Temperature and pH effect on reaction mechanism and particle size of nanostructured Co₃O₄ thin films obtained by sol-gel/dip-coating

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Abstract
This article reports the preparation of Co₃O₄ phase films by sol-gel. Initially, the precursor solution was prepared by the reaction of cobalt acetate tetrahydrate with methanol. Clean glass substrates were dipped into the solution for 4 times with a speed of dipping of 2 cm per minute. Afterwards, the films deposited were thermally treated at 500 °C to produce the Co₃O₄ phase. FTIR, UV-Vis and XRD techniques were used to analyze the effects of temperature and pH on reaction carried out on the precursor solution. While the microstructural characterization of thermally treated films was performed through XRD and SEM techniques. In parallel, were studied the thermal decompositions of both Co(CH₃COO)₂ phase as precursor solution S2 powders using TGA-DTA techniques. The results show that Co₃(CH₃COO)₂OH phase was identified as the precursor to the Co₃O₄ phase. It was observed that the synthesis temperature promotes the formation reaction of Co(CH₃COO)₂OH. While the decrease in pH by addition of citric acid had 2 effects. The first was to delay the formation reaction, and the second was to decrease the particle size of phase Co₃O₄ < 10 nm.

1. Introduction

The recent techno-revolution ‘industry 4.0’ or ‘smart factory’ is the emerging technologies era; that are radically changing humanity’s way of life. Industrial processes are characterized by digital transformation through the integration of automation, robotics, the Internet of All Things (IoT) and data analysis and exchanges. The high impact of intelligent systems will require an increase in connectivity and energy demand. Recent generation in green energy is still not enough and does not ensure stable energy production at the industrial level, especially in high powered applications, due to renewable sources are variable, unpredictable, and intermittent [1]. Thus, energy storage becomes relevant, because it can ensure and regulate, the supply of energy in industrial processes.

Batteries and supercapacitors have been the most widely used storage devices to ensure the mobility and Internet connection of personal devices. They have evolved into solid-state devices, improving safety aspects and mechanical and electrical properties [2]. In this context, fuel cells and dielectric capacitors have emerged as devices of interest to store energy. Dielectric capacitors, unlike electrolytic capacitors, have a higher power density [3], a feature that could be of interest in both automotive and drone industries. Thus, new areas of opportunity are opened in research and development, in the topic of energy storage to increase energy density in dielectric capacitors whose future projection is towards the high energy density of portable and consumable storage [4].

Thus, disruptive technologies such as nanotechnology are proposing innovative solutions that significantly change the current context in power generation, storage, and savings. Increasing energy density in dielectric capacitors could be achieved with nanomaterials with high dielectric constant. Specifically, the Co₃O₄ phase is commonly used as an electrode in electrolytic capacitors and lithium batteries [5]. It could be used as dielectric in parallel plate capacitors to evaluate its dielectric property as a nanostructured phase (<100 nm) [6]. Nanomaterials synthesis requires knowledge of the nature of the manufacturing process and control of
Table 1. Methods of synthesis to obtain Co₃O₄.

| Reference | Synthesis methods | Particle size (nm) | Morphology | Properties |
|-----------|-------------------|-------------------|------------|------------|
| [7]       | Microwave          | 24                | Nodular (high agglomeration) | Super capacitor/519Fg⁻¹ Eg = 2.43 eV |
| [8]       | Microwave          | 20–60             | Spherical | Super paramagnetic |
| [9]       | Thermal decomposition | 30–50           | Spherical | 2.02 eV. Ferromagnetic ‘semiconductor’ |
| [10]      | Chemical Precipitation | 15–55            | Spherical | K = 70 Eg = 2 Semiconductor |
| [11]      | Hydrothermal       | 15–30             | Cubes     | —          |
| [12]      | Mechanical alloyed | —                 | Nodular   | —          |
| [13]      | Reactive milling   | 5–25              | Nodular   | —          |
| [14]      | Sol-gel           | 50–100            | spherical | Eg = 3.53 eV |

Table 2. Synthesis conditions.

| Synthesis | Temperature | Citric acid (C₆H₈O₇, 99%, Aldrich) added | pH |
|-----------|-------------|------------------------------------------|----|
| S1        | Room temperature | —                                    | 7  |
| S2        | 60 °C      | —                                      | 7  |
| S3        | 60 °C      | 0.35 mmol  | 5  |

operation variables. Table 1 shows the physical and chemical processes so cobalt spinel has been synthesized and the electrical properties that derive from its morphology and particle size achieved.

The application of the Co₃O₄ phase in dielectric capacitors requires thin films whose properties have reported variations depending on the synthesis method and the deposit technique. Miquelot et al [15] show that Co₃O₄ phase synthesized by chemical methods, such as sol-gel, chemical precipitation and spray pyrolysis showed an increase in resistivity, while by using physical methods such as MOCVD (metal organic chemical vapor deposition) and ALD (atomic layer deposition) the conductivity increased.

Sol-gel is a chemical method, widely used for its ease, low cost, and generation of high purity products, which also allows the control of the structural characteristics of the final material by modifying operating parameters, such as temperature and pH. Thus, Tototzintle et al [16] reported that by means of sol-gel method and dip-coating technique; nanoparticles were generated with an average diameter of 40 nm. On the other hand, Armelao et al [17] determined particle sizes of 15 nm in films deposited by dipping the substrate into a precursor solution obtained from the reaction of Co(CH₃COO)₂ 4H₂O and CH₃OH at room temperature. The reaction mechanism of sol-gel synthesis at 60 °C of the same precursors was proposed by Vikas et al [18]. In its work, it is proposed that the product of the synthesis be CoO(OH)₂, which by heat treatment oxidizes to produce the cobalt spinel.

\[
\text{Co(CH₃COO)₂} \cdot 4\text{H₂O} + \text{CH₃OH} \rightarrow \text{CoO(OH)₂} + 2\text{CH₃COOCH₃} + 4\text{H₂O}
\]

\[
\text{CoO(OH)₂} \rightarrow \text{carbonic compounds} \xrightarrow{\Delta \text{air}} \text{Co₃O₄} + \text{H₂O}
\]

The goal of this research is to establish in detail the cobalt spinel synthesis mechanism using the sol-gel method to understand the influence of temperature and pH parameters on phase formation and microstructural characteristics, specifically about particle size. This, as the basis for future dielectric evaluation and subsequent application on energy storage devices.

2. Experimental procedure

To determine the effect of temperature and pH were prepared 3 precursor solutions from the reaction of 4 mmol of cobalt acetate tetrahydrate (Co(CH₃COO)₂ 4H₂O, 99%, Aldrich) mixed with 197 mmol of methanol (CH₃OH, 99.97%, Aldrich). The temperature and pH conditions for each solution are shown in Table 2. The mixtures were kept under stirring for 1 h in a closed reactor. After that, clean glass substrates were dipped 4 times on each solution at a speed of 2 cm per minute to obtain each film. Between each dip the films were dried at room temperature for 15 min. Subsequently, they were thermally treated at 500 °C for 1 h under oxidizing atmosphere.
A second set of solutions were prepared and dried until obtaining powders, they were analyzed to identify the products of the reaction. The S1 solution was dried at room temperature (48 h) while those of S2 and S3 solutions were dried at 60 °C for 4 h.

The tracing of the reaction was performed through UV-Vis absorption and FTIR spectroscopies. For the UV-Vis absorption analysis, a Perkin Elmer model Lambda 35 spectrometer was used. The preparation of the samples consisted of extracting an aliquot of 0.2 ml of each solution at different reaction times (0, 1, 5, 10, 15, 30, 60, 90, and 120 min) and diluting it with 50 ml of CH3OH. Each sample was immediately measured employing quartz cells and CH3OH as a blank. The FTIR analyzes were carried out in a Perkin Elmer spectrometer (model Spectrum 100) employing KBr pellet with 0.05 ml of the sol, the samples were prepared at the same reaction times as those samples monitored by UV-Vis.

The films and dried powders were characterized by x-ray diffraction (XRD). The powders were analyzed in the range of 2θ from 5 to 50° with a scanning rate of 0.3 s per step, in a Bragg Brentano configuration. While the films were analyzed by employing the grazing incidence technique to avoid the substrate signal, the scans were performed from 30 to 50° with a scanning rate of 10 s per step and incidence angle of 1°. A Bruker D8 Advanced diffractometer equipped with a copper source (Kα = 1.5406 Å), a nickel filter was employed to avoid fluorescence for both analyses.

The morphology and particle size of the films and dried powders were observed by Scanning Electron Microscopy employing a JEOL (JSM-6701F) microscope. Additionally, the films were scratched with a cutter to release the film from the substrate, in this way, the thickness could be observed and measured. In addition, thickness also was measured with a Veeco Dektak 150 surface Profilometer. The average thickness was calculated from the measurement of a set of 5 films obtained from each precursor solution.

Finally, thermogravimetric (TGA) and Differential Thermal Analysis (DTA) were carried out to determine the decomposition and oxidation temperatures of the dried powders. The measurements were performed with a Netzsch (STA2500) calorimeter in an air atmosphere with a heating rate of 10 °C min⁻¹.

3. Results and discussion

3.1. Analysis of precursor solutions

3.1.1. X-Ray diffraction of the powders

To identify the products of the sol-gel reaction, which are the starting point to the formation of the Co3O4 films, the powders and the films without thermal treatment were analyzed by XRD, the patterns are presented in figure 1. In all samples, it has been identified well-defined peaks, the highest is located around 2θ = 7.4°. These peaks were assigned to cobalt acetate hydroxide (Co3(CH3COO)2(OH)), according to the chart [00–022–0582] [19]. The crystalline structure of cobalt acetate hydroxide has not been identified and the planes are not specified in the figure. In the pattern of the powder S1 (figure 1(a)), also the presence of a small amount of the bi-hydrated cobalt acetate hydroxide (Co3(CH3COO)2(OH)2H2O) phase was observed [00–022–0583]. Concerning the diffractograms of the powders obtained from the syntheses carried out at 60 °C, S2 and S3, they also present the peaks corresponding to Co3(CH3COO)2(OH) but no other phase was identified in these samples. These results indicate that cobalt acetate is transformed into cobalt acetate hydroxide during the sol-gel reaction and that this transformation is improved by temperature.

The patterns of the films are shown in figure 1(b). A strong contribution of the amorphous substrate is observed from the very broad band ranging from 15 to 35°. In the patterns of the S2 and S3 films, it is observed a high intensity and well-defined peak at 7.4° which indicates the presence of Co3(CH3COO)2(OH). On the contrary, this reflection is broad and barely visible in the spectrum of film S1 showing that the film is low crystalline. This could be explained if the degree of transformation of the precursor during the sol-gel synthesis at room temperature (S1) and 60 °C (S2 and S3) was different. In addition, the shape of the peak observed in the pattern of the film S3, deposited from the sol obtained at 60 °C and pH = 5, also could be a sign of a certain reaction progress promoted by the citric acid.

From these results it was determined that the product of the sol-gel synthesis is the cobalt acetate hydroxide, however, temperature and pH affect reaction and crystallization processes. It is also clear that the drying process also promoted the formation of Co3(CH3COO)2(OH). To clarify the effect of temperature and pH of the sol-gel synthesis in the formation of Co3(CH3COO)2(OH), the reaction was tracked by UV-Vis and FTIR spectroscopies.

3.1.2. UV-Vis spectroscopy

Figure 2 shows the UV-Vis absorption spectra of the syntheses, the presented data correspond to the times where significant changes occurred. The spectrum enregistered at the beginning of the reaction (t = 0 min) corresponds to the precursor. It presents a peak at 520 nm associated to the Co–O plasmon (pCo–O) of cobalt
acetate tetrahydrate \[20\], and a peak at 210 nm related to the \(\sigma-\sigma^*\) transition of the C–H bond \(\langle T\sigma-\sigma^* \rangle\) from methanol, which is not evident due to its very high intensity \[21\].

The spectra of the synthesis performed at room temperature and pH \(= 7\) (S1) show the same transitions without any apparent decrease in intensity as a function of time. In particular, the spectrum corresponding to 15 min shows a negative slope which suggests the presence of colloids in the sol at that time \[22, 23\]. This slope is no longer observed at 60 min, due to the agglomeration of the precursor colloids. These results reveal that there is no precursor transformation process despite the high degree of dissolution of cobalt acetate tetrahydrate. Then, at room temperature there is not enough energy to promote the reaction between cobalt acetate and methanol.

Figure 1. XRD patterns of (a) powders and (b) films obtained from precursor solutions.

Figure 2. UV-Vis spectra of S1, S2 and S3 syntheses registered at different reaction times.
On the contrary, the spectrum of the synthesis carried out at 60°C (S2) shows important changes since the first minute of reaction. The intensity of the precursor peak (pCo–O) strongly decreases and almost disappears at 15 min of reaction. On the other hand, it appears a peak at 270 nm assigned to the n–π* transition of the carbonyl ion of the carboxylic acid (Tn–π*), this transition decreases in intensity as the reaction occurs. The formation of nanoparticles is evidenced by the negative slope of the spectra recorded since 15 min. The spectra recorded from 15 to 120 min also show the slope, the intensity of the Tσ–σ* peak remained constant and the Tn–π* signal becomes a shoulder. Patently, increasing the temperature of the reaction to 60°C promoted the transformation of the precursor and the formation of phases containing carbonyl group as well as greater production of colloidal particles.

According to the spectra of sample S3, temperature and pH promote the gradual disappearance of the pCo–O peak. The Tn–π* transition is present from 15 min and at 120 min it is still observed as a small shoulder. In addition, the colloids formation occurs after 15 min.

Figure 3 shows the tracing of the 3 syntheses from the normalized intensity of the Co–O plasmon peak corresponding to the precursor (Co(CH3COO)2·4H2O) in the UV-Vis absorption spectra. For S1 synthesis, the intensity of the peak is relatively constant indicating that the concentration of the precursor does not significantly change. The intensity of the synthesis S2 strongly decreases during the first 5 min (~ 90%), later the decrease is moderate and after 20 min it remains at values close to zero. This means that the reaction temperature promotes the transformation of the precursor, being almost complete after 20 min of reaction. As the pH of the reaction mixture is modified by the addition of the citric acid in synthesis S3, the normalized intensity gradually goes down indicating that the reaction rate is low. These results indicate that citric acid retards the reaction.

3.1.3. FTIR spectroscopy
In this section, the FTIR spectra of the 3 syntheses, recorded from 0 to 120 min, are analyzed and presented in figure 4. Only the spectra of the samples that showed significant changes are presented.

The tracing of the reaction S1 is observed in the spectra of figure 4(a). The main vibrations of the precursor (Co(CH3COO)2·4H2O), which are presented in table 3, correspond to the spectrum of the S1 synthesis at t = 0, they were identified from literature [24–27]. The highest intensity peaks at 1550 and 1422 cm⁻¹ correspond to the asymmetric stretching (νCOas) and symmetric stretching (νCOS) of the C–O bond, respectively. The distance between these vibrations (128 cm⁻¹) is smaller than that reported for free acetate ions (143 cm⁻¹ [25], 164 cm⁻¹ [24]) which indicates a bidentate coordination [26, 28]. The frequency of the asymmetric bending (δC–Has) of the C–H bond is located at 1447 cm⁻¹ while the symmetric bending (δC-Hs) appears at 1333 cm⁻¹. The symmetric bending vibration of the acetate group occurs at 679 cm⁻¹ (δCOs). In the high frequency region, a very wide band can be seen with a well-defined minimum at 3340 cm⁻¹ that corresponds to the symmetric
stretching of the OH bond (νO–Hs). Also, a low intensity, but well-defined peak is observed at 3493 cm⁻¹ which is assigned to intramolecular hydrogen bonds [25]. Sobolev et al [29] proposed a structure of cobalt acetate tetrahydrate where Co is centrosymmetric (coordination number = 6) [30] and the acetate ions are in trans position. In this structure, uncoordinated oxygen atoms form intramolecular hydrogen bonds with structural water molecules. On the other hand, the 4 structural water molecules also form intermolecular hydrogen bonds with neighboring molecules. Consequently, the bandwidth of O–H vibrations is the result of the contribution of the structural water bonds into the molecule and of the intra and intermolecular hydrogen bonds. Finally, being the precursor a specie with four structural water molecules, these form strong hydrogen bonds [31], the rotation of these water molecules is hindered in the x (Rocking H₂O), y (Wagging H₂O) and z axis (Twisting H₂O) [32]. These vibrations have been reported for Co(CH₃COO)₂·4H₂O and Co(CH₃COO)₂·2H₂O [24]. In the spectrum of Co(CH₃COO)₂·2H₂O, these vibrations occur between 2900 and 1900 cm⁻¹ (where they are called A, B, and C) and between 1000 and 600 cm⁻¹ (where they are called T, W and R H₂O). In the spectrum of the precursor the A band is wide and of low intensity and appears at 2850 cm⁻¹, the B band is located at 2350 cm⁻¹ and overlaps with the absorption of the C-O bond of the acetate molecule, while the C band is almost

| Vibration (cm⁻¹) | Intensity | Assignment     |
|-----------------|-----------|----------------|
| 621             | very weak | Rocking H₂O, R H₂O |
| 679             | medium    | CO bending, δCOs |
| 809             | very weak | Twisting H₂O, T H₂O |
| 885             | medium    | Two modes phonon H₂O, TP H₂O |
| 1027            | medium    | CH₃ rocking, ρCH₃ |
| 1333            | strong    | CH₃ symmetric bending, δC–Hs |
| 1422            | strong    | CO symmetric stretching, νCOas |
| 1447            | medium    | CH₃ asymmetric bending, δC–Has |
| 1550            | very strong | CO asymmetric stretching, νCOas |
| 2350            | weak      | B band, water molecule |
| 2850            | weak      | A band, water molecule |
| 3340            | strong    | OH symmetric stretching, νOHs |
| 3493            | weak      | intramolecular H bonding |

Figure 4. FTIR spectra of the S1, S2 and S3 syntheses recorded at different reaction times.
imperceptible (1973 cm\(^{-1}\)). The vibrations T\(\text{H}_2\text{O}\) (809 cm\(^{-1}\)) and R\(\text{H}_2\text{O}\) (621 cm\(^{-1}\)) have very low intensity while the vibration W\(\text{H}_2\text{O}\) (740 cm\(^{-1}\)) is imperceptible. In addition, the so-called two phonon vibration (TP\(\text{H}_2\text{O}\)) is also observed at 885 cm\(^{-1}\), it corresponds to vibrations of the rocking and twisting movements of the crystallization water molecules [24].

Concerning the S1 synthesis, there is no significant change in the spectra recorded from 0 to 120 min, for this reason in figure 4(a) only the spectra obtained at initial and final time are presented. However, some subtle changes can be observed over time. The vibrations belonging to the structural water disappear, this is evident for the A and TP\(\text{H}_2\text{O}\) bands and may be an indication of the partial loss of these molecules. On the other hand, the changes can be observed over time. The vibrations belonging to the structural water disappear, this is evident for reason in\(\text{O}^{\cdot}\)obtained at 120 min. Zhu et al. [27] reported that the vibrations of O–H bonds of metallic transition hydroxides are in the range of 440 to 480 cm\(^{-1}\) [33–35]. This reveals that during sol-gel reaction, bonds have been formed between cobalt and hydroxyl groups from detached water molecules. Concerning the vibrations located at 1250 and 934 cm\(^{-1}\), according to the literature [36, 37], these correspond to the symmetric deformation vibrations (s) of the O–H and C–H bonds (this last has also been assigned to the vCO bond, [26, 36]) of the acetic acid molecule in its monomeric form. The formation of monomeric acetic acid during the reaction is confirmed in the same spectrum with the appearance of the vCO band at 3536 cm\(^{-1}\) [26, 37, 38] and with the increase in the intensity of the vCO\_as vibration in 1728 cm\(^{-1}\).

In the spectrum of the sample obtained at 120 min of reaction, Co–OH bond and acetic acid vibrations become more intense. Therefore, it is established that the use of heat in the reaction promotes the transformation of the precursor into a cobalt acetate hydroxylated phase, identified by XRD as\(\text{Co}_2(\text{CH}_3\text{COO})_2\cdot\text{OH}\), and the formation of acetic acid as a by-product.

From the spectra of the S3 synthesis (figure 4(c)), it is deduced that the dehydration of the precursor molecule occurs at longer reaction times (>15 min) if compared with S2 synthesis. The described changes are perceivable up to 120 min of reaction. The vibrations corresponding to structural water disappear while those belonging to the hydroxylated phase of cobalt acetate and to acetic acid appear. It should be noted that the widening of vCO\_as and vCO vibrations (from 1800 to 1300 cm\(^{-1}\)) can be assigned to the contribution of citric acid [39, 40], whose most intense vibrations are in this region. These results indicate that in this synthesis, citric acid worked as a reaction retardant without preventing the formation of the hydroxylated phase of cobalt acetate, possibly due to the steric effect [41].

These results confirm that during the sol-gel reaction at room temperature there is no transformation of the precursor. The transformation occurs almost completely during the drying process of the sol but partially during the drying of the films, as observed in XRD. Concerning the syntheses performed at 60 °C, the formation of\(\text{Co}_2(\text{CH}_3\text{COO})_2\cdot\text{OH}\) occurs spontaneously however the presence of citric acid diminishes the reaction rate.

3.1.4. Reaction mechanism

From the previous results it was determined a reaction mechanism in which\(\text{Co}_3(\text{CH}_3\text{COO})_2\cdot\text{OH}\) is obtained as the main product and acetic acid as a by-product. It was identified that due to the nature of the sol-gel process, the transformation of the\(\text{Co}(\text{CH}_3\text{COO})_2\cdot\text{4H}_2\text{O}\) molecule could follow the saponification mechanism, also known as alkaline hydrolysis of esters, which is shown in figure 5.

In stage I, the electrostatically bounded water molecules are separated from Co by the interaction with\(\text{CH}_3\text{OH}\), this dehydration occurs gradually at room temperature and quickly at 60 °C. In stage II, the hydroxyl ion, which is a nucleophile, attacks the carbon of the carbonyl group, causing the splitting of the C=O double bond and generating a tetrahedral structure. Because of the splitting generates charge instability, the equilibrium is reestablished in stage III, releasing the oxygen bounded to Co by the breaking of the covalent C–O bond. In this way an acetic acid molecule is formed and a ‘cobalt alkoxide’ is separated. In stage IV, a quick transfer of the proton occurs, that means the hydrogen bounds to the\(\text{O}^{\cdot}\). This occurs, according to the results, promoted by the reaction temperature.
It should be noted that the proposed mechanism would only occur in 1 of 3 precursor molecules, this modified molecule being bonded with two cobalt acetate molecules in a polycondensation process. The final molecule is formed by electrostatic bonds between Co and O, as proposed by Su et al.\cite{42}, conforming the cobalt acetate hydroxide molecule. The proposed structure of Co\(_3\)\((\text{CH}_3\text{COO})_5\text{OH}\) is shown in figure 6.

Regarding the synthesis S3, the citric acid diminishes the reaction rate, according to UV-Vis and FTIR results. This could be explained by a combined influence of the steric effect and the formation of a Stern layer, both promoted by the dissolution of citric acid into the reaction mixture. The interaction of citric acid into the sol is proposed in figure 7. The Stern layer was yielded by hydrogens of structural water unlinked and hydronium ions produced by the reaction of citric acid and water\cite{43}. While the steric effect was occurred by the presence of citric acid between another molecules, it avoided free interaction of precursor with solvent\cite{44}.

Due to the low concentration of citric acid, it interacts with a limited number of precursor molecules. Nevertheless, the interaction is enough to avoid the immediate formation of cobalt acetate hydroxide, as it was observed for synthesis S2. In addition to that, also the formation of big agglomerates is also affected by citric acid promoting the presence of colloids as suggested from UV–V is analysis.

3.2. Analysis of Co\(_3\)O\(_4\) products

3.2.1. TGA-DTA analysis

Thermogravimetric analysis was performed to understand the decomposition process of cobalt acetate and cobalt acetate hydroxide and the formation of Co\(_3\)O\(_4\). Four steps were identified for precursor and powders. Figure 8 shows the curves of the precursor and S2 powder which is representative of the phenomena that occurred for the 3 powders.

![Figure 5. Alkaline hydrolysis of esters mechanism proposed for sol-gel reaction.](image)

![Figure 6. Proposed structure of Co\(_3\)\((\text{CH}_3\text{COO})_5\text{OH}\) molecule.](image)
The first step consists of dehydration, in the case of the precursor it occurs by the elimination of structural water molecules in an endothermic process (seen in DTA). It starts at 70 and ends at 130 °C with a mass loss of 19%, which is below the theoretical value of 29%. In the graph of the S2 powder, a small drop of approximately 5% in mass is observed due to the evaporation of the water absorbed from the environment (from 30 to 80 °C).

The second step corresponds to the multistage partial decomposition of the acetate molecule. In the precursor, this step begins at 185 °C and ends at approximately 295 °C. In this interval 3 small decompositions are observed with a mass loss of 12.82% which corresponds to the decomposition of 27% of the acetate groups present in the precursor molecule. In DTA curve a possible oxidation process (exothermic) is observed at the beginning of decomposition, in which hydroxylated and oxidized phases of cobalt acetate can be formed, as
proposed by Wanjun (Co(OH)\textsubscript{2}(CH\textsubscript{3}COO))\textsubscript{2-x} in N\textsubscript{2})\textsuperscript{45} and by Grimes \textit{et al} (Co\textsubscript{4}(CH\textsubscript{3}COO))\textsubscript{6}O in Ar\textsuperscript{46}. In contrast, the powder from the S2 synthesis presents a small mass loss of 10.22\% between 230 \textdegree C and 290 \textdegree C that corresponds to the decomposition of 16.93\% of the acetate present in the Co\textsubscript{3}(CH\textsubscript{3}COO))\textsubscript{5}OH molecule, it occurs in an endothermic process, observed in the DTA curve around 250 \textdegree C.

The third step is related to the total decomposition of the acetate and the formation of Co oxides of different chemical composition. In the precursor, this step ends until 350 \textdegree C and corresponds to a total mass loss of 42\%. This percentage is lower than that reported for the decomposition of the precursor in inert atmospheres\textsuperscript{45}, there the mass loss was of 46.7\% indicating the formation of CoO. According to our results, it can be deduced the formation of Co\textsubscript{3}O\textsubscript{4} and/or Co\textsubscript{x}O\textsubscript{1-x} which corresponds to a mass loss of 38.85\% in the steps 2 and 3. The DTA curves indicate an exothermic (350 \textdegree C) process promoted by the crystallization of cobalt oxides.

In the case of S2 powder, the total decomposition is achieved at 357 \textdegree C, the experimental total mass loss is 55.58\% corresponding to the formation of 3CoO (theoretical mass loss of 54.03\%). Also, an exothermic process is observed during the formation of cobalt oxide crystals.

Finally, in the fourth step, a final oxidation process was identified for the complete transformation of small amounts of Co\textsubscript{x}O\textsubscript{1-x} and CoO that may exist into the Co\textsubscript{3}O\textsubscript{4} phase. In the precursor, this process is very small because only a gain of mass around 1\% is identified, while for the S2 powder the gain is about 5\%.

These results indicate that for precursor and synthesis powders, the acetate molecule decomposes in several steps until an approximate temperature of 300 \textdegree C and totally around 350 \textdegree C, later the obtained oxide continues its oxidation to transform into Co\textsubscript{3}O\textsubscript{4} at 500 \textdegree C.

From the above results, the formation process of Co\textsubscript{3}O\textsubscript{4} was depicted and presented in figure 9. Four steps were identified; the first one consists of the dehydration of the cobalt acetate hydroxide; water molecules were absorbed from the ambient. During steps 2 and 3 the acetate molecule decomposes giving place to the formation of CoO. Finally, at temperatures higher than 350 \textdegree C the oxidation becomes complete to obtain Co\textsubscript{3}O\textsubscript{4}.

3.2.2. Thickness of the films
After thermal treatment, the films were analyzed. Films S1 and S3 were transparent and brownish colored while S3 film was opaque and dark and looked thicker. No cracks were observed in any sample. The differences in the appearance of the films have their origin in the characteristics of precursor solutions. Both films and solutions are presented in figure 10. Solutions of synthesis S1 and S3 were translucent with dark violet color, this indicates the existence of a solution of the Co(CH\textsubscript{3}COO))\textsubscript{2}·4H\textsubscript{2}O. On the other hand, the solution of synthesis S2 is a dense light pink colloidal solution that produces dense and thick films. These results are in accordance with those obtained from UV-Vis and FTIR analyses, from which it was elucidated that the reaction of S2 was carried out more quickly and efficiently than that of S1 and S3.

![Figure 9. Mechanism of decomposition and oxidation for obtaining Co\textsubscript{3}O\textsubscript{4}.](image-url)
Figure 11 shows the profilometry graphs of the films obtained from precursor solutions S1, S2, and S3 as well as their respective SEM images of the thicknesses. The thickness of film S1 is homogeneous along the measured length, an average value of 140 nm was considered, while the thickness observed from the SEM image was around 130 nm. A non-homogeneous surface can be noticed from the graph of S2 film, a thickness of around 1000 nm was estimated. However, as observed in the corresponding image the thickness was 259 nm; this variability is due to the poor homogeneity of the film. The graph of the film S3 shows good homogeneity with some flaws. The determined thickness of around 105 nm is close to that observed from the SEM image. The thickness of the films and their homogeneity is consistent with the characteristics of the precursor solutions used for the deposit by dip-coating.

3.2.3. Morphology of Co₃O₄ films
The morphology of the Co₃O₄ spinel films and their particle size distribution are shown in the images in figure 12. The images were taken at 200,000X in high contrast conditions to favor the visualization of morphology. All films have a homogeneous and smooth surface with semi-spherical particles. The film obtained from the synthesis at room temperature and neutral pH (S1) presents less defined particles and some coalescence. On the other hand, the film obtained from the synthesis at 60 °C and neutral pH (S2) shows more defined particles but also with a certain degree of coalescence. The film obtained from the synthesis at 60 °C and
with acid pH has well-defined particles without apparently coalescence. The difference of the Co$_3$O$_4$ particles sizes is clearly seen in the size distribution plot. The films obtained from the neutral pH syntheses have a wider size distribution and larger average particle sizes, being 11.8 and 10.4 nm for S1 and S2, respectively. On the contrary the S3 film has an average particle size of 8.1 nm and narrow size distribution. The decrease of pH in the synthesis favors the formation of Co$_3$O$_4$ films with smaller nanometric particle size due to steric effect and Stern layer formation during the sol-gel reaction, which limited the growing of the particles. Then, during the thermal treatment the growing of the particles was restricted by the size of the original particles formed during the reaction and the deposition of the films.

3.2.4. X-ray diffraction of the films
The XRD patterns of the films after heat treatment at 500 °C are shown in figure 13. Because of the low thickness of the films, the patterns present a noise signal. The three films show the same diffraction peaks, indicating that after heat treatment at 500 °C they are all composed of cobalt oxide crystalline phase. The most intense peaks are located around $2\theta = 31.2^\circ$ and $2\theta = 36.8^\circ$, according to the diffraction charts (00–080–1532) these peaks correspond to the planes (220) and (311) of Co$_3$O$_4$ cubic phase (Fd3m).

4. Conclusions
The main results of this research indicate that there is an effect of the temperature and pH of the precursor solution on the reaction mechanism and consequently on the average particle size and thickness of films of Co$_3$O$_4$ phase synthesized. It was observed that in synthesis S1, the reaction did not occur. However, the Co$_3$O$_4$ phase was obtained from this solution by direct decomposition of Co(CH$_3$COO)$_2$, as is showed by TGA-DTA results. The effect of temperature was seen in the S2 synthesis, the action of temperature promoted the formation of the precursor phase Co$_3$(CH$_3$COO)$_5$OH, and the reduction of the particle size by generating a greater number of colloids in the solution (seen in UV-Vis). Finally, the decreased of pH until 5 in the precursor solution S3, generated a combined effect of reduction of particle size and delay in the reaction rate by a steric effect due to the presence of citric acid molecules and hydronium ions generated an electrostatic layer that avoid free interaction.
of species and that prevent the agglomeration of the colloids. Therefore, after a thermal treatment at 500 °C, both particle average size and thickness of film S3 were the smallest, 8 nm and 105 nm, respectively.

Acknowledgments

This work was supported by IPN-SIP contracts 20195455, 20194917, 20200503 and 20200561, M.E. Andrade-Sanchez thanks to CONACYT for a PhD grant and to IPN for BEIFI grant.

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References

[1] Yoo Y, Jung S, Kang S, Song S, Lee J, Han C and Jang G 2020 Dispatchable substation for operation and control of renewable energy resources Applied Sciences 10 1–13
[2] Kilic I. 2020 Industry 4.0 and Internet of things implementation at siseam energy management system Journal of Polytechnic-Politeknik Dergisi 23 (4) 1167–1175
[3] Razaa W, Alib F, Razac N, Luoa Y, Kimf K, Yanga J, Kumare S, Mehmooda A and Kwond E E 2018 Recent advancements in supercapacitor technology Nano Energy 52 441–73
[4] Jua J, Ma J, Wang Y, Cui Y, Han P and Cui G 2019 Solid-state energy storage devices based on two-dimensional nano-materials Energy Storage Mater. 20 269–90
[5] Li Y, Tan B and Wu Y 2008 mesoporous Co3O4 nanowire.pdf Nano Energy 6 1–265–70
[6] Kruis F E, Fissan H and Peled A 1998 Synthesis of nanoparticles in the gas phase for electronic, optical and magnetic applications—a review J. Aerosol Sci. 29 311–35
[7] Vijayakumar S, Kiruthika Ponnalagi A, Nagamuthu S and Muralidharan G 2013 Microwave assisted synthesis of Co3O4 nanoparticles for high-performance supercapacitors Electrochim. Acta 106 500–5
[8] Anandha Babu G, Ravi G, Hayakawa Y and Kumaresavanji M 2015 Synthesis and calcinations effects on size analysis of Co3O4 nanospheres and their superparamagnetic behaviors J. Magn. Magn. Mater. 375 184–93
[9] Salavati-Niasari M, Khansari A and Davar F 2009 Synthesis and characterization of cobalt oxide nanoparticles by thermal treatment process Inorganica Chim. Acta 362–14 4937–42

Figure 13. XRD patterns of the Co3O4 films obtained after thermal treatment at 500 °C.
10. Makhlof S A, Baki Z H, Aly K I and Moustafa M S 2013 Structural, electrical and optical properties of Co$_3$O$_4$ nanoparticles Superlattices Microstruct. 64 107–17
11. Lester E, Aksomiayte G, Li J, Gomez S, Gonzalez-Gonzalez J and Poliaikoff M 2012 Controlled continuous hydrothermal synthesis of cobalt oxide (Co$_3$O$_4$) nanoparticles Prog. Cryst. Growth Character. Mater. 58 3–13
12. Garcia-Pacheco G, Cabañas-Moreno G J, Yee-Madeira H, Cruz-Gandarilla F and Urgemoto M 2002 Production of nanostructured Co$_3$O$_4$, Co$_3$S$_4$, and NiO particles by mechanically induced reactions J. Metastable Nanostruct. Mater. 13 281–6
13. Garcia-Pacheco G, Cabañas-Moreno G J, Yee-Madeira H and Cruz-Gandarilla F 2006 Co$_3$O$_4$ nanoparticles produced by mechanochemical reactions Nanotechnology 17 2528–35
14. Venella A B, Mangalaraj D, Muthukumarasamy N, Agilan S and Hemalatha K V 2019 Structural and optical properties of Co$_3$O$_4$ nanoparticles prepared by sol–gel technique for photocatalytic application Int. J. Electrochem. Sci. 14 5355–52
15. Miqaelot A, Despotopoulou M, Vahlas C, Villeneuve C, Dragoe N, Prud’homme N and Debieux O 2020 Morphological, structural, optical, and electrical study of nanostructured thin films: charge transport mechanism of p-type Co$_3$O$_4$ Mater. Chem. Phys. 240 122059
16. Tototzintle-Huitle H, Prokhorov E, Mendoza-Galván A, Urbina J E and Gonzalez-Hernández J 2003 Study of the formation of Co$_3$O$_4$ thin films using sol–gel method 64 973–80
17. Armelao L, Barreca D, Gross S, Martucci A, Tieto M and Tondello E 2001 Cobalt oxide-based films: sol–gel synthesis and characterization J. Non-Cryst. Solids 295 477–82
18. Sen Vikes Patil S, Josh P and Chougule M 2012 Synthesis and characterization of Co$_3$O$_4$ thin film Soft Nanostruct. Lett. 21–7
19. Doremiex J L 1967 Thermal evolution of tetrahydrated cobalt acetate in a stream of nitrogen at room temperature. Bull. Soc. Chim. Fr. 14 4593
20. Risch M, Ringlef B, Kohlhoff M, Bogdanoff P, Cherney P, Zahraveia I and Dau H 2015 Water oxidation by amorphous cobalt-based oxides: in situ tracking of redox transitions and mode of catalysis Energy Environ. Sci. 8 661–74
21. Bandala E R, Pelaez M A, Dionysiou D G, Veloso S, Garcia J and Macias D 2007 Degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) using cobalt-peroxymonosulfate in Fenton-like process J. Photochem. Photobiol. A Chem. 186 357–63
22. Pandey O K, Shahi A K and Gopal R 2015 Magnetic colloid by PLA: optical, magnetic and thermal transport properties Appl. Surf. Sci. 347 461–70
23. Bala T, Arumugam S K, Pasricha R, Prasad B L V and Sastry M 2004 Foam-based synthesis of cobalt nanoparticles and their subsequent conversion to core@coreshell nanoparticles by a simple transmetallation reaction J. Mater. Chem. 14 1057–61
24. Nickolov Z, Georgiev G, Stoilova D and Ivanov I 1995 Raman and IR study of cobalt acetate dihydrate J. Mol. Struct. 354 119–25
25. Ito K and Bernstein H J 1996 The vibrational spectra of the formate, acetate, and oxalate ions Can. J. Chem. 34 170–8
26. Socrates G 2001 Infrared and Raman characteristic group frequencies Third Edition (England: John Wiley & Sons Ltd) Tables and charts. 978–0–470–09307–8 (https://doi.org/10.1021/ja0153520)
27. Heyns A M 1972 The low-temperature infrared spectra of the copper(II)acetates J. Mol. Struct. 11 93–103
28. Palacios E G, Juárez-López G and Monhemius A J 2004 Infrared spectroscopy of metal carboxylates: II. Analysis of Fe(III), Ni and Zn carboxylate solutions Hydrometallurgy 72 139–48
29. Sobolev A N, Miminoshvili E B, Miminoshvili K E and Sakvareilidze T N 2003 Cobalt dicarboxytrihydrate Acta Crystallogr. Sect. E Struct. E 59 10
30. Henschel H, Klockner J P, Nicholls I A and Proschen M H 2012 Computational and structural studies on the complexion of cobalt(II) acetate by water and pyridine J. Mol. Struct. 1007 45–51
31. Ristova M and Soptrajanov B 1984 Infrared spectra of protiated and deuterated cobalt acetate dihydrate J. Mol. Struct. 115 355–8
32. Lepodise L M, Horvat J and Lewis R A 2013 Collective librations of water molecules in the crystal lattice of rubidium bromide: experiment and simulation Phys. Chem. Chem. Phys. 15 20232–61
33. Zhu Y, Li H, Koltypin Y and Gedanken A 2002 Preparation of nanosized cobalt hydroxides and oxyhydroxides assisted by sonication J. Mater. Chem. 12 729–33
34. Xu Z P and Zeng H C 1999 Interconversion of brucite-like and hydroxalate-like phases in cobalt hydroxide compounds Chem. Mater. 11 67–74
35. Mockenhaupt C, Zeiske T and Lutz H D 1998 Crystal structure of brucite-type cobalt hydroxide β-Co(OH, D)12–Neutron diffraction, IR and Raman spectroscopy J. Mol. Struct. 443 191–6
36. Babkov L M, Vashchinskaya V V, Kovner M A, Punchkovskaya G A and Fialkov Y Y 1979 Vibrational spectra of acetic acid monomer D. Chem. Phys. Lett. 70 15–27
37. Makhlouf S A, Bakr Z H, Aly K I and Moustafa M S 2013 Structural, electrical and optical properties of Co$_3$O$_4$ nanoparticles Superlattices Microstruct. 64 107–17
10. Makhlof S A, Baki Z H, Aly K I and Moustafa M S 2013 Structural, electrical and optical properties of Co$_3$O$_4$ nanoparticles Superlattices Microstruct. 64 107–17