



# Article Fe<sub>2</sub>O<sub>3</sub> Microcubes Derived from Metal–Organic Frameworks for Lithium-Ion Storage with Excellent Performance

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**Abstract:** Transition metal oxides are regarded as a potential electrode material for lithium-ion storage due to it features high theoretical capacity and low cost. In this study, the possibility of  $Fe_2O_3$  microcubes as an electrode material for lithium-ion storage was investigated, where the anode electrode of  $Fe_2O_3$  microcubes were created through Prussian blue (PB) metal–organic frameworks (MOFs) and followed by the calcination process at high temperature. The results showed that the  $Fe_2O_3$  microcubes electrode obtained by the calcination process at 500 °C exhibited superior electrochemical performances than that of  $Fe_2O_3$  obtained by the calcination process at 700 °C. The increase in calcination temperature will lead to the further sintering reaction between the particles and the formation of cracks and voids in crystals that eventually lead to the breakup of microcube and so lower stable structure of the  $Fe_2O_3$  microcubes electrode.  $Fe_2O_3$  microcubes exhibited an excellent/stable lithium storage performance and thus is a promising anode material for LIBs.

Keywords: Fe<sub>2</sub>O<sub>3</sub>; metal–organic-framework; anode; lithium-ion battery



1. Introduction

Burning fossil fuels (coal, natural gas, oil, etc.) released huge amounts of air pollutants that are harmful to environment. The development of new energy storage devices could lessen the air pollution [1–4]. Lithium-ion batteries (LIBs) are the most versatile energy storage devices, which are widely used in in electric vehicles, gas–electric vehicles, and different electronic products [5,6]. However, the theoretical capacity of graphite anode widely used in LIBs is 372 mAh g<sup>-1</sup>, which cannot meet the requirements of high energy density for the next generation of LIBs. Therefore, it is necessary to develop new anode materials with high stability and theoretical capacity for LIBs [7].

Transition metal oxides (TMOs) are promising electrode materials for LIBs because of their low cost, good thermal stability and high theoretical capacity [8]. However, the large volume changes of TMOs during the cycle will make the electrode materials agglomerate and pulverize, and thus deteriorating the performance and service life of the battery [9,10]. Consequently, TMO-type electrode materials with a stable structure and good resistance to volume change are expected to be developed [11,12]. Many studies reported that metal–organic frameworks (MOFs) are ideal precursors for creating TMOs, and thus are promising electrode materials for LIBs, owing to the fact that MOFs have a stable structure, uniform particle size and crystal morphology [13–17]. Lu et al. [18] made the porous, nanostructured  $Co_3O_4$  from Co-bearing MOFs precursors, and found its reversible capacity is 838 mAh g<sup>-1</sup> at the current density of 1 A g<sup>-1</sup> after 300 cycles. The research regarding the preparation of nano-Fe<sub>2</sub>O<sub>3</sub> as an anode for LIBs by using MOFs as self-sacrificing templates is widely reported. Abhik et al. have made porous  $\alpha$ -Fe<sub>3</sub>O<sub>3</sub> nanospindles from Fe-bearing MOFs [19]. Xu et al. used the mesoporous spindle-like Fe<sub>2</sub>O<sub>3</sub> prepared from Fe-bearing MOFs as an



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). anode material for LIBs [20]. Guo [21] reported the mesoporous  $Fe_2O_3$  with yolk–shell shape prepared from MIL-53 MOFs has the discharge capacity of 744 mAh g<sup>-1</sup> at the current density of 1 A g<sup>-1</sup>.

In this work,  $Fe_2O_3$  microcubes were prepared through Prussian blue (PB) metalorganic frameworks (MOFs), following by the calcination process at high temperature to obtain the anode electrode for lithium-ion batteries (LIBs). Then, the morphology and electrochemical performances of the  $Fe_2O_3$  microcubes were investigated.

# 2. Materials and Methods

# 2.1. Synthesis of Fe<sub>2</sub>O<sub>3</sub> Microcubes

By using the precipitation method, Fe<sub>2</sub>O<sub>3</sub> microcubes were prepared through Prussian blue, where the used chemical reagents of Polyvinylpyrrolidone (K30, Aldrich), K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O (99%, Aldrich), HCl (Longxi), ethanol (99.7%, Aldrich) are analytically pure without further purification. Figure 1 shows the preparation route of Fe<sub>2</sub>O<sub>3</sub> microcubes. Firstly, 20 g of polyvinyl pyrrolidone was dissolved in 250 mL of HCl (0.2 mol L<sup>-1</sup>), and mixed by using magnetic stirring until the polyvinyl pyrrolidone was completely dissolved. Then, 0.6 g K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O were added into the solution and left to stand for 20 h at 80 °C without stirring. Next, the precipitates obtained from the solution were washed three times in centrifugally, and subjected to vacuum drying at 70 °C, then the Precursors Blue (PB) were obtained (Figures 2 and 3a). Finally, the precursors blue were calcined at the different temperature of 500 and 700 °C for 2.5 h in the air, respectively, then Fe<sub>2</sub>O<sub>3</sub> microcubes were made (labeled as Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700, where the number, i.e., 500 and 700, represents the calcination temperature).



Figure 1. Schematic of the synthesis of Fe<sub>2</sub>O<sub>3</sub> microcubes.



Figure 2. XRD patterns of (a) precursors blue and (b) Fe<sub>2</sub>O<sub>3</sub> samples.



Figure 3. SEM images of (a) precursors blue, (b)  $Fe_2O_3$ -500 and (c)  $Fe_2O_3$ -700. TEM images of (d)  $Fe_2O_3$ -500 and (e)  $Fe_2O_3$ -700.

#### 2.2. Characterization

The sample structure was identified by X-ray diffractometer (XRD, Rigaku Minflex-600) with Cu K $\alpha$  radiation ( $\lambda$  = 0.15418 nm). The microscopic morphology and structure of Fe<sub>2</sub>O<sub>3</sub> samples were characterized by Scanning Electron Microscope (SEM, FEI NanoSEM 450, Portland, OR, USA) and Transmission Electron Microscope (TEM, Tecnai F30, Portland, USA). While CR2016 button cells were assembled so as to evaluate the electrochemical performances of Fe<sub>2</sub>O<sub>3</sub> electordes. In addition, the chemical composition of the material surface and the chemical price of each element are charactered by X-ray Photoelectron Spectroscopy (XPS, Ulvac PHI PHI5000 Versaprobe-II, Osaka, Japan).

For a piece of current collector of copper foil (the thickness of the electrode material on the copper foil is about 30  $\mu$ m), the working electrode consists of Fe<sub>2</sub>O<sub>3</sub> power, super P and binder PVDF (7:2:1). A lithium plate was regarded as a counter electrode, where 1 M LiPF<sub>6</sub> dissolved in ethylene carbonate/dimethyl carbonate (EC/DEC, 1:1) as electrolyte. By the battery test system (LAND CT2001, Wuhan, China), the electrochemical performances of the Fe<sub>2</sub>O<sub>3</sub> microcubes were investigated with the voltage range of the galvanostatic current test is 0.01–3.0 V. In addition, a Metrohm Autolab electrochemical workstation was used to recorded Electrochemical Impedance Spectroscopy (EIS, PGSTA 302N, Herisau, Switzerland) of electrodes after 50 cycles and a range of 0.1 Hz to100 kHz.

# 3. Results and Discussion

The crystalline phases of precursors blue and Fe<sub>2</sub>O<sub>3</sub> microcubes were identified through a XRD measurement. As shown in Figure 2a, all the characteristic peaks of precursors blue correspond to Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub> (JCPDS No. 01-0239), which implies the pure Prussian Blue MOF is made [22]. The elements in precursors blue were investigated by XPS, and the results are supplemented in Figure S1. Powder X-ray diffraction patterns of the Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700 are shown in Figure 2b. Both of Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700 contain  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phases. The characteristic strong peaks observed at 24.1°, 33.1°, 49.5°, 54.1°, 67.6° and 64.0° can be indexed to the (012), (104), (024), (116), (018), (300) crystal plane of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS No. 33-0664), and the rest of characteristic peaks match the XRD peaks of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS No. 39-1346) very well [20,21]. Therefore, both of XPS and XRD analysis confirmed Fe<sub>2</sub>O<sub>3</sub> is created.

The morphologies and microstructure of precursors blue and  $Fe_2O_3$  microcubes were examined by SEM and TEM. Figure 3a shows precursors blue are a cubic shape with smooth surfaces, and the particle size is 300 to 600 nm. The reason why  $Fe_2O_3$  exhibited the microcubes shape could be attributed to the preferential growth of  $Fe_2O_3$  crystals along its preferential orientation so as to reduce the free energy of a system that could also be explained by Wulff construction [23]. Compared with the microcubes of Fe<sub>2</sub>O<sub>3</sub>-700, Fe<sub>2</sub>O<sub>3</sub>-500 microcubes exhibited more uniform particle size (mean particle size ~450 nm) and the smoother surfaces (Figure 3a). Figure 3b shows Fe<sub>2</sub>O<sub>3</sub>-700 microcube is a mess block consisting of smaller and rough particles (mean particle size ~ 90 nm). The particle size distribution of Fe<sub>2</sub>O<sub>3</sub>-700 microcube might be attributed to the further sintering reaction between the particles, and the formation of cracks and voids in crystals leading to the breakup of microcube. Figure 3c,d show the TEM images of Fe<sub>2</sub>O<sub>3</sub>-700 microcube exhibited cracks and voids.

The electrochemical performances of Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700 anode electrodes are evaluated. Figure 4a,b show the discharge/charge profiles of Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700 electrode at 200 mA g<sup>-1</sup>, respectively. The discharge/charge curves of those two samples are similar. Initial discharge capacity of Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700 is 1310.4 and 1384.1 mAh g<sup>-1</sup>, respectively. There is a plateau between 0.91 and 0.77 V in the first discharge curve. The first coulombic efficiencies of Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700 are 0.68 and 0.65 V, respectively. The low first coulombic efficiency might be attributed to the occurrence of side reactions and the formation of solid electrolyte interphase [23–25]. Both of those two samples have the high reversible capacity in the 2nd and 100th cycle, indicating that the well electrochemical stability of the Fe<sub>2</sub>O<sub>3</sub> microcubes. The dQ/dV curves are calculated based on galvanostatic discharge/charge cycling curves of Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700 and the results are supplemented in Figure S2. Compared with the peak offset in Figure S2, it can be found that Fe<sub>2</sub>O<sub>3</sub>-500 exhibited better cyclic stability than that of Fe<sub>2</sub>O<sub>3</sub>-700.



**Figure 4.** Discharge/charge profiles of (**a**) Fe<sub>2</sub>O<sub>3</sub>-500 and (**b**) Fe<sub>2</sub>O<sub>3</sub>-700 for the 1st, 2nd, 100th cycles. (**c**) Cycling performance of Fe<sub>2</sub>O<sub>3</sub>. (**d**) Long-cycling performance of Fe<sub>2</sub>O<sub>3</sub>. (**e**) Rate capability of Fe<sub>2</sub>O<sub>3</sub>.

The cycle performances of Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700 at 200 mA g<sup>-1</sup> current density are shown in Figure 4c. The specific capacity of Fe<sub>2</sub>O<sub>3</sub>-500 initially at 900 mAh g<sup>-1</sup>, decreases to the minimum value of 490 mAh g<sup>-1</sup> at 50 cycles, and then increases for the rest of cycles. Meanwhile, the specific capacity of Fe<sub>2</sub>O<sub>3</sub>-700, initially at 900 mAh g<sup>-1</sup>, decreases to the minimum value of 570 mAh g<sup>-1</sup> at 40 cycles, then increases to a maximum value of 750 mAh g<sup>-1</sup> at 110th cycles, and finally decreases again for the rest of cycles. The decrease in capacities during the first 40 to 50 cycles may be attributed to the structural degradation and rearrangement that a polymeric gel-like film on the active materials are formed. The polymeric gel-like film is due to kinetically activated electrolyte decomposition, which can store excess Li<sup>+</sup> ions through the so-called pseudo-capacitance-type behavior, resulting in an increase in capacity in the following cycles. Fe<sub>2</sub>O<sub>3</sub>-500 shows an excellent capacity retention, and delivers a specific capacity of 974.7 mAh g<sup>-1</sup> after 200 cycles which is larger than

that of Fe<sub>2</sub>O<sub>3</sub>-700 (414.5 mAh g<sup>-1</sup>). The reason why the discharge capacity of Fe<sub>2</sub>O<sub>3</sub>-700 decays after 110 cycles may be contributed to the active material gradually pulverized during the Li ions intercalation/deintercalation process. The long-term cycling performance are tested under the 400 cycles with 1000 mA g<sup>-1</sup> current density. After 400 cycles, the reversible capacity of Fe<sub>2</sub>O<sub>3</sub>-500 retains 775.1 mAh g<sup>-1</sup>, the capacity retention rate is 70% with respect to that of value at second cycle. While the reversible capacity of Fe<sub>2</sub>O<sub>3</sub>-700 is 456.1 mAh g<sup>-1</sup>, the capacity retention rate is 53%. To reveal the cycling stability of Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700, the morphologies of the disassembled cells were investigated by SEM. The SEM images of samples after 300 cycles at 1000 mAh g<sup>-1</sup> are supplemented in Figure S4. It is found that the structural stability of Fe<sub>2</sub>O<sub>3</sub>-500 is better that that of Fe<sub>2</sub>O<sub>3</sub>-700 (Figure S4a) shows the bulk morphology. This finding is consistent with the electrochemical tests, suggesting the cyclic stability of Fe<sub>2</sub>O<sub>3</sub>-500 is better than that of Fe<sub>2</sub>O<sub>3</sub>-700.

Figure 4e shows the rate capability of  $Fe_2O_3$ -500 and  $Fe_2O_3$ -700 at the current densities from 100 to 2000 mA g<sup>-1</sup>.  $Fe_2O_3$ -500 exhibits better rate capability than that of  $Fe_2O_3$ -700. For  $Fe_2O_3$ -500, the average capacities of 1009.2, 832.5, 683.6, 570.4, and 481.2 mAh g<sup>-1</sup> correspond to the current densities of 100, 200, 500, 1000, and 2000 mA g<sup>-1</sup>, respectively. When the current density drops again to 0.1 A g<sup>-1</sup>, the average reversible capacity of  $Fe_2O_3$ -500 recovers rapidly to 786.1 mAh g<sup>-1</sup>, while that value for  $Fe_2O_3$ -700 is 460 mAh g<sup>-1</sup>. Therefore, it could be concluded that  $Fe_2O_3$ -500 has superior rate performances than that of  $Fe_2O_3$ -700.

Furthermore, electrochemical impedance spectroscopy (EIS) was carried out on the battery after 50 cycles. Figure 5 presents the Nyqueist plot and the fitted equivalent circuit model, and EIS curves consist of semicircles and oblique lines. In the equivalent model,  $R_s$  and  $R_f$  represents the electrolyte resistance and the interface impedance, respectively [26–28]. In addition, the semicircles in the medium-frequency region corresponds the charge transfer impedance ( $R_{ct}$ ). The fitting data of  $R_s$ ,  $R_f$  and  $R_{ct}$  are shown in Table 1. EIS results reveal that Fe<sub>2</sub>O<sub>3</sub>-500 possesses lower  $R_f$  and  $R_{ct}$  than those values of Fe<sub>2</sub>O<sub>3</sub>-700, indicating Fe<sub>2</sub>O<sub>3</sub>-500 has better lithium-ions diffusion performance and stability than those of Fe<sub>2</sub>O<sub>3</sub>-700.



Figure 5. Nyquist plots of Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700 electrodes after 50 cycles.

Parameters	Fe <sub>2</sub> O <sub>3</sub> -500	Fe <sub>2</sub> O <sub>3</sub> -700
$R_s(\Omega)$	4.61	6.54
$R_f(\Omega)$	2.73	6.16
$R_{ct}^{\prime}(\Omega)$	29.7	57.7

Table 1. Simulated resistance values (*R<sub>s</sub>*, *R<sub>f</sub>*, *R<sub>ct</sub>*) of Fe<sub>2</sub>O<sub>3</sub>-500 and Fe<sub>2</sub>O<sub>3</sub>-700 electrodes.

### 4. Conclusions

In this study, the potential of  $Fe_2O_3$  microcubes as an electrode material for lithium-ion storage is investigated. First, the  $Fe_2O_3$  microcubes are created through Prussian blue, following by the calcination process at high temperature to obtain the anode electrode for lithium-ion batteries. Then, the electrochemical performances of  $Fe_2O_3$  microcubes are investigated. The main results are:

- (1) Fe<sub>2</sub>O<sub>3</sub> microcubes electrode obtained by the calcination process at 500 °C exhibited superior electrochemical performances than that of Fe<sub>2</sub>O<sub>3</sub> obtained by the calcination process at 700 °C. The increase in calcination temperature will lead to the further sintering reaction between the particles and the formation of cracks and voids in crystals that eventually lead to the breakup of microcube and thus lower stable structure of Fe<sub>2</sub>O<sub>3</sub> microcubes electrode.
- (2) For Fe<sub>2</sub>O<sub>3</sub> microcubes obtained by the calcination process at 500 °C, the discharge capacity is 974.7 mAh g<sup>-1</sup> after 200 cycles, and the specific discharge capacity is 775.1 mAh g<sup>-1</sup> at 1000 mA g<sup>-1</sup> current density after 400 cycles.
- (3) Fe<sub>2</sub>O<sub>3</sub> microcubes prepared by precipitation method combined with appropriate heat treatment conditions exhibits an excellent/stable lithium storage performance, and hence is a promising anode material for LIBs.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10 .3390/cryst11080854/s1, Figure S1: XPS spectra for PB precursor (a) XPS spectrum, (b) Fe 2p, (c) C 1s, (d) N 1s, Figure S2: The Differential capacity plot of (a) Fe<sub>2</sub>O<sub>3</sub>-500 and (b) Fe<sub>2</sub>O<sub>3</sub>-700, Figure S3: The Cycling performance of (a) Fe<sub>2</sub>O<sub>3</sub>-400 and (b) Fe<sub>2</sub>O<sub>3</sub>-600, Figure S4 SEM images of (a) Fe<sub>2</sub>O<sub>3</sub>-500 and (b) Fe<sub>2</sub>O<sub>3</sub>-700 after 300 cycles at 1000 mA g<sup>-1</sup>.

**Author Contributions:** Conceptualization, J.L. and H.Z.; methodology, J.L.; software, C.Z. and Y.L.; validation, J.L. and H.Z.; formal analysis, C.Z.; investigation, Y.L.; resources, J.L.; data curation C.Z.; writing—original draft preparation, C.Z. and J.L.; writing—review and editing, H.Z. and J.L.; visualization, Y.L.; supervision, C.Z. and H.Z.; project administration, H.Z.; funding acquisition, J.L. and H.Z. All authors have read and agreed to the published version of the manuscript.

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