Synthesis and Application of Inverse Spinel NiFe2O4 Produced by EDTA-citrate Method: Structural, Vibrational, Magnetic, and Electrochemical Properties

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Synthesis and application of inverse spinel NiFe$_2$O$_4$ produced by EDTA-citrate method: structural, vibrational, magnetic, and electrochemical properties

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Abstract

In this paper we studied the production of single-phase NiFe$_2$O$_4$ powders synthesized by the complexation method combining EDTA-citrate. The structural, optical, magnetic, and electrochemical properties of were studied as a function of the synthesis pH. Powders obtained with pH 9 showed larger crystallite sizes (73 nm) in comparison to those produced with pH 3 (21 nm). The band gap energy was found to be inversely proportional to the crystal size (1.85 and 2.0 eV for powders with crystallites of 73 nm and 21 nm, respectively). The synthesized materials presented an inverse spinel crystalline structure. The samples obtained at higher pH conditions were found to be fully magnetic saturated with a saturation magnetization of 50.5 emu g$^{-1}$, while that synthesized at pH 3 is unsaturated with a maximum measured magnetization of 48.4 emu g$^{-1}$. Cyclic voltammetry and charge-discharge curves indicate a battery-type behavior, with an better performance for the material obtained at pH 9 (65 C g$^{-1}$ at a specific current of 3 A g$^{-1}$). The remarkable performance of the associated with its by microstructural characteristics (particle size, particle agglomeration and porosity). This work offers an alternative synthesis route for obtaining spinel ferrites for magnetic and electrochemical applications.

Keywords: Powder synthesis; EDTA-Citrate method; Electrochemical performance; Battery-type electrodes.

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1. **Introduction**

The production of nanoscale ceramic materials promises to lead the industry to a new standard capable of revolutionizing modern science [1]. Ferrites are ferrimagnetic ceramics [2, 3] composed of a mixture of 3d transition ions which have a general molecular formula \((X_{1-z}Fe_z)[X_2Fe_{2-z}]O_4\), where \(z\) is the degree of inversion. Ferrites crystallize in the spinel-type structure with tetrahedral (A-sites, cations in parentheses) and octahedral (B-sites, cations in brackets) sites occupied by divalent (X) and trivalent (Fe) cations [4].

Depending on the distribution of cations in the A and B sites, ferrites are classified as normal, inverse or partially inverse. The degree of spinel inversion depends upon the synthesis method and the synthesis parameters such as pH of the solution, temperature, heating rate, temperature and time of calcination, surfactant, chelating agents, and ratio of cations, among others [5, 6]. The magnetic properties of these oxides depend also on their degree of inversion [7, 8].

Spinels with \(X^{2+}\) and \(Fe^{3+}\) magnetic cations have distinct properties such as high saturation magnetization, high ferrimagnetic transition temperature, high magnetic permeability, and a wide range of coercivity fields. The electrochemical performance of spinels ferrites has also been studied for their applications as supercapacitors [9] and battery-type electrodes [10]. These materials have also been studied as photocatalysts for water splitting [5, 11–13], gas sensors [14, 15], electrocatalysis for the oxygen evolution reaction (OER) [16, 17], degradation of organic compounds by heterogeneous Photo-Fenton reactions [18–22], and biomedical applications [23, 24].

Within the spinel family of oxides, nickel ferrite \((NiFe_2O_4)\) has attracted considerable scientific interest due to its physical and chemical properties allowing these materials to be applied in electrochemical devices [10, 16, 25]. Besides, nickel ferrites have a band gap in the visible light region [26] due to the electronic excitation of the O-2p level (valence band) to the Fe-3d level (conduction band) [27], which is an interesting property for application in photocatalysis. Nickel ferrites may crystallize in an inverse spinel structure [28], however, the literature also reports several examples where Ni cations occupy both tetrahedral and octahedral sites [8, 10, 29–31], leading to a partial inverse spinel.

Several synthesis methodologies have already been used to produce ferrites including co-precipitation [14, 32], proteic sol-gel [10], hydrothermal [33–35],
solvothermal [36–38], conventional sol-gel [29], combustion [39], solid state reaction [40], solution blow spinning [16], and complexation [41]. The sol-gel process is one of the most accepted methods for producing ferrites where chelates are formed through a complexation reaction between multivalent ions and citric acid, a multidentate ligand [30, 42]. However, the possibility of using transition metals with different oxidation states to produce a wide variety of ceramic materials requires a versatile complexing agent such as ethylenediamine tetra-acetic acid (EDTA). EDTA can be combined with metal ions in the proportion 1:1, regardless of the cation charge, the exception standing for alkali metals that do not chelate with EDTA. This molecule has six donor groups of electron pairs for bonds with metal ions, EDTA has four carboxylic groups and two amino groups, thus, it is classified as a hexadentate ligand [42].

The prerogative to use the EDTA-citrate method in this study is that it allows the formation of a more stable chelating complex than that obtained by using only EDTA or citric acid [43]. Citric acid acts as an auxiliary complexing agent in this synthesis process [44]. This methodology allows adjusting parameters such as heating time, heating rate, calcination temperature, initial pH of the synthesis, and the stoichiometric ratio chelating/cations, thus reaching nanoparticles with different morphologies, high purity, high degree of crystallinity and precise stoichiometric control [45–48]. In this synthesis process, the ions in solution are organized at an atomic level within an organic matrix formed by complexing agents [49]. This allows the crystallization process to occur at lower temperatures, resulting in particles with nanometric sizes [43].

In this work, we studied the production of inverse spinel-type NiFe$_2$O$_4$ nanoparticles ($Z = 1$) by using the EDTA-citrate complexation method under acid (pH = 3) and basic (pH = 9) conditions. The pH influence on the morphological, optical, magnetic, and electrochemical properties of nickel ferrites was investigated using several materials characterization techniques. To the best of our knowledge, this is the first report on the practical investigation of the relation between NiFe$_2$O$_4$ physico-chemical properties and the pH of the EDTA-Citrate route of production.

2. Materials and Methods

2.1 Synthesis of nickel ferrites

Nickel ferrites (NiFe$_2$O$_4$) were synthesized by the combined EDTA-citrate complexation method [46, 50] using Ni(NO$_3$)$_2$·6H$_2$O (98%, Sigma Aldrich), Fe(NO$_3$)$_3$·9H$_2$O (98%, Sigma Aldrich), EDTA acid (C$_{10}$H$_{16}$N$_2$O$_8$, 99.4%, Synth),
ammonium hydroxide (NH₄OH, 28%, CRQ), citric acid (C₂H₄O₂, 99.5%, Synth), and nitric acid (HNO₃, 70%, Synth) as starting materials. Initially, 7.56 g of EDTA was dissolved in 76 ml of NH₄OH at 313 K. Then, 2.53 g of Ni(NO₃)₂·6H₂O and 6.96 g of Fe(NO₃)₃·9H₂O were added to the solution. The mixture was heated up to 313 K and further stirred until thoroughly dissolve and homogenize the solution, which took 15 minutes. Afterwards, 7.41 g of citric acid was added, and the resulting solution was warmed up to 353 K and kept under stirring. NH₄OH and HNO₃ were used to adjust the initial pH (3 or 9). The volume of the solution decreased and the viscosity increased until a dark brown gel was formed, with no visible precipitate or turbidity. Finally, the obtained gel was pre-calcined in air at 503 K for 3 h. Then, it was subsequently calcined in air at 873 K for 6 h using a heating rate of 10 °C.min⁻¹.

2.2 Microstructural Characterization

The crystalline structure of samples was studied by X-ray diffraction (Shimadzu, XRD-7000) at room temperature using Cu-Kα radiation (λ = 1.5406 Å). The data were collected at a rate of 1 °/min, with a step size of 0.02 °, in the angular range 2θ = 10-80 °. Lattice parameters were obtained by the Rietveld refinement method using the Total Pattern Analysis Solution software (TOPAS, version 4.2, Bruker). The powder morphology was inspected by field emission scanning electron microscopy (FESEM, Carl Zeiss, model Supra 35-VP).

2.3 Vibrational Characterization

Raman spectra were recorded at room temperature using a laser with a wavelength of 532 nm as the excitation source. Data were recorded in the frequency range of 100-1000 cm⁻¹. The laser interacting with the sample was diminished to 1 mW to avoid overheating. We used an acquisition time of 20 s and an accumulation of 30 (Horiba, model HR-Evolution).

UV-vis diffuse reflectance spectra (UV–vis DRS) were recorded at 300 K in a UV-Vis NIR spectrometer (Cary, model 5G) in the range of 200-800 nm. Barium sulfate (BaSO₄) was used as a reference sample.

2.4 Mössbauer spectroscopy and magnetic characterization

The ⁵⁷Fe Mössbauer spectra were recorded in the transmission mode, at 12 K, with a ⁵⁷Co:Rh source, using a spectrometer from SEECo equipped with a He closed
cycle cryostat from Janis. The isomer shift (IS) values are related to α-Fe at 300 K. The Mössbauer spectra were fit using the software Normos-95.

The magnetic measurements were performed at 5 K using a Physical Properties Measurements System (PPMS) equipped with a vibrating sample magnetometer (Quantum Design, model Dynacool).

2.5 Electrochemical characterization

Cyclic voltammetry (CV), charge-discharge galvanostatic (GCD) and impedance spectroscopy (EIS) measurements were carried out using a three-electrode setup (in a 3 M KOH electrolyte) on a PGSTAT204 (Metrohm Autolab) with FRA32M module. Ag/AgCl and Ni foam were used as reference and counter electrodes, respectively. The working electrode was prepared using a homogeneous slurry of NiFe2O4 with carbon black acting as a conductive additive and polytetrafluoroethylene acting as a binder in an isopropyl alcohol solution with a weight ratio of 80:10:10, respectively. The prepared slurry was sonicated for about 30 min at room temperature. Then, inks containing each powder were drop-casted on Ni foams (1 cm2) and further heated at 373 K for 12 h in a vacuum oven. The mass loading of the electrode material on Ni foam was about 2.5 mg cm\(^{-2}\). CV was performed between 0-0.5 V vs. Ag/AgCl at different scan rates (from 5 to 100 mV s\(^{-1}\)) and, for comparison, blank Ni foam was also studied under the same conditions. GCD was conducted in a potential window of 0-0.45 V at different specific densities (from 1 to 10 A g\(^{-1}\)) and EIS was carried out under open circuit potential (OCP) in the frequency range 0.01-100 kHz using a voltage amplitude of 5 mV.

3. Results and Discussion

3.1 Microstructural characterization

3.1.1 X-ray Diffraction

The calcined nickel ferrite powders (NiFe\(_2\)O\(_4\)) obtained using different pH values were analyzed by X-ray diffraction (XRD) with Rietveld refinement analysis. The XRD patterns, shown in Fig. 1, revealed that all peaks \{\(111\), (220), (311), (222), (400), (422), (511), (440), (620), (533), (622)\} belong to the cubic phase NiFe\(_2\)O\(_4\) with lattice parameter \(a = 8.337 \, \text{Å}\), (JCPDS card n° 86-2267, space group Fd-3m (227)) [10, 16]. The samples did not show secondary phases such as α-Fe2O3 or NiO,
demonstrating the effectiveness of the EDTA-Citrate method to synthesize single-phase nickel ferrite powders. The lattice parameters, crystallite sizes and Rietveld Refinement agreement factors are presented in Table 1. The lattice parameters of the NiFe$_2$O$_4$ phase obtained in acidic (a = 8.334(8)) and basic media (a = 8.333(9)) are in good accordance with those reported in the JCPDS card n° 86-2267. $\chi^2 \leq 2$ suggested a good agreement between the experimental data and the proposed fitting structure profile.

Fig. 1: Refined XRD patterns of NiFe$_2$O$_4$ nanoparticles.
The average crystallite size, cell parameter, volume, and density of the samples are listed in Table 1 together with the data obtained from the standard card, JPCDS 86-2267. It was found that with increasing the initial pH of the synthesis solution also increases the crystallite size while the cell parameter remains nearly constant [28].

Table 1: Structural parameters of NiFe₂O₄ powders obtained by Rietveld refinement.

| Sample             | Crystallite size (nm) | Lattice parameter (Å) | Density (g/cc) | V (Å³) | Agreement factors |
|--------------------|-----------------------|-----------------------|----------------|--------|------------------|
|                    |                       |                       |                |        | Rwp (%) | Rexp (%) | χ²    |
| pH 3               | 21.6                  | 8.334(8)              | 5.377          | 579.01 | 28.08    | 24.81    | 1.13  |
| pH 9               | 73.8                  | 8.333(9)              | 5.379          | 578.82 | 28.24    | 25.18    | 1.12  |
| Standard card, 86-2267 | -                     | 8.333(7)              | 5.379          | 578.78 | -        | -        | -     |

The synthesis method we used proved to allow a better organization of cations in organometallic complexes, as a result of that high purity nanocrystalline materials are expected to be produced, even when the precursors are thermally treated at low temperatures [44] in comparison to other synthetic approaches that use higher temperatures to obtain NiFe₂O₄ [10, 29, 30, 51]. The high degree of chelation of the metallic ions in the solution is thought to be responsible for the good homogeneity of metallic constituents in the precursors, which leads to the fore mentioned result [50].

3.1.2 Raman spectroscopy

Raman spectra of NiFe₂O₄ samples are shown in Fig. 2. The spinel-type structure of the space group Fd - 3m has five active Raman modes, A₁g + E₉ + 3T₂g [52]. These active modes can be used to distinguish the tetrahedral and octahedral sites [53]. The Raman bands for NiFe₂O₄ have as a peculiar characteristic the presence of a shoulder on the left side of the active Raman modes between 600 and 800 cm⁻¹ revealed through the curve deconvolution (Fig. 2) [10, 54].
Fig. 2: Room temperature Raman spectra of NiFe$_2$O$_4$ nanoparticles synthesized with (a) pH 3 and (b) pH 9.
The nature of the tetrahedral sites is revealed in the $A_{1g}$ mode which occurs due to the symmetrical elongation of the oxygen atoms in the metal-oxygen (M-O) bonds. The $E_g$ mode is a consequence of the symmetrical flexion of oxygen atoms in relation to metal ions. $T_{2g}$ mode (1) is attributed to the translational movement of the tetrahedron (metallic ion in the tetrahedral place together with four oxygen atoms). The $T_{2g}$ (2) and $T_{2g}$ (3) modes correspond to the vibrations of the octahedral group, where asymmetric oxygen flexion and asymmetric Fe/Ni-O elongation are attributed to $T_{2g}$ (3) [52]. The Raman peaks over the region of 660 – 720 cm$^{-1}$ reflect the nature of the tetrahedra in ferrites, while those in the 460 – 640 cm$^{-1}$ region reflect the nature of the octahedra [55]. The 480 cm$^{-1}$ and 654 cm$^{-1}$ positions in the Raman spectra are attributed to Ni$^{2+}$ ions in the octahedral and tetrahedral sites, respectively [5,7], indicating that the synthesized spinel presents inversion, a fact corroborated with the results of Mossbauer spectroscopy, because when observing the relationship between the areas of these peaks, it appears that the areas of the peaks referring to the octahedral sites are larger than the areas of the tetrahedral sites. The Raman spectra are of good quality and match with those reported earlier [52, 56].

3.1.3 Field emission scanning electron microscopy

The morphology of the NiFe$_2$O$_4$ powders was inspected by FESEM. Fig. 3 (pH 3 (a-c) and pH 9 (d-f)) reveals that the synthesized samples consist of agglomerates of undefined particle shapes and different sizes, which is typical of a heterogeneous nucleation process [46]. The porous structure is attributed to the release of gases during the calcination process, which is mostly related to the combustion of citric acid and EDTA matrix.
Fig. 3: FESEM images of NiFe$_2$O$_4$ nanoparticles: pH 3 (a-c) and pH 9 (d-f).

These images show that individual particles are larger than crystallite (21.6 nm and 73.8 nm for samples prepared at pH 3 and 9, respectively) values obtained from Rietveld refinement of the XRD data, evidencing the polycrystalline nature of the powders. It is observed that in both pH conditions the nickel ferrite was obtained free of impurities, as confirmed by XRD patterns. Besides, the acidic condition yields lower crystal size (see Fig. 3), which can be explained by the fact that the acid pH of the solution leads to a delay in the complexation process between metal ion and EDTA that is caused by the H+ competition with the metal ions for EDTA [44].
It is known that at high pH, the OH\(^-\) competes with EDTA for metal ions which may precipitate in the form of metal hydroxides or form non-reactive hydroxide complexes, and the use of citric acid as an auxiliary complexing agent serves to stabilize the complexation process [44]. However, unlike what occurred in acidic pH, the basic pH causes an increase in the size of crystals and agglomerates since during the calcination process there is a smaller amount of volatile products, which provided a faster evaporation and consequently crystallization and growth of the crystals were favored.

### 3.2 Optical properties

The optical band gap energy of the nickel ferrite nanoparticles is shown in Fig. 4. It is reported in the literature that the optical band gap of semiconductor oxides can be calculated by the method proposed by Wood & Tauc [57], as shown in Equation (1):

\[
\alpha (hv) = k. (hv - E_{gap})^n
\]  

Where \(\alpha\) is the absorbance, \(hv\) is the photon energy, \(k\) is the absorption constant that depends on the properties of the material, \(E_{gap}\) is the range of the optical band, and "\(n\)" represents the nature of the electronic transition in the material (0.5 or 2 for allowed direct or allowed indirect transitions). Nickel ferrite is reported as a semiconductor that has a direct allowed electronic transition [27, 39, 58–60], hence the optical band gap for the absorption peak can be obtained by extrapolating the linear portion of the plot \((\alpha hv)^2\) vs. \(hv\) to zero [21, 58] as shown in Fig. 4 for samples produced at pH 3 and 9.
Fig. 4: UV-vis diffuse reflectance spectra acquired at room temperature for NiFe$_2$O$_4$ powders obtained in acid (pH=3) and basic media (pH=9).

The band gap energy values of 1.85 and 2.0 eV were found for powders obtained at pH 9 and 3, respectively. These results follow the trend reported by Dhiman et al. [58]. They prepared nickel ferrite by the hydrothermal method and observed the lowest band gap value for the largest crystallite size. Kalam et al. [21] synthesized cobalt ferrite by the modified solvothermal method and measured band gap values of 2.5, 2.6 and 2.65 eV for nanoparticles with sizes of 15 nm, 12.38 nm and 11.85 nm. Accordingly to those authors, the band gap is affected by several factors, such as the crystallite size, lattice parameter, presence of impurities, and degree of disorder of the crystalline structure [31, 39, 58, 59]. In the light of our XRD and SEM analysis, we can conclude that the trend related to the the band gap of the herein synthesized nickel ferrites is due to their difference in the crystallite size.

3.3 Mössbauer spectroscopy study
The spectra at 12 K were recorded with a maximum velocity of 12 mm/s to clearly show all the possible Fe-oxide phases. The experimental spectrum is fit to two sextets (each spectrum has six peaks), each sextet is ascribed to a Fe$^{3+}$ in tetrahedral (A-site) and octahedral (B-site) oxygen coordinated Fe sites in NiFe$_2$O$_4$, as shown in Fig. 5.

![Mössbauer spectra](image)

Fig. 5: $^{57}$Fe Mössbauer spectra recorded at 12 K for samples prepared at pH = 3 and pH = 9. The empty circles are the experimental data, the blue and black lines are the sextets ascribed to Fe at B and A sites, respectively.

Each sextet is due to a Zeeman interaction, i.e. when the $^{57}$Fe nuclear spin moment ($I$) is under a magnetic field, the ground ($I_g = 1/2$) and excited ($I_e = 3/2$) degenerate nuclear levels split into several states. The transitions between the split excited and ground levels lead to a six quantum transitions, these events are represented by a sextet and the velocity distance between the first and sixth peaks is proportional to the magnetic field. In absence of an external magnetic field, the internal effective magnetic field (Bhf) is due to the Fe own partially filled d-electron and s-electrons. The isomer shift (IS) is due to a monopole interaction between the nuclear charge and the s-electron density overlapping the nuclear volume. The IS is sensitive to the Fe-O bonding and to the available volume occupied by the $^{57}$Fe ion, the interaction shifts the spectrum along the velocity scale. Finally, the quadrupole splitting (QS) is due to the
electric interaction between the nuclear electric quadrupole moment and the electric gradient field due to the Fe valence electrons and ligands. As shown in Fig. 5, there are not additional phases contributing to the spectrum, indicating that the method used to prepare the samples allows synthesizing a high purity sample.

Table 2 presents the hyperfine parameters obtained from the fits, the IS of both sextets are 0.25 mm/s, 0.36 mm/s and are ascribed to a high spin Fe$^{3+}$ ($S = 5/2$), as shown by Gütlich et al. [61]. Greenwood showed [62] that the Bhf and IS for Fe in A-site are smaller than that at B-site. Therefore, the sextet that has the smaller Bhf (and IS) of $\approx 49$ T ($\approx 0.25$ mm/s) is related to Fe in A-site. Furthermore, from the relative absorption areas (RAA) of each sextet one can determine the inversion degree of the spinel structure.

Table 2- Mössbauer parameters obtained from fits using the software Normos90. IS and QS in mm/s, Bhf in Tesla, and RAA in %.

| Sample | Sextet 1 (A-site) |  |  |  | Sextet 2 (B-site) |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  | IS | Bhf | QS | RAA | IS | Bhf | QS | RAA |
| pH = 3 | 0.254 | 50.7 | 0.0020 | 49.7 | 0.366 | 55.1 | 0.0110 | 50.3 |
| pH = 9 | 0.255 | 51.0 | 0.0085 | 49.6 | 0.361 | 54.9 | 0.0103 | 50.4 |

The chemical formula unit of Ni ferrite can be written as: (Ni$_{1-z}$Fe$_z$)$_2$[Ni$_z$Fe$_{2-z}$]O$_4$, where $z$ is the degree of inversion, which is defined as the fraction of Fe ions occupying the tetrahedral sites. In the above formula, cations enclosed in parenthesis and squared brackets are Fe$^{3+}$ in A and B sites, respectively. Ferrites are normal spinel when $z=0$, inverted when $z=1$, and partially inverted when $0<z<1$. The inversion degree can be calculated from the ratio of RAA for sextet due to Fe in A and B sites, i.e. RAA(A)/RAA(B)=$(f_A/f_B)z/(2-z)$, where $f_B/f_A=0.99$ is the ratio of recoilless fractions at low temperature for Fe$^{3+}$ in B and A sites [63]. From the RAA values shown in Table 2, one can obtain $z$ values of 0.995 and 0.980 for the sample prepared at pH=3 and pH=9, respectively. Therefore, their chemical formula units will be of (Ni$_{0.005}$Fe$_{0.995}$)[Ni$_{0.995}$Fe$_{1.005}$]O$_4$ and (Ni$_{0.020}$Fe$_{0.980}$)[Ni$_{0.980}$Fe$_{1.02}$]O$_4$. Therefore, both samples are mostly inverse spinel Ni ferrites. The hyperfine parameters found for the Fe in A and B sites are similar to those reported for NiFe$_2$O$_4$ samples.
3.4 Magnetic study

The isothermal M-H measurements at 5 K are shown in Fig. 6. Samples are subjected to a maximum magnetic field of 10 Tesla. The data indicate that the sample prepared with pH = 9 is fully magnetic saturated, meanwhile the sample prepared at pH = 3 does not saturate, and the magnetic hysteresis confirms the prepared ferrite material is magnetically ordered [66].

![Fig. 6](image.png)

**Fig. 6:** a) M-H measurements recorded at 5 K. b) Enlarged view of the M-H loop.

The remanence magnetization (Mr) and coercivity field (Hc) are obtained directly from the Fig. 6 (B). These values are 17.9 emu/g (233 Oe) and 16.5 emu/g (419 Oe) for samples prepared with pH=9 and pH=3, respectively. It is noticed that the ascending and descending curves merge at a magnetic field larger than 3 T. Thus, the saturation magnetization ($M_s$) and magnetocrystalline anisotropy ($K_1$) can be determined by fitting the high field data ($H > 8$ T) using the law of approach to saturation (LAS) (Fig. 7) [67] given by the Equation (2):
Where: $4/15$ is a coefficient that holds for samples with uniaxial magnetic anisotropy and $K_1$ is the magnetocrystalline anisotropy. The obtained $M_s$ values are 50.5 emu/g and 48.5 emu/g, and the $K_1$ values are $3.39 \times 10^5$ J/m$^3$ and $7.77 \times 10^5$ J/m$^3$ for samples prepared with pH=9 and pH=3, respectively. The density of NiFe$_2$O$_4$ is 5.38 g/cc [68]. The ratios $M_r/M_s$ are 0.340 (pH=3) and 0.354 (pH=9), these values are smaller than the expected for a sample with cubic magnetocrystalline anisotropy (of $M_r/M_s \sim 0.8$) and a bit smaller than $M_r/M_s \sim 0.5$ for a sample with uniaxial magnetocrystalline anisotropy. Thus, the choice of uniaxial magnetic anisotropy is in agreement with the $M_r/M_s$ values. The $K_1$ values are an order of magnitude larger than the one expected for a polycrystalline sample, these results may be ascribed to induced surface anisotropy due to their small particle size [68].

$$M = M_s \left[ 1 - \frac{4}{15} \left( \frac{K_1}{M_s H} \right)^2 \right]$$ (2)

Fig. 7: $M$-$H^2$ curves and their fits to the law to the approach to saturation.
NiFe$_2$O$_4$ is ferrimagnetic, it has two magnetic sublattices formed by the octahedral and tetrahedral sites, in each sublattice the magnetic moments are aligned ferromagnetically. Furthermore, there is an antiferromagnetic interaction between these magnetic sublattices leading to an effective magnetic moment, this moment is the difference between the magnetic moments from both sublattices. Since the inversion degree $z$ is close to 1, mostly all Ni$^{2+}$ are located in octahedral sites and nearly half of the Fe$^{3+}$ cations are also located in the octahedral sites. Thus, if we consider the high spin moments (in units of Bohr magnetons) for Ni and Fe as $S$(Ni$^{2+}$) = 2$\mu_B$ and $S$(Fe$^{3+}$) = 5$\mu_B$, and from the chemical formula units obtained from the Mössbauer results we will get theoretical values of saturation magnetization of 50.5 emu/g and 48.4 emu/g, which are in close agreement with the Ms obtained by using the LAS equation.

3.5 Electrochemical characterization

The electrochemical assessment of NiFe$_2$O$_4$ nanoparticles has been probed through CV, GCD and electrical impedance spectroscopy (EIS) measurements in 3 M KOH electrolyte at room temperature. The CV curves were recorded at different scan rates (5-100 mV s$^{-1}$) in a potential window of 0-0.5 V vs. Ag/AgCl (Fig. 8 a,b). The CV curves of all samples show clearly separated peaks, which are related to oxidation and reduction processes of reactions occurring on the surface of NiFe$_2$O$_4$ based electrodes, which implies that in our samples a faradic charge storage mechanism is predominant [9, 69]. With increasing the scan rate the anodic and the cathodic peaks shift in the direction of +ve and –ve potential regions, respectively, characterizing a rapid diffusion of ions in the KOH electrolyte [70]. Redox peaks attributed to the dispersal of electrolyte in the materials suggest that NiFe$_2$O$_4$ based electrodes are showing battery-like behavior [71, 72]. This battery-like behavior and the surface faradaic redox reaction mechanism can be attributed to the redox transitions of Ni$^{2+}$/Ni$^{3+}$ and Fe$^{2+}$/Fe$^{3+}$, which may merge because of the similar redox potential [73, 74] (Fig. 8 a), or not, as shown by the two reduction peaks of NiFe$_2$O$_4$ prepared at pH 3, as previously reported in the literature [75, 76]. The redox processes take place in two sequential steps in an alkaline medium (3M KOH), as shown in Equation (3) [77, 78]:

\[
\text{NiFe}_2\text{O}_4 + 2e^- + 2H^+ \rightarrow \text{NiFe}_2\text{O}_4 + 3\text{H}_2\text{O}
\]
NiFe$_2$O$_4$ + OH$^-$ + H$_2$O $\leftrightarrow$ NiOOH + 2FeOOH + e$^-$ \hspace{1cm} (3)

For comparison, a blank Ni foam (1 cm$^2$) was also studied at a constant scan rate of 100 mV s$^{-1}$ (Fig. 8 c). As can be seen in Fig. 8 (c), the area under the CV curve of the blank Ni foam is very small only compared to those of the NiFe$_2$O$_4$ based electrode prepared at pH 3, showing that Ni foam does not influence the electrochemical performance.

Fig. 8: CV curves of (a) pH 9 and (b) pH 3 NiFe$_2$O$_4$ based-electrodes at different scan rates in 3 M KOH, (c) Comparison of CV curves recorded at 100 mV s$^{-1}$, (d) Plots of $i_p$ versus $v^{1/2}$ with scan rates varied from 0.5 to 100 mV s$^{-1}$.

Fig. 8d shows the near-linear relationship between peak current ($i_p$) $vs$ square root of scan rate ($v^{1/2}$) extracted from the CV plots. The slope ($b = i_p/v^{1/2}$) values are 266 and 158 (anodic currents) and -251 and -157 (cathodic currents) for samples synthesized with pH 9 and 3, respectively. These values indicate diffusion rates with surface redox reactions characteristics of charge storage processes that are controlled by diffusion, confirming the battery-like behavior [79]. Besides, the rates of reversible surface redox
reactions for the NiFe$_2$O$_4$ based-electrode synthesized with pH 9 are faster than those for the Ni ferrite made with pH 3.

Figs. 9 (a e b) display the GCD curves recorded at different specific currents (1 to 10 A g$^{-1}$) in a potential window of 0-0.6 V vs. Ag/AgCl. The GCD curves of all NiFe$_2$O$_4$ based-electrodes are typical of battery-like electrodes [71, 72, 80]. For this reason, the specific capacities ($Q_s$) were calculated by using the following Equation (4):

$$Q_s = \frac{i \Delta t}{m}$$

(4)

where $i$ is the discharge current (A), $\Delta t$ is the discharge time (s) and $m$ is the mass of the active material (g) [79, 81]. As shown by the GCD curves, the electrode made with powders synthesized with pH 9 has significantly higher charging and discharging times in comparison to the electrode derived from the powder obtained with pH 3. Fig. 9 (c) shows the specific capacity of the electrodes. The superior discharge time of the NiFe$_2$O$_4$ based-electrode prepared at pH 9 becomes clearly prominent as the specific current increases (24, 49, 65, 58, and 51 C g$^{-1}$ at specific currents of 0.5, 1, 3, 5, and 10 A g$^{-1}$, respectively) in comparison to those of the NiFe$_2$O$_4$ based-electrode prepared at pH 3 (4.3, 2.9, 3.3, 3.5, and 5 C g$^{-1}$ at specific currents of 0.5, 1, 3, 5, and 10 A g$^{-1}$, respectively) at the same specific currents.
Fig. 9: CGD curves of (a) pH 9, (b) pH 3 and (c) specific capacity at specific currents ranging from 1 to 10 A g\(^{-1}\), (d) Nyquist plots of electrodes with inset showing the high frequency region.

Interestingly, the enhanced electrochemical performance of the electrode made with the powder obtained at pH 9 indicates that its morphological characteristics have contributed positively to enhance the charge storage mechanism. This can be explained by the addition of ammonium hydroxide to obtain the NiFe\(_2\)O\(_4\) particles at pH 9. It promotes reactions of combination of organic compounds with hydrogen ions that are eliminated during the calcination process, leading to the most porous microstructure. In this way, the microstructure of the electrode obtained at pH 9 acts as channels favoring the wettability of the electrode by the electrolyte [17]. It ensures that more intermediate species (OH\(^{-}\)) reach as many active sites as possible [82]. Besides, despite of the proximity between the ESR values of the electrodes (Fig. 9d), their morphological characteristics (particle size, agglomeration and porosity) play a vital role on limiting their electrical conductivities, once grain boundary density acts as spreaders of charge carriers [83].
4. Conclusions

Nickel ferrites were successfully synthesized by the combined EDTA-Citrate complexation method. The effect of the synthesis pH on the powder crystallite size was assessed by Rietveld refinement analysis. Raman spectroscopy was performed to assess the distribution of Ni and Fe cations at the tetrahedral and octahedral sites. The analysis of UV–vis DRS showed that the samples have band gap energy values of 1.85-2.0 eV. Mössbauer spectroscopy reveals that both samples are inverse spinel-type ferrites. Magnetic data indicate that the sample prepared with pH = 9 is fully magnetically saturated. Cyclic voltammetry and charge-discharge curves indicate improved performance for the sample synthesized at pH 9. The enhanced electrochemical performance of NiFe₂O₄ synthesized at pH 9 is due to an increase in pharyngeal reactions driven by the difference in porosity on the surface of the sample agglomerates and the boundary limits of the grains responsible for a lower resistance to charge transfer, confirmed by impedance spectroscopy. The complexing method combining EDTA-Citrate offers an alternative for the production of nickel ferrites for magnetic and electrochemical applications.

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