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Morphology control strategies have been widely used to boost the tolerance of anode materials against dramatic volume change during charge/discharge processes. Herein, we found solid scientific evidence demonstrating that electrochemical properties of cavity contained materials are superior to their solid counterparts.

Due to its high energy density compared to conventional rechargeable batteries, the lithium ion battery dominates the market of portable devices and is considered as one of the most promising battery options for electric vehicles (EVs). However, present-day micro-size electrode materials can only operate at low currents and may cause polarization and pulverization while operating at high currents. Thus, it is critical that new electrode materials with enhanced electrochemical performance for EVs are developed. Nanomaterials have attracted great attention for use in lithium ion batteries, as their low dimensions provide shorter pathways for fast lithium ion migration; therefore, achieve high power for EVs.

However, no matter how advanced the design for nanomaterials, it is inevitable that electrode materials will suffer from volume change during charge/discharge processes, due to the volume expansion/shrinkage caused by intercalation/de-intercalation of lithium ions. To alleviate the stress of electrode materials during charge/discharge, many attempts have been made in preparing novel structured materials with void buffer spaces, including mesoporous, hollow spherical and yolk-shell structured materials. Bruce et al. developed a series of ordered mesoporous structured materials for lithium ion batteries. The internal mesopores of 2 - 50 nm can be flooded with electrolyte, ensuring a high surface area of electrolyte/electrode interphase, and hence a high flux of lithium across the interface. Compared with the random porosity between the nanoparticles, the ordered mesoporous structure ensures that this is an even distribution of electrolyte in contact with the electrode surface and a uniform buffer space for electrode expansion. Meanwhile, several of ordered mesoporous structured electrode materials were widely investigated by other research groups. Lou et al. have devoted to hollow structured electrode materials for lithium ion batteries. The hollow structures (spheres, boxes, core-shell etc.) with high surface area and different shell morphologies (e.g. nanopolycrystals, nanosheets) can provide efficient active sites and short pathways for lithium ion migration. Moreover, the hollow inner cavity can buffer the volume change during charge/discharge. Recently, a yolk-shell structure has received much interest because of its unique core-shell structure and void space between core and shell, which may be applied to applications such as nanoreactors, energy storage and drug delivery. Cui et al. recently reported a novel yolk-shell structured sulphur-TiO$_2$ composite, by partially dissolving sulphur in S-TiO$_2$ core-shell particles. The yolk-shell composite accommodates the volumetric expansion of sulphur in the void space, and presents a high specific capacity and excellent long term performance for lithium-sulphur batteries.

The above mentioned reports reveal an electrochemical performance of electrode materials by raising a hypothesis of volumetric expansion depression. However, none of them provide systemic scientific evidence to explain the enhancement, especially in respect to electrochemistry. To investigate the morphology effect of void space in materials, herein, we prepared two groups of Fe$_2$O$_3$ materials with/without cavity, nanorods vs. nanotubes and nanodisks vs. nanorings, and measured the electrochemical performances as anode materials for lithium ion batteries. Furthermore, activation energy of as-prepared materials can be obtained by electrochemical impedance spectroscopy (EIS) method, giving instructive comparison in each group.

Nanostructured Fe$_2$O$_3$ materials were prepared by a facile hydrothermal method (experimental details in supporting information). Figure 1 shows the scanning electron microscopy (SEM) images of nanostructured Fe$_2$O$_3$ materials, which demonstrate the morphologies of as-prepared materials (nanorods, nanotubes, nanodisks and nanorings). Figure 1(a) presents the SEM image of Fe$_2$O$_3$ nanorods, illustrating a large scale of spindle-like nanorods with lengths of about 1 micron and widest diameters of around 150 - 200 nm. Figure 1(b) shows the SEM image of Fe$_2$O$_3$ nanotubes, demonstrating the similar size in length and diameter to nanorods as shown in Figure 1(a). The high resolution SEM image as shown in the inset of Figure 1(b) clearly presents the open-end tip, implying a tubular structure. Figure 1(c) shows the SEM image of Fe$_2$O$_3$ nanodisks obtained in a higher concentration of H$_3$PO$_4$ solvent.
The high resolution image in Figure 2(b) implies the fringe structure in Figure 2(a) confirms the solid structure morphology of nanorods. The TEM image as shown in Figure 2(c) clearly shows the inner hollow structure of Fe$_3$O$_4$ nanotubes. The HRTEM image in Figure 2(d) confirms the crystal structure of alpha-phase Fe$_3$O$_4$ nanotubes. Figure 2(e) shows the TEM image of Fe$_3$O$_4$ nanodisks, demonstrating convex-disk-like structure with a diameter of about 100 nm. The HRTEM image in Figure 2(f) demonstrates the lattice structure of nanodisks, which presents the view perpendicular to the [012] direction. The Figure 2(g) shows the TEM images of Fe$_3$O$_4$ nanorings with typical ring-like structure. The HRTEM of Fe$_3$O$_4$ nanorings as shown in Figure 2(h) implies the polycrystalline structure of nanorings, with the exposed [012] directions at random.

As a result, the dissolution process continuously proceeded along the [001] direction to form the hollow structure (tubes or rings).

The X-ray diffraction patterns of nano-structured Fe$_3$O$_4$ materials are shown in Figure S1. The Fe$_3$O$_4$ nanorods and nanotubes show pure rhombohedral hematite structure (JCPDS No. 33-0664). For the Fe$_3$O$_4$ nanodisks and nanorings, minor impurity exists in both products, which can be indexed to the Fe$_3$(PO$_4$)$_2$(OH)$_3$ (JCPDS 42-0429), the same as the published literature. This is owing to the higher concentration of H$_2$PO$_4$ anion in reactant for the formation of nanodisks and nanorings than that of nanorods and nanotubes. The nitrogen sorption isotherms and corresponding pore size distributions of Fe$_3$O$_4$ products are shown in Figure S2. The specific surface area of Fe$_3$O$_4$ nanorods, nanotubes, nanodisks and nanorings are 42.4, 68.4, 52.1 and 89.6 m$^2$g$^{-1}$, respectively, as summarized in Table S2, calculated by the Brunauer-Emmett-Teller
Cyclic voltammetry (CV) measurements of nanorods, nanotubes, and nanodisks Fe₂O₃ were carried out to investigate the diffusion of lithium ions in the solid state of electrode materials, as shown in Figure 3. The CV curves of Fe₂O₃ nanorods and nanotubes are the typical shape of alpha phase hematite material, which is similar to previous reports. For instance, in Figure 3 (a), the board peak that appeared at about 0.61 V in the cathodic process in the first scanning cycle could be contributed to the reduction reaction from Fe³⁺ to Fe²⁺. In addition, this cathodic process is also associated with electrolyte decomposition to form the solid electrolyte interphase (SEI) layer and the reversible conversion reaction of lithium ion intercalation to form Li₂O. An anodic peak is present at about 1.80 V, corresponding to the reversible oxidation of Fe²⁺ to Fe³⁺. In the subsequent cycles, the cathodic peak potential shifts to 0.78 V. The CV curves of the Fe₂O₃ nanorods and nanotubes are identical from the second cycle, indicating high reversibility and good capacity retention at a low scanning rate (0.1 mV s⁻¹). For the CV curves of Fe₂O₃ nanodisks and nanorings electrodes, as shown in Figures 3 (c) and (d), both present an additional cathodic peak in each cycle. In the first cycle, the additional cathodic peak appears at about 0.61 V in the cathodic process which is similar to previous reports.

For lithium ions intercalation reaction, the apparent activation energy (Eₐ), namely, the energy barrier between reactant and product, interprets different value for each material. The Eₐ for lithium intercalation and exchange current (iₜ₀) can be calculated from the equation:

\[ i_{t_0} = \frac{R T}{n F R_a} \exp(-E_a / RT) \]

where R is the gas constant, T is the absolute temperature, n is the number of transferred electrons, F is the Faraday constant, R_a is the charge transfer resistance, and A is a temperature-independent coefficient. The electrochemical impedance spectra tested at different temperatures of 35, 40, 45, 50 °C and their Arrhenius plots of log iₜ₀ versus the reciprocal of absolute temperature (1/T) are summarized in Figure 4 (b). The activation energies are 65.09, 42.19, 52.76 and 22.19 kJ mol⁻¹ for Fe₂O₃ nanorods, nanotubes, nanodisks, and nanorings, respectively, calculated by the above mentioned equations. Interestingly, the activation energies of Fe₂O₃ materials with a hollow cavity are lower than their counterparts. The lower activation energy of Fe₂O₃ nanotubes and nanorings, as well as their lower charge transfer resistances, can be attributed to the facile charge transfer and lithium diffusion dynamics at the lower dimensional size in Fe₂O₃ nanotubes and nanorings, as they provided a higher surface area and shorter pathway for lithium ion diffusion, compared with their counterparts. This reduction of the charge transfer resistances and activation energies are beneficial in improving charge and electron kinetics in the electrode materials, and hence, enhance the electrochemical performance for lithium storage.

The galvanostatic charge/discharge measurements of nanorods, nanotubes, nanodisks and nanorings Fe₂O₃ electrode materials were carried out at testing currents of 0.1, 1 and 10 A g⁻¹ (approximate to...
The discharge capacities are 1098, 1150, 1107, and 1151 mAh g\(^{-1}\) after 100, 100 and 1000 cycles.

In the second cycle, the capacities of nano-structured Fe\(_3\)O\(_4\) are 89.3%, 96.3%, 91.4% and 96.2%. It is noticed that the capacities of nanorods and nanodisks are superior to previous reports of alpha-phase with different morphologies. The electrochemical enhancements of nanotubes and nanorings electrodes compared with their counterparts, especially in high rate performances, can be attributed to the benefits of the hollow structure. The higher surface area of nanotubes and nanorings can provide more active sites for lithium ion intercalation so that charges and electrons can go through electrode materials in short period. The lower dimensional size in nanotubes and nanorings ensure faster lithium ion diffusion kinetics. The intrinsic advantages such as lower charge transfer resistance and lower activation energy of hollow structured materials enhance the reactivity and intercalation dynamics.

In conclusion, two groups of nanostructured Fe\(_3\)O\(_4\) materials (with/without cavity) were prepared by a facile hydrothermal method. The physical properties and electrochemical performance of Fe\(_3\)O\(_4\) anode materials are summarized in Table 1. Compared with their solid counterparts, the hollow structured materials (nanotubes and nanorings) have higher specific surface area, smaller dimensional size, lower charge transfer resistance and lower activation energy. These advantages are beneficial in enhancing the lithium diffusion dynamics, and hence, achieve excellent electrochemical performance for lithium ion batteries. The Fe\(_3\)O\(_4\) nanotubes and nanorings exhibited higher specific capacities, better retentions and superior high rate performances, compared with their solid counterparts (nanorods and nanodisks). The Fe\(_3\)O\(_4\) nanotubes and nanorings electrodes can achieve capacity of 391 and 447 mAh g\(^{-1}\) at a discharge current of 10 A g\(^{-1}\) after 1000 cycles. These results would be instructive for comparative studies of other nano-structured materials for lithium ion batteries.

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GXW appreciates the support from ARC Future Fellow Project (FT1101100800). HL would like to thank the support from UTS Chancellor’s Post Doctoral Fellowship (CPDF). The overall electrochemical performance of nanotubes and nanorings is superior to previous reports of alpha-phase with different morphologies. The electrochemical enhancements of nanotubes and nanorings compared with their counterparts, especially in high rate performances, can be attributed to the benefits of the hollow structure. The higher surface area of nanotubes and nanorings can provide more active sites for lithium ion intercalation so that charges and electrons can go through electrode materials in short period. The lower dimensional size in nanotubes and nanorings ensure faster lithium ion diffusion kinetics. The intrinsic advantages such as lower charge transfer resistance and lower activation energy of hollow structured materials enhance the reactivity and intercalation dynamics.

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