Characterisation of Fe Doped Layered Cathode Material as Nano-Rechargeable Batteries

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Abstract. This research focuses on the layered doped lithium conductive metal oxides with the universal form Li MO\textsubscript{2} (M = Co, Ni, Ag or Fe doped solutions) adjustment of cathode electrodes for lithium-ion cells (LIBs). Preparation in a low temperature combustion reaction promotes its electrochemical efficiency. The modification starts with the preparation of the LiCo\textsubscript{0.5}Ni\textsubscript{0.45}Fe\textsubscript{0.5}O\textsubscript{2} (LCNFO) powder with citric acid, which is used as fuel, along with deionized water (DW). As binding materials, nitrate of ions (Li\textsuperscript{+}) and ions (Fe\textsuperscript{3+}) were added to this mixture to create a uniformed mixture. The required amount of citric acid and de-ionised water was added to this unified mixture to create a powder. This powder was cautiously heated to 150 \textdegree C \textendash 200\textdegree C initially, and finally annealed at a range from 600 \textdegree C to 1000 \textdegree C for six hours. The resulting product was submitted to a thermal analysis (TGA), which is a useful tool to explore a wide array of polymer properties. This research demonstrates the different applications of TA methods in the field of polymer-nanomaterial research and displays several examples of implementation of the differential scanning calorimeter (DSC). TGA was deployed to investigate the performance of thermal characteristics, which vary with the temperature, for the illustrative purposes and structural characterisation, X-ray Diffraction (XRD) and analysis. A meticulous annealed temperature will output pure, single phase LCNFO / NP material with electrochemical behaviour. The powder was studied, and the dimensions of the cathode material were designed approximately for the XRD data using the Scherer’s equation. Furthermore, we used the Fourier transform for the IR (FT-IR) and surface morphology EDS and SEM analysis. The results focused on modifying the LiCoO\textsubscript{2} of the cathode materials by adding materials that are similar to Ni and Fe because these materials are documented as being their own state and not contaminated with the hexagonal geometry arrangement and R three m (gap assembly). We noticed that doped Fe has material that will perform better according to the capacity, power, rate capability stability and low cost, with increased storage capacity due to the nano-size effects.

1. Introduction

Energy embodies a significant function in our life. Industries have pollution, global warming and finite ordinary energy supplies and resources, which make electricity, along with the use of green energy, a global precedence [1]. Nanomaterials are imperative due to their unique mechanical, electrical and elective properties that are measured in a run of one–100 nm. Batteries are gadgets that change the vitality that is discharged by unconstrained chemical responses to power. They have a few advantages can store and recover electrical vitality [2]. There is an increasing importance to ensure that electrical components (energy storage units) fit the requirements, such as the upcoming plug in hybrid electric vehicles (PHEVs), as renewable resources are rare [3,4]. A contemporary community progressively controls additional electricity. The component’s progress enables it to store minor energy directly or indirectly, which could be a definite subject for the 21st century [5].
LiBs are electrochemical vitality capacity gadgets that can realise the vitality capacity / discharge using charge / release LiB cells. LiBs are composed of the following three primary components: the anode, cathode and electrolyte. Li-ion battery innovation provides the ideal capacity vitality. For all these applications, to attain commercial victory, the batteries must have a long lifecycle and calendar life, sufficient energy / power, be tolerant of damaging conditions, not be harmful and operate securely. The cathode material is an exceptionally critical part of the supporting particle [3, 5].

The Li-ion cell’s structure is well-organised as it supplies portable devices using superior authority necessities. The contemporary cell phones for technology-based civilisation depends on transportable electronics with slim energy resources, and investigations into slim layer cells have increased to accomplish this [6]. It is our responsibility to report the difficulties regarding synthesis, electrochemical stability, performance and security matters of these three phases of lattices from the perspective of Li+ ion motion. The aim of this study is to discover the consequences of new investigations into Li, Li ion and Li-free slim-layer cells, along with crystalline LiCoO₂ electrodes, and to summarise and characterise the remarkable characteristics of the nano- and microcrystalline layers in the FeLiO system. The LCNFO / NP’s electrode material has more power than LiCoO₂ [7,8].

Firstly, there are additional motives for regulating the stoichiometry of electrode materials. Substitution and decreasing electrode sources enhance the sources’ electro-chemical behaviour in association with the exact power and interfacial density of energy (Li et al. 2002; Park et al. 2001; Veluchamy et al. 2001) [8]. Secondly, it may well steady the source and enhance cycling recital (Fey et al. 2003). Thirdly, it might reduce the cost of manufacturing by reducing the use of some luxurious metals, such as cobalt, and using less luxurious metals, such as as Mn or Fe (9). Finally, it may decrease the material’s toxicity and promote a healthier and safer environment.

This work describes an improved preparation of LCNFO / NP using a solid reaction in the air and considers the electrochemical characteristics of the resulting powder and the consequences of the annealed on the crystallisation of the manufactured LCNFO / NP. As a result of the disadvantages of LiCoO₂, LiNiO₂ and LiMnO₂, in the current research, a new cathode material LCNFO / NP was synthesised using the combustion technique using citric acid as energy and D.W as the binding material [10,11].

Figure 1: How to reduce Co₂ using LCNFO nanoparticles of a combustion reaction.
2. Experiment

2.1 Powder

Figure 2 displays a chart of the experimental trial for the preparation of nano-fine particles [9–11]. Burning the synthesis of LCNFO in the form of powder, which was made from lithium nitrate \{LiNO$_3$ (7.064 g)\] nitrate crystal, cobalt (II)- nitrate \{Co(NO$_3$)$_2$·6H$_2$O (14.909 g)\], nickel (II)-nitrate \{Ni(NO$_3$)$_2$·6H$_2$O (13.409 g)\] nitrate crystal, ferric nitrate \{Fe(NO$_3$)$_3$·.9H$_2$O Fe(NO$_3$)$_3$·9H$_2$O (2.069 g)\] and citric acid anhydrous C6H8O7 (15.158 g), they were resulted from HARRIS chemicals cooperation in England with decontamination 99%. It was reduced to nano-size using a low preparation temperature of 150 °C under atmospheric pressure until firing produced a fine powder material. This produced eight to ten gm of pure cathode. Then, we used a thermal analysis to obtain the optimum annealing temp and divided it into three batches at 600, 800 and 1000 degrees centigrade [12,13].

![Diagram of the experimental trial for the preparation of nano-fine particles](image)

**Figure 2.** The schism state of the reaction of combustion.

2.2 Thermal Analysis (TGA).

The purpose of this test was to calculate the optimum temperature that eliminated the impurities and phase configuration with the resulting crystallisation. TGA was created using a thermal analyser (STA PT-1000 Model) at a heating rate of 25 co / min through ambient ambiance to conclude the maximum temperature for state configuration and / or the overall solidification of the powder illustration.

2.3 X-Ray Diffraction for the Powder

The powder of LCNFO was defined using the experiments of the X-ray. The measurement was executed and correlated with the American Society of Testing Materials cards by applying Philips PW 1840 X-ray diffract meter of \(\AA\) from Cu-K. The elements with impurities that were found in the powder targets were analysed by applying the X-ray fluorescence source with the model OLYMPUS \(\backslash\) DELTA.

2.4 FT-IR Spectrophotometer

The optical feature of the powder that was examined by transmission by FTIR was absorption spectroscopy. The measurable wave number area relied on the sensor that was used; the main detectors were TGS (PLATINUM-ATR) 400–7800 cm$^{-1}$ and the semiconductor-type sensor ALPHA. The low sensing limit is approximately 650 cm.

2.5 EDS and SEM of LCNFO Cathode Powder

We examined the morphology, focusing on the particle size distribution of the material. We also had topographic considerations and conducted a microstructure examination. The voltage went up to 30000 v (Ministry of Science and Technology Production Engineering and Metallurgy). The image shows a 3D tomography component. Tescan Vega III, Czech Republic, (USA).
3. Results and Discussion

In Figure 3, the TGA curve shows three obvious parts of weight loss by m1by m3. The first part (m1-m2) was due to water loss. The second division (m2-m3) was because of the disintegration of the convinced remaining hydrocarbons that did not react. The third part (m3) referred to the disintegration of FeNiO3 and the creation of the uncontaminated phase of the layered LCNFO compound and the de-lithia ion of the layered LCNFO by the Li vaporisation. There were weight losses, corresponding masses and molar weights for every part [13,14].

As a result, the TGA/DSC thermal profile of the LCNFO powder should be studied for the recognition of a convenient annealing temperature that will not have consequences in the creation of the metal / conductivity metal oxide contaminates in the annealed module. For this pattern, the temperature should be high enough to produce pure LCNFO material by-transitory a laser temperature of creation of the metal / conductivity metal oxides. Basically, for well electrochemical facial appearance of the (LCNFO) material, the selected annealing temperature should be more than 973 K, and the samples should be placed in a fully heated furnace of an appropriate temperature. The elevated temperature will enforce the Fe ions into the LiICONiO2 lattice to produce stoichiometric LCNFO material. The selected annealing temperature will produce pure, single phase LCNFO material, as well as electrochemical behaviour. [9,15]. The mass losses of every part are shown in Table 1.

![Figure 3: TGA (mass loss and heat flow curves) of the thermally analysed powder.](image)

| Part | T (OC) | Mass (mg) | Mass loss (mg) | Structure |
|------|--------|-----------|----------------|-----------|
| M1   | 25     | 23.4892   | 0.0            | LiCO0.5 Ni0.45Fe0.5O2 + H2O + Co2 + FeNiO3 |
| M2   | 545.8  | 22.8892   | 0.6            | LiCO0.5 Ni0.45Fe0.5O2 (from XRD patterns) |
| M3   | 692.3  | 21.7892   | 1.1            | LiCO0.5 Ni0.45Fe0.5O2 |

3.1 Fourier Transforms IR (FT-IR)

An analysis of the Fourier infrared is necessary to gain spectral visual knowledge about the composite materials, as it indicates the bonds’ strength or length in a particular spectral region using the vibrations.
Figure 4. FTIR pattern of the LCNFO / NP (a) at RT °C at 1000 °C and (b) after annealing.

Figures 4a and b display the FTIR spectra of the prepared powder at various temperatures subject to the ambient. The IR is inactive in the area around 2000–4000 Cm\(^{-1}\), which could be due to temperature exposure, as when it is increased, the mass of the particles increases. This is illustrated in Figure 4a. Three absorption areas at 1300–1409.50 Cm\(^{-1}\) peak at a broad weak intensity because of bond (C–H), and the area around 1804.20–2500 Cm\(^{-1}\) peaks at broad medium. The intense strength comes from bond (C=H). Finally, area 3000–3737 Cm\(^{-1}\) IR is inactive because there is no dipolar bond (C=C) or off bond (H-OH). Figure 4b displays the peaks at 421.77–570.62 Cm\(^{-1}\), which is equivalent to the iron-oxide bond Fe–O in the tetrahedral sites. When the group at 916 Cm\(^{-1}\) corresponds to the stretching vibration mode, it should correspond with the M–O absorption band. The bigger absorption peak that is located at 3500 Cm\(^{-1}\) could refer to the widening of the -OH/HO- assemblies of the arcade water molecules with the hydrogen–hydroxyl bounded groups in both CO and Fe(OH)\(_2\). The peaks at approximately 2000–2374.96 Cm\(^{-1}\) are due to C=H stretching and the C–O bending vibrations. The shape of the peak at the broadband at 400 and 570 Cm\(^{-1}\) is attributed to the stretching vibrations of Fe\(^{3+}\)-O\(^2-\), which are considered in all the ferrite modules. The broad at 3653 Cm\(^{-1}\) could be due to the vibration state of the chemically bonded hydroxyl groups. The peaks at around 3833.81–3500 Cm\(^{-1}\) are attributed to H–OH stretching [12,13].

3.2 -X-Ray Diffraction (XRD)
Figure 5 reviews the annealing procedure, which decreases lattice deformations and damage. However, this technique can create the grains’ adhesion. This prejudiced the amplified mean particle dimensions for nanoparticles and the grain dimension from 37.59 nm–484 nm, along with the temperature increase. The determined range of the lattice stricture of the LCNFO / NP modules were in accordance with the...
reference statistics tag (system 98-016-2293) [12]. Model grains are sub-micron dimensional particles with a sphere shape, which are sufficient for improved electrochemical effectiveness. As the heating duration is raised, the diffraction peaks become sharper and superior due to the raise in the crystallinity of the resulting product.

LCNFO powders that were gained through these wet-chemistry procedures showed the precise XRD pattern and the hexagonal doublets (006) / (102) and (018) / (110), along with an obvious splitting. This signalled a higher degree of crystallinity, good hexagonal characteristics and a better layered facial appearance. The XRD consequences proved the configuration of the pure state [14,15].

![XRD patterns of LCNFO with various annealing temperatures of 600 °C, 800 °C and 1000 °C for a, b and c, respectively.](image)

**Figure 5** XRD patterns of LCNFO with various annealing temperatures of 600 °C, 800 °C and 1000 °C for a, b and c, respectively.

### 3.3 Energy Dispersive Spectroscopy of LCNFO Cathode Active Material

Figure 6 reviews the EDS of the LCNFO cathode active material. The EDS results before and after the annealing state that the weight percentages of the cobalt, nickel and iron were 37.80, 31.44 and 3.76, respectively, without changes after the annealing process. These results were in accordance with the compositional structure of the conducted material, as determined from the XRD results [9–16].
3.4 Scanning Electron Microscopy of the LCNFO POWDER

The morphological alterations of the arranged LCNFO powder at various annealing temperatures have been tested by SEM, and the consequences are displayed in Fig. 7a. Previously, annealing had a spherical and springy shape with a length of the small dimension nanoparticles being less than 37 nm. As the temperature rises, the size becomes larger and the accumulation becomes significant, as shown in the SEM image in Fig. 7b. This was in accordance with the results from the XRD measurements [17,18,19].

![Figure 6 EDS of the LCNFO cathode (active).](image)

![Figure 7 (a, b) Upper SEM images of LCNFO powders that were prepared through combustion and annealed at various temperatures: (a) before annealing, and (b) 1000 °C. The lower images display the statistical distribution of the LCNFO powder.](image)
This growth of the uneven, average LCNFO dimensions could be associated with the straight exposure of the annealing temperature on the powder structure. As the temperature rises, the superior energy is utilised by the substance, and there is a possibility to form great particles due to the increased ion distribution and grain creation [20, 21, 22, 23].

Conclusion

LiCo$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ layered nanoparticles are defined as developed cathodes with simple transition-metal layered dioxides, in which at least one lithium ion per transition-metal ion could be reversed by extracting / inserting while keeping the materials’ cost and toxicity low, and they were successfully synthesised by a firing reaction at low temperature. This was proven through characterisation using an X-ray and EDS with SEM. These materials are important for use in future lithium-ion batteries. Fe doped with LiNiCoO$_2$ makes the movement of the lithium-ions easy due to layered structures, which progress the performance of the electrochemical cells. The TGA curve demonstrates the decomposition of the modules in the single stage. The topographical SEM images show that LCNFO may illustrate encouraging electro-chemical features as intercalation, and the de-intercalation of Li$^+$ is thought to increase the capacity of the cathode hosts by focusing on nano-sized powders and amorphous materials.

Acknowledgments

Authors sincerely acknowledge to the support of the Nanotechnology team in Ministry of Industry & Mineral, and the Nanotechnology team in State Company for Electrical Industries/Baghdad/Iraq.

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