Electrodeposition of nano-Cu, Ni and binary Ni/Cu into nano-porous AAO layer for high-efficiency black spectrally selective coating

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Abstract
Background: Anodic aluminum oxide (AAO) template is widespread due to its diverse metal nanostructures. Various solar selective black coatings on aluminum oxide template were investigated. Spectrally selective nano-coating of nickel, copper and nickel–copper on anodized aluminum was produced.

Results: The coatings were performed via electrodeposition and evaluated by measurement of coating thickness, hardness and optical properties. Also, these coatings were analyzed by scanning electron microscope, energy-dispersive X-ray spectroscopic and polarization studies in 3.5% NaCl solution. The anodized aluminum showed higher corrosion resistance (4.8284 KΩ) and lower corrosion rate (0.02189 mm/year). However, the electro-colored Al with Cu for 60 min showed the highest corrosion rate of 0.1942 mm/y, compared with other Al samples. The effect of anodizing time on the metal density and the optical efficiency of black copper coating was studied.

Results: The obtained solar panels exhibit low values of solar reflectance within the visible range and high solar absorption efficiency. These coatings are highly efficient and adequate for any solar system.

Keywords: Electrodeposition, Nickel, Copper, Selective coating

Background
Metal nanostructures continue to attract considerable attention because of their size- and shape-dependent catalytic, electronic, optical, and magnetic properties (Baig et al., 2021). Anodic aluminum oxide (AAO) template is widespread due to its diverse metal nanostructures. A porous oxide layer is formed upon oxidation of aluminum; the pore diameter, the pore density, and the pore depth depend on the applied potential, temperature, and the electrolyte composition (Ghaddar et al., 2009). Nano-porous anodic oxide coating can be colored by electrolytic coloring methods. The coloring methods included the immersion of the specimens of anodized aluminum in solutions containing organic dyes. However, because of the limited stability of the colors obtained by organic dyes, these methods have been replaced by other processes such as integral and electrolytic coloring. In the electrolytic coloring process, the metal atoms are incorporated into the porous matrix of anodized aluminum that is obtained by anodization. The metal, which is employed as the coloring agent, exits in the electrolyte as a cation, and the characteristics of the resultant color depend on the concentration of metal ion in the solution and the type of electrolyte. Pastore et al. (1989) and Shih and Huang (2008) reported that obtaining the darkest shade of black color on the aluminum surface is a challenge but worthwhile. Hence, the process starts by forming an anodic film on aluminum and

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then obtaining the darkest shade of black color using an electrolytic method. The parameters that impact on the coloring process are bath temperature, voltage, electrolyte concentration and time duration (Shih and Huang 2008). Generally, electrolytic coloring technique is more conversational exhibiting stable and high-quality color (Girginov et al., 2012; Nozari Nezhad et al., 2014). Consequently, the electrolytic deposition method is utilized in decorative applications, solar energy storage and conversion systems. Hence, the black electrolytic coloring of Al materials, which are light in weight, low in cost, and good at thermal as well as electrical conductivities, has been gradually developed and applied in the manufacturing process of the solar energy source plate (Awad et al. 2015a, 2015b). In addition, multilayer alloys are metallic composite structures, comprising of alternating layers of two different metals, periodically deposited on a pure metal substrate or alloy substrate, by electrodeposition or vacuum deposition techniques. Moreover, the electrodeposition of multilayers has been reviewed by Ross (1994) and has a great interest owing to the fact that these multilayers exhibit enhanced magnetic, electrical, diffusion and mechanical properties as compared to those that of the corresponding pure metals (Alper et al., 1993; Dakua 2015). Nickel–copper alloys are potentially incorporated in the industrial applications where resistance to corrosion and thermoelectric characteristics is required. Its corrosion resistance makes it suitable for use as a protective coating in marine and corrosive environments. In the literature, they have involved work on Ni–Cu alloys primarily on planar electrodes. In fact, there are a relatively few studies that exist on the electrodeposition of copper nickel alloys, and none completely characterize the deposition process (Amrit 2003; Chassaing and Quang 1987). Electrolytic coloring showed high stability and quality of the color produced, and it could be used in different applications (Kaplanoglu et al. 2006; Shaffei et al. 2021). Moreover, Mennucci et al. (2021) presented several electrodeposition procedures to produce nickel black coatings as greener and less toxic alternatives to Cr(VI)-based coatings used in different applications. In this study, the electrolytic black coloring of nano-porous anodized aluminum by copper and nickel was investigated, an enhancement of metal density and maximum absorbance was achieved by co-deposition of nickel–copper alloy compared by black coating based on copper ions only, so several black selective coatings will be presented in this work to enhance the efficiency of any solar system.

### Methods

#### Materials

Aluminium sheet of alloy 99.5% was cut into similar samples of dimension 10 × 3 cm; lead was used as counter electrodes in anodization step. Aluminum samples were subjected to the preliminary treatment, which involves degreasing from oils by acetone then followed by etching in 10% sodium hydroxide for 10 min., rinsed by distilled water then followed by neutralization in 20% nitric acid for 30 s. and rinsed by distilled water. The anodization was carried out in 170 g/l H2SO4 at 15–17 V and temperature ranged (15–17) °C. Copper and nickel sulfate solutions were prepared for the electrolytic coloring step; the chemical composition of each coloring solution is listed in Table 1.

#### Electrolytic coloring

Electrolytic coloring step uses electrolytic cell of AC power supply connected to working electrode and stainless-steel electrode or nickel electrode (in case of nickel coating). The anodized aluminum samples were transferred to different coloring baths including copper and nickel sulfate, the coloring time was fixed at 10 min. and the applied AC voltage was 15 V.

#### Characterization

**Instruments**

GW Lab DC Power Supply GPR-3030 was used as a source of DC current. Moreover, AC power supply MIO-523/RI Contact voltage 1000 VA output 0–250 V, single-phase 50 Hz was used as a source of AC current during electrolytic coloring step. Also, the optical measurements were recorded by Spectrophotometer V-570 UV/VIS/NIR. Scanning electron microscope (SEM–EDX) was investigated using Inspect S (FEI Company, Holland). The metal density (lg/cm^2) was determined by atomic absorption analysis, Agilent Technologies, 200 Series AA. The colored samples were subjected to the polarization resistance investigation using AUTO LAB potentiostat. A solution of 0.5 M NaCl was used as the aggressive corrosion medium.

#### Results

Aluminium surface after electrolytic coloring by electrodeposition of Ni and Cu and mixture of Ni and Cu at constant anodization time of 30 min and electrolytic coloring time of 10 min is shown in Fig. 1. Also, electrolytic coloring of aluminium by electrodeposition of copper for

### Table 1 Chemical composition of electrolytic coloring bath

| Type of bath | Chemical composition | pH  |
|--------------|----------------------|-----|
| Copper bath [3] | 40 g / l CuSO4, 10 g/l Mg SO4 | 2   |
| Ni bath [15] | 60 g Ni SO4, 7 H2O, 40 g H3BO3, 20 g MgSO4, 30 g NiCl2 | 4   |
10 min using different anodization times of 20, 30 and 60 min was studied as shown in Fig. 2.

Scanning electron microscope and EDX analysis
As shown in Fig. 3, all samples (1–5) of FESEM images showed the formation of nano-porous oxide film after anodization and electrolytic coloring with a slight variation in the density and distribution of oxide layer according to the anodization and coloring time.

Furthermore, EDX analysis in Fig. 4 showed the presence of nano-metals deposited into nano-porous oxide layer after electrolytic coloring, where nano-nickel (2.27%), nano-co-nickel and copper (2.14 and 0.3%) and nano-copper (1.82, 6.34 and 4.25%) were detected.

Atomic absorption and determination of metal content
As shown in Fig. 5, the highest content of nickel 2.8 mg/cm² was detected after electrolytic coloring in nickel bath and copper content detected in copper bath was 1.75 mg/cm². However, the summation of Ni and Cu detected was 2.3 mg/cm² in the mixture of nickel and copper bath. On the other hand, the content of copper was determined in the aluminum sample electrolytically colored for constant time 10 min and after different anodization time 20, 30 and 60 min. It was found that the amount of Cu
was increased as the anodization time increased, where Cu detected was (2.7 mg/cm$^2$) after 60-min anodization time. While the amount of Cu detected was decreased to 1.75 mg/cm$^2$ after anodization for 30 min, lower amount 1.3 mg/cm$^2$ was detected after anodization time 20 min, as shown in Fig. 6.

Measurements of thickness and hardness

As given in Table 2, the sample anodized for 60 min and colored by Cu showed the highest thickness 20 μm due to adequate time to build up a thick anodized layer. Then, the thickness determined of Al samples anodized at 30 min and electrolytically colored with Ni was 16 μm and Cu 11 μm and the measured mixture Ni/Cu was 10 μm, while the lowest thickness was 8 μm of the sample electrolytically colored with Cu and anodized for 20 min. Moreover, the hardness was also determined, and it was found that it is affected by anodization time (Table 3). The sample anodized for 60 min and colored by Cu showed the highest hardness 54 HB due to enough time to build up anodized layer. Then, the hardness determined of Al samples anodized...
with Ni was 53 and Cu 51 and mixture Ni/Cu was 51 HB, while the lowest hardness was 50 HB of the sample electrolytically colored with Cu and anodized for 20 min.

Optical characteristics and reflectance measurements
Optical characteristics of electrolytically colored aluminum samples are essential for reflectance and absorbance of the surface. The uniform black coatings of aluminum surface play an important role for high
absorbance in the wavelength visible regions (350–850 nm), as shown in Fig. 7.

**Effect on anodizing time on reflectance**

Figure 8 illustrates the effect of anodizing time on the reflectance (optical efficiency) of black colored anodized aluminum samples that were colored by copper metal ion. The optical measurements were recorded at wavelength range of (0–2500) nm. From these data, it is clear that increasing anodizing time from 20 to 60 min., the colored aluminum samples showed lowest reflectance in

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### Table 2  Tafel parameters of aluminum and anodized aluminum samples

| Sample          | $\beta_a$ (V/dec) | $\beta_c$ (V/dec) | $E_{corr.}$ (V) | $i_{corr.}$ (μA/cm²) | Corrosion rate (mm/year) | Polarization resistance (KΩ) |
|-----------------|-------------------|-------------------|-----------------|-----------------------|--------------------------|-----------------------------|
| Al substrate    | 125.67            | 106.99            | −800.61         | 7.8914                | 0.08603                  | 3.1803                      |
| Anodized Al     | 24.8550           | 219.33            | −723.64         | 2.008                 | 0.02189                  | 4.8284                      |

### Table 3  Tafel parameters of aluminum and electrolytically colored aluminum samples Ni, Ni + Cu and Cu at constant anodization time 30 min

| Sample                  | Coloring time (min) | $\beta_a$ (V/dec) | $\beta_c$ (V/dec) | $E_{corr.}$ (V) | $J_{corr.}$ (μA/cm²) | Corrosion rate (mm/year) | Polarization resistance (KΩ) |
|-------------------------|---------------------|-------------------|-------------------|-----------------|----------------------|--------------------------|-----------------------------|
| Al substrate            | –                   | 125.67            | 106.99            | −800.61         | 7.5914               | 0.08603                  | 3.1803                      |
| Al colored by Ni        | 30                  | 220.1700          | 319.55            | −723.28         | 3.7446               | 0.04082                  | 3.2004                      |
| Al colored by Ni + Cu   | 30                  | 118.0990          | 190.24            | −728.09         | 2.3794               | 0.06594                  | 2.0165                      |
| Al colored by Cu        | 30                  | 23.6590           | 262.91            | −718.54         | 7.8257               | 0.09114                  | 1.4446                      |

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![Fig. 7](image_url) Reflectance measurements of colored samples by Ni, mixed Ni and Cu, Cu (20 min), Cu (30 min) and Cu (60 min)

![Fig. 8](image_url) Comparison between reflectance measurements of samples colored by Cu at different anodization times of 20, 30 and 60 min
spite of variation of anodization time in the visible range of spectrum.

**Linear polarization and corrosion resistance measurements**

The study of linear sweep voltammetry (LSV) of aluminum samples was studied in aggressive solution of 3.5% NaCl relative to both the surface of aluminum substrate and anodized aluminum before coloring step.

As shown in Figs. 9, 10 and Table 2, the corrosion potential \( (E_{\text{corr}}) \) of anodized aluminum surface was shifted to more anodic potential \( (E_{\text{corr}} = -723.640 \text{ V}) \) more than aluminum substrate \( (E_{\text{corr}} = -800.610 \text{ V}) \), and it revealed also corrosion current density \( (i_{\text{corr}} = 2.0080 \mu\text{A/cm}^2) \) lower than aluminum substrate \( (i_{\text{corr}} = 7.8914 \mu\text{A/cm}^2) \). This indicates that anodized aluminum sample revealed higher corrosion resistance due to the anodic oxidation and smooth passive film formed over aluminum surface. The anodized aluminum showed higher corrosion resistance \( (4.8284 \text{KΩ}) \) and lower corrosion rate \( (0.02189 \text{ mm/year}) \), while aluminum substrate has lower corrosion resistance \( (3.1803 \text{KΩ}) \) and lower corrosion rate \( (0.08603 \text{ mm/year}) \). This could be demonstrated by the formation of two protection layers: one is compact barrier thin film \( (5 \mu\text{m}) \) of aluminum oxide and the other is thick porous \( \text{Al}_2\text{O}_3 \) layer \( (25 \mu\text{m}) \) after anodization treatment and passivation of virgin aluminum surface. The corrosion resistance was decreased by electrodeposition of nano-metal Ni, Ni–Cu and Cu, where it decreased to 3.2004, 2.0165 and 1.446 KΩ (Table 3).

The high conductivity of metals decreased the insulation of anodized aluminum. Nano-Cu deposited into nanoporous layer AAO led to the lowest corrosion resistance due its high conductivity \( (5.98 \times 10^{-7} \text{S/m}) \) more than Ni conductivity \( (1.46 \times 10^{-7} \text{S/m}) \).

(https://www.thoughtco.com/electrical-conductivity-in-metals-2340117). Furthermore, the copper density of nano-Cu electrodeposited in nano-porous AAO layer has highly impact on the surface activity. As shown in Fig. 11, the corrosion potential is shifted toward anodic potential as the content of Cu decreased. So, Cu (20) deposited after anodization for 20 min showed the highest corrosion potential and lower icorr. Corrosion resistance was influenced by the content of nano-Cu, where corrosion resistance was decreased from 3.1803 to 1.4446, 1.4758 and 0.5619 KΩ as the time of electrodeposition of Cu increased to 20, 30 and 60 min, respectively (Table 4). Also, the corrosion rate revealed
the increase as the Cu content increased, where the electro-colored Al with Cu for 60 min showed the highest corrosion rate of 0.1942 mm/y, compared with other Al samples electro-colored for 20 (0.07114 mm/y) and 30 min (0.14445 mm/y). Figure 12 shows the overall results of linear polarization of Al samples at different conditions. The results revealed that the anodized sample showed the highest corrosion resistance due to the insulation of anodized layer, while other samples showed lower corrosion resistance after electrodeposition of nano-metals with enough electric conductance. This rendered to the variation of electric conductance and atomic size of Ni and Cu, where the electric conductance of Ni (1.46 × 10^7 S/m) is lower than Cu (5.98 × 10^7 S/m). This indicates that the highly resistance non-conductance porous AAO layer was turned to low conductance layer after electrodeposition of nano-Ni and turned to high conductance layer after electrodeposition of nano-Cu.

### Discussion

A new approach was executed for electrolytic coloring of aluminum using electro-co-deposition of nickel and copper into the nano-porous layer of anodized aluminum after anodization process.

### Scanning electron microscope and EDX analysis

Anodic oxide layer was built up on the aluminum surface after anodic oxidation, where firstly the gelatinous aluminum oxide hydroxide (Boehmite γ-AlO(OH)) forms and crystallizes in the orthorhombic di-pyramidal system and is typically massive. Then, it was turned to bundles of hexagonal nano-porous crystal structure of aluminum oxide as shown in Fig. 3. Moreover, the EDX analysis indicates the black color formed due to the presence of nano-metals Ni, Cu and Ni/Cu imparting the scattering light of black color.

### Atomic absorption and determination of metal content

The content of Ni and Cu per surface area (1 cm²) was determined in aluminum samples after electrolytic coloring using the atomic absorption technique. The data reveal the presence of nano-Ni more than nano-Cu in the electrolytically colored aluminum samples. Moreover, the measurements of EDX analysis revealed that the variation of electrodeposition of Ni and Cu showed different metal densities detected. This rendered to the variation of electric conductance and atomic size of Ni and Cu, where the covalent radius of Ni (124 ppm) is lower than Cu (132 ppm) (https://www.webelements.com/copper/atom_sizes.htm). This indicates that the high probability of filling nano-porous AAO layer with nano-Ni is higher than filling it with nano-Cu. So, the content of nano-Ni is more than the content of nano-Cu electrolytically deposited at the same conditions of anodization and electrolytic coloring steps. As shown in Fig. 6, the increase of metal content with anodization time is attributed to the continuous widening of pores of AAO thin film. Also, continuous increase of column height build ups excess oxide layer due to anodic oxidation. Moreover, the Cu/Ni
deposited into anodized aluminum enhanced the metal density within the porous layer compared with Cu/AAO (the electrolytic coloring by copper bath), where it was increased from 1.8 to 2.4 mg/cm² after constant anodization time of 30 min.

Measurements of thickness and hardness

The thickness of anodic oxide layer formed after the anodization and electrolytic coloring of aluminum surface was determined (Table 5). The anodization time impacts the thickness of nano-porous layer. Moreover, the hardness was also determined, and it was found that it is affected by anodization time (Table 6). This indicates that the anodization time influences the hardness of aluminum samples after anodization and electrolytic coloring. This could be demonstrated by the increase in thickness of nano-AAO layer with long time of anodization step. Furthermore, continuous widening and increase of pores wall thickness and height lead to the increase of hardness of Al electrolytically colored by Cu. The anodization time (60 min.) was high in hardness value than the colored by Cu after anodization time 30 and 20 min., respectively.

Optical characteristics and reflectance measurements

As shown in Fig. 7, aluminum samples after electrolytic coloring with Ni, Cu and mixture Ni/Cu showed the lowest reflectance in the range of visible region with a slight difference. This indicates the high absorptivity of aluminum surface, and uniform black color was obtained. Regarding the results, it can be observed that the nickel samples showed the minimum reflection in the visible region comparing with other samples. The co-deposition of copper–nickel alloy showed also a low reflectance value. This was achieved due to the high blackness of the surface of these samples and consequently the high absorbance of solar radiation.

Linear polarization and corrosion resistance measurements

After anodization and electrolytic coloring, new nano-metals like Ni, Cu and both Ni and Cu were deposited into the nano-porous layer of Al₂O₃. So, the corrosion resistance was higher than aluminum surface but slightly lower than anodized sample. As shown in Fig. 10, the corrosion potential of Al samples after anodization and electrolytic coloring was shifted to anodic potential, while the Al sample of anodized and colored with Cu showed the higher $i_{corr}$ more than other samples.

Conclusions

The electrodeposition of copper, nickel and copper–nickel on anodized aluminum produced highly efficient spectrally selective coatings. These types of nano-coatings showed minimum reflectance values within the visible range, which gives high absorption efficiency surfaces. The increase of time of anodizing enhances the hardness and the thickness of colored anodized aluminum samples. The sample anodized for 60 min and colored by Cu showed the highest thickness 20 μm due to adequate time to build up thick anodized layer. From studying of linear sweep voltammetry (LSV) of aluminum samples in aggressive solution of 3.5% NaCl, it was concluded that the anodized aluminum showed higher corrosion resistance (4.8284KΩ) and lower corrosion rate (0.02189 mm/year). However, the corrosion rate increased as the Cu content increased, where the electro-colored Al with Cu for 60 min showed the highest corrosion rate 0.1942 mm/y, compared with other Al samples.

Abbreviations

AAO: Anodic aluminum oxide; EDX: Energy-dispersive X-ray analysis; FESEM: Field emission scanning electron microscope; LSV: Linear sweep voltammetry; $E_{corr}$: Corrosion potential; $\beta_p$: Anodic Tafel constant; $\beta_c$: Cathodic Tafel constant, $i_{corr}$: The corrosion current; Boehmite γ-AlO(OH): Gelatinous aluminum oxide hydroxide; HB: Brinell hardness number.

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Authors' contributions
All authors participated in the development and implementation of the research plan and subsequently written it. The first author HS carried out the experimental work and shared in writing and discussion of results, MF shared in the idea of work, discussion of results and implementation of the research plan, AM shared in writing, development of research and all authors read and approved the final manuscript.

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Availability of data and materials
The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare that they have no competing interests.

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