Self-Assembled Fe$_3$O$_4$ Nanoparticle Clusters as High-Performance Anodes for Lithium Ion Batteries via Geometric Confinement

Soo Hong Lee,$^{†,‡}$ Seung-Ho Yu,$^{†,‡}$ Ji Eun Lee,$^{†,‡}$ Aihua Jin,$^{†,‡}$ Dong Jun Lee,$^{†,‡}$ Nohyun Lee,$^{†,‡}$ Hyungyung Jo,$^{§}$ Kwangsoo Shin,$^{†,‡}$ Tae-Young Ahn,$^{||}$ Young-Woon Kim,$^{||}$ Heeman Choe,$^{§}$ Yung-Eun Sung,$^{*,†‡}$ and Taeghwan Hyeon$^{*,†‡}$

$^†$Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 151-742, Republic of Korea
$^‡$School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea
$^§$School of Advanced Materials Engineering, Kookmin University, Seoul 136-702, Republic of Korea
$^{||}$Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Republic of Korea

Supporting Information

ABSTRACT: Although different kinds of metal oxide nanoparticles continue to be proposed as anode materials for lithium ion batteries (LIBs), their cycle life and power density are still not suitable for commercial applications. Metal oxide nanoparticles have a large storage capacity, but they suffer from the excessive generation of solid—electrolyte interphase (SEI) on the surface, low electrical conductivity, and mechanical degradation and pulverization resulted from severe volume expansion during cycling. Herein we present the preparation of mesoporous iron oxide nanoparticle clusters (MIONCs) by a bottom-up self-assembly approach and demonstrate that they exhibit excellent cyclic stability and rate capability derived from their three-dimensional mesoporous nanostructure. By controlling the geometric configuration, we can achieve stable interfaces between the electrolyte and active materials, resulting in SEI formation confined on the outer surface of the MIONCs.

KEYWORDS: Nanoparticles, lithium ion batteries, self-assembly, solid—electrolyte interphase, iron oxide, anodes

For the extensive applications of lithium-ion batteries (LIBs) to consumer electronics and electric vehicle, high performance electrode materials with high energies, high power densities, and good cyclic stabilities should be developed. In the last two decades, many transition-metal oxide nanostructures based on conversion reactions have been extensively investigated as potential LIB anodes because they have higher theoretical specific capacities (≈1000 mAh g$^{-1}$) than the currently commercially used graphite (372 mAh g$^{-1}$) and they show significantly improved reversibility.\textsuperscript{1–3} Furthermore, nanostructured materials are known to provide short diffusion pathways for lithium ions, resulting in high rate capabilities.\textsuperscript{4} Despite these advantages, these nanostructured materials face two major challenges for practical commercial applications. First, they generally suffer from poor capacity retention, which is attributed to their huge volume expansion during lithiation/delithiation processes. Although the mechanical stress associated with volume expansion and contraction during cycling can be reduced with small-sized nanoparticles,\textsuperscript{5} such particles are likely to aggregate into larger particles that are pulverized again after long cycles, ultimately leading to rapid capacity fading. Second, the solid—electrolyte interphase (SEI) layer formed by electrolyte decomposition on the surface of anode materials can degrade battery performance tremendously. Repeated expansion and contraction upon cycling can cause fracture, which can provide new active surfaces for SEI growth. The continuous SEI formation associated with additional exposure of the active material upon each cycle leads to consistent consumption of electrolytes and lithium ions, and the resulting SEI layer retards the diffusion of lithium ions. Furthermore, SEI can weaken the electrical contacts between the current collector and the anode material, resulting in mechanical degradation of anodes. Consequently, the design of a stable SEI at the interface between the electrolyte and active material is critically important to achieve a more stable and enhanced battery performance.\textsuperscript{6} The stable SEI requires elasticity, flexibility, and uniform morphology to relax nonuniform electrochemical reactions, which can provide good passivation to the anode materials.\textsuperscript{7} However, nanoparticles (NPs) provide a huge surface area over which electrolytes can decompose, and a thick SEI layer can be formed easily and continuously with each charge/discharge cycle. To overcome these limitations, a wide variety of nanostructures such as metal oxide/carbon composites,\textsuperscript{8–10} mesoporous structures,\textsuperscript{11–15} hollow structures,\textsuperscript{16–20} and inactive/active composites\textsuperscript{21,22} have been developed. Among them, three-dimensional (3D) mesoporous metal oxide materials have attracted much attention because they can provide not only a short lithium ion path by facilitating electrolyte contact with the pores, but also
free space that can accommodate volume changes during cycling. Recently, various coating methods such as conformal carbon coating,\textsuperscript{23} tubular carbon coating,\textsuperscript{24,25} and silica shell coating\textsuperscript{6} have been employed in nanostructured silicon-based anode materials, leading to the improved mechanical strength, higher conductivity, and most importantly stable SEI formation. Herein, we report the successful preparation of mesoporous iron oxide nanoparticle clusters (MIONCs) with carbon coatings through bottom-up self-assembly approach. Owing to the 3D-ordered and mesoporous structures, the MIONCs exhibited higher cyclic stability than random aggregates of iron oxide nanoparticles (RAIONs) and commercialized bare iron oxides (CBIOs) by confining stable SEI layer on the outer surface. Iron oxide NPs were selected as the representative component NPs because of their well-characterized properties and facile production.\textsuperscript{26}

Among various synthetic strategies for the preparation of 3D mesoporous metal oxides,\textsuperscript{27−29} we used a bottom-up self-assembly strategy because the secondary structure exhibits not only the characteristics of individual constituting NPs, but also new collective properties derived from the self-assembled structure.\textsuperscript{30}

The overall synthetic procedure of the MIONCs and RAIONs is shown in Figure 1a. Fe$_3$O$_4$ NPs (11−12 nm) stabilized with oleic acid were synthesized by thermal decomposition of an iron−oleate complex using the previously reported method.\textsuperscript{26} Transmission electron microscopy (TEM) image (Figure S1a) revealed that the synthesized NPs are uniform-sized with a particle size of 11 nm. For the synthesis of MIONCs, the Fe$_3$O$_4$ NPs were self-assembled into colloidal nanoparticle clusters (CNCs) using the method detailed in the previous report.\textsuperscript{31} Fe$_3$O$_4$ NPs in chloroform were emulsified into an aqueous solution containing dodecyltrimethylammonium bromide (DTAB) for use in an oil-in-water emulsion system. Subsequently, the solution was heated to evaporate the oil phase in

Figure 1. (a) Schematic illustration of the preparation of MIONCs and RAIONs. (b) TEM image of MIONCs. (c) HRTEM image obtained from cross-sectioned MIONCs by microtoming.
the emulsion droplet, leading to the production of densely packed CNCs. At least two cycles of hexane/acetone washing process after the synthesis of Fe3O4 NPs were necessary to produce densely packed CNCs (Figure S9) because oleic acid surfactant can act as a cosurfactant in an oil-in-water emulsion system.44

Further incorporation of polyvinylpyrrolidone (PVP) polymers stabilized the CNCs through repulsive steric interactions and directed the CNCs into a more ordered structure. The TEM image (Figure S1b) and dynamic light scattering (DLS) data (Figure S1c) showed that the average size of the CNCs was 174 nm with a relative standard deviation of 26% in water. The CNCs were then dried in vacuum and heated at 500 °C for 5 h in Ar to yield mesoporous iron oxide nanoparticle clusters (MIONCs) with carbon coating. Figure 1b clearly shows that the morphology of the MIONCs remained intact even after the heat treatment at 500 °C. A high-resolution TEM (HRTEM) image was obtained after a microtoming process to confirm the
internal structure of the MIONCs. Figure 1c shows uniform pores between neighboring Fe₃O₄ NPs, and such well-aligned ensembles were observed throughout the MIONCs.

To prepare a comparison group, Fe₃O₄ NPs in chloroform were dried in a vacuum oven and then calcined directly in Ar without any modification, resulting in the formation of random aggregates of iron oxide nanoparticles (RAIONs). To make sufficient carbon coating in the RAIONs, the Fe₃O₄ NPs were dispersed in chloroform without washing process. A TEM image of the RAIONs (Figure S2a) showed that no sintering occurred between the constituting Fe₃O₄ NPs. An HRTEM image of these RAIONs (Figure S2b) revealed that the individual Fe₃O₄ NPs were distinctly visible in a carbon matrix with high crystallinity.

Figure 2a shows a low-magnification TEM image of microtomed sections of the MIONCs. Although some parts were cracked and sliced during the microtoming process, most of the MIONCs maintained their mesoporous structure. Interestingly, black sintered parts were sometimes observed, as shown by the red circle in Figure 2a. For the analysis of the structure and composition of the sintered particles, HRTEM images and selected-area electron diffraction (SAED) patterns were obtained. The HRTEM image demonstrated that the black sintered particles had a different phase, which was distinct from the neighboring Fe₃O₄ NPs (see the regions in the red and blue squares in Figure 2b). From the SAED patterns, it was determined that the phase in the red square corresponds to metallic Fe (Figure 2c) and that in the blue square to Fe₃O₄ (Figure 2d). In our system, PVP polymers were gradually degraded with concomitant evolution of H₂ gas to give rise to a reductive environment. Because the degradation temperature of PVP starts at 380 °C and peaks at 435 °C, metallic Fe NPs might be expected to form more easily in such an environment. Consequently, PVP polymer acts as a structure-directing agent for the self-assembly as well as a reductant for the generation of metallic iron. Advantageous roles of these metallic iron species in LIBs are discussed below.

When the CNCs were heated at 500 °C for 5 h in air instead of Ar, the resulting NPs showed a completely different morphology and crystalline phase. TEM images revealed that each component Fe₃O₄ nanoparticle coalesced, and large pores were generated on the surfaces (Figure S4a,b). The crystalline phase was a mixture of hematite (α-Fe₂O₃) and magnetite (Fe₃O₄) (Figure S4c). Therefore, calcination in an Ar flow is necessary to prevent severe coalescence and maintain the original CNC structure. Figure 3a depicts the X-ray diffraction (XRD) pattern of the MIONCs and shows Fe and Fe₃O₄ phases. The most intense diffraction peaks at 44.9° and 65.2° indicate the formation of metallic Fe. The major diffraction peaks apart from these two peaks can be indexed to the inverse spinel phase of Fe₃O₄. The mean crystalline size of metallic Fe, calculated using the Scherrer equation, was estimated to be ~80 nm, which is roughly eight times larger than that of the component Fe₃O₄ nanoparticles. The ratio of Fe₃O₄ to Fe was determined by Rietveld refinement to be 94:6 wt % (Figure S5). In comparison, the XRD pattern of the RAIONs indicated the presence of highly crystalline Fe₃O₄. Small-angle X-ray scattering (SAXS) measurements on the MIONCs and RAIONs were carried out to verify the long-range ordering (Figure 3b). The primary peak was observed at 1.7° for the MIONCs, which corresponds to a d-spacing of approximately 5.2 nm (from λ = 2d sin θ), indicating a
well-ordered assembled structure even after the calcination. However, in the case of the RAIONs, no clearly distinguishable peak was observed, indicating random assembly of nanoparticles within the aggregates.

For further verification of the surface area and porous structure, nitrogen adsorption–desorption isotherms were obtained. The MIONCs showed a type-IV isotherm (Figure 3c), which was ascribed to a mesoporous structure with uniform pores, as reported previously.33 The Brunauer–Emmett–Teller (BET) surface area of the MIONCs was measured to be 55.4 m² g⁻¹. A uniform pore distribution with an average size of 3.5 nm was determined from analysis of the desorption curve (inset of Figure 3c). Furthermore, a broad peak at around 40 nm was found for the MIONCs, corresponding to the mesopores among the clusters (Figure S6a). In comparison, we obtained a type-IV isotherm for the RAIONs with an H3-type hysteresis loop attributed to an interconnected mesoporous system as is frequently observed for porous materials with broad pore-size distributions (Figure 3d).34 The BET surface area was measured to be 144.6 m² g⁻¹. The pore-size distribution for the RAIONs is shown in the inset of Figure 3d and indicates the formation of randomly distributed pores. There were no additional pores with diameters of more than 25 nm (Figure S6b). Elemental analysis showed that the MIONC and RAION samples contained 7.7 and 24.0 wt % carbon, respectively. To analyze the characteristics of the carbon layer within the samples, we performed Raman spectroscopy on the two samples (Figure S6c). In the case of the MIONCs, the signal peaks showed a D band at 1315 cm⁻¹ and a weaker G band at 1580 cm⁻¹, with an I_D/I_G ratio of 1.15. In comparison, the RAIONs had a D band at 1322 cm⁻¹ and a G band at 1578 cm⁻¹ with similar intensities (I_D/I_G ratio of 0.99). As reported in the literature,35 the D band is ascribed to sp² carbon and defects such as topological defects, dangling bonds, and vacancies, whereas the G band is attributed to ordered sp² carbon. Therefore, the I_D/I_G ratio represents the degree of disorder in the carbon materials on the surfaces of the MIONCs and RAIONs, which can be considered to be disordered nanocrystalline graphite.36 In addition, HRTEM images, a scanning TEM (STEM) image, and energy-dispersive X-ray spectroscopy (EDS) line scan data of MIONCs and RAIONs were acquired, respectively (Figures S10, S11).

The potential of MIONCs and RAIONs as LIB anode materials was characterized by an electrochemical test using coin-type cells. Figure 4a and b represent the cyclic voltammograms of the MIONCs and RAIONs, respectively. In the cathodic process, both samples showed large peaks at 0.58 and 0.64 V, respectively, in the first cycle; this indicated the reaction Fe₂O₃ + 8Li⁺ + 8e⁻ → 3Fe⁰ + 4Li₂O with the formation of the SEI layer. The two samples commonly showed a peak below 0.5 V, which was mainly due to the reaction of lithium with carbon. In the first anodic process, two peaks were observed at approximately 1.66 and 1.87 V in both samples, attributed to the oxidation of Fe⁰ to Fe²⁺ and Fe³⁺, respectively. These results are in agreement with the previous studies, especially those involving Fe/FexOy/C⁵² and Fe₂O₃/C⁵⁷ composite anode materials. The difference between the peaks in the first cycle and subsequent cycles can be ascribed to activation processes, including the conversion to nanosized metal particles dispersed in the Li₂O matrix or the formation of the SEI. These similar features were also observed in the galvanostatic charge–discharge voltage profiles determined at a current density of 100 mA g⁻¹ (Figures S7a, S7b).

For the confirmation of the durability of the electrodes, the MIONCs, RAIONs, and CBIOs were charged and discharged galvanostatically in the range of 0.01–3.00 V (vs Li⁺/Li) at a current density of 100 mA g⁻¹ (Figure 4c). The reversible capacity of the MIONCs was around 867 mAh g⁻¹ in the first cycle. Interestingly, the specific capacity initially decreased until 10 cycles and then started to increase until around the 80th cycle. This capacity increase can be attributed to the existence of some activation process, as reported earlier.38,39 After 80th cycle, the specific capacity was maintained up to 100 cycles (Figure S12). More importantly, the MIONCs showed high cyclic stability up to 100 cycles even though capacity slightly decreased in the initial ~10 cycles. In contrast, the RAIONs showed a high specific capacity of 970 mAh g⁻¹ initially and maintained about 76.6% of the initial capacity after 80 cycles. The first charge capacity of the RAIONs was higher than the theoretical specific capacities of Fe₂O₄ (926 mAh g⁻¹) and graphite (372 mAh g⁻¹). This excess specific capacity can be attributed to the carbonaceous materials present that showed higher specific capacities than graphite, as reported earlier.38 The increase might also be due to other reactions such as the reversible growth of a polymer/gel-like film caused by decomposition of the electrolyte on the transition-metal oxide during the conversion reaction.40 CBIOs showed a capacity of 800 mAh g⁻¹ initially but faded very rapidly until 50 cycles. At 50 cycles, they exhibited only 19.6% of capacity retention, and the measurement was ceased. Clear capacity fading was observed in the RAIONs and CBIOs, compared to the MIONCs. The initial Coulombic efficiencies (CEs) of the MIONCs and RAIONs were 73.4% and 69.0%, respectively. The CEs of the MIONCs increased steadily after several cycles and rapidly reached up to 99.7%. In contrast, the RAIONs exhibited an oscillating CE of 95–97% after two cycles, indicating their lower reversibility than that of the MIONCs. Because the loss of 1% CE in each cycle can cause nearly complete degradation of the balanced full cell after 100 cycles,41 this difference in CE demonstrates the superior reversibility of the MIONCs.

This stable performance was also manifested in the rate performance at various current densities (Figure 4d). At low current densities (less than 400 mA g⁻¹), the specific capacities of the MIONCs were lower than those of the RAIONs. However, at high current densities (higher than 800 mA g⁻¹), the MIONCs exhibited higher reversible capacities than the RAIONs. Even at 1600 mA g⁻¹, the reversible capacity delivered by the MIONCs (473 mAh g⁻¹) was 61% of the value at 100 mA g⁻¹; this is even higher than the theoretical capacity of commercially available graphite (372 mAh g⁻¹). On the other hand, only 27% of the capacity at 100 mA g⁻¹ was delivered at 1600 mA g⁻¹ in the RAIONs. Clearly, the change in the geometric configurations allows lithium ions to reach the active materials of the MIONCs rapidly, despite their larger overall size.

By comparing the electrochemical performances of the MIONCs and RAIONs, we can speculate on the attractive features of the MIONCs, which showed more stable and higher rate performances. First, metallic iron particles, which are inactive toward lithium ions in the voltage range 0.01–3 V, can act as a buffer to reduce electrode swelling when intimate contact is made between inactive and active components, as reported in the previous study.22 To prove this, we compared XRD patterns of the CBIOs and MIONCs before and after cycling (Figure S13). Although CBIOs were converted into amorphous state during the first cycle, metallic Fe in MIONCs was still present after the first cycle, showing that metallic Fe particles in MIONCs are nearly inactive toward lithiation. In addition, metallic iron has much greater electrical conductivity (2 orders of magnitude higher) than Fe₂O₄; this supplies an electrical
not exhibit a high surface area exposed to electrolytes and additional layer during cycling (Figure 5). On the other hand, the RAIONs surface exposure upon cycling, resulting in excessive SEI formation. Randomly distributed pores can cause a concentration gradient of lithium ions, consequently stress relaxation and the overall morphology can be preserved without any aggregation of primary nanoparticles after long cycles. In addition, the mesoporous structure provides short diffusion paths for lithium ions, resulting in a high rate capability. The RAIONs also have randomly distributed pores that can accommodate volume expansion. Furthermore, carbon coating, which can provide some mechanical strength against deformation, seemed to supply electron-transfer channels. To confirm the effects of carbon coating, we compared two RAION samples with different carbon contents of 24 wt % and 17 wt % (Figure S14). The RAIONs with a low carbon content of 17 wt % exhibited rapid capacity decay, demonstrating that the proper amount of carbon coating is essential for the high battery performance. However, the random distribution of the pores and carbon coatings originated from the ligands of the Fe3O4 NPs is not sufficient to prevent the aggregation of particles. Finally, the MIONC structure can maintain its morphology with a stable SEI layer during cycling (Figure 5). On the other hand, the RAIONs exhibit a high surface area exposed to electrolytes and additional surface exposure upon cycling, resulting in excessive SEI formation. Randomly distributed pores can cause a concentration gradient of lithium ions, consequently stress relaxation and SEI formation cannot be controlled efficiently. As confirmation of this assumption, the MIONCs and RAIONs (Figure 6a,b) were subjected to different cycling processes, and the resulting structures were characterized by scanning electron microscopy (SEM) and TEM. The MIONCs exhibited a stable SEI layer on their individual surfaces exclusively (Figure S8a). However, a thick SEI layer was formed on the RAIONs after one lithiation/delithiation cycle in the whole region (Figure S8d). This difference was visible more clearly on the electrode surfaces after 20 cycles. The morphology of the MIONCs can be resolved clearly with a limited SEI layer on their surfaces (Figures 6c, S8b), but the RAIONs are buried under thick SEI layers (Figures 6d, S8e). TEM images after 20 cycles showed a thin and compact SEI layer on the surface of each cluster with clear pores inside the MIONCs (inset of Figure 6c), while an excessive SEI layer was formed on the RAIONs (inset of Figure 6d). Because excessive SEI formation is related to rapid capacity fading and low rate capabilities and CEs, the MIONC structure enables an outstandingly stable battery performance and high-power rate capabilities. To confirm the material stability, which is directly related to battery cyclic stability, we performed selective etching of the SEI, as reported previously. After the removal of the SEI, the MIONCs exhibited a morphology similar to that before cycling (Figures 6e, S8c). However, after SEI removal from the RAIONs, the SEM images indicated more aggregated morphology than in the initial state (Figures 6f, S8f). The TEM image after SEI removal from the MIONCs also showed that their morphology was similar to that before cycling, demonstrating high mechanical stability (Figure 6g). However, the results for the RAIONs after etching of the SEI layer revealed that some Fe3O4 NPs were aggregated (Figure 6h) and showed a different morphology from the initial state. This maintenance of the MIONC structure suggests that we can confine SEI formation to the outer surface of the MIONCs simply by changing their geometric configuration. Thus, the application of a bottom-up self-assembly method imparts new collective properties such as a stable SEI formation and resistance to mechanical degradation, which was not observed in the case of primary nanoparticles. Both the MIONC and RAION materials manifested an amorphous nature after battery cycling, as seen by their ED patterns (insets of Figure 6g,h).

In summary, mesoporous iron oxide nanoparticle clusters with carbon coating were synthesized successfully and tested as anode materials for LIBs. The unique structure endowed the MIONCs with enhanced capacity retention, rate capability, and Coulombic efficiency. More importantly, the results demonstrated that changing the geometric configuration can lead to the confinement of SEI layer formation, resulting in stable battery performance. This synthetic strategy can be considered a model framework and applied to other metal oxide NPs such as Co3O4 and NiO with high specific capacities. These findings further confirm that bottom-up self-assembly of active materials can improve battery performance.
MIONCs and RAIONs, galvanostatic discharge heated under air, pore-size distribution and Raman spectra of coalesced and sintered particles generated from the CNCs. TEM image of CBIOs, TEM image and XRD pattern DLS data of CNCs, TEM images and HRTEM image of Experimental details, TEM image of Fe$_3$O$_4$ NPs, TEM image and

![Figure 6. Comparison of MIONC and RAION electrodes before and after cycling. SEM images of initial (a) MIONCs and (b) RAIONs before cycling. SEM images of (c) MIONCs and (d) RAIONs after 20 cycles. Insets of c and d show high-magnification TEM images. The two electrodes correspond to the delithiated state. SEM and TEM images of initial (a) MIONCs and (b) RAIONs. Insets of TEM images (g, h) show ED patterns of corresponding cycles in which the SEI was removed selectively by chemical etching. MIONCs (e, g) and RAIONs (f, h) are shown respectively after 20 cycles. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: thyeon@snu.ac.kr; ysung@snu.ac.kr.*

**Author Contributions**

S.H.L. and S.-H.Y. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We would like to acknowledge the financial support by the Research Center Program of Institute for Basic Science (IBS) in Korea.

**REFERENCES**