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Preparation and Characterisation of Fe_2O_3 Carbon Composite Anode Material for Li-ion Cells

Retty P. Reji*
M.Sc. Student, Department of Physics, St. Stephens College, Kerala University, Kerala, India

Abstract**: Electronics for everyday use frequently utilize lithium-ion batteries. They have one of the finest energies-to-weight ratios, a high open circuit voltage, a low self-discharge rate, no memory effect, and a modest loss of charge when not in use, easy to dispose making them one of the most popular types of rechargeable batteries for portable gadgets. It has several disadvantages despite its general benefits.it is delicate and needs a protection circuit to continue operating safely. With the majority of Li-ion batteries, aging is a concern. Whether the battery is being used or not, after a year there is some capacity for degradation. Due to their high theoretical capacity, non-toxicity, low cost, and better safety, oxides like Fe_2O_3 and Fe_3O_4 have recently attracted more attention as extremely promising anode materials for rechargeable Li-ion batteries. The current study focuses on hydrothermal modification of iron oxide carbon composite anode material. In order to analyze the iron oxide nanoparticles created by this approach, methods including x-ray diffraction for structural study and FESEM imaging for morphological analysis are used. Following that, we assess the viability and potential of Fe_2O_3 carbon composite nanoparticles as an anode material for Li-ion batteries based on our inferences from the structural and microstructural study.**

Keywords**: anode material, FESEM, Fe_2O_3, hydrothermal, Li-ion, low cost, nontoxic, nanoparticles, rechargeable batteries, XRD batteries.**

1. Introduction

Primary batteries are also referred to as throwaway or single-use batteries. Every year, some 15 billion basic batteries are discarded globally and essentially end up in landfills. Batteries are hazardous because of the poisonous heavy metals and potent acids and alkalis they contain. The secondary battery sector has risen and is replacing the primary battery in high-end products.

Rechargeable batteries or storage batteries are alternative names for secondary batteries. They are a form of electrical battery that can be charged, discharged into a load, and recharged numerous times. Electrochemical cells comprise one or more secondary batteries - also known as an "accumulator". Lead-Acid, Zinc-Air, Nickel-Cadmium (NiCd), Nickel-Metal Hydride (NiMH), Lithium-ion (Li-ion), Lithium iron Phosphate (LiFePO4), and Lithium-ion polymer are just a few examples of the various electrode materials - electrolytes combinations used to make rechargeable batteries (Li-ion polymer). Lithium-ion batteries are more expensive than Nickel-Cadmium batteries but have higher energy densities and can function over a wider temperature range.

Lithium-ion batteries convert chemical energy into electrical energy to function. Electrochemical reactions of the electrodes switch between anode and cathode. Lithium salt in an organic solvent serves as the electrolyte. The most widely used commercial anode (negative electrode) is graphite, while the positive electrode is made of an intercalated lithium compound [2]. In Li-ion cells, the separator role is crucial. Graphite is frequently utilized as the anode while layered LiCoO2 is typically used as the cathode. The total charge transported across electrode-electrolyte interface affects the cell capacity. It is based on the external circuit's current during charging and discharging [3]. Lithium may build up on the negative electrode and at the electrolyte interface when the Li-ion flux during the charge transfer process exceeds that of the positive electrode. As the concentration of lithium ions rises above a particular saturation point, a huge growth of Li could be observed. This deposition results in electrode surface deformation, internal short circuits, and battery thermal runaway. The main goals of lithium-ion battery research are to increase charge speed, decrease cost, improve safety, and extend lifetime. The objective of current research is to improve these goals by utilizing nanotechnology.

Li-ion batteries' electrochemical capabilities are influenced by the materials they use for the anode. Carbonaceous graphite's layered structure makes it easier for lithium ions to enter and exit its lattice space. To satisfy the needs for higher energy and power densities, carbon alternatives with higher energy densities and improved safety are needed [4].

Metal oxides are another family of anode materials with high capacity. Metal oxides typically have low conductivities however accurately tailored nanoscale metal oxides exhibit promising properties. The main focus of this study is to create MxOx/carbon composites and nanomaterials {Transition metal oxides (MxOx, M= Mn, Fe, Co, Ni, Cu, etc.)} [4].

Oxyhydroxides and iron oxides are common in nature. They are chemical mixtures made of oxygen and iron. Earth contains a variety of iron-based oxides, including magnetite (Fe_3O_4) and maghemite (-Fe_2O_3) hematite (-Fe_2O_3), and others. For biological applications, magnetite and maghemite are the two most preferred phases. They are utilized in biomedical applications due to their biocompatibility, high stability, low cost, non-toxicity, and non-corrosive nature. In nature, iron

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*Corresponding author: rettyreji112@gmail.com oxide exists in many forms such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite (α- Fe_2O_3). It has a rhombohedral structure. Maghemite is a very common mineral on the earth's surface. It occurs in soils as a weathering product of the heating of other iron oxides [5]. Both maghemite and magnetite crystallize in the inverse spinal cubic structure. Maghemite is metastable with respect to hematite and forms continuous solid solutions with magnetite. In hematite, oxygen ions are in a hexagonal close-packed arrangement, with Fe (III) ions occupying in octahedral sites. In the case of magnetite, and maghemite the oxygen ions are in a cubic close-packed arrangement. Magnetite has an inverse spinal structure with Fe (III) ions that are distributed randomly between octahedral and tetrahedral sites and Fe (II) ions in octahedral sites [6]. Maghemite has also a spinal structure similar to magnetite but with vacancies in the cation sublattice. The stability increases for smaller nanocrystals of maghemite, because its surface energy is lower than that of hematite. At ambient conditions, both magnetite and maghemite phases become less stable than hematite [1], [3].

Maghemite exhibits soft ferromagnetic properties at room temperature and a curie temperature of 928K. It also has a small magnetic anisotropy due to no orbital angular momentum. Maghemite is unstable at high temperatures and loses its susceptibility with time. However, it can be stabilized by doping it with other metal ions. The magnetic properties of iron oxide nanoparticles are affected by surface effects. As a result, their net magnetization decreases at a faster rate with increasing temperature than that of corresponding bulk material [12].

Iron oxides are extensively investigated as anode materials for lithium-ion batteries because of their low cost, eco-friendliness, high theoretical capacity (1007 $mAhg^{-1}$), and high conversion capability during lithiation and de-lithiation. However, during cycling, they experience significant volume fluctuations that cause anode pulverisation and a loss of electrical connection. As a result, the iron oxide anodes' capacity retention deteriorates, and it should be enhanced for commercial use. This was accomplished by directly pyrolyzing Fe-based zeolitic imidazolate frameworks at 620°C in the presence of air, to create ultra-small Fe_2O_3 nanoparticles contained in nitrogen-doped hollow carbon shells. By using this technique, the main pulverisation issue was resolved, which speeds up electrochemical kinetics and successfully prevents the aggregation of Fe_2O_3 nanoparticles during de-lithiation. The in-depth study of metal oxides also revealed that their capacity retentions were constrained by two important factors: their low conductivity and their irreversible morphological changes brought on by volume expansion and contraction throughout the lithiation and de-lithiation processes. In order to attain higher capacity retention during long-term cycling, innovative composites must be created. Because of this, recent research has focused on the higher performance of a synthetic Fe_2O_3/C/carbon nanotube composite as compared to a compound made by combining commercially available Fe_2O_3 and CNT. These samples were deposited using cold spraying, supersonic deposition, and non-vacuum deposition techniques. A new method for quickly and uniformly depositing nanomaterial on substrates that are flexible and non-flexible is cold spraying. This approach can be used in a roll-to-roll process and is both scalable and economically viable. The bonding energy significantly contributes to the good adhesion between the substrates and the deposited materials as a result of the high-speed impact of particles on the substrate. This causes active material to be downscaled in order to achieve faster Li+ diffusion, which in turn causes the manufacture of Fe_2O_3 particles that are smaller than those of commercially available particles. As a result, the Fe_2O_3/C/CNT combination offers a greater capacity for energy storage. Additionally, it enhances the LIB anode's steady electrochemical performance [8].

2. Objectives of Study

- Synthesis of pure iron oxide and iron oxide carbon composites using hydrothermal method.
- Characterization of synthesized iron oxide carbon composites using various structural characterization techniques to understand their possibility as anode material.

3. Results and Discussion

In this section, experimental procedures followed for the preparation of Fe_2O_3 carbon composite anode material using the hydrothermal method is detailed along with the characterization carried upon the prepared samples. The hydrothermal method is used for Fe_2O_3 nanoparticle synthesis. The solution obtained after the hydrothermal method is centrifuged and the residue is dried, ground, and then annealed to get the final product. The prepared Fe_2O_3 nanoparticles after annealing are subjected to various characterization techniques such as X- Ray diffraction technique and Scanning electron microscopy.

A. Experimental Procedure

1) Preparation of Fe_2O_3 precursor solution

4.04 g of Fe $(NO_3)_3$ and 10 ml of deionized water were taken in a beaker, and mixed with the help of a magnetic stirrer for about 10 to 15 minutes to obtain a completely soluble solution. The ammonia solution was dropwise added to the above prepared $Fe(NO_3)_3$ solution with constant stirring and the pH of the solution was controlled. As the pH of the solution reached, further addition of ammonia was stopped; the pH of the solution was maintained and again kept at constant stirring for 1 hour. After 1 hour the solution obtained after magnetic stirring was transferred to a Teflon beaker and further into an autoclave and kept in a hydrothermal furnace at 180°C for 12 hours. The solution was centrifuged at 8000 rpm for 20 minutes using water and ethanol. This technique was repeated five times, resulting in a pure residue. The residue was dried for 12 hours at 90 0C in an oven. A solid substance was formed after heating, which was ground into powder and annealed at 400° C for 1 hour. Hydrothermal synthesis, often known as "hydrothermal technique" is a unique process for crystallizing compounds from high-temperature aqueous solutions at high vapour pressures. The term "hydrothermal" comes from geology. It's essentially a solution-reaction-based method. Hydrothermal synthesis is a single-crystal synthesis process that relies on the solubility of minerals in hot water under high pressure. The crystal growth is carried out in an autoclave, which is a pressure vessel made of steel, in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end, the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal [1]. The autoclaves are usually thick-walled steel cylinders with a hermetic seal that must withstand high temperatures and pressures for prolonged periods of time. Furthermore, the autoclave material must be inert with respect to the solvent. After 1 hour of magnetic stirring, the slurry obtained was transferred to a Teflon beaker and further into an autoclave and kept in a furnace at 180℃ for 12 hours. The solution was centrifuged at 8000 rpm for 20 minutes using water three times and ethanol two times. This technique was repeated five times, resulting in a pure residue. The residue was dried for 12 hours at 90 ℃ on oven heating. A solid substance was formed after heating, which was ground into powder and annealed at 400º C for 1 hour.

2) *Preparation of Fe_2O_3 carbon composite precursor solution*

In order to prepare carbon composite nanoparticles, take 1.8 g of glucose dissolved in 10 ml of deionized water with the help of a magnetic stirrer to obtain the glucose solution. The obtained glucose solution was added to the Fe $(NO_3)_3$ solution.

Fig. 1. Magnetic stirring of Fe $(NO_3)_3$ solution

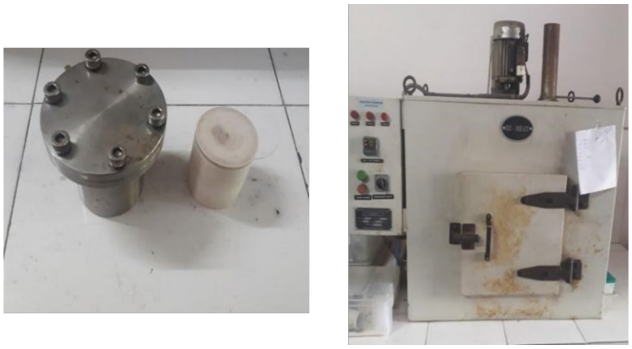

Fig. 2. (a) Autoclave and Teflon beaker (b) Hydrothermal furnace

Fig. 3. The beaker containing residue after centrifugation

Fig. 4. Fe_2O_3 nanoparticles after annealing

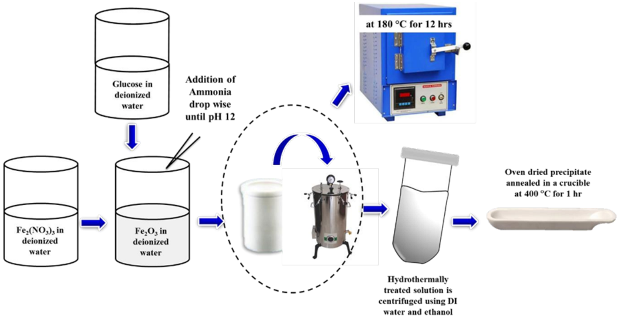

Fig. 5. The schematic representation of the preparation procedure of Fe_2O_3 carbon nanocomposites through hydrothermal method

3) *Characterization of Fe_2O_3 and carbon composite nanoparticles*

Field emission scanning electron microscopy:

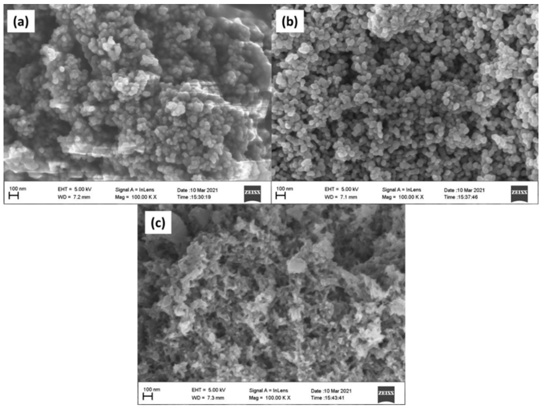

Fig. 6. SEM micrographs of pure Fe_2O_3 nanoparticles (a) before annealing and (b) after annealing and Fe_2O_3/carbon nanocomposites (c) before annealing

The morphology of the pure Fe_2O_3 nanoparticles and Fe_2O_3 carbon nanocomposites can be studied using the FESEM technique. The FESEM images of the samples are given in figure 6. From the figure, we can confirm that the overall morphology of the samples is homogenous and generally spherical in nature for the pure Fe_2O_3 nanoparticles. In the case of the Fe_2O_3 carbon nanocomposites before annealing, the nanoparticles are found to be smaller in size but agglomerated. We did not anneal these samples, as we presumed further aggregation of the sample after annealing. However, the carbon-incorporated samples are porous in nature. For a detailed understanding of the effect of carbon addition, we need to synthesize Fe_2O_3 carbon nanocomposites with varying compositions of carbon addition. Using ImageJ software, we determined the size of the Fe_2O_3 and Fe_2O_3/carbon composite, around 40 nm [16], [17].

XRD diffraction analysis:

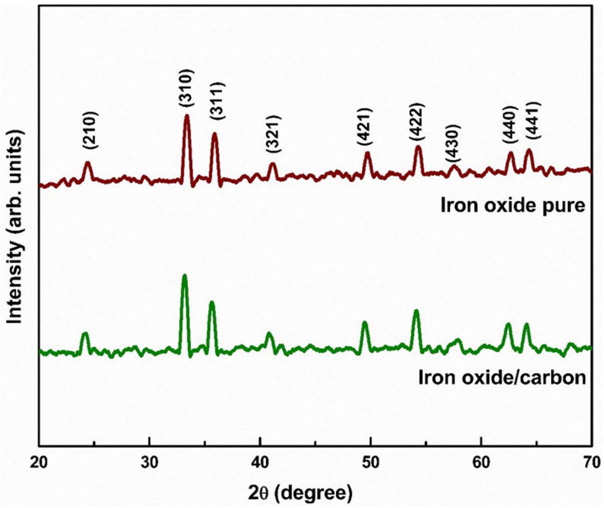

Fig. 7. XRD pattern of pure Fe_2O_3 and Fe_2O_3/carbon nanocomposites

The XRD patterns help us to determine the crystalline phase and the structural character of the concerned samples. Figure 7, represents the X-ray diffraction patterns of pure Fe_2O_3 nanoparticles and Fe_2O_3/carbon nanocomposites. A definite line broadening of the XRD peaks indicates that the prepared material consists of particles in the nanoscale range. The iron oxide compounds when synthesized through the hydrothermal route are generally found to be less crystalline in nature. The peak intensities are relatively low when compared to other oxide compounds. The XRD peak positions match exactly with the JCPDS Card No. 39-000-1346 for maghemite Fe_2O_3. The incorporation of carbon, has not altered the crystal structure of maghemite Fe_2O_3.

In order to evaluate the mean crystallite size of the particles, the Debye–Scherrer formula was used.

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

Where 0.9 is Scherrer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle, and β is the full width at half-maximum (FWHM) of the diffraction peak. The average particle size of the pure Fe_2O_3 and Fe_2O_3/carbon nanocomposite was found to be 27.2 nm and 13.7nm, respectively which is derived from the FWHM of more intense peaks in their XRD patterns using Scherrer's formula.

The maghemite Fe_2O_3 structure was confirmed and the surface morphology was generally of nanospheres. However, we saw that incorporating carbon into the Fe_2O_3 synthesis procedure causes a decrease in particle size but causes aggregation of these nanoparticles which is reflected as line broadening in the corresponding XRD pattern. This prompted us to avoid the further annealing of Fe_2O_3/carbon composite samples, as this may aggravate the state of aggregation of nanoparticles.

Fe_2O_3 nanoparticles with a large surface-to-volume ratio exhibit extremely high-rate capability and outstanding cycling performance, which could be attributed to the unique 3D pore-solid architecture. It not only favors relatively short ion and charge diffusion pathways and high transport rates of both lithium ions and electrons but also can partially accommodate the volume expansion during cycling [18]. The literature survey and our experimental observations conclude that the mesoporous Fe_2O_3/carbon composite could be effectively modified to exhibit excellent cycling performance suited for lithium-ion anodes. The incorporation of carbon should be controlled based on how far it can reduce the charge transfer resistance and thereby increasing its potential as anode material.

4. Conclusion

This paper presented an overview on preparation and characterisation of Fe_2O_3 carbon composite anode material for Li-ion cells.

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