Interconnected $\alpha$-Fe$_2$O$_3$ nanosheet arrays as high-performance anode materials for lithium-ion batteries

Dandan Cai$^{a,b,1}$, Dongdong Li$^{a,c,1}$, Liang-Xin Ding$^a$,*, Suqing Wang$^a$, Haihui Wang$^{a,c,*}$

$^a$School of Chemistry & Chemical Engineering, South China University of Technology, Wushan Road, Guangzhou 510640, China
$^b$School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources (Ministry of Education), Guilin 541004, China
$^c$School of Chemical Engineering, the University of Adelaide, Adelaide, South Australia 5005, Australia

**Abstract**

The electrode materials with structure stability and binder-free are urgently required for improving the electrochemical performance of lithium-ion batteries. In this work, interconnected $\alpha$-Fe$_2$O$_3$ nanosheet arrays directly grown on Ti foil were fabricated via a facile galvanostatic electrodeposition method followed by thermal treatment. The as-prepared $\alpha$-Fe$_2$O$_3$ has an open network structure constituted of interconnected nanosheets and can be directly used as integrated electrodes for lithium-ion batteries. The $\alpha$-Fe$_2$O$_3$ nanosheet arrays exhibit a high reversible capacity of 986.3 mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$. Moreover, a reversible capacity of ca. 425.9 mAh g$^{-1}$ is achieved even at a superhigh current density of 10 A g$^{-1}$, which is higher than the theoretical capacity of commercially used graphite. The excellent performance could be attributed to the efficient electron transport, the large electrode/electrolyte interfaces and the good accommodations for volume expansion from the interconnected nanosheet arrays structure.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Rechargeable lithium-ion batteries (LIBs), as the most promising energy storage devices, are the heart of technologies in developing electric vehicles and hybrid electric vehicles due to their high energy density, environmental friendliness and safety [1,2]. Graphite is currently the main commercial anode for LIBs due to its low cost and long cycle life. Unfortunately, the low theoretical specific capacity (372 mAh g$^{-1}$) and poor rate performance cannot fulfill the challenge of the increasing requirements [3]. Therefore, it is currently an urgent task to find alternative anode materials with higher specific capacities and better rate performance.

Nowadays, various materials have been explored as promising anode materials for LIBs, such as metal oxides [4–7], nitrides [8], chalcogenides [9], lithium-alloying materials [10], non-graphitic carbon [11,12] and their composites [13–15]. Among them, transition metal oxides have been regarded as appealing candidates because of their high theoretical capacity, abundance and low cost. Particularly, $\alpha$-Fe$_2$O$_3$, possessing a high theoretical specific capacity (1007 mAh g$^{-1}$), has attracted much attention in the recent years [16–23]. In principle, it is generally believed that the high specific capacity of $\alpha$-Fe$_2$O$_3$ derives from the reversible conversion reaction mechanisms (Fe$_2$O$_3$ + 6Li$^+$ + 6e$^-$ $\rightarrow$ 2Fe + 3 Li$_2$O). Despite of these intriguing features, the electrode still suffers from rapid decay in capacity due to the drastic volume change during charge/discharge process. In addition, the sluggish kinetics for charge transfer and ionic diffusion will lead to the limited rate capability. In order to overcome the above-mentioned barriers, one of the generally accepted strategies is to decrease their particle size to the nanoscale level, such as nanoparticles [16,17], nanorods [18] [19], nanotubes [20], nanofoakes [21] and nanosheets [22] etc. It was demonstrated that the Fe$_2$O$_3$ nanomaterials with different morphologies can improve the electrochemical properties due to the short paths of lithium-ion diffusion and more active reaction sites. However, the undesirable interfaces among nanomaterials, the insulating binders and conductive agents will greatly decrease the electrical conductivity of the electrodes. Additionally, the nanomaterials tend to agglomerate during the cycle process, which would inevitably lead to the poor rate performance. As a result, the rate capability and cycling stability cannot meet the demands for practical use, yet.

http://dx.doi.org/10.1016/j.electacta.2016.02.010
0013-4686/© 2016 Elsevier Ltd. All rights reserved.
Recently, the direct growth of one-dimensional (1D) and/or two-dimensional (2D) $\text{Fe}_2\text{O}_3$ arrays on current collectors to form integrated three-dimensional (3D) electrodes has been successfully synthesized and all exhibit enhanced electrochemical performance for LIBs [24–27]. For example, Chen et al. prepared $\text{Fe}_2\text{O}_3$ nanorod arrays on Ti substrate by solution-phase growth and chemical etching. The robust $\text{Fe}_2\text{O}_3$ nanorod arrays with optimized interstices could form a novel 3D anodes with improved rate capability (350 mAh g$^{-1}$ at 30 A g$^{-1}$) and good cycling stability (retain 801 mAh g$^{-1}$ after 500 cycles at 5 A g$^{-1}$) [25]. Lou’s groups have reported porous $\text{Fe}_2\text{O}_3$ nanosheets on conductive substrates by solvothermal approach coupled with post-annealing. The as-obtained integrated binder-free electrode showed high reversible capacity of 1009 mAh g$^{-1}$ and a high capacity of 908 mAh g$^{-1}$ can be still obtained after 60 cycles [26]. The constructed architecture can provide sufficient free space and robustness to accommodate the volume changes during the lithiation/delithiation process, thus dramatically improving the cycling stability. Moreover, each electroactive nanostucture with direct adhesion to the substrate can facilitate the electrons transport and lithium-ions diffusion, largely reducing the polarization and enhancing the rate performance [24–28]. Thus, it is reasonably deducible that the mentioned $\text{Fe}_2\text{O}_3$ nanosheet arrays directly grown on current collecting substrates has great potential to achieve superior electrochemical performance for LIBs. Generally, $\text{Fe}_2\text{O}_3$ nanosheets grown on different substrates as the anode materials for lithium-ion batteries have been obtained by hydrothermal technologies [26,27]. However, the mentioned hydrothermal methods require relatively high temperatures and pressures, which restrict the large-scale production and potential applications. So the development of facile and effective method to synthesize $\text{Fe}_2\text{O}_3$ nanosheet arrays with interconnected and porous structure as well as the enhanced electrochemical performance is still considered to be a huge challenge. The galvanostatic electrodeposition technology is the most effective way to synthesize metal oxides ($\text{Fe}_2\text{O}_4$ [29–31], $\text{CoO}$ [32], $\text{NiMoO}_4$ [33] and $\text{Fe}_2\text{O}_4$ [34] et al) nanoarrays because of its direct growth pattern on well-designed conductive substrates. In addition, the constant current in the deposition process could effectively control the growth of the crystal nucleus, leading to the nanoarrays composed of the homogenous nanocrystal and forming porous structure. To the best of our knowledge, there has been no report on interconnected and porous $\text{Fe}_2\text{O}_3$ nanosheet arrays on Ti foil by galvanostatic electrodeposition.

Based on the above considerations, a facile galvanostatic electrodeposition method combined with post-annealing was proposed to fabricate $\text{Fe}_2\text{O}_3$ nanosheet arrays on titanium (Ti) foil and the electrochemical performance for LIBs was investigated. The $\text{Fe}_2\text{O}_3$ electrode with the ingenious integrated architectures is expected to show high reversible capacity, enhanced cycling stability and excellent rate capability.

2. Experimental

2.1. Synthesis of the interconnected $\text{Fe}_2\text{O}_3$ nanosheet arrays on Ti foil

All the reagents used in this experiment were analytical grade purity. Prior to the electrodepositing, the Ti foils (99.99%, 1.5 cm$^2$) were mechanically polished using SiC emery paper from 300 to 800 grits, then dipped in HCl solution (5%) and ultrasonically cleaned using acetone and distilled water. The details of the fabrication are described as follows: The interconnected $\text{Fe}_2\text{O}_3$ nanosheet arrays on Ti foil were electrodeposited from an alkaline aqueous solution consisting of 0.5 M NaOH, 0.04 M $\text{Fe}_2\text{(SO}_4\text{)}_3$3H$_2$O, and 0.25 M tri-ethanol-amine (TEA). It should be pointed out that the mixture solution displayed no turbidity and a pale-green homogeneous color. The iron oxide precursor nanosheets were formed under stirring at a constant current density of 3 mA cm$^{-2}$ using a simple two-electrode electrolytic cell set-up maintained at 50°C for 10 min. The graphite electrode was used as a counter electrode (spectral grade), while Ti foil was served as the working electrode. Finally, the as-obtained precursor was further annealed at 400°C in the flowing argon for 2 h.

2.2. Materials characterization

X-ray diffraction (XRD, Bruker D8 Advance) using Cu/Kα radiation was employed to identify the crystalline phase of the as-obtained sample. The elemental composition of the $\text{Fe}_2\text{O}_3$ nanosheet arrays on Ti foils and the valence states of metal elements were probed with the ESCALAB 250 X-ray photoelectron spectroscopy (XPS) instrument. All XPS spectra were corrected using the C 1s line at 284.6 eV. The structure and morphology were characterized by field emission scanning electron microscopy (FE-SEM) (JSM-6330F) and transmission electron microscopy (TEM, FEI, Tecnai™ G2F30).

2.3. Electrochemical measurements

The electrochemical properties were evaluated by galvanostatic cycling using CR2025 coin-type half cells. The interconnected $\text{Fe}_2\text{O}_3$ nanosheet arrays were directly used as the working electrodes without adding any binders and conducting carbon black. Then, the lithium foil was used as the counter electrode, and the Whatman GF/B glass fiber membrane was used as the separator. The electrolyte was composed of 1 mol L$^{-1}$ LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) (1:1 by volume). The coin cells were assembled in an argon-filled glove box (Mikrouna, super 1220) where the oxygen and moisture contents were less than 1 ppm. The cells were galvanostatically discharged/charged using a Battery Testing System (Neware Electronic Co., China) between 0.01 and 3.0 V at different current densities. Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (Zahnner IM6ex) at a scan rate of 0.2 mV s$^{-1}$ over the potential range of 0.01–3.0 V vs. Li/Li$^+$. The electrochemical performances were calculated from the galvanostatic cycling data, the cyclic voltammetry data, and the coulometric data.

3. Results and discussion

3.1. Microstructure characterization

To clarify the phase of the as-prepared material on Ti foil, XRD was carried out. As shown in Fig. 1, the diffraction peaks at 38.4°, 40.1°, 52.9° and 70.6° can be indexed to the Ti foil substrate. Apart from the diffraction peaks of the Ti substrate, the other diffraction
peaks at 33.1°, 35.6°, 54.1° and 62.5° can be unambiguously assigned to (104), (110), (116) and (214) planes of the rhombohedral phase of hematite (α-Fe₂O₃). JCPDS 33-0664), which is in good agreement with the previous reports [26,27,35,36]. The XRD result indicates that the crystalline α-Fe₂O₃ phase has been formed without any impurities by the galvanostatic electrodeposition method combined with post-annealing. To further determine the chemical compositions and the valence state of the interconnected α-Fe₂O₃ nanosheet arrays on Ti foil, XPS was carried out. The spectra are referenced to the C 1s peak (284.6 eV). Fig. 2 shows XPS spectra of the Fe 2p and O 1s core levels obtained from the as-prepared sample. As shown in Fig. 2a, the two strong peaks at 724.1 eV and 711.1 eV corresponded to Fe 2p₁/₂ and Fe 2p₃/₂ of the Fe₂O₃ nanosheets, respectively [22,36–39]. The shakeup satellite peak at 718.2 eV (region between Fe 2p₁/₂ and Fe 2p₃/₂) is characteristic of Fe²⁺ in Fe₂O₃ [22,24,37,38]. The appearance of the satellite peak further confirms that the as-obtained sample is Fe₂O₃ rather than Fe₃O₄. Additionally, the O 1s spectra in Fig. 2b can be deconvoluted into two peaks at 529.7 eV and 531.3 eV, generally assigned to the lattice oxygen in the Fe₂O₃ and the oxygen in hydroxide ions, respectively [24]. These results coincide with the XRD results and further suggest that the formation of Fe₂O₃ nanosheets on Ti foil was obtained by a simple electrodeposition and calcination.

The morphologies of the as-prepared materials on Ti foil were primarily characterized by SEM. Fig. 3 shows the representative SEM images viewed from the top. As shown in Fig. 3a, the precursor on Ti foil before thermal treatment has an open-up network structure assembled by interconnected nanosheets. It can be clearly observed that the nanosheets are uniformly grown on the Ti substrate. Moreover, as presented in Fig. 3b-d, the morphologies of α-Fe₂O₃ could be well preserved after a simple thermal treatment, suggesting that the nanosheets arrays are robustly adhere to the Ti foil. It can also be seen that the Fe₂O₃ nanosheets are generally interconnected with each other and perpendicular to the plane of the Ti substrate, assembling into tremella-like domains (Fig. 3c). From the magnified SEM images, the open space between nanosheets is relatively large. In addition, the single nanosheet has a smooth surface and the thickness is about 25 nm on average (Fig. 3d). Furthermore, these nanosheets present a large effective area, which would be potentially significant for electrochemical performance for LIBs [26,27].

To further investigate the morphology and structure of the as-synthesized Fe₂O₃ nanosheets, typical TEM images are presented in Fig. 4. The TEM image of the edge of a nanosheet is shown in Fig. 4a. The rolled-up edge is due to the surface tension, suggesting the thickness of the nanosheet is small, which concurs well with the SEM observation [40]. The magnified image (Fig. 4b) clearly shows the uniform distribution of many nanopores throughout the whole nanosheet. The unique structure might be mainly derived from the release of gas in the process of heat treatment. Furthermore, the selected area electron diffraction (SAED) pattern (inset of Fig. 4b) shows a set of diffraction rings, which further demonstrate that the porous Fe₂O₃ nanosheets are polycrystalline.

### 3.2. Electrochemical performance

Fig. 5 depicts the representative CV curves of the α-Fe₂O₃ electrode for the initial three cycles in the potential range of 0.01–3.0 V (vs. Li/Li⁺) at ambient temperature at a scanning rate of 0.2 mV s⁻¹. Obviously, the first cycle, especially for cathodic process, is different from the subsequent cycles. During the first cycle, three cathodic peaks at 1.72, 1.40 and 0.68 V are detected, which could be related to a multi-step lithiation process [25–27]. First, the peak at 1.72 V may be ascribed to lithium insertion into the crystal structure of the as-obtained Fe₂O₃ nanosheet arrays without change in the structure. Second, another small peak at 1.40 V could be due to phase transition from hexagonal LiₓFe₂O₃ to cubic LiₓFe₂O₄. The third sharp reduction peak at about 0.65 V can be attributed to the reduction of both Fe²⁺ to Fe⁺ and the irreversible reaction related to the decomposition of electrolyte. Meanwhile, two broad anodic peaks at 1.61 and 1.82 V correspond to the reversible oxidation of Fe⁺ to Fe²⁺ and then to Fe³⁺, which agrees well with the previous reports [21,22,24–27,41]. In the subsequent cycles, both cathodic and anodic peaks are slightly shifted due to the structural modification after the first cycle. It is noteworthy that the second and third cycle of the voltage-current curves almost overlaps with each other, suggesting the good reversibility and stability of the electrochemical reaction.

The galvanostatic discharge/charge curves of the as-prepared Fe₂O₃ interconnected nanosheets grown on Ti foil at a current density of 100 mA g⁻¹ in the voltage range of 0.01 – 3.0 V (vs. Li/Li⁺) were displayed in Fig. 6. Clearly, the discharge/charge curves of the electrode have a sloped region between 1.5 and 0.9 V and a long plateau at 0.83 V, which matches well with the peaks of the CV curves. Significantly, the interconnected Fe₂O₃ nanosheets exhibit high initial discharge and charge capacities of 1442.4 mAh g⁻¹ (504.8 mAh cm⁻²) and 986.3 mAh g⁻¹ (345.2 mAh cm⁻²), respectively. However, The capacity loss in the first cycle may be mainly caused by the irreversible reactions involved in the formation of the SEI layer and the decomposition of electrolyte, which is a common phenomenon for nanostructured anodes [22,26]. The reversible specific capacities are 952.5 mAh g⁻¹ (333.4 mAh cm⁻²) and 951.5 mAh g⁻¹ (333 mAh cm⁻²) for the second and third cycles.

---

*Fig. 2. XPS spectra of (a) the Fe 2p and (b) the O 1s performed on the as-obtained interconnected α-Fe₂O₃ nanosheet arrays on Ti foil.*
respectively, which is very close to the theoretical capacity of $\alpha$-Fe$_2$O$_3$ (1007 mAh g$^{-1}$). Moreover, the similar reversible specific capacities for the subsequent two cycles show a good reversibility of the integrated electrode for LIBs. It should be pointed out that the loading density of $\alpha$-Fe$_2$O$_3$ on the Ti foil ($\sim$0.35 mg cm$^2$) was estimated for the integrated 3D anode. The low loading density seems to be a common problem associated with nanoarrays grown on planar substrates [22,24–27], which could be further solved by adding electrodeposition time or using substrates with 3D structures.

The rate performance of LIBs anodes is very crucial, especially for high-power applications in power grids and electric vehicles. It should be pointed out that the cell was discharged/charged for initial three cycles at a low current density of 100 mA g$^{-1}$ to activate the cell. The rate capabilities of the Fe$_2$O$_3$ integrated 3D electrode were first evaluated at various current densities ranging from 200 to 10000 mA g$^{-1}$, as shown in Fig. 7. The electrode
delivered charge specific capacity of 892.5, 814.0, 750.2, 686.3 and 575.2 mAh g\(^{-1}\) obtained at the current densities of 200, 500, 1000, 2000 and 5000 mA g\(^{-1}\), respectively. More interestingly, a capacity of about 425.9 mAh g\(^{-1}\) (149.1 mAh cm\(^{-2}\)) is retained even at a high current density of 10000 mA g\(^{-1}\). The capacity is still much higher than the theoretical capacity (372 mAh g\(^{-1}\)) of commercially used graphite anodes, suggesting its potential application in the future high-rate batteries. The rate capability is superior to those reported for the mesoporous Fe\(_2\)O\(_3\) nanoparticles (450 mAh g\(^{-1}\) at 1000 mA g\(^{-1}\)) [16], the α-Fe\(_2\)O\(_3\) nanorods (300 mAh g\(^{-1}\) at 5C) [19], and the α-Fe\(_2\)O\(_3\) nanowall arrays (440 mAh g\(^{-1}\) at 5C) [27]. The results suggest that the Fe\(_2\)O\(_3\) electrode exhibits an obvious advantage in rate capability. Moreover, the high reversible capacity of Fe\(_2\)O\(_3\) nanosheets can be restored to 939.4 mAh g\(^{-1}\) (328.8 mAh cm\(^{-2}\)) when the current density is switched from 10000 to 200 mA g\(^{-1}\), implying good reversibility.

To further explore the rate capability, the cycling performance and coulombic efficiency of the Fe\(_2\)O\(_3\) nanosheet arrays at a high current density of 500 mA g\(^{-1}\) were presented in Fig. 8. The as-prepared α-Fe\(_2\)O\(_3\) electrode achieved a reversible capacity of 801.9 mAh g\(^{-1}\) (280.7 mAh cm\(^{-2}\)) at a high current density of 500 mA g\(^{-1}\) at the first cycle, and the reversible capacity slightly increased with the increasing of the cycle number. A reversible specific capacity of 900.9 mAh g\(^{-1}\) (315.3 mAh cm\(^{-2}\)) can be achieved after 100 cycles and no fading tendency can be seen in the subsequent cycles. The reversible specific capacity is higher than those reported previously for the porous hematite nanorod arrays (707 mAh g\(^{-1}\) at 0.5C) [24] and the porous α-Fe\(_2\)O\(_3\) nanosheets (809 mAh g\(^{-1}\) at 500 mA g\(^{-1}\)) [26]. The phenomenon of the gradual increased capability of the α-Fe\(_2\)O\(_3\) electrode in the 100 cycles is due to the larger active surface caused by the nanosize effects and the possible activation process that is caused by the gradual wetting by the electrolyte soaking into the pores of the nanosheets [22,42]. Such similar phenomenon has been commonly found in the previous reports for metal oxides with nanostructure based anode materials [22,25,32,33]. Meanwhile, the corresponding coulombic efficiency could be maintained at about 98% after the first cycle at the current density of 500 mA g\(^{-1}\). The result indicates the high cycling stability of the α-Fe\(_2\)O\(_3\) nanosheet arrays at a high current density. To further investigate the excellent cycling performance, the morphological analysis of electrochemical tested α-Fe\(_2\)O\(_3\) nanosheet after first cycling at 500 mA g\(^{-1}\) is conducted. As shown in Fig. 9, the nanostructure almost no change compared to the fresh electrode indicating high structure stability. So, the superior performance of α-Fe\(_2\)O\(_3\) nanosheet arrays electrodes could attribute to the following reasons: (i) the robust nanosheet arrays directly grown
on Ti foil can accelerate the transfer speed of electrons and lithium-ions. (ii) The interconnected structure can accommodate the volume expansion during the lithium-ion insertion/extraction. (iii) The open spaces between Fe2O3 nanosheets could increase the electrochemically active sites and provide large electrode/electrolyte contact area.

4. Conclusions

The α-Fe2O3 nanosheet arrays were successfully prepared by a simple and effective galvanostatic electrodeposition method and subsequent thermal treatment. The porous and interconnected α-Fe2O3 nanosheets directly grown on Ti foil were investigated as integrated and binder-free anodes for LIBs. The large open spaces between the interconnected nanosheets on current collector could provide the fast electron transfer and large electrode/electrolyte interfaces, resulting in the excellent rate capability. A reversible specific capacity of 425.9 mAh g⁻¹ (149.1 mAh cm⁻²) is achieved at an ultrahigh current density of 10000 mAh g⁻¹. Furthermore, the Fe2O3 electrode exhibits a high reversible specific capacity of 900.9 mAh g⁻¹ (315.3 mAh cm⁻²) after 100 cycles at a high current density of 500 mAg⁻¹. The above study demonstrates that the Fe2O3 nanoarray electrode obtained by galvanostatic electrodeposition technique may hold great promise in high-performance LIBs.

Acknowledgements

This work was financially supported by National Science Fund for Distinguished Young Scholars of China (No. 212255625) and the National Natural Science Foundation of China (No. 21306057) and the Fundamental Research Funds for the Central Universities, SCUT (2013ZM0064) and Guangxi Natural Science Foundation (No. 2015GXNSFBA139025) and the Australian Research Council (ARC) through the Future Fellow Program (FT140100757). D. Li thanks the China Scholarship Council (201506150052).

References

Electrodeposition of iron oxide nanorods on carbon nanofiber scaffolds as an anode material for lithium-ion batteries, Electrochim. Acta 55 (2010) 3240.

Hierarchical hollow spheres of Fe₂O₃@polyaniline for lithium ion battery anodes, Adv. Mater. 25 (2013) 6250.

Nanostructured reduced graphene oxide/Fe₂O₃ composite as a high-performance anode material for lithium-ion batteries, ACS Appl. Mater. Interfaces 6 (2014) 7189.

