Impedance and Electric Modulus Studies on Polyaniline/Nickel Ferrite (PANI/NiFe$_2$O$_4$) Composites

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Abstract

Conducting polyaniline/nickel ferrite (PANI/NiFe$_2$O$_4$) composites are synthesized by employing interfacial polymerization method. The composite has been synthesized with 10, 30 and 50 wt.% of nickel ferrites in PANI. The prepared samples were characterized by FTIR and SEM with EDS. The dominant peaks in FTIR graph confirm the formation of PANI/NiFe$_2$O$_4$ composites. The XRD pattern confirms the formation of composites. The surface morphology of these composites was studied by scanning electron microscope (SEM). Impedance and electric modulus of these composites was investigated in the frequency range of 10$^2$ Hz to 10$^5$ Hz. It is found that Debye type relaxation has been confirmed by the Cole-Cole plot and electrical modulus is inversely proportional to the conductivity of these composites.

1. Introduction

The conducting polymers are a new group of synthetic polymers which combines the chemical and mechanical properties of polymers with the electronic properties of metals and semiconductors [1]. Conducting polymers are used in many applications such as microwave absorption, electronic displays, corrosion protection coating, electrochemical batteries, supercapacitors, sensors, and electrodes [2-6]. They have extended p-conjugation with single- and double-bond alteration along its chain. They behave as a semiconductor material with low charge carrier mobility [7] and their conductivity is increased to reach the metallic range by doping with appropriate dopants [7]. Polyaniline is the most widely studied conducting polymer because of its facile synthesis, low synthetic cost, high electrical conductivity, good environmental and thermal stability [8-12]. Polyaniline can be easily prepared either chemically or electrochemically from acidic aqueous solutions [13, 14]. The most common preparation method is by oxidative polymerization with ammonium persulfate as an oxidant.

Ferrites belong to a special class of magnetic materials, which have a wide range of technological applications. Due to their low cost, ferrite materials are used in various devices like microwave, transformer cores, magnetic memories, isolators, noise filters, etc [15-18]. The spin-glass state in ferrites exhibits the most interesting magnetic property that causes high field irreversibility, shift of the hysteresis loops, and anomalous relaxation dynamics [19, 20].

Nickel ferrite (NiFe$_2$O$_4$) is one of the most important spinel ferrites that have been studied. Stoichiometric NiFe$_2$O$_4$ is considered as n-type semiconductor [21]. It exhibits different kinds of magnetic properties such as paramagnetic, superparamagnetic or ferrimagnetic behavior depending on the particle size and shape.

In our earlier paper, we reported AC conductivity and dielectric properties of PANI/NiFe$_2$O$_4$ composites [22] and in the present paper, the preparation of PANI/NiFe$_2$O$_4$ composites, its characterization through FTIR spectra, scanning electron microscope, impedance spectroscopy and electric modulus is reported.

2. Experimental Methods

2.1 Synthesis of Polyaniline/NiFe$_2$O$_4$ Composites

The polyaniline/NiFe$_2$O$_4$ composites were prepared via interfacial polymerization method with different weight percentage of NiFe$_2$O$_4$ (10, 30 and 50 wt.%). One gram of aniline was dissolved in 40 mL of CHCl$_3$. 0.1 M ammonium persulphate was dissolved in 1 M HCl and the NiFe$_2$O$_4$ particles prepared by combustion method in the weight percent of 10, 30 and 50 were added to the above mixture of aqueous and organic phase. After 5 minutes dark green precipitate formed slowly at the interface and then gradually diffused into aqueous phase. After 24 hours, the entire aqueous phase was filled homogeneously with dark green color film, organic layer observed shows orange color due to the formation of aniline oligomers. The aqueous phase was then collected and washed with ethanol and water to remove the unreacted aniline. The residue of polymer thus obtained is purified and dried in vacuum oven at 40 °C for 36 hours. In this way 3 different polyaniline-NiFe$_2$O$_4$ composites with different wt.% of NiFe$_2$O$_4$ in polyaniline have been synthesized as reported [22, 23]. The dried polymeric composite sample was used for structural characterization and further used to study the electrical properties.

2.2 Characterization

The above synthesized samples were structurally and morphologically characterized by using different techniques like FTIR, XRD and SEM. The FTIR spectra of samples were recorded on Thermo Nicolet, Avatar 370 spectrometer in KBr medium at room temperature. The X-ray diffraction patterns of the prepared samples were obtained by employing Bruker AXS D8 advance X-ray diffractometer using CuKα radiation (λ=1.5418 Å) in the 2θ range 10° to 65°. The surface morphology of polyaniline-NiFe$_2$O$_4$ composites were studied by using Joel model JSM-6390 LV scanning electron microscope (SEM). To measure the AC conductivity, the pellets of the prepared samples were coated with silver paste on either side was held between two nominally spring-loaded copper plates and the AC parameters were measured using N4L-PSM 1735 Numetrix Q programmable LCR meter in a frequency range 10 to 10$^5$ Hz.

3. Results and Discussion

3.1 FTIR Spectral Studies

Fig. 1 (a) shows FTIR spectra of pure polyaniline and Fig. 1 (b-d) shows that of polyaniline/nickel ferrite (10, 30 and 50 wt.%) respectively. Careful
The crystalline size was determined by Scherrer's formula. The prominent peaks corresponding to 2\(\theta\) = 29.98°, 53.79° and 75.12° are due to (220), (400) and (511) crystal planes of NiFe\(_2\)O\(_4\) respectively. By comparing the XRD patterns of the composite (50 wt\% NiFe\(_2\)O\(_4\)) to the XRD patterns of the pure NiFe\(_2\)O\(_4\), it can be seen from the Fig. 5 and Table 2, the NiFe\(_2\)O\(_4\) particles are uniformly dispersed in polyaniline. The presence of Ni, Fe and O elements in the EDS spectrum indicates the formation of composite along with small traces of sulphur and chlorine.

### 3.2 XRD Characterization

The X-ray diffraction pattern of polyaniline, pure NiFe\(_2\)O\(_4\) and polyaniline–NiFe\(_2\)O\(_4\) composite (50 wt\%) is shown in Fig. 2. From Fig. 2(a) by investigating carefully, the X-ray diffraction profiles of polyaniline has amorphous nature with an expansive peak centered at 2\(\theta\) = 20.7° and 25.29°. This is the distinctive peak of polyaniline, which is attributed to the periodicity in parallel and perpendicular directions of the polymer chains respectively [26]. XRD spectra of polyaniline, demonstrates an expansive reflection at lower Bragg angle 2\(\theta\) estimation of 25.29° comparing to (200) diffraction plane of HCl doped PANI of FSI structure [27, 28].

![Fig 2 X-Ray diffraction patterns of (a) polyaniline (b) pure NiFe\(_2\)O\(_4\) (c) polyaniline – NiFe\(_2\)O\(_4\) composite (50 wt\%)](image)

### 3.3 SEM Study

Fig. 3 shows the SEM image of polyaniline/NiFe\(_2\)O\(_4\) composite with 50 wt\%. NiFe\(_2\)O\(_4\) in polyaniline. High magnification SEM image reveals that, the surface of composites was rough and exhibit, more or less, spherical morphology. From the image it is clear that, the PANI can minimize the aggregation of particles because of the repulsive force between magnetic particles and PANI. It also noticed that, the PANI layers are wrapped on the surface of NiFe\(_2\)O\(_4\) particles appearing as small aggregated globules [30].

SEM images of samples were not well resolved, because samples are highly magnetic and intensity of electron beam of SEM may not be sufficient to provide the required resolution to make estimates of sample sizes. Particle size distribution was determined by using Image J software to obtain the maximum size distribution range by selected area of the SEM image of the samples.

Fig. 4 shows the particle size pie graph and the maximum size distribution range of polyaniline – NiFe\(_2\)O\(_4\) composites are found to be 24 nm to 123 nm. An energy dispersive X-ray spectroscopy (EDS) analysis of polyaniline – NiFe\(_2\)O\(_4\) composite (50 wt\%), it can be seen from the Fig. 5 and Table 2, the NiFe\(_2\)O\(_4\) particles are uniformly dispersed in polyaniline. The presence of Ni, Fe and O elements in the EDS spectrum indicates the formation of composite along with small traces of sulphur and chlorine.
3.4 Impedance Spectral Studies

The real and imaginary part of impedance (Z' & Z") and electric modulus (M' & M") parameters have been calculated by the recorded values of equivalent capacitance (Ceq), dissipation factor (D), phase angle (θ) and parallel equivalent resistance (Req) using LCR meter at selected frequency range. Fig. 6 shows the variation of real impedance as a function of frequency of imaginary impedance (Cole-Cole plot) of polyaniline – NiFe2O4 composites. It is observed from the above graph that the semi circles of Cole-Cole plot suggest the dominance of Debye type relaxation has been confirmed. It is observed that resistance of the composites is inconsistent because of the change in the allotment of NiFe2O4 particles in polyaniline. A mechanism for the charge motion through the pressed pellets of conducting polymers was hypothesized. In the Fig. 7 the points on the diagram represent the experimental data, while the continuous line represents the polynomial fitting based on the non-linear least square fitting.

<table>
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<th>Element</th>
<th>Mass %</th>
<th>Atom %</th>
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Fig. 5 EDS spectrum of polyaniline/NiFe2O4 composite (50 wt.%)