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Co-Mg ferrite nanocomposite as a humidity sensor device prepared by Co-Precipitation method

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Abstract

In the present study, the humidity sensing properties of Co-Mg nanocomposite prepared by chemically co-precipitated have been investigated by impedance analysis. The correlation between the impedance patterns and relative humidity have shown remarkable results for further investigation. Whereas, the humidity measurement capability of the sensor was high at low frequencies. Also, we identified that this ability was continuously diminished at higher frequencies. So, the hysteresis value for successive adsorption and desorption of the humidity on ferrite nanocomposite material was also determined as small and also the long time measurement stability was excellent. The response and the recovery times for nanocomposite materials were identified as 60 s and 300 s respectively. Finally, a direct relationship between the active electron and transport mechanism of the humidity onto the nanocomposite has been identified as an advanced investigation.

Keywords: Ferrite nanocomposite, Humidity sensor, Co-Precipitation method, Response and recovery time, Impedance.

1. INTRODUCTION

The sensors are the converters a physical response to another one like from pressure to electricity, from humidity to electricity, from light to electricity, etc. In today's world, we can come across lots of different sensors in a different field of the life from our homes to advanced technological devices. So, the novel exploration, development an also improvement of the materials which is used in the sensor production, have gained more attention among scientists and technologists for last three decades [1]. The sensor usage in our life is almost an obligation to run and control lots of machines and tools to increase their life quality and standards [2]. The humidity or moisture is a critical parameter for many industrial applications and daily life requirements especially in food, paper, wood, textile, electronic industries and etc. Moisture regulation and its control are also a necessity for a lot of industrial production processes and moisture sense requiring devices like air conditioners and refrigerators as a simple sample [3]. In the light of these explanations, we can see that the humidity sensing and measurement can be applied to full range materials like polymer [4], crystal [5], thin film [6,7] and ceramic [8]. The higher impedance gap versus higher sensitivity [9], the stability in an extended period of time measurements [10], narrow hysteresis [11] properties of the sensors are sought as the essential requirements of the humidity sensor. The desired material, which should have lower response-recovery time interval, is another challenging issue of scientific studies [12]. In addition to these above, the economy of the sensor is another important factor to produce this material and so, it should be cheaper, durable, small size and constant resistivity towards ambient gases [13]. When we think about the mentioned

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properties of the humidity sensors, exploring the right material providing all features mentioned above is almost impossible. So, in much sensor-based research, scientists try to improve the optimization of the certain properties of the sensor materials.

In recent years, ferrite-based nanoparticles have been investigated as a newly discovered nanoparticle family [14]. Many experimental and theoretical studies have been conducted on this particle to illuminate their electrical, magnetic and structural properties and their applications in different fields [15-17]. However, their humidity sensing feature has not been already reviewed comprehensively and their humidity sensing capability and applicability in ambient weather conditions is considered as a remarkable topic in recent years [18]. The humidity sensor applicability tests of the materials can be performed by considering some physical analysis like impedance measurements [19,20], frequency shifting [21,22], capacitance [23,24] and current-resistance [25]. Therefore, phase quartz crystal microbalance, impedance, and two temperature [26] methods have been utilized in many different researches. However, lots of methods are still employed to control the relative humidity in different aspects to determine humidity with a humidifier or saturated salt solution [27,28].

In the current study, ferrite-based Co-Mg containing ferrite nanocomposite material was synthesized, and its applicability of humidity sensor was illuminated by impedance measurements giving the water by dropwise to the analysis environment. Thus, the conduction mechanism and the performance of nanocomposite material in sensor were clarified to verify the applicability of synthesized ferrite nanoparticles for the long-life humidity sensor.

2. EXPERİMENTAL

$Co(NO_3)_2 6H_2O$, $Mg(NO_3)_2$, $Fe(NO_3)_3 9H_2O$ and NaOH were purchased from (Merck, Germany, >99.0%) and directly used for the synthesis of $Co_{0.5}Mg_{0.5}Fe_2O_4$ based ferrite nanoparticle sample without further purifications. All aqueous solutions were prepared with deionized water (Milli-Q ultrapure water). Ferrite nanoparticle was synthesized according to the chemical co-precipitation procedure [29]. All preparatory steps are shown in Fig. 1.

3. RESULTS AND DISCUSSIONS

The morphology and microstructures of the Co-Mg ferrite characterized by a scanning electron microscope (SEM, model JEOL—JSM 6060 LV) at an acceleration voltage of 20 kV. Fig. 1 shows SEM images of the sample. As seen from the figure, there is dewetting on the powder sample which also prevents us from commenting on grain size. However, some planar and spinel formations were observed. It means that such a structure is likely to make the adsorption process of water molecules easier because of the capillary pore and large surface area.

The energy dispersive X-ray (EDX) analysis result was also given in Fig. 2, to analyze the chemical composition of Co-Mg ferrite nanocomposite. All the peaks belong to the main elements of Fe, Co, O and Mg and there is no impurity. According to EDX results, the sample was successfully formed in the desired composition.

In the current study, the Fig. 3 represents the relationship between impedance frequency and humidity map of the ferrite nanoparticles. The figure apparently put forwards that the sample has extraordinary humidity map. According to the figure, it is noteworthy that the humidity value is obviously changed against tested frequency gap. The impedance value of the investigated sample was decreased in a constant humidity condition. The adsorbed water molecules on the sample have prevented the rotation against applied emd [30]. It is clear that the impedance values decreased exponentially in the frequency range between 20Hz-10kHz. For example, in 20 Hz test frequency, the impedance values were rapidly reduced from 4.44×10^7 ohm to 3.4×10^4 ohm. Especially at low frequencies, the rapid increase in the conductivity may be attributed to a result of the contribution to the conductivity of the water molecules. In that conditions, the conductivity occurs via surface conductivity mechanism. The rapid increase of the conductivity was related to the adsorbed water molecules from the sample surface [31]. It means that the sample absorbed more water molecules on its surface at low humidity and low-frequency conditions. We can even say that this value is almost decreased linearly in higher frequency values greater than 10 kHz. As a remarkable result that impedance value is almost independent of the humidity at the frequency higher than 1 MHz. The decreasing impedance value with increasing relative humidity (RH) value can be explained by the adsorption mechanism of the water molecules. Also, there is an impedance dispersion at low frequencies, and it shows a shift towards higher frequencies with increasing ambient humidity values [32]. We can interpret that the investigated sample has a hydrophobic structure at a higher humidity than 70 % and up to 10^5 kHz frequency value that the impedance value almost stable in this humidity and frequency interval [33].

The above results, which are logarithmically decreased, are well fitted to the Eq. 1.

$$Z = a\exp(-H/b) + c \qquad (1)$$

Here, R^2=0.99399, a, b and c values are -184036 ohm, 876584220 and 7.5 ohm respectively.

The humidity measurement sensitivity of the investigated sample was calculated with Eq. 2

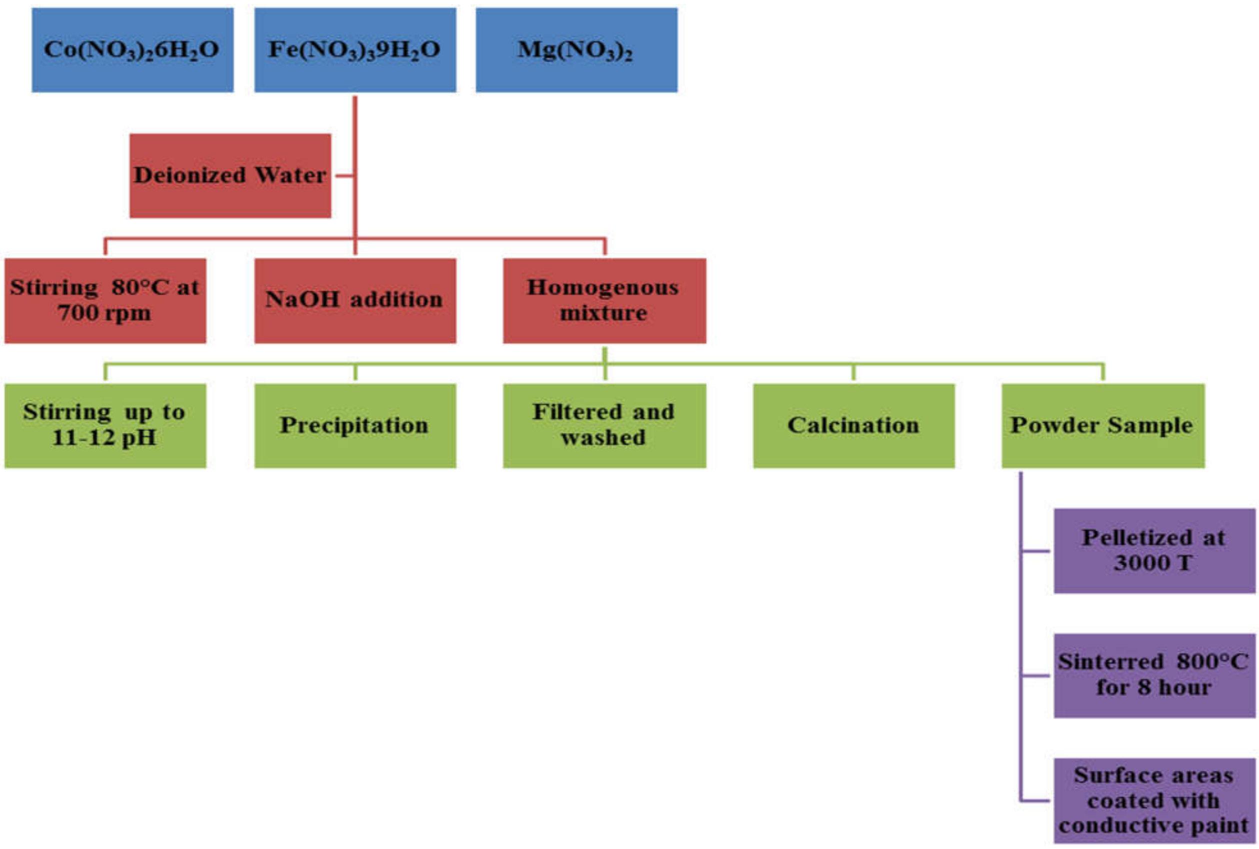
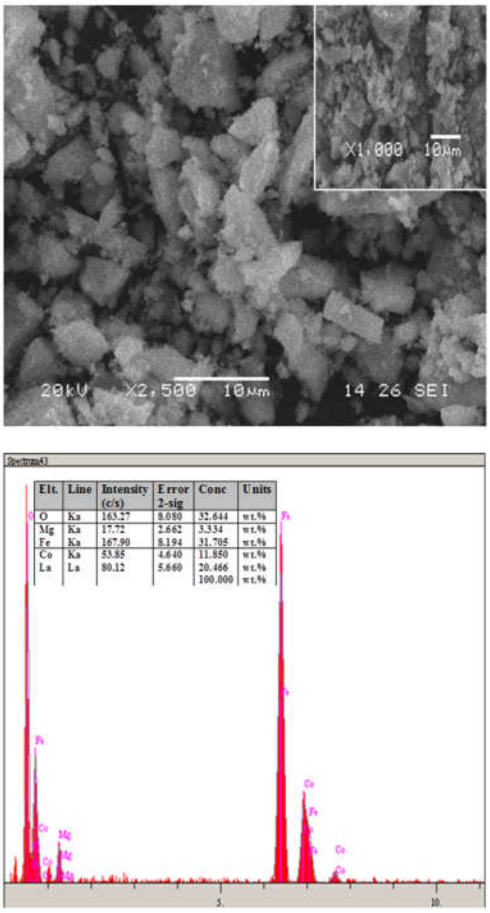


Figure 1. Preparation steps.



Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
O	Ka	163.27	8.080	32.644	wt.%
Mg	Ka	17.72	2.662	3.334	wt.%
Fe	Ka	167.90	8.194	31.705	wt.%
Co	Ka	53.85	4.640	11.850	wt.%
La	La	80.12	5.660	20.466	wt.%
				100.000	wt.%

Figure 2. SEM micrographs at different magnitude and EDX analysis of Co-Mg ferrite nanoparticle

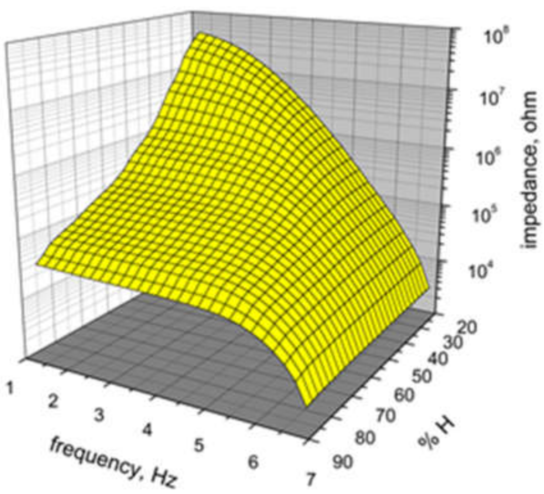


Figure 3. Humidity, impedance and frequency map of Co-Mg ferrit.

$$S\% = \left|\frac{Z_{measured} - Z_{20}}{Z_{20}}\right| x100 \qquad (2)$$

In this equation, Z_{20} and $Z_{measured}$ values belong to the impedance values at 20% humidity and measured [34]. The moisture measurement sensitivity versus ambient humidity for some different frequencies was given in Fig. 4. It can be clearly seen from the figure that the sensitivity is higher at low-frequency values. The sensitivity values lower than 1 kHz are more and more reliable, and their measurement accuracy for 40% RH increases up to 95% sensitivity. It is because of rapid changing of impedance with humidity at low frequencies. The sensitivity values increase with increasing ambient humidity. When the ambient humidity decreased below 40%, the sensitivity was also decreased rapidly. This situation is a result of slow changes in impedance values at the lower frequency region.

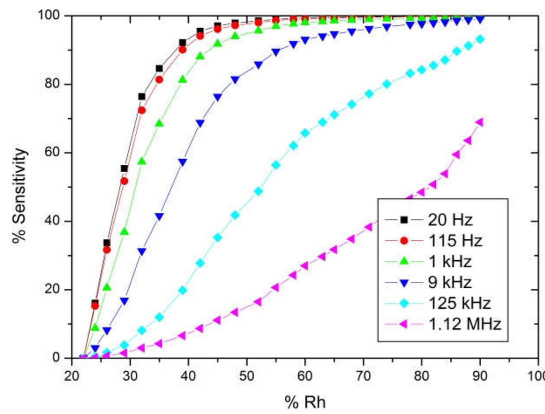


Figure 4. The sensitivity of the sensor device.

In the literature, impedance measurements were made for the definition of the answer of changing humidity in sensing materials. Hysteresis loop of humidity exhibits adsorption and desorption process of humidity sensors [35]. It is one of the critical parameters for the humidity sensor. Naturally, a hysteresis characteristic is used for testing a sensor's reliability [36]. Fig. 5. shows the hysteresis loops between adsorption and desorption processes that measured whole humidity range for seven % RH value, at 1 V, 10 kHz, and room temperature, and results given as a function of RH%. Co-Mg ferrite impedance decrease in a range of 22%-90% with increasing RH%. This figure demonstrates that the impedance values within desorption process nearly settle the amounts under the adsorption. This is the general feature of humidity sensors. As clearly seen from the figure Co-Mg ferrite exhibits a narrow hysteresis loop and this is one of the most desirable properties of humidity sensors for stability. Nevertheless, the sensing curves did not overlap. Instead, a closed loop was noticed in the range of middle humidity.

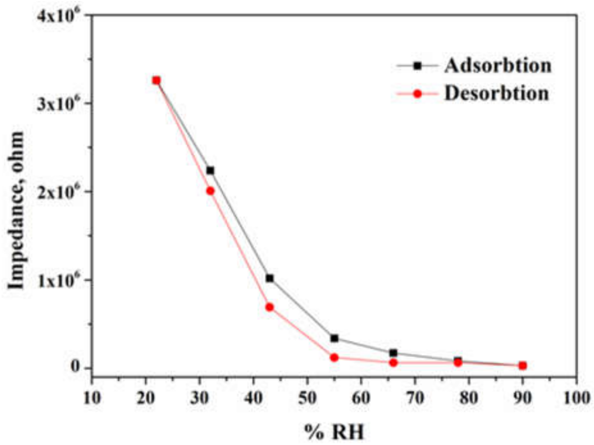


Figure 5. Humidity Hysteresis loop of the Co-Mg sample.

Response and recovery time is one of the key feature demonstrating the performance of the device. Fig. 5. shows response and recovery time of Co-Mg nanocomposite ferrite material. During the adsorption and desorption process, impedance measurements were made as a function of time, at 10 kHz and between 22% - 90% RH. As seen from the Fig. 6 that the response and the recovery curve is repeated. Response and recovery time is known as elapsed time of the total impedance change of the sample to the value reached in amounts corresponding to 90% during adsorption and desorption. According to this, the response time of the sample is 300 s while recovery time is 60 s. Thus, recovery time is shorter than response time. The reason for this is because adsorption is faster than desorption of the sample. The point to be noted here, in the laboratory conditions value of RH is 20%. It may be thought that these times will be shortened by lowering to smaller humidity values. Furthermore, as seen in the figure, the repeatability of the assay was confirmed.
In this study, Co-Mg ferrite measured different relative humidity. Fig. 7. demonstrates long-term stability at five different RH% levels. Impedance was measured every ten days for 60 days (first 10 days, it was measured more frequently). As seen, no significant changes have been observed in impedance at lower humidity. For all that, there is a small charge at 90% humidity. These results underline that Co-Mg ferrite has an excellent stability and it can be correctly applied to practical humidity sensors [37].

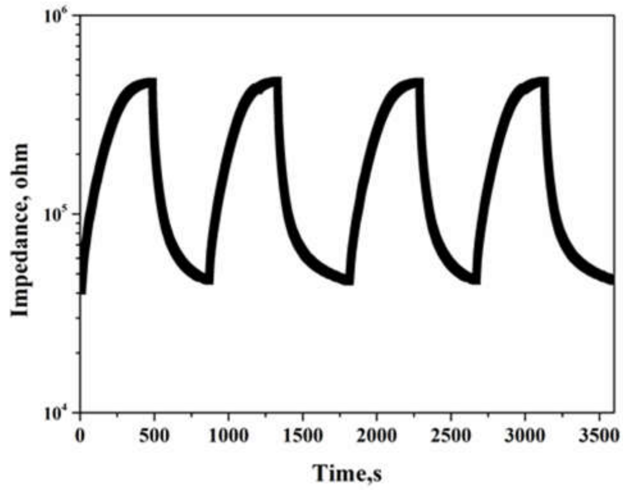


Figure 6. Response and recovery loops.

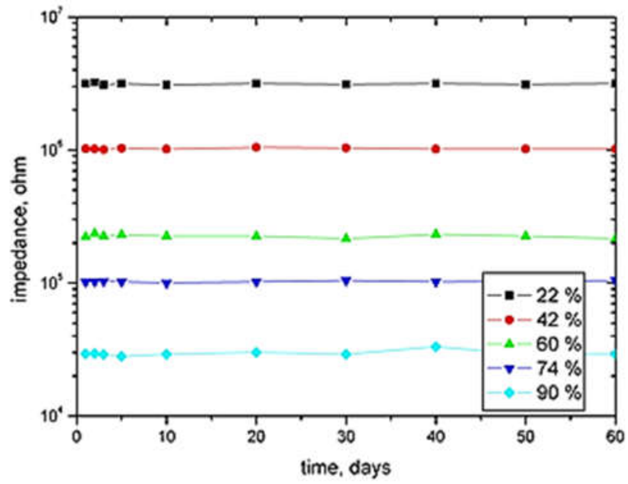


Figure 7. Long time stability of the sample at from humidities.

Nyquist's plots are necessary to introduce the sample conductivity mechanism. In Fig. 8. Nyquist plots of the sample being investigated are shown. These curves reveal one of the intrinsic features of impedance which belongs to sample [38]. A tail at low-frequency region represents the ionic case. However, as seen from all curves, tail, which is not the low-frequency side, has the meaning of appropriate electronic conductivity mechanisms. Undefined half circles at low humidities show that electronic conductivity mechanism is still active at much lower frequencies. Completed half loops are seen at 48% and higher humidity values. For these circuits, although electronic conductivity mechanism is completely active, this means a sign for possible ionic conductivity. The essence of the matter, the absence of ionic conductivity with increasing humidity is a cause of non-increased conductivity. Semicircle suppressed by the low frequency indicates the Havriliak-Negami type relaxation mechanism. This situation defines the equivalent circuit formed by the parallel connected resistor-capacitor combination [39]. Equivalent circuits' resistance decreases from $5x10^7$ ohm to $2.5x10^4$ ohm, capacitor decreases from 18 pF to 3 pF while RH increase from 22% to 90%. This behavior of half loops means that same conductivity mechanism works for all RH values.

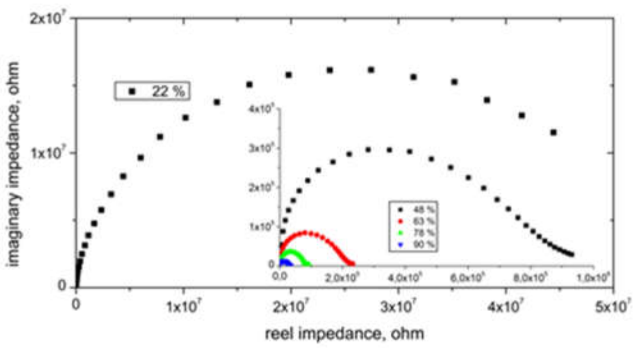


Figure 8. Co-Mg ferrites impedance measurement for Argand diagram.

4. CONCLUSION

Co-Mg ferrite nanoparticle prepared by chemical co-precipitation was studied as a humidity sensor material. Many features that are important for humidity sensors have been researched. Along with this investigation examined sample reveals excellent humidity, impedance and frequency map. According to this map, higher precision humidity measurements have demonstrated at the low-frequency region. According to design for a possible device, the low-frequency impedance-humidity fitting curve has been found to decrease logarithmically. Also, hysteresis curve, during adsorption and desorption, seems to be normal range. Although response and recovery times are a bit long, measurements covering a long time have shown, impedance remains stable for different humidity values. Finally, electronic conductivity mechanism has understood to be suitable for increasing relative humidity. According to these features, the investigated sample is interesting for humidity sensor application.

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