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I-CReST 2025:115-078 – A Synthesis and Characterisation of Doped Dysprosium in $LiMnTiO_4$ Cathode Materials for Lithium-Ion Batteries

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ABSTRACT

The demand for enhanced performance in Li-ion batteries necessitates the development of advanced cathode materials. This study investigates the synthesis and characterisation of dysprosium (Dy)-doped $LiMn_{1.9}Ti_{0.1-x}Dy_xO_4$ (x = 0.00, 0.01, 0.05) cathode materials, focusing on their structural, compositional, and morphological properties. The primary objective is to understand how dysprosium substitution at the titanium site influences these properties and the overall electrochemical performance of the material. Using the self-propagation combustion synthesis method, high purity and single-phase formation with reduced particle sizes were achieved. The thermal properties were studied by Simultaneous Thermal Analysis (STA). Structural analysis through X-ray diffraction (XRD) revealed significant changes in the crystal lattice parameters, confirming successful doping. Field emission scanning electron microscopy (FESEM) provided detailed insights into the morphology of the material. These results suggest that dysprosium-doped $LiMnTiO_4$ is a promising candidate for next-generation Li-ion battery cathodes. In conclusion, this research demonstrates the potential of dysprosium doping in enhancing the properties of $LiMnTiO_4$ cathode materials, offering valuable insights for the development of high-performance and sustainable energy storage solutions.

Keywords: Cathode; lithium-ion; $LiMnTiO_4$; dysprosium(Dy)

1. INTRODUCTION

The advancement of lithium-ion batteries has resulted in the creation of lithium-polymer batteries. These batteries use a solid polymer compound as the electrolyte instead of a liquid organic solvent, which makes them even more useful in more situations [1]. Lithium-ion batteries are leading the way in modern materials electrochemistry due to immense impact on the energy storage [2]. Lithium-ion battery technology is developing into large Li-ion battery packs energy storage system with lower costs [3].

These recent years, $LiMnTiO_4$ has garnered significant attention as a potential cathode material for lithium-ion batteries due to its promising electrochemical properties. Research has shown that solvothermal synthesized Ti-rich $LiMnTiO_4$ exhibits high lithium storage capacity, making it a viable candidate for cathode material in lithium-ion batteries [4]. Dy compounds have been found to exhibit strong magnetic behaviour, making them suitable for applications in magnetic materials and devices [5],[6]. Additionally, Dy oxide has been identified as having important chemical and physical properties, such as electrical property, large energy bandgap, high chemical and thermal stability, making it useful for various technological applications [7].

Doping Dy into $LiMnTiO_4$ cathode materials can potentially improve their electrochemical properties, such as capacity, cycling stability and rate capability. The synthesis of doped Dy in $LiMnTiO_4$ cathode materials involves the incorporation of Dy into the structure of the material, known as crystal lattice. Previous studies have demonstrated the effectiveness in doping element such as boron in improving the structural ability and electrochemical performance of cathode materials [8]. Furthermore, a study focused on the improved performance of rare-earth-doped $LiMn_2O_4$ cathodes, demonstrating the impact of rare-earth elements, including Dy, on the crystal structure and electrochemical performance of the cathode materials [9]. In addition to the synthesis process, the characterisation process of doped Dy in cathode material is important.

This research aims to contribute to the existing scientific knowledge by investigating the interactions between the characterised and synthesized properties of doped Dy in $LiMnTiO_4$ in cathode materials. The outcomes of this study are expected to offer insights into optimizing the design of cathode materials for enhanced Li-ion battery performance, addressing critical aspects of energy storage to improve sustainable and advanced energy solutions.

2. MATERIALS AND METHOD

2.1 Synthesis by Modified Self Propagating Combustion Method (SPC)

The synthesis of all the samples was conducted using the self-propagation combustion method. Initially, stoichiometric amounts of lithium nitrate, manganese (II) nitrate hydrate, titanium (IV) nitrate and dysprosium (III) nitrate hydrate were dissolved in distilled water. Triethanolamine, TEA which act as a combustion agent was added to the solution. This mixture was continuously stirred until homogeneous mixture were obtained and then was heated at a temperature of 300 °C, where a self-propagating combustion reaction took place, resulting in a fine powder. The samples were characterised for their thermal properties using a Simultaneous Thermogravimetric Analyzer (STA). Then, the precursors were annealed at 700 °C for 24 hours in a furnace before final product was obtained.

2.2 Characterization of Samples

The methods used for characterization of the samples were Simultaneous Thermogravimetric Analysis (STA), X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM) analysis. STA was a technique that combines Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) in a single measurement, allowing for the simultaneous collection of data on mass changes and heat flow in a material as it was heated, cooled, or held at a constant temperature. The methodology involved preparing a representative sample, setting the temperature program and atmosphere, and also collecting real-time data on mass changes and heat flow. Data analysis involved examining TGA curves for decomposition, mass loss and DSC curves for endothermic and exothermic events.

XRD was a method used to analyze the crystalline structure of materials. It works by directing X-rays at a sample while the angles and intensities of the rays that are diffracted by the crystal's atoms were measured. This diffraction pattern provides detailed information about material's crystal structure. The XRD analysis was conducted using a PANalytical X'Pert Pro X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.5406 Å). The prepared samples were placed on a sample holder and packed uniformly. The samples were scanned from 10° to 90° 2θ with a step size of 0.02°. Diffraction data were collected using X'Pert

HighScore Plus Software. The observed diffraction patterns were compared with standard reference patterns from the International Centre for Diffraction Data (ICDD) database and peaks were identified.

FESEM analysis was conducted for sample $LiMn_{1.9}Ti_{0.1-x}Dy_xO_4$ (x = 0.00, 0.01, 0.05) using JEOL JSM-7600F. It was equipped with a comprehensive range of detectors, making it well-suited for applications in nanotechnology, material science, compositional analysis, and structural analysis since it provides exceptional resolution and stability allowing for the detail examination of nanostructures at magnifications ranging from 25 to over 1,000,000 times with a resolution of 1 nm.

3. RESULTS AND DISCUSSION

3.1 Simultaneous Thermogravimetric Analysis (STA)

In this study, STA analysis was performed to characterize the thermal stability and composition of the synthesized $LiMn_{1.9}Ti_{0.1-x}Dy_xO_4$ (x = 0.00, 0.01, 0.05) cathode material doped with Dy.

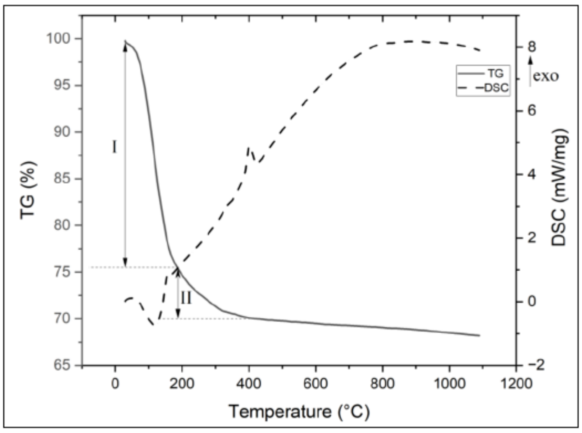

Fig. 1. STA results for $LiMn_{1.9}Ti_{0.1}O_4$ sample

In Fig. 1, the TG curve shows the mass loss of the sample was about 24 %. This indicates a major decomposition or loss of components that could possibly be organic materials or volatile compounds. The mass loss slows significantly after 289 °C, which is only 5 %. The sample stabilizing around 70 % mass remaining at temperatures above 1000 °C, suggested that the remaining material is stable and resistant to thermal degradation. An endothermic peak is observed at 115 °C indicates crystalline transformations or phase changes occurring within the material upon heating. A significant exothermic peak around 400 °C is observed that may signify the formation of new phases or structural rearrangements within the material during thermal treatment.

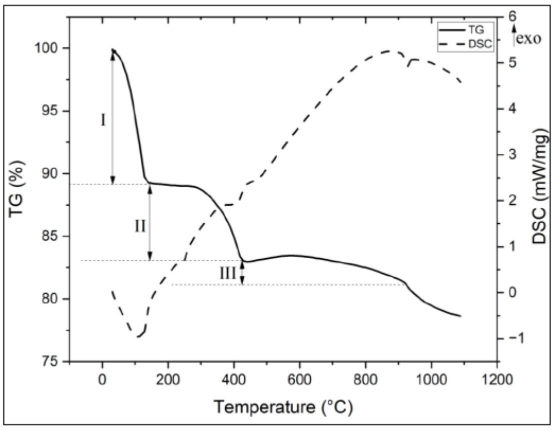

Fig. 2. STA results for $LiMn_{1.}9Ti0_{.09}Dy_{0.01}O_4$ sample

TG curve for $Dy_{0.01}$-doped $LiMnTiO_4$ is shown in Fig. 2. An initial weight loss starting at 37 °C, stabilizing briefly before a sharp decline, corresponds to the first weight loss of 10 %, likely indicating loss of physically adsorbed water. A significant weight loss occurs between 128 °C and 429 °C, when sample weight is 6%. This might indicates a decomposition or loss of volatile components. Beyond 429 °C, the weight loss rate decreases significantly, which is 2% and nearly flattens out beyond 900 °C, suggested that most volatile substances have been expelled, leading to the final residue of 79 % at 1089 °C. A DSC curve shows endothermic peak at 114 °C and 929 °C that signify phase transitions, decomposition processes, or other thermal events specific to the material.

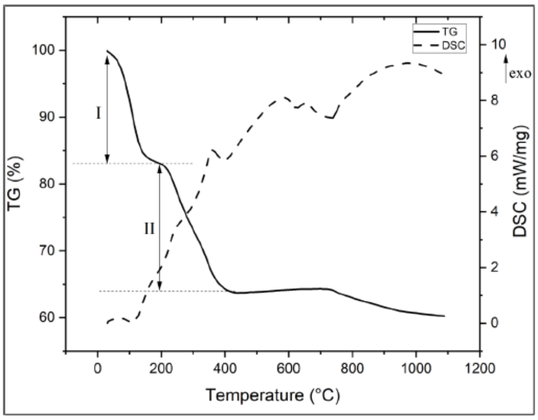

Fig. 3. STA results for $LiMn_{1.9}Ti_{0.05}Dy_{0.05}O_4$ sample

In Fig. 3, starting from room temperature up to 211 °C, there is a minor but gradual decline in mass, which is 17 %, likely indicating the loss of adsorbed moisture or other light volatiles. The curves decrease significantly from 211 °C to 409 °C, with the weight decreasing about 18 %. This substantial loss could be due to the decomposition of organic materials and related to the breakdown of structural components within the sample, especially if there are any organic binders or volatile constituents. The remaining material is more thermally stable and may consist of non-volatile, more inert components such as ceramics or metals that do not decompose under the conditions of the test. A curve representing DSC observed an exothermic peak at 359.6 °C and 738.8 °C. One possible explanation for this peak could be related to phase transitions or structural changes within the material. An endothermic peak at 618.7 °C also link to the insertion of lithium ions into the material's structure. In the case of lithium-ion battery cathodes, the insertion of lithium ions into the cathode material can lead to endothermic peaks in DSC curves, reflecting the energy required for this process.

3.2 X-Ray Diffraction (XRD)

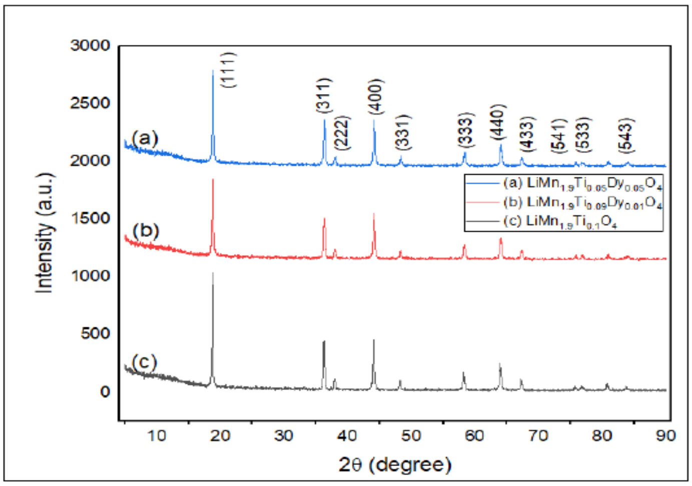

Fig. 4. XRD results patterns of $LiMn_{1.9}Ti_{0.1-x}Dy_xO_4$ (x = 0.00, 0.01, 0.05)

The X-ray diffraction pattern (XRD) of $LiMn_{1.9}Ti_{0.1-x}Dy_xO_4$ (x = 0.00, 0.01, 0.05) are shown in Fig. 4. Patterns shows strong diffraction peaks at 2θ of 18.80°, 36.25°, 37.93°, 44.04°, 48.16°, 58.16°, 63.88°, 67.19°, 75.73°, 76.71° and 83.79° corresponds to ICDD No. 00-035-0782 indexing from XRD. The entire fingerprint peaks of (111), (311), (222), (400), (331), (333), (440), (433), (541), (533) and (543) respectively, were observed clearly for each sample. No additional peaks were observed, suggesting complete incorporation of Dy into the lattice. The diffraction patterns of all samples could be refined in $Fd\bar{3}m$ space group. The major peaks correspond to the spinel structure of the undoped sample, indicating that the crystal structure remains consistent upon doping.

A study shown that the absence of additional peaks in XRD analysis of doped materials in lithium-ion battery cathode materials signifies the successful incorporation of dopants into the crystal lattice without the formation of new phases, contributing to enhanced performance in lithium-ion batteries. Based on the results, different amount of Dy substituted into Ti create different effect on the first peak of XRD pattern indicates the crystallinity of the materials.

3.3 Field Emission Scanning Electron Microscope (FESEM) analysis of sample

Fig. 5. FESEM for sample $LiMn_{1.9}Ti_{0.1}O_4$, annealed at 700 °C

FESEM for sample $LiMn_{1.9}Ti_{0.1}O_4$, annealed at 700 °C is shown in Fig. 5. It shows the sample exhibits irregular shapes, and noticeable aggregation features. The important of these structural features are for the material's application in Li-ion batteries, indicating that the annealing process effectively optimized the structure. This cathode material developed a polyhedral structure with average diameter of 176.1 nm.

4. CONCLUSION

In conclusion, this research has investigated the impact of Dy substitution at the titanium site in $LiMnTiO_4$ cathode materials for Li-ion batteries. These findings indicate that Dy substitution has improves the structural integrity and electrochemical performance of $LiMnTiO_4$ and higher concentrations of Dy, (x = 0.05) showing better improvements. The combustion synthesis method proved effective in achieving high purity, single-phase formation, and reduced particle size, which are critical for battery performance.

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