
Study on the Effect of Humidity on Electrical Properties of Copper-Silica Aerogel

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Abstract

Copper-silica aerogel was synthesized by the sol-gel method and was heated at 400, 500 and 600°C for 3 h in the air. The gained materials were named as sample (a), (b) and (c) respectively. Then all samples were characterized by FE-SEM, EDX and FTIR spectroscopy. For resistance measurements the pulverized material was pressed to form a disk-type sensor. The measurements of resistance in the relative humidity range of 11.3-84.3% were performed for all samples. For the following experiments sample (a) was chosen. Then the response time and stability properties were examined. The response time of 7.5 minutes was obtained and the stability graphs showed that in the higher RH the sensor was more stable.

Keywords: Humidity Sensor, Silica Aerogel, Electrical Properties, Copper-Silica Composite, Resistance Measurements

1. Introduction

Humidity is a common component in atmosphere though its measurement and control have received much attention in recent years [1]. Humidity sensors are used in a broad range of fields like industry, agriculture and also domestic applications [2,3]. So far, different kinds of humidity sensors have been invented for adjusting different working conditions [2]. Although different mechanisms have been developed for detecting humidity, its precise measurement is a very difficult process [1]. Among the different ways of sensing

humidity like contraction of materials, optical methods, etc., exploiting electrical properties of materials is more compatible with recent compact humidity sensors because the size of sensors can be minimized in this way [4].

Humidity sensors which use the changes of electrical properties of materials with humidity can be divided into two groups including the resistive type and the capacitive type. In the resistive type, the adsorption of water molecules causes changes in the resistance of the sensor. These humidity sensors are classified into two groups: ionic and electronic. In the ionic type, the resistance decreases with an increase in

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humidity. Microstructure and intrinsic impedance of materials are parameters affecting the performance of this type. On the other hand, in the electronic type, the resistance decreases or increases depending on whether the semiconductor is of n-type or p-type [3,5].

So far, different materials have been studied as humidity sensors. These materials include three groups of electrolytes, polymers and ceramics. Ceramics and metal oxides are more favorable because of their high thermal, physical and chemical stability. Porous ceramics with nano pores provide fast and easy adsorption of water molecules and, as a result, the fast response of sensor which is an important factor in evaluating a sensor [6].

There are many studies on silica and silica composites as humidity sensors. Some research showed that mesoporous silica had high sensitivity to humidity and fast response time [7-9]. A study by Tongpool *et al.* [10] showed that adding silica to ironoxide improved the humidity sensing properties of iron oxide. They concluded that iron oxide-silica nanocomposite had fast and reversible response time.

Aerogels are porous materials that possess unique properties. Among the aerogels silica aerogels have specific characteristics of high surface area (up to 1000 m²/g), high porosity (75-99%) and small pore size of 1-100 nm [11]. Also, the hydroxyl groups on the surface of the silica aerogel prepared by wet solution chemistry accelerate the adsorption of water vapor. Li *et al.* [12] showed that the hydroxyl groups on the surface of silica aerogel remained after exposure to water vapor. Wang *et al.* [13] prepared thin films of

silica aerogel on alumina substrates. They concluded that silica aerogel is highly sensitive to humidity over 40% RH and it can be a viable material for future humidity sensors because of its stability and reproducibility. Wang and Wu [14] investigated the effect of thickness and pore structure on electrical properties of silica aerogel. They found that the film with greater thickness was more suitable for high relative humidity. On the other hand, the thinner film could be used in low relative humidity because of high response rate. They also reported a hysteresis of 3.3% and response and recovery time of 51 and 44 s for the silica aerogel film, respectively.

In this study, a new humidity sensor has been introduced based on copper-silica aerogel. This composite has the advantages of large surface area and high pore size of aerogel together with the high conductivity of copper. Copper provides another advantage, adding a second metal to the aerogel makes it more suitable for shaping to act as a sensor [15]. These properties would result in providing a humidity sensor with high sensitivity in DC measurements.

2. Materials and methods

2-1. Preparation of humidity sensor

Copper-silica aerogel was synthesized by the sol-gel method according to the procedure illustrated in [16] and a powder-shaped hydrophobic material was obtained. The sample was placed in an oven for about 3 hours in the air at temperatures of 400, 500, and 600°C. The resulting samples were labeled as sample (a), (b) and (c) respectively.

To obtain a compact form of copper-silica

aerogel powder for performing electrical measurements, certain amount of calcined material was ground properly. Then it was pressed to shape a disk-type sensor (15 mm in diameter, 0.5 mm in thickness). The resistance of the sensor was measured using two copper wires attached to the sensor by silver paste. A schematic diagram of the sensor prepared is shown in Fig. 1.a.

Different relative humidity environments were prepared in glass vessels using different saturated salt solutions of LiCl, CH₃CO₂K, MgCl₂.6H₂O, K₂CO₃, Mg(NO₃)₂.6H₂O, NaBr, NaCl, KCl. The corresponding RH values at 25°C were 11.3, 22.5, 32.8, 43.2, 52.9, 57.6, 75.3 and 84.3% respectively [17]. A time of 10 h was considered to reach to the equilibrium conditions.

The disk-type sensor was then placed in different environments with different relative humidities and the resistance was measured by a digital Megger (Mastech MS5201) with various DC voltages including 250, 500 and 1000 V. Fig. 1.b shows the configuration of devices used for measurements. The voltage was applied by Megger through the two copper wires attached to the sensor and the sensor was in the glass vessel in which the air was kept at constant temperature and relative humidity.

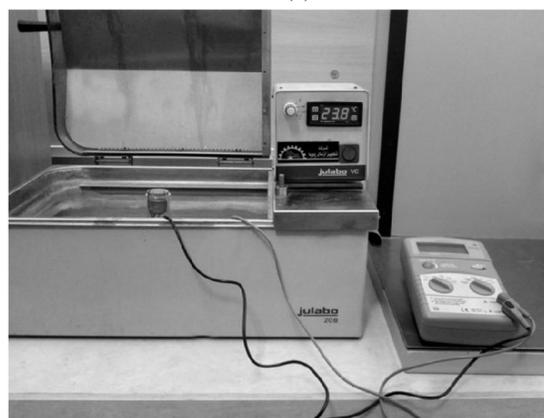
2-2. Characterization

Field Emission Scanning Electron Microscopy (MIRA3 FE-SEM, Tescan, Czech) was presented for morphology analysis and Energy Dispersive X-ray spectrometer (Scanning Electron Microscopy: Tescan Vega device, model TS5136MM, equipped with EDX spectrometer) was performed to investigate

the compositions of the samples. FTIR spectra of samples were measured on a Fourier transform infrared spectrometer (FTIR, Mattson, model Unicam 4600). The samples were ground properly into powder and well-mixed with KBr. The solid mixtures were then pressed to shape a pellet for performing analyses.



(a)



(b)

Figure 1. Schematic sketch of the humidity sensor prepared and the set up used for measurements.

3. Results

3-1. Structure characteristics

Fig. 2a displays the FE-SEM photograph of a sample containing 4.1% weight of copper content calcined at 450°C. The image reveals that the material contains a porous structure with spherical particles. It also confirms the presence of nanopores in the sample which provides the easy adsorption of water molecules. As denoted in [16], the structure of the material did not vary considerably with copper content. So this image can be evidence for our samples with a close copper content to be nano structure material, too. For further information about the structural properties, reference [16] can be useful. EDX analysis of the sample (a) is represented in Fig. 2b. It is obvious that the amount of Cu in the composite is lower than other elements and the quantitative weight percentages of the elements show that the amount of copper in the composite is around 15%.

Fig. 3 shows FTIR spectra of copper-silica aerogel samples which were calcined at 400, 500 and 600°C. The transmittance peaks between 1000 and 1300 cm^{-1} are attributed to asymmetric Si-O-Si bands [18]. The strong peak at 450 cm^{-1} is related to O-Si-O band. Another important peak at 810 cm^{-1} is due to CuSiOxy band which proves the existence of copper in the composite.

In the calcination process, the $-\text{CH}_3$ termination groups were removed and $-\text{OH}$ bands were substituted. The peaks between 2900 and 2950 cm^{-1} indicate $-\text{CH}_3$ groups which are weak, therefore the complete calcination of the samples is confirmed. The transmittance peaks between 3000 and 3700 cm^{-1} are assigned to different types of $-\text{OH}$ bands [19].

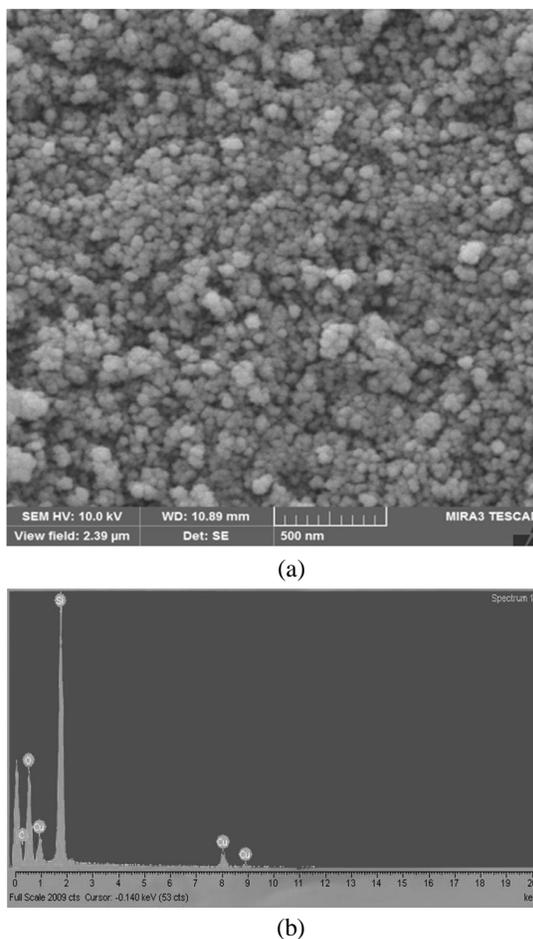


Figure 2. The FE-SEM image of the copper-silica aerogel containing 4.1% weight of copper content, calcined at 450°C [16] and EDX spectra of sample (a).

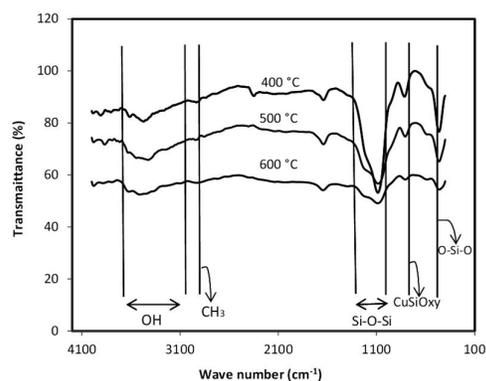


Figure 3. FTIR spectroscopy obtained for copper-silica aerogel samples calcined at 400, 500 and 600°C.

3-2. Humidity sensitive properties

The resistance measurements were conducted to evaluate the materials for use as humidity sensor. For this purpose, the following conditions were applied: DC voltage of 1000 V, relative humidity range of 11.3-84.3% and temperature of 25°C. The results obtained for sample (a) revealed that, the resistance at relative humidities below 43.2% was higher than 2 GΩ which is out of range of the device. This high resistance of copper-silica aerogel can be attributed to the highly porous structure of the aerogel consisting of 90% air which is an insulator and does not conduct electricity well.

Further increasing the relative humidity resulted in a decrease in the resistance. Fig. 4a shows the variations of resistance at the

relative humidity of 43.2%. The resistance changes greatly in the first moments while the changes become lower at the continuation. The resistance tends finally to a constant value.

Fig. 4b shows the resistance change where the relative humidity is 52.9%. Similar to the previous case, here, the resistance decreases with time, however, it tends to a lower final value compared to the previous case (relative humidity of 43.2%). By further increasing the relative humidity the resistance decreased more. The results have been plotted in Fig. 4c to e. A comparison between various graphs obtained for different humidity values revealed that, the resistance attains its final value more quickly where the humidity is higher.

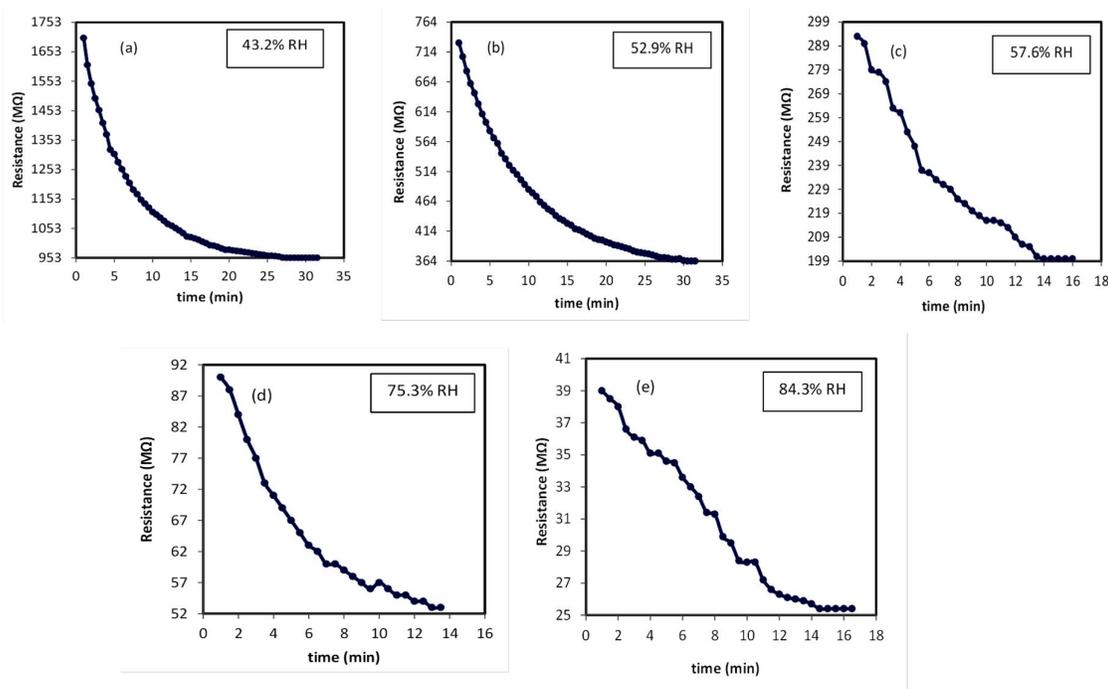


Figure 4. The variations of resistance of sample (a) with time.

The results obtained for sample (b) are presented in Fig. 5. For this sample the resistance at the relative humidity of 11.3% was above 2 GΩ. However, increasing the relative humidity and adsorbing the water

molecules by sensing material reduced the resistance of the sample. The results for the relative humidity values ranging from 22.5% to 75% (Fig. 5e to f) revealed a similar decreasing trend to the sample (a). Further

increase in the relative humidity causes more decrease in the resistance. The graph obtained for RH of 84.3% (Fig. 4g) shows a much

different trend; the changes took place more slowly. This may be attributed to the capacity of the material in adsorbing water

molecules. When the humidity is changed step by step, the sensor adsorbs water molecules gradually. In high humid environments, the material adsorbs water molecules as it can, so the sensor cannot adsorb water and the resistance would change slowly and stepwise.

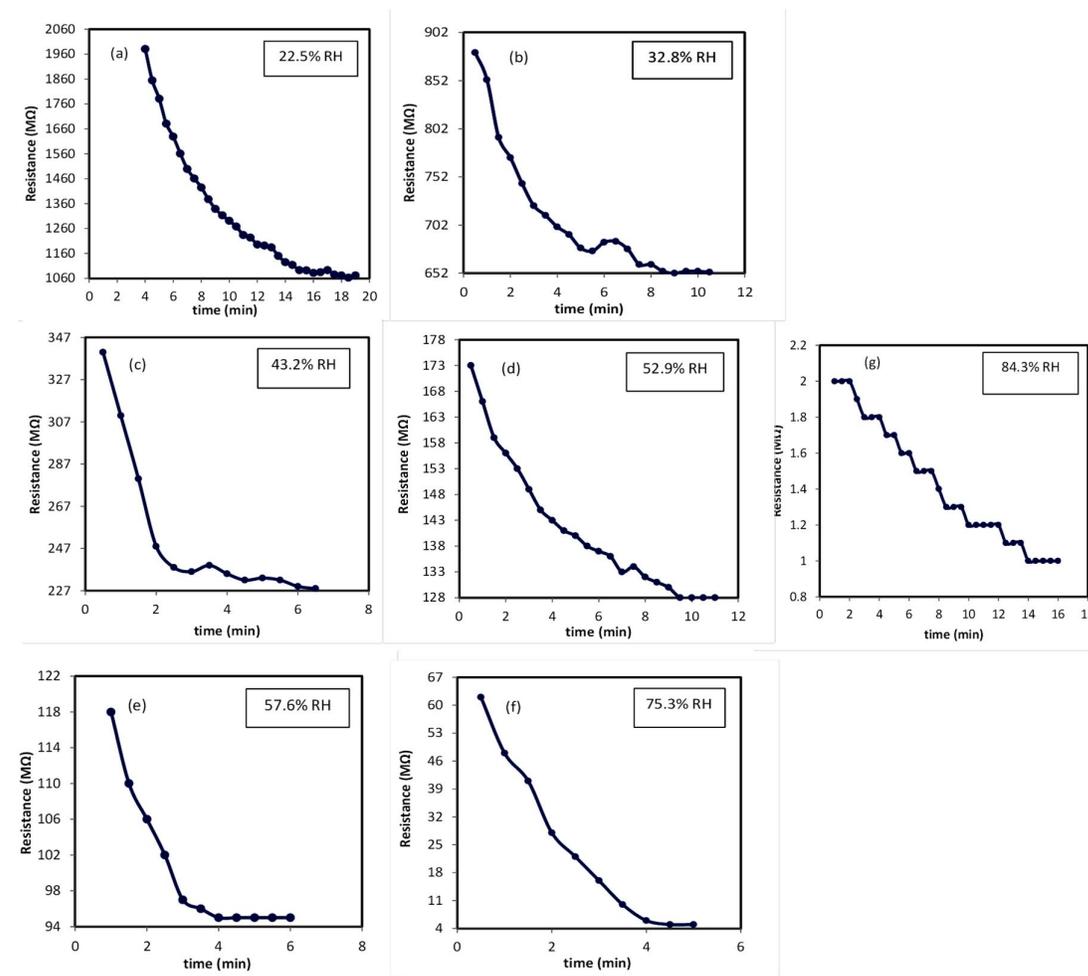


Figure 5. The variations of resistance of sample (b) with time.

The results of measurements for sample (c) are presented in Fig. 6. According to Fig. 6.a by increasing the relative humidity the resistance begins to decrease from a high value to a lower value. Fig. 6.b to g shows the effect of increasing the relative humidity on this sample.

Fig. 7 depicts the RH dependence of

resistance for samples (a), (b), and (c). A comparison between various resistances obtained at a certain RH value revealed that the resistance decreases by increasing the calcination temperature. The latter is due to the sample absorbing more water molecules. By increasing the calcination temperature more hydroxyl groups were

substituted. As a result, the material could adsorb more water molecules and the resistance decreases.

Comparing the amounts of resistance obtained in various humidity values reveals a

dramatic change of the resistance for the samples. Defining the change in resistance as sensitivity, copper-silica aerogel has an acceptable sensitivity to the humidity.

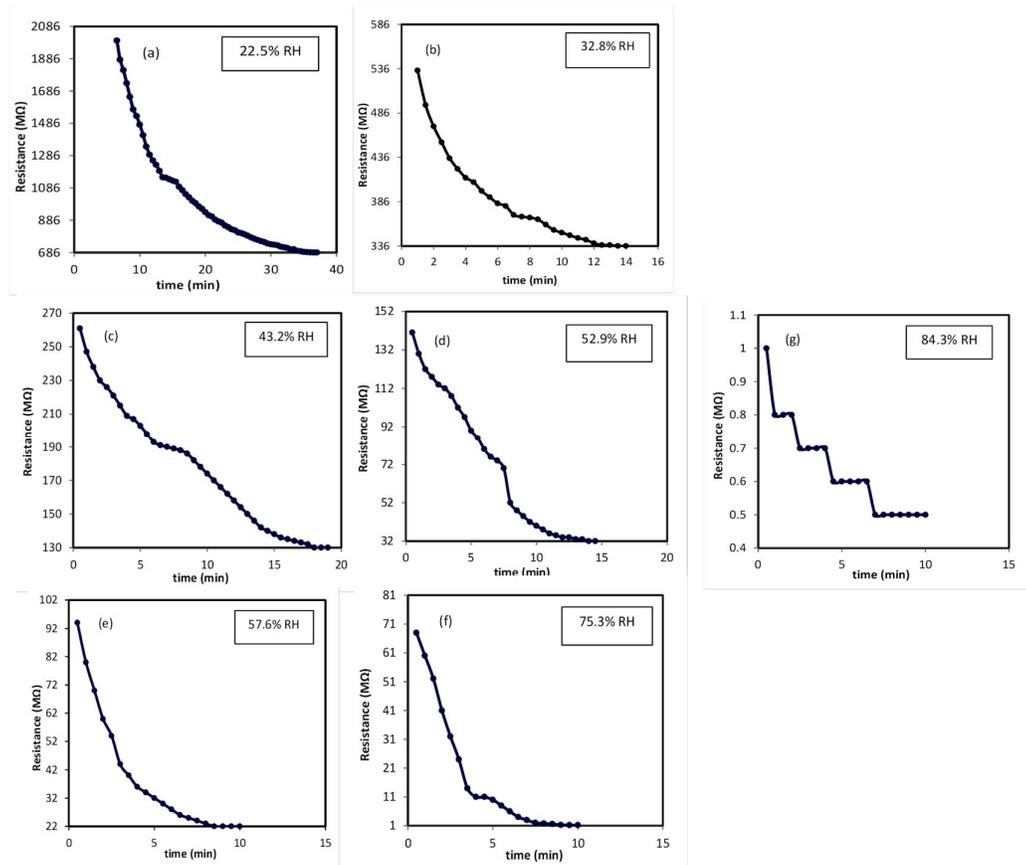


Figure 6. The variations of resistance of sample (c) with time.

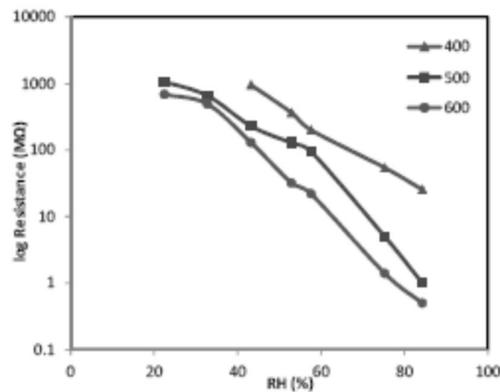


Figure 7. The RH dependence of resistance for samples (a), (b) and (c).

The amount of change for the sample calcined at temperature of 600°C, which is about 3 orders of magnitude, is more than that of the other samples. This proves the greater capability of this sample to adsorb water molecules. For the following parameters sample (a) was chosen.

The time it takes the sensor to reach 90% of its final resistance is defined as the response time [20]. The response characteristic curve of sample (a) is shown in Fig. 8. The response time (to perform the

humidification process from 11 to 84.3%) is about 7.5 minutes (including the time required to reach the equilibrium humidity). This time is much less than time calculated for the other values of relative humidity.

The stability of sample (a) was examined during three weeks. For this purpose, the sensor was placed in all humid environments introduced previously and its resistance was measured. The results presented in Fig. 9 reveal that, the stability of the sample changes more where the relative humidity is lower

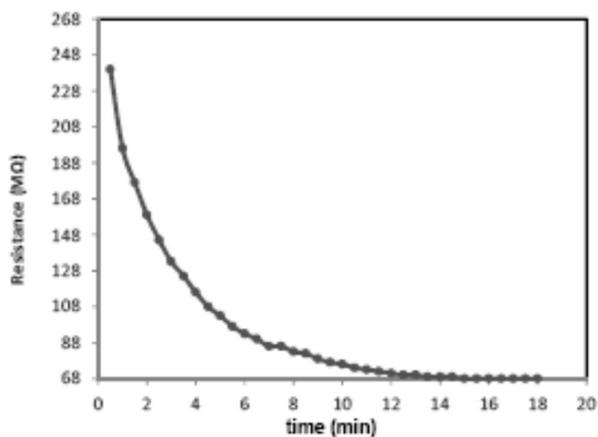


Figure 8. The response time obtained for sample (a).

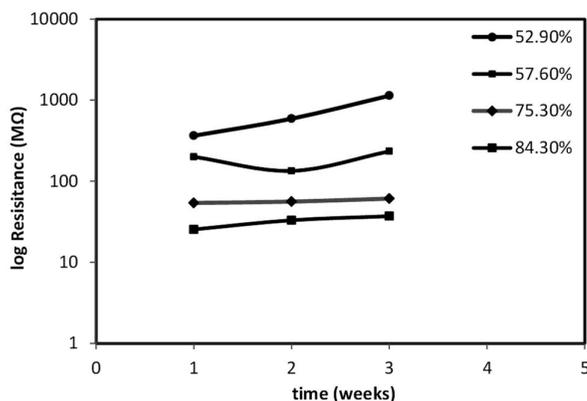


Figure 9. The variations of stability of sample (a) with time.

4. Conclusions

The copper-silica aerogel was calcined at different temperatures and used as humidity sensor. For all the samples applied, the resistance decreased by increasing the humidity. Comparing the results of resistance measurements at a specific relative humidity revealed that by increasing the calcination temperature the resistance decreased. All three samples studied showed good sensitivity to the humidity whereas sample (c) (calcined at a temperature of 600°C), with more than three orders of magnitude change in resistance, showed the best sensitivity. The response time for sample (a) (calcined at a temperature of 400°C) was 7.5 minutes and the stability experiments conducted on this sample showed that more changes occurred in lower humidities.

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