The influence of lithium on the optical and electrical properties of CoLi$_x$Fe$_{1-x}$O$_4$ nanoferrites

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HIGHLIGHTS

- The crystalline nature of the synthesized nanoparticles decreased with increasing Li content.
- SEM analysis reveals cubic structure.
- The calculated bandgap energies tended to decrease with increasing Li concentration.
- The discharge (charge) capacity and coulombic efficiency shows 1258 mAh g$^{-1}$ (1010 mAh g$^{-1}$) and 80%.

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ABSTRACT

Current research on the application of nanofermites as an electrode material for Li-ion batteries (LIBs) has reached a tremendously high level. The structural, electrical, and optical properties of nanofermite materials for LIBs have been characterized in several studies. The intention in the present study was to introduce new ferrite materials for improving the cyclic property and efficiency of Li batteries and to provide further characterization of the optical and electrical properties of these CoLi$_x$Fe$_{1-x}$O$_4$ nanoferrite synthesized using a sol-gel combustion technique. Moreover, the synthesized CoLi$_x$Fe$_{1-x}$O$_4$ ferrite samples were characterized by identifying their structural, electrical, and optical properties. A UV analysis illustrated a decrease in the bandgap energy values with increasing Li concentration, while a Fourier transform-infrared spectroscopy study confirmed a spinel ferrite structure. Electrochemical performance of the synthesized CoLi$_x$Fe$_{1-x}$O$_4$ nanoferrites showed an initial coulombic efficiency of 80% and an initial discharge capacity of 1258 mAh g$^{-1}$.

1. Introduction

Ferrites are a great class of oxides with exceptional magnetic properties, which have been examined and applied over the past 50 years [1,2]. Their usage covers an extraordinary range of applications ranging from integrated circuitry with millimeter wave to simple permanent magnets, power handling, and magnetic recording [3–5]. For some applications, ferrites cannot be exchanged by ferromagnetic metals; nevertheless, they frequently compete with metals due to commercial reasons, among others [2]. The possibility of producing nanosized ferrites has opened a new, innovative research field with revolutionary capabilities that are applicable not only in electronics but also in the field of biotechnology [6].

Research on ceramic compounds mixed with iron oxide and one or more metals has fascinated the relevant scientific community owing to their novel properties and technological applications, especially when the particle size approaches the nanometer scale, as more novel electrical and magnetic behavior has been observed in comparison with their bulk counterparts [7,8]. In general, the transport properties of nanomaterials are primarily controlled by the grain boundaries rather than the grains [9]. Based on this finding, these magnetic materials have been explored for use in an extensive range of practical applications and thus are currently replacing conventional materials [10].

It is evident that the phases, crystallite size, and morphology of ferrites have a significant impact on their magnetic and electrical properties, and potential applications; thus, the meticulous fabrication of nanostructured materials with novel morphologies has recently drawn considerable attention [11–13]. Since iron is a conventional magnetic material, nanoferrites have been used in various fields because of their unique electrical and magnetic properties [14,15]. Numerous innovative and effective approaches have been developed to yield nanoferrites with various shapes such as nanowires, nanorods,
nanotubes, etc. [16–19]. Nanoferrites have suitable properties and have shown excellent efficiency in the fields of lithium-ion batteries (LIBs), wastewater treatment, microwave devices, solar cells, and drug delivery [20–25].

In this study, Li-substituted cobalt ferrites were synthesized using a sol-gel combustion method with various concentrations of lithium. Subsequently, the synthesized samples were characterized using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) to elucidate their structures, and using UV spectroscopy and Fourier transform-infrared (FTIR) spectroscopy to ascertain their optical properties. In addition, their band-gap energy values were calculated and electrochemical performance examined by conducting coin-cell testing.

2. Experimental methods

2.1. Sample preparation

The nanoferrite samples were synthesized using commercially available nitrates as source materials: analytical-grade chromium nitrate (99% purity, Sigma-Aldrich Co., USA), nickel nitrate (99% purity, Sigma-Aldrich Co., USA), iron nitrate (99% purity, Sigma-Aldrich Co., USA), and citric acid (99% purity, Sigma-Aldrich Co., USA). The Li-doped cobalt ferrites were synthesized using a sol-gel combustion method. Metal nitrates, citric acid, and polyvinyl alcohol (PVA) were dissolved in distilled water and stirred continuously for 3 h (the PVA was used as a chelating agent). Additionally, they were subjected to heat treatment, as previously reported [26].

2.2. Characterization

The synthesized Li-doped cobalt nanoferrites were characterized using XRD with a Bruker D8 Advance X-ray diffractometer and CuKα radiation (1.54056 Å). The particle sizes of the samples were confirmed using SEM (Zeiss Euva 8). An FTIR spectroscopic study was carried out in a KBr medium using a Shimadzu FTIR-8400 in the wave number ranging from 400 to 4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) and a UV-diffusion reflectance spectra study was performed using a Jasco UV–Visible Spectrophotometer (V-670 PC). The electrochemical performance was evaluated using a standard coin-cell test with the synthesized nanoferrites as the working electrode and Li metal as both the counter and reference electrodes. The electrolyte was 1.0 M LiPF\(_6\) in a solution of ethylene carbonate (EC) and diethylene carbonate (DEC) mixed at a volume ratio of 3:7. Galvanostatic test (CTS-Lab, BaSyTec, Germany) was conducted at a constant current of 100 mA g\(^{-1}\) in the voltage window between 3.0 V and 0.01 V vs. Li\(^+\)/Li at 25°C.

3. Results and discussion

The XRD patterns of the CoLi\(_x\)Fe\(_{1-x}\)O\(_4\) (x = 0.2, 0.4, 0.6, 0.8, and 1) nanoferrites are displayed and compared in Fig. 1; they exhibit peak patterns similar to those of pure cobalt ferrite [27]. The (220), (311), (400), (422), (511), and (440) planes in the XRD patterns reveal the cubic structures of the samples. At the same time, it is seen that the crystalline nature decreases with increasing Li concentration. Moreover, this decrease in intensity is also observed in the XRD patterns with increasing Li concentration [28]. This is associated with an increase in structural disorder as the crystalline nature decreased with increasing Li concentration, which led to different inter-atomic distances between the nanoparticles’ surface layers relative to those at their cores and a smaller mass of substituent ions [29,30]. The average particle size ranged from 20 to 78 nm. The observed pattern indicates a single-phase structure since there are no additional peaks of any impurities.

Based on the SEM analysis in Fig. 2, the morphological features of the CoLi\(_x\)Fe\(_{1-x}\)O\(_4\) nanoferrites with different amounts of Li are compared, showing that they all possess cubic morphology. The observed morphology is in good agreement with TEM analysis reported in previous literatures [31–33]. In addition, the optical properties of the CoLi\(_x\)Fe\(_{1-x}\)O\(_4\) nanoferrites are analyzed and compared in Fig. 3. The
bandgap-energy values of the Li-substituted Co ferrites according to the concentration of Li are observed. Tauc plots of \((\alpha h\nu)^2\) vs. photon energy (eV) are used to calculate the indirect bandgap energy values of the Li-substituted Co ferrite by extrapolating the curve to zero absorption. The slope of the \((\alpha h\nu)^2\) values denotes the phonon involvement in an optical process \[34,35\]. The results show a decrease in bandgap energy with increasing Li concentration as \(E_g = 0.5\ \text{eV}, 0.4\ \text{eV}, 0.3\ \text{eV}, 0.2\ \text{eV}, \text{and} 0.1\ \text{eV}\) for \(x = 0.2, 0.4, 0.6, 0.8, \text{and} 1\), respectively. Based on the observed results, the conductivity of the Li-substituted Co ferrites steadily improves with increasing Li concentration. Therefore, the results from the UV studies suggest that the synthesized Co\(\text{Li}_{x}\text{Fe}_{1-x}\text{O}_4\) nanoferrite materials are applicable in LIBs.

On the other hand, Fig. 4 shows the absorption bands for different Li concentrations as a function of wavelength, which originated primarily from the absorption and scattering of UV radiation by the magnetic nanoparticles in agreement with the previously reported results in the literature \[36\]. Thus, it is evident that the Co ferrites showed a significant blue shift in the absorption peak relative to the bulk absorption, which might have been associated with the quantum size effect that arose due to the very small size of the nanoparticles \[37\].

Fig. 5 shows the FTIR spectroscopy analysis recorded in the rage of 4000–400 cm\(^{-1}\) for the Li-substituted Co ferrites with varying composition. The peaks around 500 cm\(^{-1}\) show the common characteristics of spinel ferrites \[38\]. The frequency-absorption band lies in the range of 500–600 cm\(^{-1}\), which is fixed for the vibration of the tetrahedral metal complex consisting of a bond between the oxide ion and the tetrahedral site metal ion (O-M). The existence of a higher frequency band is confirmed by the stretching vibration within the bonds between molecules/ions, whereas the lower frequency band is originated from the bending vibration. These band locations are in good matching with the typical infrared absorption bands of Co ferrites \[39\]. In addition, the bands near 1650 and 3500 cm\(^{-1}\) are due to the C-H stretching vibration band and O-H stretching interaction through the H band \[40,41\].

Fig. 6a and b illustrates the voltage profiles of the Co\(\text{Li}_{x}\text{Fe}_{1-x}\text{O}_4\) nanoferrites and the cyclic performance of the Co\(\text{Li}_{x}\text{Fe}_{1-x}\text{O}_4\) at a constant current density of 100 mA g\(^{-1}\) with a voltage between 3.0 and 0.01 V. Li can be inserted and reacted with ferrite in the presence of MO and reduced to Fe and Li\(_2\)O as follows:

\[
\text{M(O)} - \text{Fe}_{2}\text{O}_3 + 6\text{Li} \rightarrow 2\text{Fe} + 3\text{Li}_{2}\text{O} + \text{M(O)}
\]  

Based on Eq. (1), the approximate theoretical capacity of Co\(\text{Li}_{x}\text{Fe}_{1-x}\text{O}_4\) nanoferrites is predicted to be 714 mAh g\(^{-1}\) because the predicted capacity is calculated based on the number of transferred electrons in the electrochemical reaction \[42\].

The initial discharge capacity (and the initial charge capacity) and the initial coulombic efficiency of the synthesized nanoferrites are measured as 1258 mAh g\(^{-1}\) (1010 mAh g\(^{-1}\)) and 80\%, respectively, and exhibit superior capacity and coulombic efficiency as compared with its predicted theoretical capacity (714 mAh g\(^{-1}\)) and previous reports \[43,44\]. Although a further systematic study is required to
define its salient mechanism and explore its optimized conditions, we demonstrate for the first time that the CoLixFe1-xO4 nanoferrites synthesize in this study can be a promising anode material of LIBs.

4. Conclusions

In this paper, we report the synthesis of Li-substituted Co ferrites using a sol-gel combustion method with various concentrations of Li. The following conclusions can be drawn:

i. The crystalline nature of the synthesized nanoparticles decreased with increasing Li concentration.

ii. The SEM analysis revealed that they all had cubic crystalline structure.

iii. The calculated and plotted bandgap energies tended to decrease with increasing Li concentration.

iv. From the FTIR spectroscopy of the Li-substituted Co ferrites with varying composition, the band positions were in good agreement with the characteristic infrared absorption bands of Co ferrites.

v. The initial discharge (charge) capacity and initial coulombic efficiency were measured as 1258 mAh g⁻¹ (1010 mAh g⁻¹) and 80%, respectively. There is still plenty of room for further development despite the successful demonstration of its potential use as an anode material of LIBs.

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