



Electrochemical performance of hematite nanoparticles derived from spherical maghemite and elongated goethite particles



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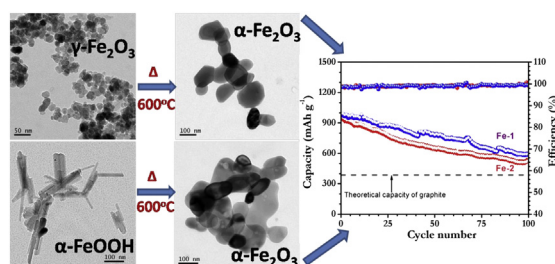
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HIGHLIGHTS

- α -Fe₂O₃ nanoparticles from maghemite nanoparticles and goethite rods.
- The α -Fe₂O₃ from maghemite exhibited a reversible capacity of ~1160 mAh g⁻¹.
- The α -Fe₂O₃ from goethite delivered a reversible capacity of ~1100 mAh g⁻¹.

GRAPHICAL ABSTRACT



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ABSTRACT

We report here an interesting observation on the electrochemical performance of hematite nanoparticles derived from cubic maghemite nanoparticles and hexagonal goethite rods prepared by a sonochemical process. We prepared hematite (α -Fe₂O₃) particles by annealing the as-prepared spherical cubic maghemite (γ -Fe₂O₃) nanoparticles and rod shaped hexagonal goethite (α -FeOOH) particles at 600 °C in air and investigated their performance as a Li-ion battery anode. Interestingly, annealing of spherical maghemite particles resulted in the formation of plate like interconnected hematite particles exhibiting unimodal pore distribution whereas rod shaped goethite has resulted in the formation of irregularly shaped porous hematite particles having a wide and multimodal pore distribution. The plate like α -Fe₂O₃ cells delivered a reversible capacity of ~1160 and the porous α -Fe₂O₃ nanoparticles exhibited a slightly lower capacity of ~1100 mAh g⁻¹. The test cells rendered a reversible capacity of ~926 and ~841 mAh g⁻¹ for nanoparticles derived from maghemite and goethite, respectively, after 40 galvanostatic cycles and a capacity of 611 and 522 mAh g⁻¹ at 0.1C rate after 100 cycles. In other words, the investigated α -Fe₂O₃ nanomaterials retained a reversible capacity of ~80 and 75%, respectively after 40 galvanostatic cycles. The basic difference in the electrochemical performance of the studied hematite particles have been attributed to the difference in the porosity of the samples. Moreover, the adopted synthesis technique is very simple and easily up scalable compared to most of the methods available in the literature for the synthesis of hematite nanoparticles.

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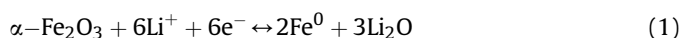
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1. Introduction

Hematite (α -Fe₂O₃) is an anti-ferromagnetic, n-type semi conducting material exhibiting unique properties such as non-toxicity,

low cost, high stability under ambient conditions and high resistance towards corrosion making it very attractive for lithium ion batteries (LIBs), gas sensors, catalysts, and adsorbents [1–6]. Owing to their novel properties leading to promising applications, interest in synthesizing hematite having different size and shape has been an area of current interest [7,8]. As an anode material in LIBs, α -Fe₂O₃ exhibits a high theoretical capacity of 1005 mAh g⁻¹. The performance of hematite in LIB's strongly depends on their structure, particle size, morphology and also to a larger extent on the porosity [9–14]. Nano-structured hematite has been demonstrated to have superior performance compared to bulk hematite exhibiting initial reversible capacities as high as 1303 mAh g⁻¹. This has been attributed to the effect of smaller particle size in decreasing the diffusion length of the Li-ions, apart from the pseudo-capacitance contribution from electrode/electrolyte interface [15]. It has also been found that porous electrode materials can facilitate the diffusion of Li-ions to active sites with less resistance and can also withstand the change of volume during the charge/discharge cycling [16–18]. Some recent investigations revealed the importance of shape of the hematite crystals in controlling the conversion reactions with Li-ions [19]. To achieve better performance with higher capacity and longer cycle life, different types of materials have been incorporated in hematite, to use them as alternative anodic materials for LIBs. For example, reduced graphene oxide (RGO)/ α -Fe₂O₃ composite used as anode in LIB exhibited higher discharge and charge capacities of 1693 and 1227 mAh g⁻¹, respectively [20,21]. Introduction of carbon coating or composite carbonaceous materials with hematite nanostructures also exhibited superior performance. The performance of LIB's is mainly governed by the reaction shown below [22,23].



In the initial stage, a small amount of Li could get inserted into the hexagonal hematite to form a hexagonal α -Li_xFe₂O₃. Further discharging reactions subsequently leads to the formation of metallic nanoparticles (Fe³⁺ to Fe²⁺ and Fe²⁺ to Fe⁰). Thus, the fine nanoclusters of Fe⁰ get dispersed in the amorphous Li₂O matrix. During charging Fe⁰ gets oxidized to Fe³⁺ resulting in the formation of ν -Fe₂O₃.

In the present work, we have compared the properties of hematite nanoparticles formed from two different host materials and their performance as anode material for LIB's. In our previous work, we had reported that drop-wise addition of hydrazine monohydrate (N₂H₄·H₂O) to an aqueous solution of 0.1 M ferric nitrate solution resulted in the formation of maghemite nanoparticles and simultaneous addition formed goethite nanorods [24]. In this work, we have prepared hematite (α -Fe₂O₃) particles exhibiting different properties by annealing the as-prepared spherical maghemite (γ -Fe₂O₃) nanoparticles and rod shaped goethite (α -FeOOH) particles at 600 °C in air. The electrochemical results indicated that the hexagonal plates derived from maghemite nanoparticles exhibit higher capacity and cycling stability than the hematite derived from goethite rods.

2. Experimental section

2.1. Synthesis of hematite nanoparticles

Ferric nitrate nonahydrate [Fe(NO₃)₃·9H₂O] GR, ethanol GR were purchased from Merck, Germany and hydrazine monohydrate (N₂H₄·H₂O) was purchased from Merck, India. The detailed synthesis of maghemite and goethite has been discussed in our previous work. [24] In brief, drop-wise addition of hydrazine monohydrate to an aqueous solution of 0.1 M ferric nitrate resulted

in the formation of maghemite whereas on simultaneous addition of hydrazine monohydrate, goethite was formed. The as prepared powders were calcined at 600 °C in a muffle furnace for 4 h at a heating rate of 60 °C/hour in air. After the heat treatment, the brownish black maghemite and the light yellow goethite were transformed into red hematite nanoparticles. The hematite nanoparticles prepared from maghemite and goethite will be designated as Fe–M and Fe–G, respectively, in the rest of the manuscript.

2.2. Structural characterization

The X-ray diffraction patterns were collected between 5° and 80° (2 θ) in a Philips X-ray diffractometer equipped with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) at a 2 θ scan rate of 2° min⁻¹. The particle size and shape were determined on a Tecnai G2 Transmission Electron Microscope (TEM) operating at 300 kV. The local crystallographic structure was studied by high resolution transmission electron microscopic (HR-TEM) studies. The dispersion for TEM analysis was prepared by sonicating a small amount of the powder in ethanol for 20 min. UV-visible analysis was carried out on a Shimadzu UV–Vis–NIR spectrometer UV–3600. Raman spectra were acquired on a Renishaw InVia Reflex micro Raman spectrometer with excitation of argon ion (514 nm) lasers and the spectra were collected with a resolution of 1 cm⁻¹. Nitrogen adsorption–desorption measurements were carried out at 77 K with a Quantachrome (ASIQ MP, Quantachrome, Boynton Beach, FL) instrument. The powders were degassed under vacuum at 250 °C for 4 h for the measurement. The surface area was obtained using Brunauer–Emmet–Teller (BET) method within the relative pressure (P/Po) range 0.05–0.20, and the pore size distribution (PSD) was calculated by Barret–Joyner–Halenda (BJH) method. The nitrogen adsorption volume at the relative pressure (P/Po) of 0.99 was used to determine the pore volume.

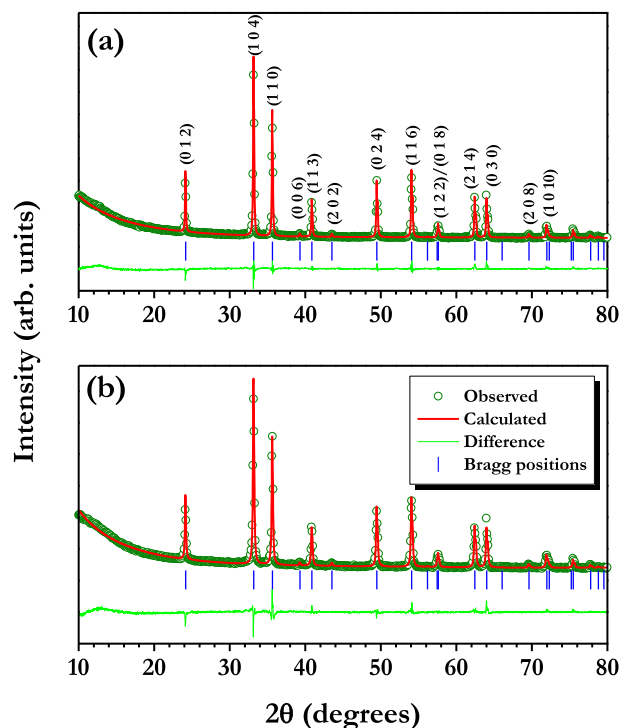


Fig. 1. Rietveld refined powder X-ray diffraction pattern of Fe₂O₃ hematite nanoparticles obtained from (a) maghemite- γ -Fe₂O₃ and (b) goethite- α -FeOOH.

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