



RESEARCH ARTICLE – PHYSICS

Investigation of Copper Anodization Products with Temperature and Chemical Solution Changes

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Article Info.	Abstract
<p><i>Article history:</i></p> <p>Received 27 February 2024</p> <p>Accepted 21 April 2024</p> <p>Publishing 30 september 2024</p>	<p>The rapid breakdown anodization (RBA) process was used to modify the copper surface and produce copper oxide powder. The effects of the temperature and inhibitors like glycerol and ethylene glycol were studied. The rate of corrosion increased dramatically at low temperatures, whereas it decreased at high temperatures. Cubic Cu₂O particles were formed on the anode. Their sizes increased with increasing temperatures. Scanning electron microscope (SEM) images show the production of semispherical particles in the powder formed at low temperatures, but these particles congregate and combine at high temperatures. After using the glycerol, octahedron and semispherical Cu₂O particles were formed on the anode and cathode, respectively. The findings confirm the concept that the anodizing process's temperature may be utilized for controlling the oxide to metal ratio. Significant slowing of the anodic process occurs at high ratios for both inhibitors.</p>

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Introduction

Anodization is an electrochemical oxidation process that modifies the surface morphology and crystal structure of metals by thickening the oxide layer on their surfaces. It is used to change the appearance of certain metals. In addition to being frequently used to shield metals from corrosion, it also coats the metallic surface and makes it possible to dye them different colors [1]. The anodized coating is strong, long-lasting, and resistant to wear and peeling. One advantage of the electrochemical process over other approaches is its ability to regulate the final copper compound films' form and atomic composition through the manipulation of potential, reaction time, and integrated charge passing through the cell. When compared to traditional procedures, this procedure is more practical, eco-friendly, and time-efficient [2].

Copper and oxygen combine to generate two chemical compounds found exclusively in nature: cupric oxide (CuO) and cuprous oxide (Cu₂O). These oxides are semiconductors, where the color of CuO is black and the color of Cu₂O is reddish [3]. Copper is utilized in electronics, alloy formation, and the manufacture of wires, sheets, and tubes. It is immune to the effects of the environment and numerous pollutants [4].

Cu₂O is a suitable material for use in water photolysis for the production of solar cells and LEDs because of these properties [5]. Cu₂O exhibits significant potential for use in supercapacitors, hydrogen generation, and sensors [6]. Cupric oxide (CuO) and cuprous oxide (Cu₂O) may also be combined to generate other phases, such as copper-rich Cu₄O₃ [7].

Several papers have examined the impact of conditional variation on the properties of the generated particles. Voon et al. used anodizing to create Cu₂O nanostructured thin films, and they found that varying the anodizing process's voltage and temperature made it simple to customize Cu₂O nanostructures with a variety of morphologies [8]. Copper oxide nanowires,

nano-leaves, and nanopore arrays were produced by Kar et al. via electrolyte switching with DI water, methanol, and EG ethylene glycol [9]. Some of the unique strategies being researched for anodizing include anodizing in novel electrolytes, viscous electrolytes, with additives, or by altering current or voltage throughout the anodizing process [10].

The purpose of this research is to study the effect of inhibitors (glycerol and ethylene glycol) and temperature on the shape and size of the oxides resulting from the anodization process.

Experimental part

Cu foil (0.3 mm thick) with a rectangular shape (1x2cm) was cleaned with alcohol and then submerged in RBA chemical solution (0.1 M HClO₄ electrolyte). Two pieces of Cu were utilized in the anodization procedure; one was used as a working electrode and the other as a counter. There was 0.5 centimeter between the two electrodes.

The applied voltage was 20 volts. The anodization process took one hour. The chemical solution has to be constantly stirred during the surface modification procedure. After the electrochemical process, the samples were cleaned with deionized water and dried at 100°C. The chemical solution temperature was varied from 5 to 90°C. To decrease the activity of Cl⁻ ions, two inhibitors were added to RBA chemical solution: glycerol and ethylene glycol, with different ratios, as illustrated in Table 1.

Table 1. The ratios of inhibitors

Solution no.	The ratio of RBA chemical solution	glycerol	Solution no.	The ratio of RBA chemical solution	ethylene glycol
Sol ₁	75%	25%	Sol ₄	75%	25%
Sol ₂	50%	50%	Sol ₅	50%	50%
Sol ₃	25%	75%	Sol ₆	25%	75%

The topographies of the surfaces and the sizes of the generated particles have been determined by means of the scanning electron microscopy (SEM) method. Germany's MIRA3 TESCAN system has a model that is currently in use. By using energy dispersive X-ray spectroscopy (EDX), the components of each particle were determined. Photos must be crystal clear with such resolution to allow fine details visibility. The elements from any photo must be explained using numbers, letters, etc. The text within a figure or photo must have the same style, shape and height as the caption.

Results and discussion

Fig. 1 illustrates the impact of raising the pure RBA chemical solution temperature. When the temperature of the anodic solution was between 5 and 50 °C, the rate of corrosion (the rate of ions transfer in the electrolyte) rose significantly. Subsequently, the rate of increase falls within the range of (50 to 90 °C).

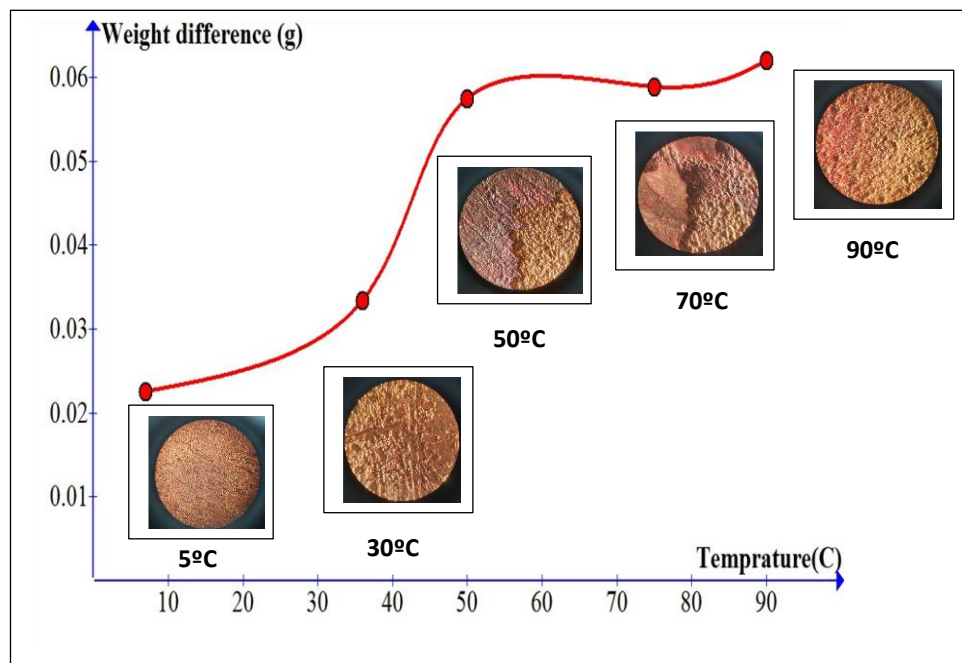


Figure.1. The variation of weight difference (WD) with temperature of anodic process. The insets are optical micrograph for anodized Cu surfaces.

Scopelianos informed that, since the higher temperature accelerated the evaporation of water and solvent, it became more difficult to consistently maintain the volume of the solution and the temperature of the electrolyte bath above 60°C. Due to the little volume of water (1 vol%), even a small water loss can have a significant impact on the electrolyte composition [11].

Since the reducing ion's activity was temperature-dependent, it was obvious that a greater temperature would improve Cl^- activity, which in turn would increase the rate of corrosion [12]. Nevertheless, at 50 °C, the corrosion rate fell rather than rose, demonstrating that corrosion ion activity was not the only factor influencing the corrosion rate.

SEM images of the anodized samples at low and high temperature are shown in Fig.2. By observing the Cu_2O cubes in Fig. 2, it can be seen that their volumes increase with increasing temperature. It was reported that higher heating temperatures produced bigger particles and greater oxidation due to the high temperature, which released more energy [13] [14] [15]. The volume increase of the produced particle after increasing temperature was attributed by Mardiansyah et al. to the increase in the amount of oxidation, i.e., the percentage of oxygen atoms in the structure of the produced particles [16]. Mahmood et al. confirmed the dependence of particle size on anodization temperature, agreeing with current results [17].

It was demonstrated by Yang et al. that as the temperature rose, corrosion weight loss or corrosion rate dramatically increased [18]. However, on occasion, the corrosion rate might also decrease if the temperature rose over a particular point [19].

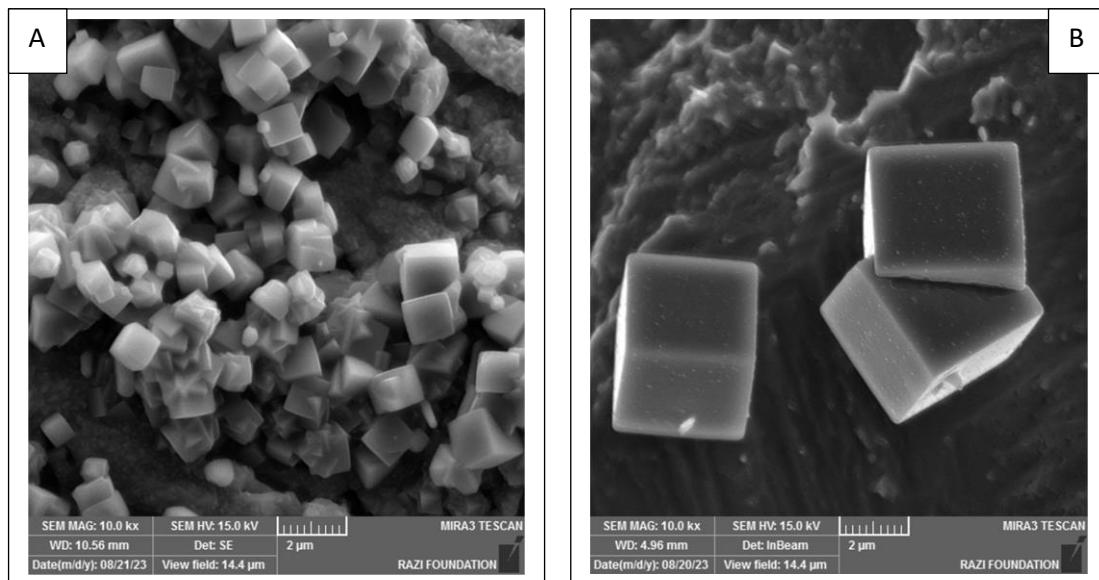


Fig.2. SEM images of anode at two temperature A: 30°C and B:90°C.

The compositions of the cubes in fig.3 were tested by EDX technique and listed in the following spectra.

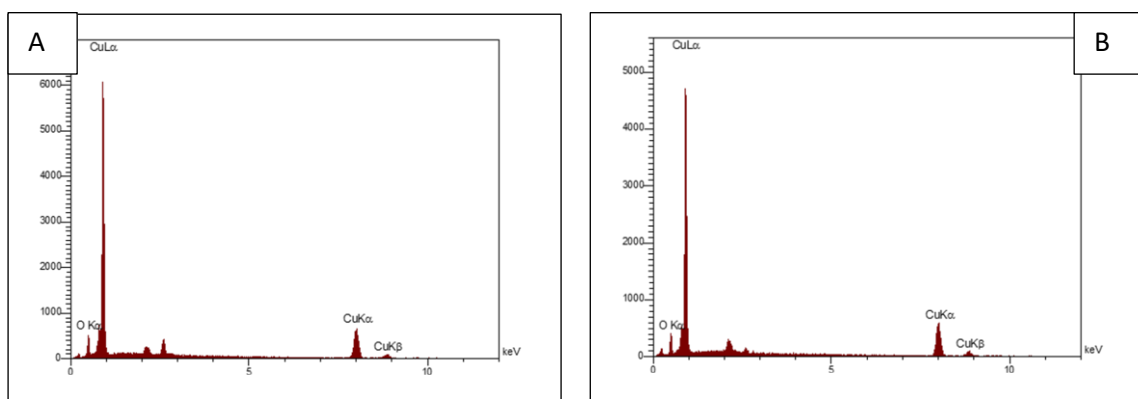


Fig.3. EDX spectra for the anodized samples at two temperature A: 30°C and B:90°C.

Table 2. wt% and at% for the anodized copper at two temperatures.

Anodized samples temp.	Element	Line	wt%	at%
30°C	O	K α	11.63	34.33
	Cu	K α	88.37	65.67
90°C	O	K α	11.18	33.33
	Cu	K α	88.82	66.67

According to the values of at% in Table 2, the cubes in Fig. 2 are composed of the Cu₂O phase, and the increasing temperature did not change this phase to another. Voon et al. reported that the temperature of the electrolyte affects the morphology but not the composition of the nanostructured thin film during the copper anodic process [8]. SEM images of the produced powders by RBA process at 30 and 90°C are shown in Fig.4.

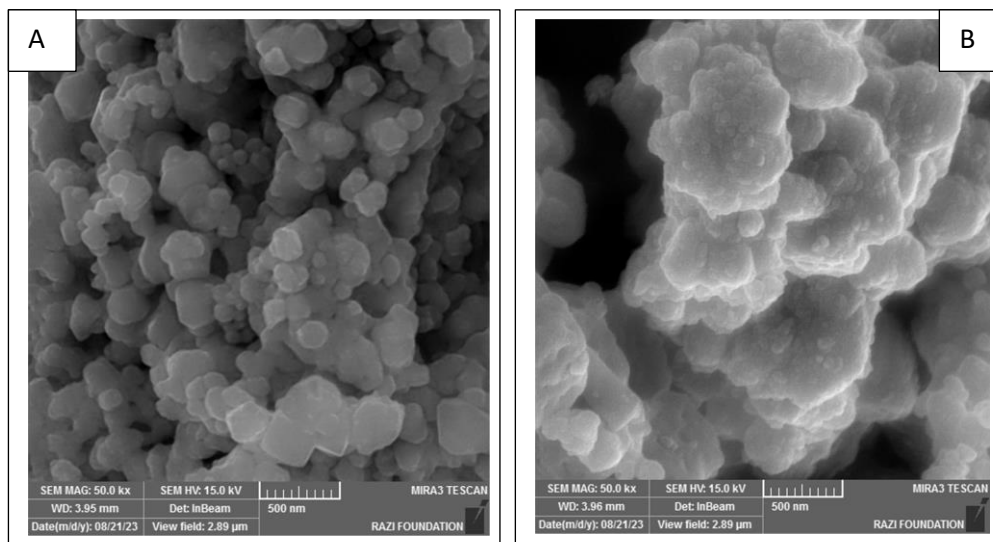


Fig.4. SEM images of the produced powders at A: 30°C and B:90°C.

The powder produced at low temperatures consists of semispherical particles. As the temperature increases to 90 °C, these particles aggregate and merge. The compositions of the powders were listed in Table 3.

Table 3. wt% and at% for the produced powders at two temperatures.

Anodized samples temp.	Element	Line	wt%	at%
30°C	O	K α	6.00	20.21
	Cu	K α	94.00	79.79
90°C	O	K α	6.08	11.21
	Cu	K α	96.92	88.79

It is clear from the at% values in Table 3 that the compositions of the produced powders are different from the formed Cu₂O cubes on the anode. The powder produced at high temperatures had a high copper content compared with that of oxygen. This result refers to the possibility of controlling the ratio of oxide to metal by the temperature of the anodizing process.

Fig.5. shows the effect of increasing the concentration of Glycerol and Ethylene glycol (as inhibitors) on the corrosion process of copper during anodization.

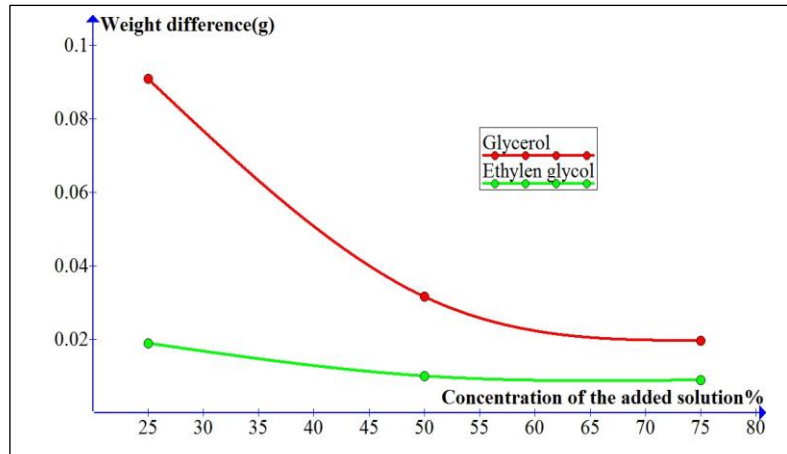


Fig.5. WD as a function to the added Glycerol and Ethylene glycol volume concentrations

Because of the high viscosity of glycerol compared with ethylene glycol, the movement and exchange of ions are slower for the former compared with the latter. As a result, the WD change is high with the increase of the glycerol ratio from 25% to 50%, but this variation is less for ethylene glycol when the same ratio is varied. At a high ratio (75%), the anodic process is strongly slowing down, and the WD has become the minimum.

SEM image of the anodized sample (anode + cathode) in chemical solution composed of (25% Glycerol +75% RBA) is shown in Fig.6.

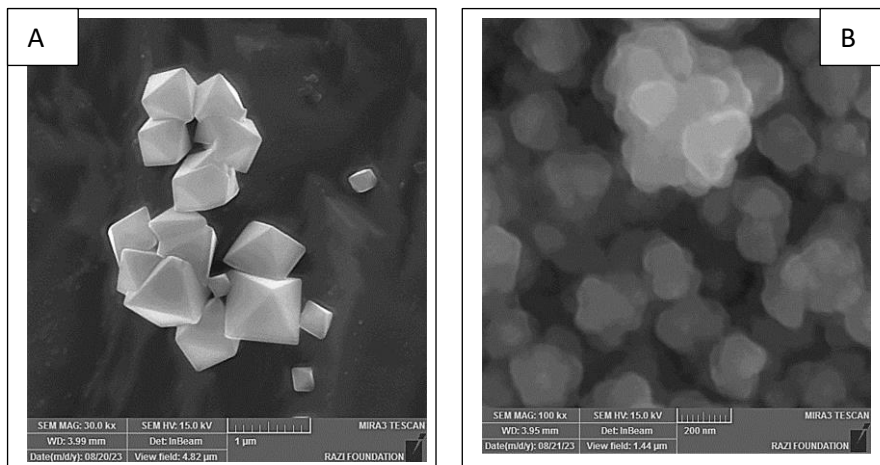


Fig.6. SEM images of the anodized sample in (25% Glycerol +75% RBA); A: anode, B: cathode.

On the anode, the shape of the formed bodies in image A is an octahedron, but semispherical bodies were formed on the cathode. The difference between these two images confirmed that the mechanism of formation of copper oxide on the anode differs from that on the cathode [20]. The compositions of the anode and cathode in fig.6 were listed in Table 4.

Table 4. wt% and at% for the produced powders with (25% Glycerol +75% RBA);

samples	Element	Line	wt%	at%
Anode	O	K α	13.07	37.39
	Cu	K α	86.93	62.61
Cathode	O	K α	11.52	34.09
	Cu	K α	88.48	65.91

The values of at% for copper and oxide confirm the formation of the Cu₂O phase on the anode and cathode.

Conclusions

For applications like gas sensors or solar cells, it is desirable to use Cu₂O sizes as small as possible to increase the reaction surface. The current study gives useful information about the effect of temperature and inhibitors on the size of Cu₂O particles and the corrosion of Cu during RBA.

Acknowledgments

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