCVD was able to deposit active materials deeply into the large-pore MSCS mesopores (infiltrating of smaller pore MSCS was less successful). The MSCS were assembled on tungsten substrates, which provide the necessary surface charge for colloidal crystal fabrication.\[^{11}\] After colloidal assembly, the MSCS-coated substrates were put into the CVD chamber and heated to 150 °C under vacuum to drive off residual moisture. After cooling to room temperature under vacuum, disilane (SiH₄) or iron pentacarbonyl (Fe(CO)₅) was introduced into the chamber, the chamber was sealed, and then heated. The resulting Fe-MSCS were then oxidized to Fe₃O₄-MSCS by heating to 400 °C under partial vacuum (10 mbar). The Si-MSCS were used as-is out of the reactor. Both the Si-MSCS and the Fe₃O₄-MSCS were then assembled into coin cells using lithium metal as the counter electrode. The MSCS serve to provide efficient charge collection and electrical contact with the active material, and their nanostructure prevents active material aggregation during cycling. We note that the MSCS-based electrodes are fragile, as they are binder-free. For this reason, experiments using a coin cell configuration, where the MSCS colloidal crystal is held in place by the separator, were more successful than when the MSCS electrode is immersed in electrolyte. Si-MSCS anodes were first tested using a standard electrolyte (1.0 M LiPF₆ in EC/DEC/DMC (1:1:1 by vol)) at different C rates. While the Coulombic efficiency is good (99% at a rate of 1 C), capacity fade is significant. After returning to the initial 0.065 C rate after 40 cycles at 1 C, the capacity loss was nearly 50%. Adding >5 wt% VC to the electrolyte significantly reduced the capacity fade (Figure 1).

It was important to tune the sCVD conditions to deposit the appropriate amount of Si in the mesopores, but not deposit a thick Si overlayer on the exterior surface of the MSCS. First, the mesoporous structure of the MSCS can only allow for the volumetric expansion of the Si during lithiation if the MSCS is not completely filled. Second, if there is a thick Si layer on the exterior surface of the MSCS, it may fragment and become electrically isolated. The mass ratio of the Si to MSCS was 5:1 (determined via weighing electrodes after each process step, balance accuracy ± 0.01 mg), and thus even though the MSCS has some inherent capacity, the majority of the capacity obtained was provided by the Si (see the Supporting Information). The calculated tap density of the Si-MSCS anode was 0.73 g cm⁻³ (0.61 g cm⁻³ Si-basis). During the first 10 cycles at a rate of 0.07 C, there is a steady capacity fade and the Coulombic efficiency is between 90% and 95%. After the tenth cycle, the cycling rate was increased to 0.25 C and the Coulombic efficiency steadily increased to 99%, even as the rate was further increased to 0.33 C (Figure 1, capacity derived from Si mass). After the initial rapid capacity fade over the first 10 cycles, Si-MSCS anode fades much more slowly during the 0.25 C cycling (areal capacity at cycle 2 was 2.83 mAh cm⁻²). When the rate is changed to 0.33 C, the capacity initially drops, recovers after a few cycles, and continues to only fade slowly through 85 cycles, with an 85 cycle specific capacity of 1500 mAh g⁻¹, resulting in an areal capacity of 1.15 mAh cm⁻². While we are not certain why the capacity drops and then recovers when the rate is changed, it is perhaps due to initially incomplete lithiation or delithiation at the higher rate which equilibrates after a few cycles. It appears that the Si-MSCS anode can accommodate the Si volume changes with cycling, and the extended mesoporous network provides efficient electron and ion transport. The VC results in a more stable SEI, perhaps because there is no binder; in at least one report, binder appears to negate the effects of adding VC to the electrolyte.\[^{29}\]

To explore the generality of the concept of using the MSCS as an active material host, and because of the observed capacity fade issues with the Si-MSCS system, an Fe₃O₄-based MSCS anode was investigated. While sCVD has been widely used for the conformal deposition of Si,\[^{30}\] Fe has generally been grown using a traditional CVD flow reactor and rough and/or discontinuous films are often formed.\[^{39–41}\] We recently demonstrated the sCVD of conformal, continuous Fe films using Fe(CO)₅ as the precursor;\[^{42}\] Fe(CO)₅ is a high vapor pressure (≈33 mbar) liquid at room temperature; as such, in Fe sCVD, the reaction chamber is evacuated and then opened to the precursor chamber. After a set time, the reaction chamber is closed and heated. There is strong selectivity for deposition of Fe on SiO₂ relative to tungsten\[^{40}\] and when a tungsten substrate is inserted into the chamber, it remains Fe-free. Our experiments have shown that the Fe CVD has near-100% deposition selectivity on the MSCS colloidal crystal compared to the glass sidewalls of the reaction chamber, and thus nearly all the Fe deposits on the MSCS, and very little on either the chamber or the tungsten substrate. The sCVD deposited Fe (on a glass substrate) was found to be 96 at% Fe, 2.5 at% O, and 1.5 at% C, by XPS,\[^{42}\] indicating minimal oxidation during deposition.

By utilizing a slow ramp rate (1 °C min⁻¹), deep sCVD infiltrating of the Fe into the mesoporous MSCS was obtained (Figure S3, Supporting Information). To verify Fe infiltration, a focused ion beam (FIB) lift-out was performed; Figure S3a in the Supporting Information shows the scanning electron microscopy (SEM) image of the Fe-MSCS composite, Figure S3b,c shows transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images, respectively. An electron energy loss spectrum (EELS) was taken on the inset of Figure S3c in the Supporting Information and shown in Figure S3d; the peaks at 700 and 713 eV correspond to the Fe-L₂ and Fe-L₃ lines (excitation of Fe 2p⁵/₂ and 2p¹/₂ electrons),\[^{43,44}\] verifying Fe deposition.

![Figure 1. Performance of Si-MSCS anode versus Li using the 5 wt% VC electrolyte at 0.07, 0.25, and 0.33 C. Capacity was calculated based on the Si mass.](image-url)
into the center of the MSCS. By changing the diffusion and heating time, along with the amount of MSCS templates, the thickness of the Fe can be controlled. For this sample, a pre-cursor diffusion time of 30 s and heating at 150 °C for 1 h were used.

The Fe-MSCS can be oxidized into an Fe$_3$O$_4$-MSCS composite lithium battery anode. Much as for the Si case, the MSCS template provides a conductive network and space for Fe$_3$O$_4$ expansion during cycling. To convert the Fe-MSCS to Fe$_3$O$_4$-MSCS, careful oxidation is needed so that neither the MSCS scaffold is oxidized nor Fe$_2$O$_3$ is formed. Figure S4a (Supporting Information) shows the calculated Ellingham diagram for the possible C and Fe oxidation reactions, indicating this is thermodynamically possible.[45] Below 843 K (570 °C), Fe$_3$O$_4$ is the first oxidation product formed. Preventing Fe$_2$O$_3$ oxidation to Fe$_3$O$_4$ keeps the higher capacity Fe$_3$O$_4$ and retains the MSCS scaffold, as Fe$_2$O$_3$ only forms after carbon is oxidized. Heating the Fe-MSCS in air at 400 °C resulted in complete carbon oxidation (i.e., removal via CO and/or CO$_2$) and oxidation of Fe to Fe$_3$O$_4$. Experimentally, it was determined that heating at 400 °C under an air partial pressure of 10 mbar fully oxidized the Fe to Fe$_3$O$_4$ without significant oxidation of the MSCS scaffold. Figure S4b (Supporting Information) shows the XRD from the Fe$_3$O$_4$-MSCS on a tungsten substrate. All peaks are indexed to either tungsten or Fe$_3$O$_4$ and no residual Fe or Fe$_2$O$_3$ peaks are observed. Using the XRD analysis software Jade, the crystallite size of the Fe$_3$O$_4$ was calculated to be 18.4 nm. While this is larger than the pore diameter, it is much smaller than the pore length. We observed similar crystallite sizes for HfO$_2$ deposited via ALD in the pores of an MSCS-scaffold.[36] These oxidation conditions were applied to the sample in Figure S3 in the Supporting Information (see Figure 2). SEM, TEM, and STEM images (Figure 2a–c) show no MSCS degradation due to oxidation. Figure 2d,e shows the reconstructed images from the inset of Figure 2c; Figure 2d is the reconstruction of only the oxygen EELS signal with Figure 2e from only the iron EELS signal. Taken together, these verify Fe infiltrates completely through the entire MSCS colloids and complete Fe conversion to Fe$_3$O$_4$.

The Fe$_3$O$_4$-MSCS anode system utilizes the same electrode design as the Si-MSCS anode. Figure 3 shows the rate performance of an underfilled Fe$_3$O$_4$-MSCS, (the Fe$_3$O$_4$ is largely confined to the mesopores). Because the mass ratio of Fe$_3$O$_4$ to C in this system is 4:1, the system gravimetric energy density is good. The tap density for the Fe$_3$O$_4$-MSCS was found to be 0.61 g cm$^{-3}$ (0.49 g cm$^{-3}$ Fe$_3$O$_4$ basis). Similar to the Si-MSCS system, over the initial ten 0.15 C cycles, there is a sharp capacity fade and the Coulombic efficiency is under 95% (areal capacity at cycle 2 was 0.73 mAh cm$^{-2}$). The Coulombic efficiency improves during cycling, aside from the one-cycle drops when C rates were changed. After 40 cycles, the Coulombic efficiency improves to over 99%. At a rate of 1.2 C, the Fe$_3$O$_4$-MSCS anode still provides a capacity of 600 mAh g$^{-1}$, 80% of the 0.5 C capacity over cycles 11–20 (750 mAh g$^{-1}$). When the rate returned to 0.5 C, the capacity returns to 700 mAh g$^{-1}$. Similar to the Si system, we suspect that the confinement of the Fe$_3$O$_4$ active material to the MSCS mesopores minimizes loss of electrical contact between the Fe$_3$O$_4$ and the current collector, which in turn minimizes the capacity fade. Following a 24 h rest period, the anode was cycled 100 cycles at 0.15 C (Figure 3b), at the end of which the specific capacity was 550 mAh g$^{-1}$ (0.34 mAh cm$^{-2}$ areal capacity), and the Coulombic efficiency averaged greater than 99%.

Along with obtaining a high Coulombic efficiency, the minimization of the charge–discharge hysteresis is important. Fe$_3$O$_4$-MSCS anodes were fabricated with varying amounts of Fe; providing insight are the two extremes, namely an underfilled

![Figure 2](https://example.com/image.png)

**Figure 2.** a) SEM image of FIB cross section of Fe-MSCS after oxidation of the Fe to Fe$_3$O$_4$. b) TEM and c) STEM of the Fe$_3$O$_4$-MSCS from (a). EELS reconstructed imaging using: d) the O signal and e) the Fe signal from the indicated region of (c).
anode similar to the anode cycled in Figure 3 and an overfilled Fe anode in which there is an Fe$_3$O$_4$ shell on the MSCS particles. The charge hysteresis was determined by taking the differential charge with respect to voltage ($dQ/dV^{-1}$) for the second charge/discharge cycle at cycling rates of 0.2 and 5 C (Figure 4). The peak near 1.0 V (1.0 V for the underfilled anode and 0.95 V for the overfilled) is the major contributor to the capacity and is generated by the reduction reaction Li$_x$Fe$_3$O$_4$ $+ (8-x)e^- = 3Fe + 4Li_2O$. Voltage peaks above 1.0 V are attributed to the structural transformation of Fe$_3$O$_4$ to an Li–Fe–O complex (Li$_x$Fe$_3$O$_4$). Due to the nanoparticle size, the structural transformation appears to completely occur and is observed in the broad shoulder peak from 1.0 to 1.6 V. Large Fe particle formation, which could suppress the transformation to the Li–Fe–O complex, appears to be prevented due to the confinement of the Fe$_3$O$_4$ active material provided by the mesopores. For the 0.2 C cycling test, the hysteresis was taken as the difference between the reduction peak and the lower voltage of the two oxidation peaks (1.6 V for the underfilled and 1.7 V for the overfilled anode), which corresponds to the oxidation of Fe$^0$ to Fe$^{2+}$. For the underfilled Fe$_3$O$_4$-MSCS anode, the hysteresis is only 0.60 V, and for the overfilled sample, the hysteresis is only 0.60 V, and for the overfilled sample, the hysteresis is
increased to 0.75 V. We suspect that confinement of the electro-
lytically active Fe₃O₄ in the mesopores limits the nanoparticle
size, reduces, and perhaps eliminates particle aggregation, and
provides an intimate current collector. Under 5°C cycling, the
two oxidation peaks merge, with both the underfilled and over-
filled samples having a similar hysteresis of 1.1 V and 1.05 V,
respectively.

To further study the effect of Fe₃O₄ filling fraction, impedance
measurements were conducted on both an underfilled and an
overfilled half-cell. The Nyquist plot is shown in Figure S6
(Supporting Information). The series resistance, comprising of
contact and electrolyte resistance, was 2.7 Ω for the underfilled
sample and 2.0 Ω for the overfilled sample. We suspect that
these differences are not significant and may just be sample to
sample variations. The charge transfer resistance was notice-
ably higher in the overfilled Fe₃O₄ sample (395 Ω) than the
underfilled sample (300 Ω). In the overfilled Fe₂O₃, some of the
pore network is blocked, which is probably why the charge
transfer resistance increases.

The unique scaffold structure provided by the mesoporous
MSCS appears to offer significant benefits for anode systems.
These carbon scaffolds provide a conductive network where the
active materials, e.g., Si and Fe₂O₃, are confined in mesopores
providing short electron transport lengths in the active material,
allowing facile electron extraction. By confining the active mat-

erial to the nanometer-sized pores, active material pulverization
and migration is suppressed and loss of capacity through mate-

rial loss or electrical isolation is minimized. In particular, con-
fining the Fe₃O₄ active material into the mesopores resulted in
high Coulombic efficiency, and most intriguingly, a low charge
hysteresis of 0.60 V at a charging rate of 0.2 C. This decrease is
attributed to the unique electrode design, a hypothesis which
is supported by experiments where the Fe₃O₄ active material
content was increased until it overfilled the mesopores and the
hysteresis was observed to increase.

Experimental Section

Formation of Carbon Template: MSCS were synthesized[35] and slightly
oxidized to impart a surface charge that improved assembly[16] as
previously reported. Nitrogen physisorption isotherms, BET specific
surface area, and pore volume were measured and calculated as
previously described.[35] Tungsten substrates (0.5 mm thick) were
sonicated for 1 h in concentrated ethanolic KOH, rinsed, dried, and
placed in a solution of known concentration (typically 0.75 wt%) of
well-dispersed MSCS in ethanol at 40°C overnight. As shown in the
Supporting Material, the carbon template was typically 10–15 µm thick.

Material Deposition: Si sCVD was conducted following previous
reports with a reduced amount of Si₂H₆.[36] Iron pentacarbonyl (Fe(CO)₅;
Sigma) was used as the iron source during Fe sCVD. Using standard
air-free techniques, ~5 mL of Fe(CO)₅ was placed in a flask purged with
nitrogen. MSCS-coated substrates were heated to 150°C for 2 h under
a vacuum of 10⁻⁵ mbar. After cooling and sealing the vacuum line, the
precursor valve was opened to allow Fe(CO)₅ vapors to enter the sample
chamber, typically for less than 2 min. The reactor was sealed and placed
into a furnace at 150°C (1°C min⁻¹ ramp) for 1 h (underfilled) or 5 h
(overfilled). To oxidize the Fe to Fe₃O₄, an Fe-coated sample was heated
under 10 mbar of air to 400°C for 3 h (16°C/min ramp). Oxidizing in
atmospheric pressure air at 400°C converted the Fe to Fe₃O₄ while
completely oxidizing (i.e., removing) the carbon template.

sCVD Characterization: SEM was conducted on a Hitachi S-4800 at
10 kV. FIB lift-outs were performed on a Helios 600i, with the polishing
doing 1.2° off vertical using 30 kV, 80 pA for the first pass; 30 kV,
40 pA for the second pass; and 8 kV, 21 pA for the 3rd and final pass.
Final thickness of the lift-outs was between 70 and 130 nm. TEM was
performed using a JEOL 2010LAB; TEM at 200 kV. STEM was performed
using a JEOL 2010F (STEM) at 200 kV.

Coin Cell Fabrication and Testing: Li-ion half cells were fabricated in
the standard coin cell configuration using Celgard spacer, Novolyte
electrolyte (1.0 M LiPF₆ in EC/DEC/DME (1:1:1 by vol)), and Li metal
as the counter electrode. Electrolyte modification was conducted by the
addition of <5 wt% VC to the Novolyte electrolyte. The cells were
cycled at room temperature under constant current at varying rates. The
Si-MSCS anode was cycled between 0.1 and 2.0 V while the Fe₂O₃-MSCS
anode was cycled between 0.1 and 3.0 V. Impedance measurements
were carried out on coin cell with an AC amplitude of 6 mV over the
range of 100 kHz to 10 mHz.

Supporting Information

Supporting Information is available from the Wiley Online Library or
from the author.

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