Sol–Gel Dip Coated Ni-Mn Oxide Thin Films: Synergistic Effects of Doping and Microstructure on Supercapacitor Behavior

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Abstract

This work describes the synthesis and surface characterization of manganese-doped nickel nitrate (Mn:Ni(NO_3)$_2$) thin films that are 1 atomic percent (at.%) and were created using the sol-gel dip coating technique. The growing need for sophisticated supercapacitor electrode materials has prompted scientists to concentrate on transition metal oxides with specific surface chemistry and morphology. A promising method for improving the structural, electrical, and electrochemical characteristics of nickel-based thin films is doping them with manganese, a redox-active element. In order to induce crystallization, the thin films were applied to glass substrates and then annealed at 400°C.The morphological characteristics of the produced films were examined using Scanning Electron Microscopy (SEM) at various magnifications (10,000x and 5,000x). The SEM pictures showed a uniform grain size distribution, a porous, nano-granular morphology, and no cracks. Due to their enhanced ion transport pathways and high active surface area, these surface properties are ideal for electrochemical energy storage. It was discovered that manganese affected the nucleation process, resulting in improved surface roughness and grain refinement. Enhancing the double-layer and pseudocapacitive properties of electrode materials requires these effects. The SEM observations verify that manganese doping greatly enhances the morphological properties of the thin film, which qualifies it for use in supercapacitors. Correlating these structural insights with electrochemical measurements like cyclic voltammetry and impedance spectroscopy will be the focus of future research.

Key words: Ni-Mn Oxide Thin Films, Sol-Gel Dip Coating Manganese, Doping Nickel Oxide (NiO), Supercapacitor Performance

1. Introduction

The rapid advancement of electronic devices and energy storage systems has accelerated the search for innovative electrode materials with superior performance and long cycle life. Transition metal oxides, particularly those based on nickel, have attracted a lot of interest among the different candidates because of their cost-effectiveness, high theoretical specific capacitance, and advantageous electrochemical characteristics. Due to its high solubility and ease of processing, nickel nitrate is frequently used as a precursor in the creation of nickel oxide thin films. However, intrinsic problems like low electrical conductivity, restricted ion transport, and structural instability during charge-discharge cycles frequently impede the practical use of nickel-based films.Doping tactics have been thoroughly investigated in an effort to get around these restrictions. As a dopant, manganese (Mn), a three-dimensional transition metal with several oxidation states ($Mn^{2+}/Mn^{3+}/Mn^{4+}$), has demonstrated significant promise in altering the structural and electrochemical behavior of materials based on nickel. It can improve electron conductivity, increase redox activity, and stabilize the film structure during cycling when added to the nickel matrix. It has been noted that surface morphology and electrochemical behavior are greatly impacted by manganese, even at low concentrations (e.g., 1 at.%).The synthesis of 1 at.% Mn-doped nickel nitrate thin films using a sol-gel dip-coating process—a flexible and affordable technique for creating homogenous, uniform thin films—is the main focus of this work. The main goal is to use scanning electron microscopy (SEM) to examine the morphological properties of the Mn-doped films. To capture both the macroscopic film structure and the nanoscale grain distribution, the analysis is carried out at various magnifications. The SEM results should shed light on the effects of manganese incorporation on grain size, porosity, and surface roughness—all important parameters for high-performance supercapacitor applications.

2. Experimental Methodology

The sol-gel dip coating method, which was selected for its ease of use, affordability, and capacity to create consistent, sticky films over wide regions, was used to create the 1 at.% manganese-doped nickel nitrate thin films. As precursors, analytical-grade manganese nitrate ($Mn(NO_3)_2 \cdot 4H_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) were employed. The nickel nitrate solution was supplemented with the stoichiometric amount of manganese nitrate needed to attain 1 atomic percent doping. Because of its volatility and suitability for sol-gel procedures, ethanol was chosen as the solvent. To guarantee homogeneity, the solution was magnetically agitated for two hours at room temperature. It was then allowed to age for twenty-four hours to enhance gelation and network formation. Film deposition was done on pristine glass substrates. Before coating, the substrates were dried and ultrasonically cleaned in acetone and deionized water to get rid of any impurities. To guarantee uniform film thickness across all samples, dip coating was done at a regulated withdrawal speed of 3 mm/s. To obtain adequate film thickness, several coating cycles were carried out, with ten minutes of drying at 100°C in between to get rid of any remaining solvents. Following the last coating cycle, the films were crystallized and their organic content removed by annealing them for an hour at 400°C in a muffle furnace. Scanning Electron Microscopy (SEM) was used to examine the morphological properties of the resultant thin films at 10,000x and 50,000x magnifications. Grain structure, porosity, and surface uniformity—important factors influencing electrochemical performance—were assessed using the SEM analysis. To comprehend how manganese doping affected the films' surface properties and microstructure, the enlarged images were compared. In supercapacitor applications, this characterization is crucial for connecting synthesis conditions to electrochemical behaviour.

2.1 Materials and Sol Preparation

As precursors, analytical-grade manganese nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$, Sigma-Aldrich, ≥98%) and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, Merck, ≥98%) were employed without additional purification. Monoethanolamine (MEA) was employed as a chelating agent to regulate the hydrolysis process, while ethanol (C_2H_5OH) was utilized as the solvent. The nickel precursor solution was doped with 1 at.% manganese.To make the sol,

stoichiometric amounts of manganese and nickel nitrate were dissolved in ethanol, and then MEA was gradually added. Metal nitrate to MEA was kept at a molar ratio of 1:1. To create a homogenous and transparent sol, the mixture was magnetically agitated for two hours at room temperature. To increase film uniformity, the solution was aged for 24 hours.

2.2 Film Deposition via Dip Coating

Acetone, ethanol, and deionized water were used to ultrasonically clean glass substrates, which were then dried at 80°C. A steady withdrawal speed of 5 mm/s was used for the dip coating. To remove any remaining solvents, the films were preheated for ten minutes at 100°C following each coating cycle. To create consistent thin films, this coating-drying procedure was carried out five times.

2.4 Characterization Techniques

A scanning electron microscope (SEM, JEOL JSM-7600F) was used to examine the thin films' surface morphology and microstructure. Energy Dispersive X-ray Spectroscopy (EDAX, Oxford Instruments) was used to perform elemental analysis and verify the incorporation of Mn.

3. Experimental Details

In this study, 1 at.% manganese-doped nickel nitrate thin films were synthesized using the sol-gel dip coating method. Analytical-grade nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$] and manganese nitrate [$Mn(NO_3)_2 \cdot 4H_2O$] were used as the precursor salts. Ethanol was employed as the solvent, and monoethanolamine (MEA) served as a stabilizing agent to control the hydrolysis rate. The sol was prepared by dissolving stoichiometric amounts of nickel nitrate and manganese nitrate in ethanol, followed by the addition of MEA under constant stirring. The molar ratio of MEA to metal nitrates was maintained at 1:1 to ensure uniform complexation. The resulting transparent solution was stirred continuously for 2 hours at room temperature to achieve complete homogenization.Cleaned glass substrates were used for thin film deposition. The dip-coating process was carried out by immersing the substrates vertically

into the sol and withdrawing them at a constant rate of 5 mm/s. The coated films were dried at 100 °C for 10 minutes after each layer deposition. This process was repeated multiple times to achieve the desired thickness. After deposition, the films were annealed at 400 °C for 2 hours in a muffle furnace to improve crystallinity and remove organic residues.The surface morphology and microstructure of the annealed thin films were analyzed using Scanning Electron Microscopy (SEM), while the elemental composition was confirmed using Energy Dispersive X-ray Analysis (EDAX). The electrochemical performance of the films was evaluated using cyclic voltammetry (CV) in a three-electrode setup with 1 M KOH electrolyte to determine their capacitive behavior. These experimental techniques collectively validate the structural integrity and supercapacitive performance of the 1% Mn-doped nickel nitrate thin films.

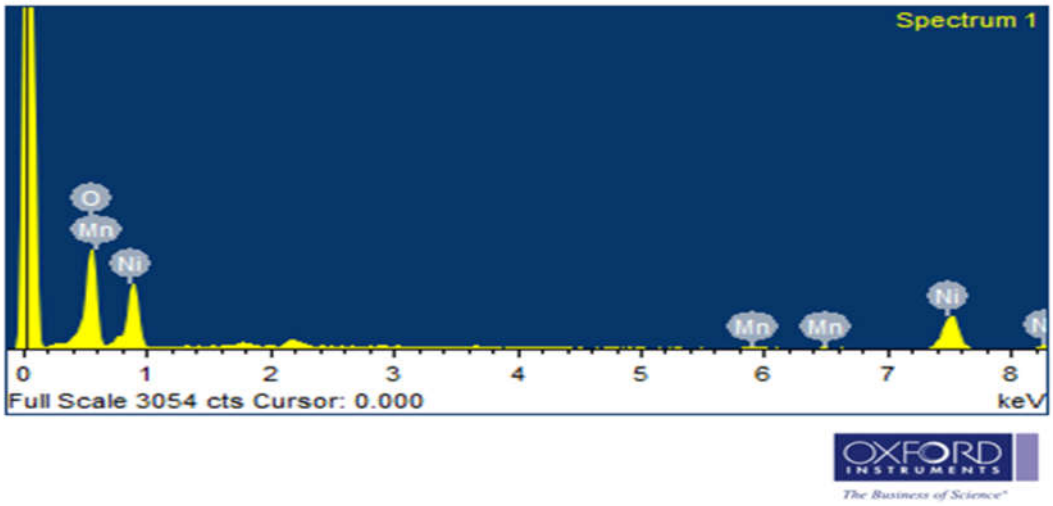
4. Results and Discussion

Using Scanning Electron Microscopy (SEM) at three magnifications—50.00x, 10,000x—the surface morphology of nickel nitrate thin films doped with manganese at a concentration of 1 at.% was investigated. The SEM pictures clearly show how manganese doping affects porosity, surface texture, and grain refinement—elements that are essential to thin film performance in supercapacitor applications. Partial crystallinity and strong film-substrate adhesion are indicated by these flake-like clusters. Cracks and open pores increase surface area, which improves ion transport and electrolyte penetration during charge/discharge cycles. These characteristics are beneficial in electrochemical applications because they promote higher capacitance and quicker ion diffusion.The image at intermediate magnification (10,000x) exhibits better homogeneity, with nanograins evenly spaced across the surface. Manganese incorporation results in improved nucleation behavior, as evidenced by this dense and compact morphology. The refined grain structure seen is explained by Mn doping, which is known to alter the host matrix's surface energy and crystallization kinetics. Stable current distribution across the electrode surface is supported and electrical resistance is decreased by the even surface coverage.A very porous, sponge-like nanostructure is visible at the highest magnification (50,00x). Diffusion pathways are shortened and the electrochemically active surface area is increased by the interconnected grains with nanoscale gaps. Double-layer formation and pseudocapacitance, which both increase energy storage capacity, are directly

influenced by these morphological characteristics. Furthermore, the homogeneity brought about by regulated Mn doping is further supported by the lack of agglomeration or isolated grain clusters.Overall, 1 at.% Mn doping results in a well-connected, nanostructured morphology with high porosity and excellent grain distribution, which are essential characteristics for high-performance supercapacitor electrodes, according to the SEM analysis.

4.1. Morphological Study

The elemental composition and doping efficiency of manganese in the nickel nitrate thin films were ascertained using Energy Dispersive X-ray Analysis (EDAX). In addition to manganese (Mn) peaks at anticipated energy levels, the EDAX spectrum verified the presence of nickel (Ni) and oxygen (O) as the primary elements. Manganese's atomic ratio was close to the target doping concentration, at about 1 at.%. This outcome demonstrates how well the sol-gel technique works to achieve exact elemental control.Additionally, elemental mapping showed that manganese was evenly dispersed across the film surface, showing no indications of segregation or clustering.For reliable electrochemical performance and structural stability, this homogeneity is essential. Stable and effective redox behavior during charge-discharge cycles is facilitated by the consistent Mn dispersion, which keeps electrochemical activity constant across the electrode surface.Furthermore, the EDAX spectrum showed no detectable foreign elements or significant impurities, indicating high purity and controlled synthesis. The effective incorporation of manganese into the nickel matrix is supported by the coexistence of Ni, Mn, and O in the anticipated stoichiometric ratios, which improves the chemical



functionality of the film.The structural conclusions drawn from SEM analysis are strongly supported by the EDAX results. The appropriateness of these films for energy storage applications is confirmed by the combination of surface morphology and compositional verification. X-ray photoelectron spectroscopy (XPS) may be used in future research to assess the oxidation states and binding energies of Mn and Ni in the film.

Figure.1 EDAX spectrum confirming the presence of Ni, Mn, and O in the thin film.

The surface morphology of 1 at.% manganese-doped nickel nitrate thin films was examined using scanning electron microscopy (SEM) at magnifications of 100,000x and 50,000×. A semi-uniform flaky surface with visible microcracks and porosity was visible in the low magnification image (100,00×). These characteristics enhance the active surface area and promote ion diffusion, which is beneficial for electrochemical applications and suggests partial densification during annealing. The film showed fine, evenly distributed grains in a densely packed granular structure at 10,000× magnification.The enhanced nucleation kinetics shown by the refined grain morphology are probably the result of Mn doping, which is crucial for reducing the growth of large grains and promoting structural homogeneity. By reducing internal resistance, this homogeneity facilitates effective charge transport across the electrode surface. Overall, manganese doping enhances surface morphology, grain structure, and porosity—all of which are crucial for maximizing the performance of thin-film supercapacitors, according to the SEM analysis.

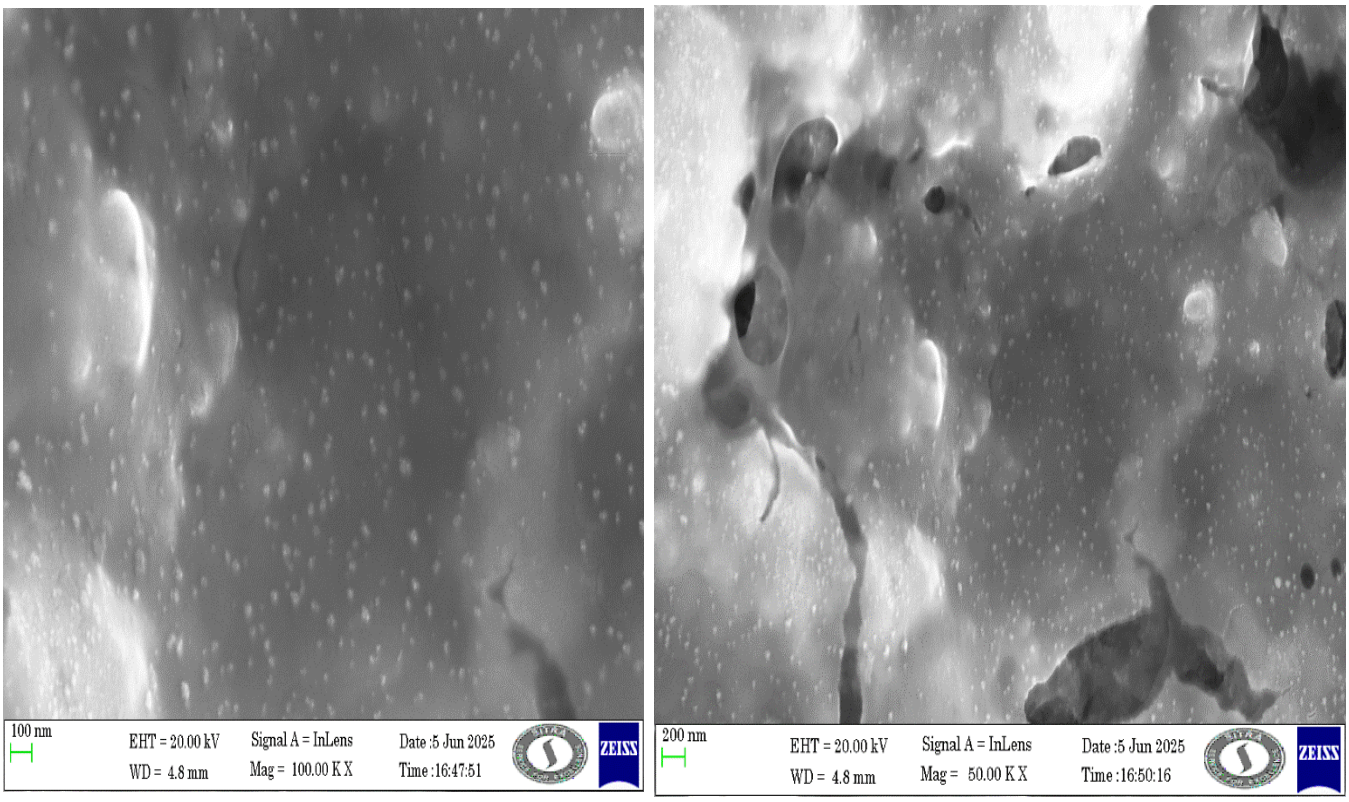


Figure. 2,3 SEM image of 1 at.% Mn-doped nickel nitrate thin film at 100,00x -50,00 x magnification.

5. Conclusion

In this study, manganese-doped nickel nitrate thin films were successfully synthesized using the sol-gel dip-coating method with a doping concentration of 1 atomic percent (at.%). They were then thoroughly morphologically analyzed using Energy Dispersive X-ray Analysis (EDAX) and Scanning Electron Microscopy (SEM). Evaluating the impact of Mn doping on the surface and structural properties of nickel nitrate thin films meant for supercapacitor electrode applications was the main goal.Significant enhancements in surface morphology and nanostructure were found by SEM analysis at different magnifications. At low magnification, the doped films displayed flake-like characteristics; at higher magnifications, they changed into evenly distributed nano-grains and sponge-like porous networks.The addition of manganese, which altered the nucleation and growth kinetics during the sol-gel process, is responsible for these modifications. The resulting microstructure offers improved roughness, surface area, and efficient ion diffusion channels—all of which are critical for the behavior of high-performance supercapacitors.Manganese was successfully incorporated into the nickel matrix with an approximate atomic percentage that was near the targeted 1%, according to the EDAX analysis.

Additionally, elemental mapping showed that the Ni, Mn, and O elements were uniformly distributed across the film surface, indicating high synthesis reliability and compositional homogeneity.These results strongly imply that manganese doping optimizes the surface conditions of the thin film for improved electrochemical interactions in addition to improving film uniformity and microstructural integrity. These films are promising candidates for energy storage systems, especially supercapacitors, due to their confirmed elemental composition and porous, nanostructured surface morphology.In the future, electrochemical tests like galvanostatic charge-discharge (GCD), cyclic voltammetry (CV), and impedance spectroscopy (EIS) will be used to determine the relationship between the structural improvements and electrochemical performance.

7. References

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