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Li Doped Nickel Ferrite/Pani Nanocomposite as an Eco-Friendly Electrode Material for Energy Storage Devices

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Abstract: - Recently transition metal oxides as capacitive electrodes are finding place in supercapacitor. However, low specific energy and poor electrical conductivity are main drawbacks for energy storage applications. This study introduces lithium doped nickel ferrite nanoparticles (LNF) and LNF/polyaniline (LNF/PAni) as an advanced option for application as electrodes in supercapacitors.

These nanocomposites were prepared by sol gel auto-combustion and in-situ polymerization method and characterized by XRD. The XRD pattern revealed the single phase of highly crystalline LNF nanoparticles and crystalline- amorphous nature of nanocomposite. The surface morphology is studied by FEG-SEM which shows cubic structure of LNF nanoparticles and formation of core-shell of nanocomposite. Capacitance was measured by electrochemical measurements to examine the impact of introducing PAni in ferrite nanoparticles. The specific capacitance value increased due to high conductivity of PAni.

Keywords: ferrite nanoparticles, polyaniline, nanocomposites, electrochemical, specific capacitance.

I. INTRODUCTION

Some of the most significant global concerns of the twenty-first century include the ever-increasing need for energy, issues with portability, and the fast-dwindling hydrocarbon fuel sources. The scientific community has been prompted by all of these problems to develop economical, environmentally responsible, and efficient alternative energy conversion and storage methods. Supercapacitors exhibit an impressive ability to store energy effectively, offering numerous advantages such as elevated power densities, substantial specific capacitance, swift charging and discharging capabilities, prolonged cycle life, and environmentally friendly electrical energy storage. One popular option for an environmentally friendly energy storage device is the supercapacitor [1-5]. Supercapacitors are unusual energy sources that operate on the basis of electrochemical energy conversion in all other respects. Supercapacitors are available in a variety of shapes and sizes and are transparent, tiny, thin, lightweight, and flexible. For portable electronics like laptops, cell phones, MP3 players, medical equipment, video cameras, and robotic vacuum cleaners, they serve as substitute power sources [6–7]. Supercapacitors have received a lot of interest because of their high-power density, long-term cycle capabilities, and high specific capacitance (SC). Three groups of materials are commonly explored for application in supercapacitors: (i) conducting polymers, (ii) metal oxides, and (iii) activated carbons [8-11].

For many years, metal oxides have served as materials for supercapacitor electrodes. MFe_2O_4 (M = Fe, Co, Ni, Mn, Cu, Zn) ferrites, however, have drawn a lot of attention for researchers. Their good conductivity, redox chemistry, ease of synthesis, abundance, eco-friendliness, and 3D diffusion pathways make them valuable, but pure metal oxides do not give satisfying electrochemical performance.

So, the plan of synthesizing hybrids of MFe_2O_4 has evolved. Out of various conducting polymers, Polyaniline is chosen over all of them due to its significantly large electrical conductivity, fairly large pseudocapacitance, quick doping/de doping kinetic during charging-discharging and moderate cost. Polyaniline and MFe_2O_4 based binary system may exhibit better electrochemical activities [12-13].

The nickel ferrite has an inverted spinel structure, with Fe3+ ions located at the tetrahedral and octahedral sites and Ni2+ ions at the octahedral sites. Li+ ions thus occupy Ni2+ sites since the ionic radius of Li (0.59 Å) is quite similar to that of Ni (0.55 Å). To improve electrochemical performance, polyaniline nanocomposite and lithium-doped nickel ferrite nanoparticles are manufactured for the current investigation.

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II. EXPERIMENTAL

A. *The synthesis of $Ni_{0.5}Li_{0.5}Fe_2O_4$ ferrite nanoparticles*

$Ni_{0.5}Li_{0.5}Fe_2O_4$ ferrite (LNF) powder was prepared using a sol-gel auto-combustion technique. The detailed procedure is as follows. Stoichiometric amounts of $Ni(NO_3)_2 \cdot 6H_2O$, $Li(NO_3)_2 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ were each dissolved in deionized water, followed by the addition of a specific quantity of lemon juice to the metal nitrate solution. These cationic solutions were then combined and stirred continuously for one hour to ensure homogeneity. Ammonium hydroxide was gradually added dropwise to adjust the pH to approximately 7.0. Subsequently, the mixed solution was heated to 90°C with constant stirring to form a dried gel, which underwent self-propagating combustion until all the gels were fully burnt, resulting in loose precursors. Finally, $Ni_{0.5}Li_{0.5}Fe_2O_4$ crystalline powder was obtained by calcining the loose precursors at 600°C for 4 hours [14].

B. *Preparation of $Ni_{0.5}Li_{0.5}Fe_2O_4$/PAni nanocomposite*

Lithium doped nickel ferrite nanoparticles/polyaniline (LNF/PAni) nanocomposite was synthesized using an in situ polymerization method. Initially, a specified amount of LNF ferrite nanoparticles was dispersed in 70 ml of 1 M HCl solution and stirred for 90 minutes to achieve a uniform dispersion. Subsequently, 2 ml of aniline (AN) monomer was added to the ferrite solution, followed by stirring for an additional two hours. A solution of 4.98 g of ammonium peroxydisulfate (ASP) in 40 ml of 1 M HCl was then prepared. This ASP solution was gradually added to the ferrite mixture under continuous stirring for two hours [15]. The resulting green solution was left to polymerize for 12 hours at temperatures ranging from 0°C to 5°C. The mixture was then filtered, thoroughly washed with 1 M HCl and double-distilled water, and finally dried in a vacuum oven at 80°C for 48 hours.

III. RESULT AND DISCUSSION

A. *Structure and Morphology*

Fig. 1 shows the X-Ray diffraction pattern of LNF ferrite nanoparticles and LNF/PAni nanocomposite. PAni shows the amorphous nature in a partially crystalline state having two diffraction peak $2\theta = 20.68°$ and 25.6° in nanocomposite XRD pattern [16-17]. The LNF ferrite nanoparticles and composites showed the polycrystalline nature. From Fig.1, we can see that between LNF ferrite nanoparticles and LNF/PAni composite, there is no significant difference in crystalline nature, except the intensity. The average crystallite size (D) of LNF ferrite nanoparticles has been calculated from XRD data using Scherer's equation.

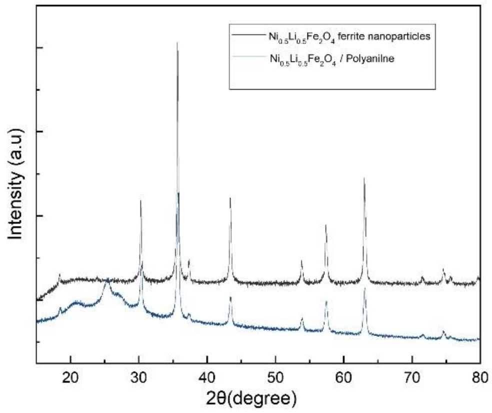


Fig. 1 XRD patterns of LNF ferrite nanoparticles and LNF/ PAni nanocomposite.

The FE-SEM images of LNF ferrite nanoparticles and the LNF/PAni nanocomposite are presented in Fig. 2 (a) and (b). In Fig.2 (a), the Lithium-doped Nickel ferrite nanoparticles exhibit a cubic structure. Fig. 2 (b) illustrates the polyaniline coating on LNF ferrite nanoparticles, where the nanoparticles are uniformly dispersed within the polymer matrix.

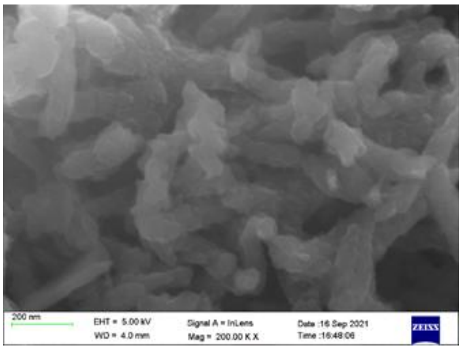
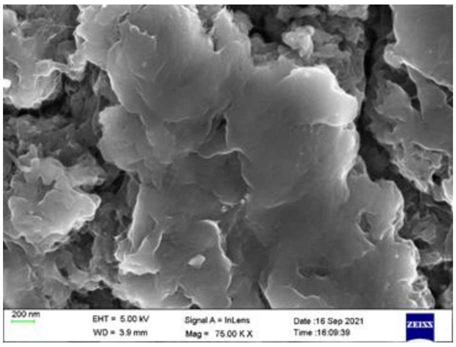


Fig. 2 (a) FE-SEM image of LNF nanoparticles



(b) FE-SEM image of LNF/PAni nanocomposite

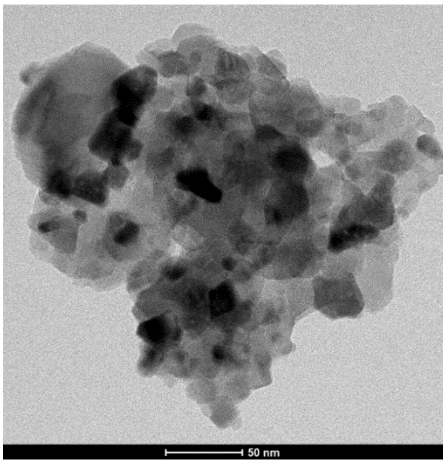


Fig. 3 (a) TEM image LNF nanoparticles

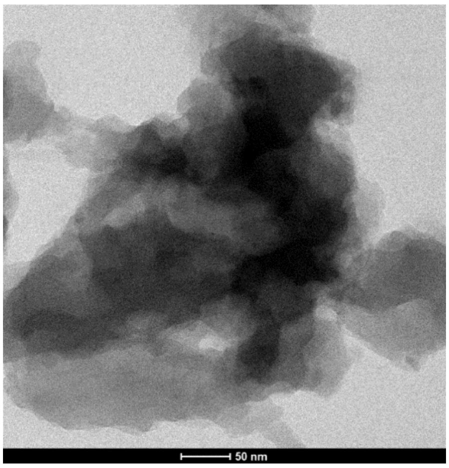


Fig. 3 (a) b) TEM image LNF/PAni Nanocomposite

The average particle size of LNF ferrite nanoparticles was determined using FEG-TEM images, yielding average particle size of 30 nm as calculated with ImageJ software. In Fig. 3 (b), the dark regions represent LNF ferrite nanoparticles, while the lighter areas correspond to amorphous polyaniline. The core of the nanocomposite consists of LNF ferrite nanoparticles enveloped by a polyaniline shell. The images clearly demonstrate that the synthesized ferrite nanoparticles are crystalline with a cubic structure and are uniformly distributed throughout the polymer matrix [18].

B. *Electrochemical characterization*

The electrochemical performance of the synthesized LNF and LNF/PAni electrodes was investigated at room temperature using a 2 M KOH electrolyte solution through cyclic voltammetry (CV). The CV plots of the prepared ferrite nanoparticles and nanocomposite electrodes in a three-electrode configuration at various scan rates (5 mV/s, 10 mV/s, 20 mV/s, 60 mV/s, 80 mV/s, and 100 mV/s) are presented in Fig. 4 (a) and (b). In Fig. 4 (a), pronounced oxidation/reduction peaks are observed for the LNF nanoparticles, indicating their pseudocapacitive properties related to electrochemical reactions at the electrode-electrolyte interface. The CV curves of the nanocomposites in Fig. 4 (b) show peaks attributable to the faradaic processes of both LNF and PAni components. The specific capacitance and surface area of the LNF/PAni nanocomposite are enhanced due to the improved conductivity of the composite. The inclusion of LNF in the PAni matrix results in a continuous conductive network that facilitates ion transport and redox reactions [19-23].

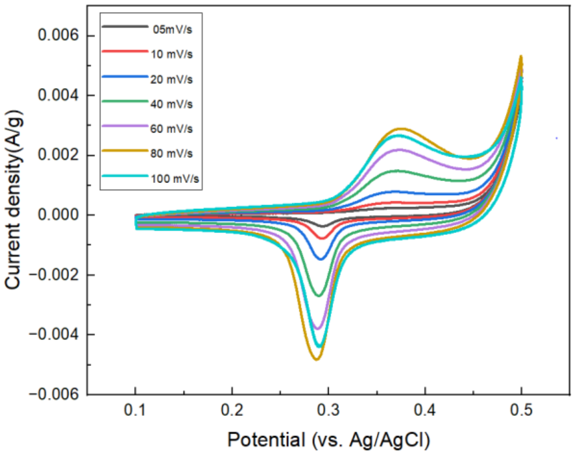


Fig. 4 C V curves of (a) NLF ferrite nanoparticles at different scan

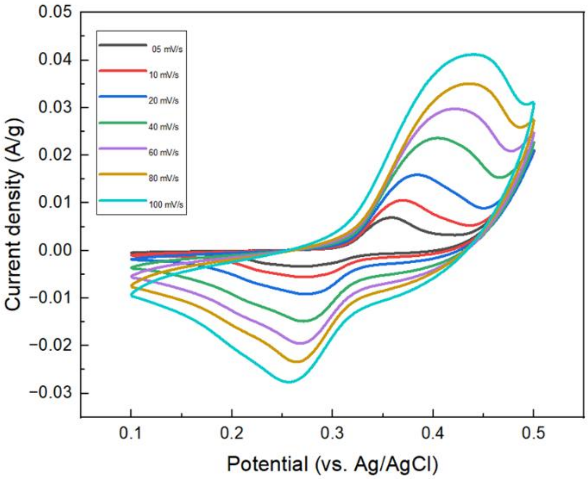


Fig. 4 C V curves of NLF/PAni nanocomposite at different scan rates and potentials.

Additionally, LNF ferrite improves the electro-chemical performance of the LNF/PAni supercapacitor electrode by minimizing charge transfer resistances and enhancing the interfacial contact between LNF/PAni and electrolyte. The specific capacitance and energy density were computed using following equations,

Specific capacitance(F/g)

$$C_s = \frac{\int I dV}{v \, x \, m \, x \, \Delta V} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where, I- Integral area - Scan rate (mVs^{-1}),

m- Mass of the composites (milligram) and

ΔV- window potential (volt).

Energy density, E (Wh/kg)

$$E = \frac{0.5 \, x \, C_S \, \Delta V^2 \, x \, 1000}{3600} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The maximum specific capacitance values calculated for LNF nanoparticles and LNF/PAni nanocomposite are 51 Fg^{-1} and 289.74 Fg^{-1}, respectively, at a scan rate of 5 mV/s. The energy density values for LNF nanoparticles and LNF/PAni nanocomposite are 0.637 Wh/kg and 14.487 Wh/kg, respectively.

IV. CONCLUSION

Lithium-doped nickel ferrite nanoparticles and Li-doped nickel ferrite/polyaniline nanocomposites were successfully synthesized using the sol-gel auto-combustion and in-situ polymerization methods. X-ray diffraction patterns confirmed the spinel cubic structure of the LNFF ferrite and the amorphous nature of polyaniline. The average particle size of the synthesized ferrite nanoparticles, determined from XRD, FE-SEM, and FE-TEM images, was approximately 30 nm. The maximum specific capacitance values for the NMF ferrite nanoparticles and LNF/PAni nanocomposite were calculated to be 17.28 Fg^{-1} and 246 Fg^{-1}, respectively, at a scan rate of 5 mV/s. The LNF/PAni nanocomposite and LNF ferrite nanoparticles have energy densities of 5.48 Wh/kg and 0.38 Wh/kg, respectively.
These findings imply that the materials that were produced are good choices for the anode electrodes of supercapacitors.

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