Al-Doped Fe$_2$O$_3$ nanoparticles: advanced anode materials for high capacity lithium ion batteries†

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Rechargeable Lithium Ion Batteries (LIBs) are the most common energy storage devices in electric vehicles with the advantages of high-power density and long cycle life. Therefore, the requirements for LIBs with a high energy density, high rate capacity, fast charge ability and excellent stability embrace the fast development of electronic technology. Metal oxides are attractive candidates for anode material in LIBs and have been studied intensively because of their high energy density and good cycle performance. In particular, Fe$_2$O$_3$ has attracted wide attention as an anode material owing to its high theoretical specific capacity (~1000 mA h g$^{-1}$), environmental friendliness and natural abundance. However, the commercialization of Fe$_2$O$_3$ has been suffocated by its intrinsic poor conductivity and the terrible capacity fading during the charging process.

To overcome the above mentioned issues, foreign metal doping into Fe$_2$O$_3$ has been developed as an effective strategy. This tactic is based on the fact that a foreign metal atom bears a different atomic radius to that of the Fe atom, and its incorporation breaks the original spatial architecture of Fe$_2$O$_3$ and modulates the electronic structure of Fe, which in turn forms a richer redox reaction, enhances the electron conductivity and consequently yields an improved electrochemical performance. For example, Co doped Fe$_2$O$_3$ demonstrated a superior initial discharge specific capacity, cycling stability and rate capacity than those of the un-doped Fe$_2$O$_3$ component competitor. Al, the most abundant metal element in the earth’s crust, is one of the most important metals for human beings, and has served human beings with a long history in the manufacturing industry. Recently, a large number of efforts have demonstrated that the introduction of the Al element into transition metal oxides/sulphides/phosphides could trigger a significantly improved performance for supercapacitors, sodium-ion batteries, electrocatalytic reaction, etc. The strong electronic interaction between Al and a transition metal is the main reason for the enhancement. Besides, an Al atom has the ability to stabilize the structure of the entity composite and raises the electron transportation. However, the utilization of Al doping to improve the electrochemical performance for LIBs has rarely been reported.

Herein, in this work, a simple fabrication method was adopted to prepare Al doped Fe$_2$O$_3$ (denoted as Al-Fe$_2$O$_3$) crystals to be used as an anode for LIBs. This achieved an initial discharge specific capacity of 1200 mA h g$^{-1}$ at a current density of 0.5 A g$^{-1}$ as well as an excellent reversible capacity of 900 mA h g$^{-1}$, much better than that of a pure Fe$_2$O$_3$ reference sample at the same working conditions. We also found that the surface controlled pseudocapacitive process is the main driving power for the elevated activity. The enhanced electrochemical performance can be ascribed to the following reasons: first, the doping of Al would trigger Fe$_2$O$_3$ volume expansion since Al and Fe exhibit different atomic radii (Al 0.143 nm and Fe 0.126 nm), which gives a greater promise to buffer the volume change. Second, the in situ formed Al$_2$O$_3$ plays a “flexible support” role, stabilizing the whole Al-Fe$_2$O$_3$ architecture. Last, Al$^{3+}$ is able to react with the electrolyte (LiPF$_6$) or the irreversible ordered solid electrolyte interphase (SEI), to produce solid acid and then optimize the non-uniform surface as well as create oxygen deficiencies, and exposure of more intrinsic active sites.

The Al doped Fe$_2$O$_3$ nanoparticles were fabricated via a facile and subsequent annealing route described in the ESI† and illustrated in Fig. S1a;† pure Fe$_2$O$_3$ without Al doping was also prepared through the same method but without Al$^{3+}$ in the original feeding stocks. The crystallinity and phase compo-
sition of the products (Al-Fe$_2$O$_3$ and pure Fe$_2$O$_3$) are firstly characterized by the X-ray powder diffraction (XRD) pattern, shown in Fig. 1a. All of the diffraction peaks of Al-Fe$_2$O$_3$ and Fe$_2$O$_3$ can be marked as Fe$_2$O$_3$ (JCPDS#33-0664). No other phase was detected, indicating the high purity of the as-prepared sample. A careful comparison of the magnified XRD patterns (inset of Fig. 1a) found that there are obvious shifts toward the negative side of the (104) and (110) peaks after Al was doped into Fe$_2$O$_3$. This movement suggests that Al doping changed the electronic structure of Fe$_2$O$_3$. According to Bragg’s law, the calculated lattice fringes for Al-Fe$_2$O$_3$ are larger than those of Fe$_2$O$_3$, indicating a widened crystal volume. Scanning electron microscopy (SEM) images are used to characterize the morphology of Al-Fe$_2$O$_3$ and Fe$_2$O$_3$, shown in Fig. 1b, d and Fig. S2.† Lots of irregular block material with rough surfaces are visually observed for both Al-Fe$_2$O$_3$ and Fe$_2$O$_3$. Fig. 1c and d show that the large bulk material is made up of numerous small nanoparticles and all of them are stacked together. We also investigated the influence of Al doping level on the XRD pattern. Fig. S3a† illustrates the XRD patterns of four samples with different Al/Fe proportions (initial mass feeding ratios of Al/Fe are 1 : 2 (A1F2), 1 : 5 (A1F5), 1 : 10 (Al-Fe$_2$O$_3$), 1 : 15 (A1F15) and 1 : 20 (A1F20)). All the diffraction peaks of these four samples can be marked as Fe$_2$O$_3$. The doping Al content affected the interlayer spacing of the Fe$_2$O$_3$ crystal plane, the peaks of (104) and (110) shifted to the negative side and this trend became more obvious with an increase of Al. Fig. S3b, c and d† depict the SEM images of the four samples; generally, the products are of a nanoparticle morphology.

A nitrogen sorption isotherm measurement is carried out to analyse the specific surface areas (BET) and porous features of Al-Fe$_2$O$_3$ and Fe$_2$O$_3$ (Fig. 1e–g and Fig. S4†). The BET of Al-Fe$_2$O$_3$ is about 19.052 cm$^2$ g$^{-1}$, nearly three-fold larger than that of pure Fe$_2$O$_3$ (7.082 cm$^2$ g$^{-1}$), which gives great promise for more exposed intrinsic active sites and an advanced electrochemical performance in comparison with that of pure Fe$_2$O$_3$. The average pore diameter and cumulative volumes are about 29.43 nm and 0.138 cm$^3$ g$^{-1}$, respectively. The generation of mesopores is caused by the different accumulation extent of small Al-Fe$_2$O$_3$ nanoparticles.⁹

The detailed structures of Al-Fe$_2$O$_3$ and Fe$_2$O$_3$ are further analysed by transmission electron microscopy (TEM) and shown in Fig. 2a, b and Fig. S5a, b.† A typical HR-TEM (Fig. 2c) image demonstrates a clear lattice fringe with a measured interplanar spacing of 0.371 nm, which ascribes well to the (012) plane of Fe$_2$O$_3$; this data is a little larger than that of pure Fe$_2$O$_3$ (0.367 nm, Fig. S5c†), verifying that Al has been successfully doped into the crystal lattice of Fe$_2$O$_3$. The average particle size of Al-Fe$_2$O$_3$ calculated from more than two hundred nanoparticles is about 85–95 nm (Fig. S6a†). Fe$_2$O$_3$ synthesized by the same method has a particle diameter of 90 nm (Fig. S6b†). In the selected area electron diffraction (SAED) profile (Fig. 2d), a clear ring-diffraction pattern also demonstrated typical crystal planes of (012), (104) and (110) of the Al-Fe$_2$O$_3$. The mapping profiles (Fig. 2e–h) also indicate a uniform distribution of O, Fe, and Al elements in the Al-Fe$_2$O$_3$ sample. In addition, the X-ray energy dispersive spectrum (EDS) (Fig. 2i) indicates, as well as Fe and O elements, that Al is also present, well consistent with the mapping results, and the doping level of Al is about 6.81 wt% in Al-Fe$_2$O$_3$ nanoparticle.

X-ray photoelectron spectroscopy (XPS) spectrum analysis is performed to investigate the element chemical states of Al-Fe$_2$O$_3$ and Fe$_2$O$_3$. In addition to the peaks for Fe and O, the peak for Al can be identified from the XPS spectra of Al-Fe$_2$O$_3$ (Fig. 3a and b), meaning the Al atoms have been doped into Fe$_2$O$_3$. The Al 2p spectrum (Fig. 3b) can be divided into two peaks at 73.9 eV and 76.8 eV, which are consistent with a previous report on doped Al materials.⁹ For the high resolution spectra of Fe 2p (Fig. 3c), two obvious characteristic peaks of Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ assigned to Fe$^{3+}$ at 708.5 and 722.4 eV for Fe$_2$O$_3$, respectively, can be observed. Note that the peaks for Fe in Al-Fe$_2$O$_3$ show a visibly negative shift to lower binding energies, indicating a strong electronic interaction between Al and Fe, which may cause the envisioned fast electron transfer and facilitate interfacial reaction kinetics.¹¹ Two obvious peaks assigned to the deficient-rich oxygen species (marked as peak A) and the full chemically bonded oxygen species (peak B) are
fitted from the deconvoluted oxygen 1s spectra (Fig. 3d). Clearly, the intensity ratio between peak A and B of Al-Fe₂O₃ is much higher than that of pure Fe₂O₃, demonstrating that there are more oxygen vacancies in Al-Fe₂O₃ in comparison with those in Fe₂O₃. As reported, oxygen vacancies are beneficial to strengthen the electrochemical behaviour of Fe₂O₃ as an anode when used in LIBs.²,¹²

We constructed LIBs with an Al-Fe₂O₃ anode and Li cathode, the composition of the LIBs is presented in the ESI and the electrochemical behaviours are studied. For comparison, LIBs constructed by pure Fe₂O₃ and other compounds with different Al-doping contents are also investigated. As disclosed in Fig. 4a, the reduction peaks of Al-Fe₂O₃ at about 1.6 V and 0.59 V during the initial discharging reflected the conversions Fe³⁺ → Fe²⁺ and Fe²⁺ → Fe⁰.¹³,¹⁴ The electrochemical performance comparison of Al doped Fe₂O₃ with various Al content demonstrates that when the Al/Fe ratio is 1:10, the cell exhibits the best electrochemical activity (Fig. S7†). Therefore, we discussed the performance of Al-Fe₂O₃ deeply. The high peak intensity suggested that Al-Fe₂O₃ exhibits a high electrochemical reactivity and excellent reduction ability. Besides, a solid electrolyte interface (SEI) layer formed during this conversion. The broad peak emerging at about 1.78 V corresponded to the reversible oxidation process of Fe⁰ to Fe³⁺. Note that the subsequent cycles (the 2nd and 3rd) almost overlapped with each other, suggesting a highly reversible process on Al-Fe₂O₃, and the whole lithiation/delithiation process is the same as previously documented.¹⁵,¹⁶ Fig. 4b shows the galvanostatic charge–discharge (GCD) curves from the 1st to the 350th cycles at a current density of 0.5 A g⁻¹ of Al-Fe₂O₃. Appreciably, the initial discharge specific capacity was above 1200 mA h g⁻¹, higher than that of Fe₂O₃ (1000 mA h g⁻¹, Fig. S8a†). The reversible capacity of Al-Fe₂O₃ is as high as 800–1000 mA h g⁻¹ in about 250 cycles, rendering Al-Fe₂O₃ comparable to or even better than previously reported Fe₂O₃ based anodes (Table S2†). Fig. 4c displays the cycling stability of the Al-Fe₂O₃ material at a current density of 0.5 A g⁻¹ and 1.0 A g⁻¹ (inset of Fig. 4c). Although the initial discharge/charge capacities fell in the first 150th cycle, they gradually increased and exhibited an excellent capacity retention of 902 and 777 mA h g⁻¹ at of 0.5 and 1.0 A g⁻¹ after a charge/discharge of 500 cycles, respectively, much better than those of Fe₂O₃ (Fig. S8b†). The rise of the capacity can be attributed to the large surface active sites created by an oxygen vacancy. In addition, Al as a defect is counterbalanced by Li⁺ ions within the plane, propping the slabs open for further redox intercalation without excessive volume expansion.¹⁷,¹⁸ Fig. 4d shows the rate performance of the Al-Fe₂O₃ electrode. The Al-Fe₂O₃ electrode delivers rate
capacities of 833.8 to 319.7 mA h g\(^{-1}\) at 0.1–3.0 A g\(^{-1}\), respectively, higher than those of pure Fe\(_2\)O\(_3\), which exhibits rate capabilities of 724–161 mA h g\(^{-1}\) at 0.1–3.0 A g\(^{-1}\) (Fig. S8†). Note that when the current density finally switched back to the initial value of 0.1 A g\(^{-1}\), an impressive reversible capacity of around 900 mA h g\(^{-1}\) was recovered.

In order to obtain the morphological and structural stability of Al-Fe\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) after cycling, we further characterized the samples after cycling tests by XRD and SEM. As can be seen from the XRD pattern in Fig. S9a† the diffraction peaks of Al-Fe\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) samples after cycling corresponded to the standard patterns of Fe\(_2\)O\(_3\) and Cu, respectively, and no phase changing is observed, indicating the strong structural stability of Al-Fe\(_2\)O\(_3\). TEM images (Fig. S9b and c†) after the cycling also demonstrated that the Al-Fe\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) materials have a good morphological and structural stability.

Electrochemical impedance spectroscopy (EIS) is widely used to investigate electrode kinetics between the electrode and the electrolyte. Fig. 4c shows the Nyquist plots of the Al-Fe\(_2\)O\(_3\) electrode before and after cycling. The simulated model and fitted impedance parameters are listed in Table S3.† The model is composed of \(R_s\) (ohmic resistance) in the high frequency region, and \(R_{SEI}\) (resistance related to Li ion passing through SEI film) in the high frequency region, \(R_{ct}\) (charge transfer resistance) in the medium frequency region, \(C_{dl}\) double capacity layer and \(Z_w\) (owing to Li ion scattering in the solid phase) in the low frequency region.19 The \(R_s\) value increased from 14.49 \(\Omega\) at the beginning to 44.83 \(\Omega\) after the cycling, which proved that the SEI film on the electrode surface is stable.20 Additionally, \(Z_w\) changed little after cycling, indicating that the ion migration ability kept no attenuation although it underwent lots of charge–discharge processes.

Fig. 4f depicts the CV cycles in various sweeping rates. The good symmetry CV shape demonstrated the outstanding redox reversibility. The anodic peak current and cathodic peak current are marked in Fig. 4f as peak 1 (red arrow) and peak 2 (dark arrow), respectively. Generally, two kinds of processes may occur for the energy storage, a diffusion controlled faradaic redox process and a surface controlled capacitive process. Here, the relationship of \(\lg i_p\) as a function of \(\lg v\) is plotted by eqn (1) to interpret whether or not there is a surface controlled capacitive process, where \(i\) represents the peak current density, \(v\) is the sweeping rate, and \(a\) and \(b\) values are adjustable parameters. The fitted slopes are 0.80 and 0.67 for the anodic and cathodic processes, respectively, recommending that a significant pseudocapacitance is the dominant process that ensures fast Li\(^+\) storage for the prepared Al-Fe\(_2\)O\(_3\) electrode.21 The contribution ratios of the diffusion/surface controlled behaviours at a scan rate of 0.5 mV s\(^{-1}\) were figured out by eqn (2), where \(k_1\) and \(k_2\) are the constants associated with the sweeping rates.22 The surface-controlled pseudocapacitive held at around 85.6%, while the diffusion-controlled process was only 15.4% (Fig. 4g). Additionally, the pseudocapacitive contributions at different sweeping rates are summarized in Fig. 4h. The pseudocapacitive contribution is about 71.6% and up to 91.3% as the sweeping rate went to 1.0 mV s\(^{-1}\). Thus, the energy storage for LIBs constructed with Al-Fe\(_2\)O\(_3\) anode is a surface-controlled capacitive process.

\[
\begin{align*}
\lg i &= \lg a + \lg v \\
i(V) &= k_1v + k_2v^{1/2}
\end{align*}
\]

Conclusions

Al doped Fe\(_2\)O\(_3\) nanocomposites as anodes for LIBs were successfully prepared. Electrochemical measurements demonstrated that Al-Fe\(_2\)O\(_3\) has superior lithium storage characteristics with a higher capacity, rate capability and a more stable cycling performance than those of pure Fe\(_2\)O\(_3\). This work provides an environmentally friendly strategy to construct ideal anode candidates for high-capacity electrodes of rechargeable LIBs.

Conflicts of interest

There are no conflicts to declare.

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References


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16 G. Li, X. Xu, R. Han and J. Ma, CrystEngComm, 2016, 18, 2949–2955.