Materials Chemistry and Physics 130 (2011) 285–292

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Structural, magnetic, electrical and electrochemical properties of $NiFe_2O_4$ synthesized by the molten salt technique

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ARTICLE INFO

Article history:
Received 31 December 2010
Received in revised form 22 June 2011
Accepted 23 June 2011

Keywords:
Spinel ferrite
Molten salt synthesis
Ferrimagnetic
Electrical conductivity pseudocapacitance
Electro-catalyst

ABSTRACT

Submicron-sized $NiFe_2O_4$ particles were synthesized by the molten salt method at 900 °C using binary melts of a NaCl and KCl mixture that acts as a flux. The X-ray diffraction pattern confirmed the single phase, high crystalline and cubic structure of $NiFe_2O_4$ with a *Fd*3*m* space group. The FT-IR spectra reveal the stretching vibration of octahedral complexes of Fe^{3+}–O^{2-} through the observed band around 552.3 cm^{-1}. The SEM and TEM image had indicated the formation of submicron-sized $NiFe_2O_4$ particles. The ferrimagnetic behavior and high saturation magnetization of 44 emu g^{-1} was elucidated by VSM. The maximum electrical conductivity of 1.42×10^{-4} S cm^{-1} was observed at 873 K. The $NiFe_2O_4$ showed a pseudocapacitive property in 1 M of a $LiClO_4$ electrolyte and exhibited a specific capacitance of 18.5 F g^{-1} at 10 mV s^{-1}. The hydrogen evolution reaction was also studied for $NiFe_2O_4$ in 1 M of a H_2SO_4 solution.

1. Introduction

Mixed metal oxides having different structures such as spinel (AB_2O_4), perovskite (ABO_3), delafossites (ABO_2), olivine ($ABPO_4$), magneto-plumbite ($AB_{12}O_{19}$) and garnet ($A_3B_2(SiO_4)_3$) are used in various applications [1]. Depending upon their crystal structure and cation distribution, the materials exhibit different electrical, magnetic and electrochemical properties. Oxide spinels are one of the mixed metal oxides, represented by the general molecular formula of AB_2O_4, where the A and B are the divalent and trivalent cations. The cations occupy tetrahedral (A) and octahedral (B) interstitial positions of the fcc lattice formed by O^{2-} ions [2]. Among the various spinels, ferrites are widely used in different fields due to their crystal structure, magnetic properties, physical flexibility, electrical resistivity, and chemical stability [3]. These materials are being used in various fields such as microwave, electromagnetics, spintronics, photovoltaics, and gas sensors [4,5]. Recently, the peculiar electrochemical properties of spinel ferrites have been used in various electrochemical devices [6,7].

Among the spinel ferrites, $NiFe_2O_4$ possess a fully inverse spinel crystal structure, a ferrimagnetic nature with low magnetic coercivity, chemical stability, mechanical hardness, and an excellent electrochemical performance [8]. Recently, $NiFe_2O_4$ has been identified as the suitable electrode material in electrochemical devices such as Li-ion batteries as a negative electrode [9] and as supercapacitors [10]. It is well known that the particle size and shape play a major role that tunes their electrochemical properties [11,12]. Hence, the synthesis procedure is the subject of much interest for the preparation of different nano/microstructures [13]. In this regard, the present work attempts a preliminary study of the synthesis of $NiFe_2O_4$ for electrodes in supercapacitors by a molten salt method. The molten salt synthesis or flux growth method is one of the simplest methods for preparing pure and stoichiometric powders of multi-component oxides [14]. Moreover, the molten salt synthesis is a simple, low-cost technique, and does not require any organic solvents or surfactants. In this method, the alkali chlorides or fluorides are commonly utilized as solvent or reacting species, or sometimes both [15,16]. The diffusion rates of the components in molten salts are much higher than those in solid-state reactions. Using this novel method, Darshane et al. have prepared $ZnFe_2O_4$ nanoparticles at 700 °C using NaCl as a growth inhibitor [17]. Recently, $NiFe_2O_4$ nanocrystals were prepared using $NiSO_4 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, NaOH and NaCl as starting compounds at 700 °C for petroleum gas sensor applications [18,19]. Other than the molten salt method, $NiFe_2O_4$ has been synthesized by a solid-state reaction [20], co-precipitation [21], a sol–gel process [22], a mechanochemical reaction [23], and hydrothermal method [24], etc.

In the present work, we have prepared submicron-sized $NiFe_2O_4$ crystals using NiO and Fe_2O_3 as starting compounds

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doi:10.1016/j.matchemphys.2011.06.043

and different ratios of KCl and NaCl as the flux. To the best of our knowledge, no comprehensive study has been reported yet on the structural (XRD, FT-IR), morphological (SEM, TEM), magnetic (VSM), electrical (a.c. conductivity, dielectric constant, and impedance spectra) and electrochemical properties of molten salt, synthesized $NiFe_2O_4$. The novelty of this manuscript is not limited to adapting a novel synthetic method, but is also a ample study of its properties. In this study, the investigation of pseudocapacitance and the hydrogen evolving reaction of the compound has been investigated using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques, respectively.

2. Experimental method

2.1. Synthesis

The metal oxides of NiO and Fe_2O_3 are used as the starting compounds, together with NaCl and KCl, as fluxes to catalyze the reaction in a liquid reaction medium for the formation of $NiFe_2O_4$. Initially, the stoichiometric quantities of NiO and α-Fe_2O_3 were ground for 2 h in an agate mortar to enhance homogeneous mixing. Subsequently, the mixture was added to different weight ratios of NaCl–KCl and heated at 900 °C for 3 h. The molten mixture was then cooled to room temperature and washed with hot distilled water and ethanol to remove the flux. The different weight ratios of NaCl–KCl were used for obtaining single phase and highly pure materials. The products were obtained employing different weight ratios of NaCl:KCl. The weight ratio of (NaCl:KCl) is 4:0, 3:1, 1:1, 1:3 and 0:4 are denoted hereafter as S1, S2, S3, S4 and S5, respectively.

2.2. Characterization

The phase structure and purity of the synthesized particles were identified by an X-ray diffractometer, Bruker D8 Advance with Cu Kα radiation. The morphology and structure of the particles were determined by SEM and TEM (JEOL-JEM 100SX microscope at an accelerating voltage of 200 kV). Fourier transform infrared (FTIR) spectrometer was used to study the structure coordination of the samples. The conductivity, impedance and dielectric measurements were carried out on a HIOKI 3532 LCR HITESTER controlled by a computer in the frequency range of 42 Hz–4 MHz. The samples were prepared by making pellets 1 cm in diameter and 2 mm thickness using a hydraulic press by applying 3.5 tons cm^{-2} pressure. For better ohmic contact silver paste was applied to both surfaces of the pellet, before being sandwiched between the two electrodes of sample holder. The magnetic behavior of $NiFe_2O_4$ was studied using a vibrating sample magnetometer from Lakeshore, USA, model 7404. The cyclic voltammetry studies of $NiFe_2O_4$ electrodes were carried out using a CHI 1120A instrument.

2.3. Electrode preparation

In order to study the electrochemical properties of the materials, the electrodes were prepared by the following procedure. The active materials of $NiFe_2O_4$ (85 wt%), carbon black (10 wt%) and polytetrafluroethylene (PTFE) (5 wt%) were ground in a mortar and a few drops of N-methyl-2-pyrrolidinone (NMP) was added to form a syrup. The desired amount of syrup was then coated on graphite sheet (area of coating, 1 cm^2). The cyclic voltammetry studies of $NiFe_2O_4$ electrodes were carried out in the potential range of 0–1.0 V at various scan rates (10–200 mV s^{-1}). 1 M of $LiClO_4$ in acetonitrile was used as the electrolyte. A platinum electrode and a saturated Ag/AgCl electrode were used as counter and reference electrodes, respectively.

3. Results and discussion

3.1. Structural and morphological analysis

Fig. 1(a)–(e) shows the XRD pattern of $NiFe_2O_4$ (S1–S5) prepared by the molten salt method. The observed high intensity and sharp, well-defined peaks indicate the high purity and the high crystalline nature of spinel $NiFe_2O_4$. No impurity phase was observed in this pattern. The diffraction peaks observed at $2\theta = 30.49$, 35.87, 37.45, 43.41, 54.06, 57.57 and 63.15 correspond to the planes of (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0), respectively. These angles measured for the $NiFe_2O_4$ (S1–S5) samples, are in very good agreement with the reported values (JCPDS card No. 44-1485). The diffraction lines provide clear evidence for the formation of cubic phase tervorite and the pure inverse spinel structure of nickel ferrite. Similarly, we prepared $NiFe_2O_4$ samples at 800 °C, and the corresponding XRD pattern elucidates the presence of an α-Fe_2O_3 phase, in addition to $NiFe_2O_4$. Hence, it can be concluded that the operating temperature for the preparation of $NiFe_2O_4$ is 900 °C.

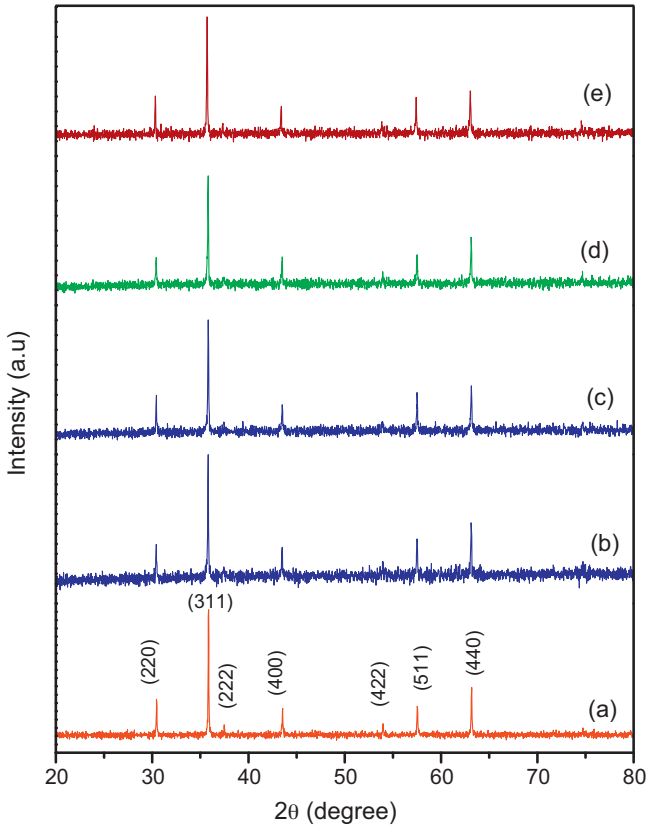

Fig. 1. XRD pattern of (a) S1, (b) S2, (c) S3, (d) S4 and (e) S5 samples of $NiFe_2O_4$ prepared at 900 °C for 3 h.

The ionic radii (r_A, r_B) and bond lengths (A–O, B–O) of spinel $NiFe_2O_4$ on tetrahedral (A) and octahedral (B) sites were calculated using the lattice parameters from the XRD pattern. The relation (Standely's equations) used for the finding the ionic radii (r_A, r_B) and bond lengths are as follows [25]:

$$\text{A–O} = \left(u - \frac{1}{4}\right) a\sqrt{3} \quad (1)$$

$$\text{B–O} = \left(\frac{5}{8} - u\right) \quad (2)$$

$$r_A = \left(u - \frac{1}{4}\right) a\sqrt{3} - r(O^{-2}) \quad (3)$$

$$r_B = \left(\frac{5}{8} - u\right) a - r(O^{-2}), \quad (4)$$

where 'u' is the oxygen ion parameter ($u = 0.381$ for $NiFe_2O_4$), 'a' is the lattice constant, and $r(O^{-2})$ is the radius of oxygen [26]. The calculated XRD parameters, such as lattice constant, grain size, X-ray density, ionic radii (r_A, r_B), and bond lengths (A–O, B–O) are given in Table 1. It can be seen that the obtained structural parameters vary with the change in the weight ratios of NaCl and the KCl flux. However, the values are well within the range for all these cases. Among the studied systems, the lattice constant (8.3431 Å) of S4 (1:3) is in agreement with the reported values (8.339 Å) [27]. Similarly, the calculated ionic radii ($r_A = 0.5430$ Å, $r_B = 0.6857$ Å) and bond lengths (A–O = 1.8930 Å, B–O = 2.0357 Å) of $NiFe_2O_4$ coincide well with the theoretical values [28]. The intensity ratio (I_{220}/I_{222}) enumerates the cation distribution of $NiFe_2O_4$ and the calculated values are given in Table 1. The intensity of (2 2 0) and (2 2 2) planes depends on the cation distribution in the tetrahedral (A) and octa-