Effect of CeO_2 and CuO oxide nanoparticles on the nickel electroplating in sulfate solution

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Received 7 Sep. 2025; Revised 29 Oct. 2025; Accepted 10 Nov. 2025; Published 28 Nov. 2025.
DOI: https://doi.org/10.54939/1859-1043.j.mst.107.2025.51-57

ABSTRACT

This study investigates the electrochemical behavior of nickel composite coatings containing CuO and CeO_2 nanoparticles using polarization and electrochemical impedance spectroscopy (EIS). The presence of CuO or CeO_2 oxide nanoparticles in the solution with the ranges between 2 and 12 g/L insignificant increased cathode polarization in the nickel sulfate plating solution. However, the EIS results showed that CuO particles had little effect on the solution resistance and plating process, while CeO_2 particles significantly increased the solution resistance, thus affecting the nickel plating rate. The solution's charge transfer resistance would rise due to the high concentration of added oxide particles, which will be detrimental to the electrode surface's deionization process, the plating solution's oxide particle content should not exceed 12 g/L.

Keywords: Nickel sulfate solution; CeO_2; CuO; Ni-CeO_2 composite plating; Ni-CuO composite plating.

1. INTRODUCTION

Composite coatings are preferable to metallic coatings because they combine the best features of the base metal and the composite material [1]. Nickel-based composite coatings are widely used in a variety of industrial applications due to their distinct mix of exceptional qualities. When compared to pure nickel coatings, these coatings exhibit superior corrosion resistance, wear resistance, and mechanical qualities [1-5]. To create a composite coating, the composite particles are distributed in the plating solution and suspended in the system through agitation. In a composite plating system, the process typically consists of five steps: (1) the formation of ion clouds around the particles, (2) particle convection toward the cathode, (3) particle diffusion through the hydrodynamic boundary layer, (4) particle diffusion through the concentration boundary layer, and (5) particle adsorption on the cathode surface, resulting in deposition on the deposited metal layer [6].

Among the particles, codeposition of nickel, copper oxide (CuO) and cerium oxide (CeO_2) nanoparticles has attracted attention due to their distinct electrical and chemical properties [2-4]. CuO nanoparticles, being semiconductive, serve as heterogeneous nucleation centers that refine grain structure and enhance the uniformity and conductivity of the deposit [4]. CeO_2 nanoparticles, on the other hand, exhibit strong dielectric properties, forming passive films that significantly improve corrosion resistance [4]. However, their effects on the electrodeposition process differ markedly, particularly in modifying charge transfer, diffusion, and interfacial capacitance.

Electrochemical impedance spectroscopy (EIS) and polarization techniques are powerful methods for exploring such behaviors. EIS provides detailed insights into interfacial resistance, capacitance, and diffusion, while polarization curves identify kinetic changes in metal ion reduction [4, 7, 8]. In this paper, electrochemical impedance and polarization measurements were used to assess the impact of oxide nanoparticles (CuO, CeO_2) on the plating process in nickel sulfate solution.

2. EXPERIMENTAL

2.1. Chemicals

Chemicals used in the study included: $NiSO_4.7H_2O$ (PA, UK), H_3BO_3, sodiumlauryl sulfate (PA, China); CeO_2 particles (Richest Group Ltd., Shanghai, China) and CuO particles (Nano Global, Shanghai, China) with sizes of 50 ÷ 100 nm.

2.2. Experimental solution

The sulfate plating solution contained $NiSO_4.7H_2O$ (50 - 350 g/L), H_3BO_3 (30 g/L), and 0.1 g/L sodium lauryl sulfate (S^o solution). The combined plating solution contained S^o solution ($NiSO_4$ 300 g/L) and x g/L CuO (x = 2 ÷ 14; symbol S^oCu^x) or y g/L CeO_2 (y = 2 ÷ 14; symbol S^oCe^y). The nanoparticles were wetted with sodium lauryl sulfate before being evenly dispersed in the solution by ultrasound. The plating solution was stirred continuously to maintain the dispersion of the nanoparticles.

2.3. Methods

The cathodic polarization curve of the Ni plating process was measured using an Autolab PG302 device (Netherlands) with a three-electrode system: a fixed nickel electrode with an area of 1 cm^2 served as the working electrode, a Ti plate measuring with an area of 10 cm^2 served as the counter electrode, and a silver-silver chloride electrode saturated Ag/AgCl as the reference electrode. The potential scanning area was from open circuit potential (OCP) to -2.0 V, the scanning speed was 10 mV/s, and the solution temperature was 50 °C.

The impedance of the Ni plating process was measured using an IM6 device (Zahner-Elektrik, Germany) with a three-electrode system: a fixed nickel electrode with an area of 0.5 cm^2 served as the working electrode, a Ti plate with an area of 10 cm^2 served as the counter electrode, and a calomel electrode served as the reference electrode. The survey range was between 100 kHz and 10 mHz, and the solution temperature was set at 50 °C.

3. RESULTS AND DISCUSSION

3.1. Cathodic polarization curves of the Ni in the plating solutions

3.1.1. Cathodic polarization curves of the Ni in the nickel sulfate solution

To investigate the influence of $NiSO_4$ concentration on plating layer quality and plating conditions, polarization potential was evaluated in solutions containing various $NiSO_4$ concentrations. The results are displayed in figure 1.

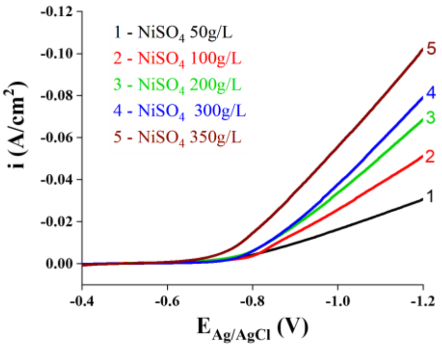

Figure 1. Cathodic polarization curves of Ni in the nickel sulfate solutions (S^o) with difference $NiSO_4$ concentrations (50 ÷ 350 g/L).

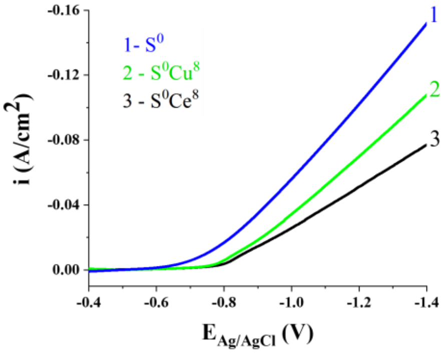

Figure 2. Cathodic polarization curves of Ni in the S^o, S^oCu^8, S^oCe^8 solutions.

Figure 1 showed that the discharge potential of Ni^{2+} in the tested solution was around -0.67V (Ag/AgCl) (line 1), which was more negative than the discharge potential of hydrogen, indicating that H_2 gas was always released during the nickel plating process [8]. In the nickel sulfate plating solution, H^+ ions were reduced first, followed by Ni^{2+} ions to produce the Ni plating layer; the Ni^{2+} ion reduction process resulted in the creation of the intermediate ion $Ni(OH)^+$ [8, 9]. The plating process in nickel sulfate solution can be described according to reactions (1) – (7), in which reactions (1) – (3) occurred simultaneously in the same potential region as reactions (4) – (7) [9]:

$$Ni + H^+ + e^- \rightarrow Ni\text{–}H_{ads} \quad (1)$$

$$2Ni\text{–}H_{ads} \rightarrow 2Ni + H_2 \quad (2)$$

$$Ni\text{–}H_{ads} + H^+ + e^- \rightarrow Ni + H_2 \quad (3)$$

$$Ni^{2+} + H_2O \leftrightarrow NiOH^+_{aq} + H^+ \quad (4)$$

$$NiOH^+_{aq} \rightarrow Ni(OH)^+_{ads} \quad (5)$$

$$Ni(OH)^+_{ads} + e^- \rightarrow Ni(OH)_{ads} \quad (6)$$

$$Ni(OH)_{ads} + H^+ + e^- \rightarrow Ni + H_2O \quad (7)$$

The findings (figure 1) reveal that when the concentration of $NiSO_4$ in the solution increased, the polarity decreased because the amount of Ni^{2+} ions in the solution increased, the plating speed increased. However, too high amount of $NiSO_4$ will be difficult to dissolve during the composting process. Therefore, the concentration of $NiSO_4$ was set to 300 g/L.

3.1.2. Effect of CeO_2 and CuO oxide particles on polarization curves in nickel sulfate plating solution

The nickel polarization curves in figure 2 demonstrated that Ni's discharge potential in sulfate solution was E* = -0.70 V (Ag/AgCl). When CeO_2 or CuO oxide particles were added to the solution (both at 8 g/L), the cathode polarization increased relative to the initial nickel sulfate plating solution, but the shape of the polarization curve remained unchanged. This is because when CeO_2/CuO oxide nano particles are present in the plating solution, Ni^{2+} ions are adsorbed onto their surfaces, bringing them to the cathode area to co-precipitate with Ni to form a composite plating layer. As a result, the concentration of free Ni^{2+} ions in the plating solution decreases, resulting in a decrease in plating speed or an increase in cathode polarization. This phenomenon is similar to other Ni composite plating layer creation processes [8].

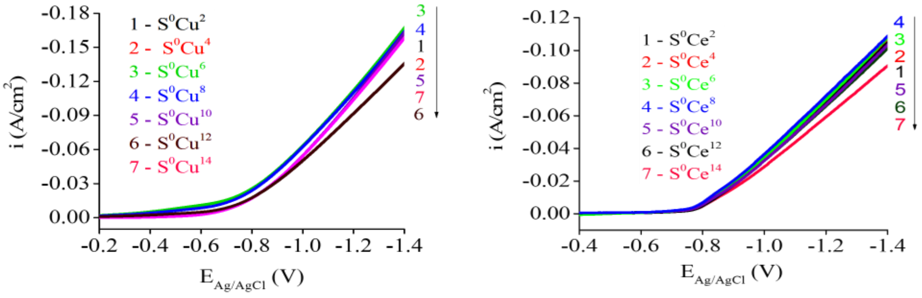

Figure 3. *Cathodic polarization curves of Ni in solutions of S^oCu^x (x = 2 ÷ 14 g/L) and S^oCe^y (y = 2 ÷ 14 g/L).*

Particle concentration and type often have a significant impact on the plating process and the characteristics of the composite plating layer that is created [6]. When the concentration of each oxide in the solution was increased from 2 to 12 g/L, the cathodic polarization of nickel remained nearly constant (figure 2). When the concentration of particles in the solution reached 14 g/L, cathodic polarization increased. The polarization curve graph shows the discharge of Ni^{2+} ions at the potential E* = - 0.66 V (Ag/AgCl) in the composite plating solution (S^oCe^y or S^oCu^x) as particle concentration changed from 2 to 14 g/L (figure 3).

3.2. *In-situ* electrochemical impedance spectra (EIS) of the studied electrode in the sulfate plating solution

3.2.1. EIS of the studied electrode in the sulfate plating solution

According to figure 1's polarization curve measurement data, the Ni discharge process in the sulfate solution started at potential E* = - 0.70 V (Ag/AgCl), or - 0.744 V (with respect to the Calomen electrode-SCE), and was steady at a potential of -0.834 V (SCE).

Figure 4 depicts the Nyquist impedance spectra of the investigated electrode measured at various potential regions in the nickel sulfate plating solution S° ($NiSO_4$ 300 g/L, H_3BO_3 30 g/L, sodium lauryl sulfate 0.1 g/L). The symbols represented the actual measured values, whereas the solid lines corresponded to the simulation lines. The results demonstrated that the simulation lines were nearly equal to the measured values. The simulation data are shown in table 1.

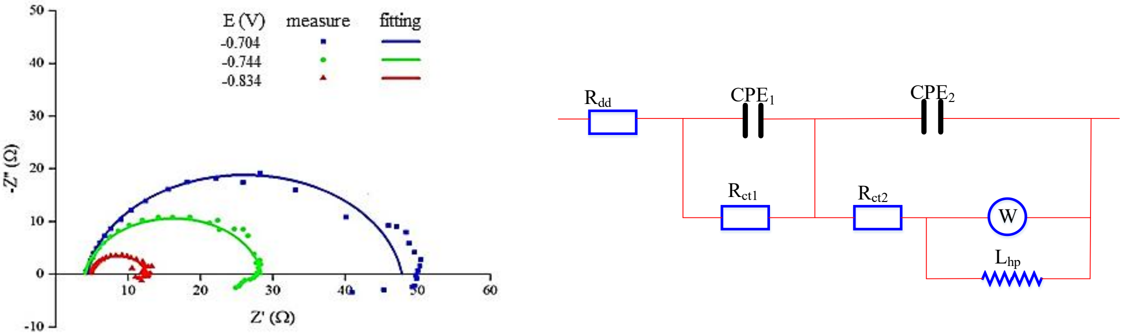

Figure 4. *Nyquist impedance spectra of the studied electrode in S° solution at different potentials and the equivalent diagram.*

The equivalent circuit design (figure 4) was made up of two consecutive semicircles: the first semicircle contained the constant phase component (CPE$_1$) and the charge transfer resistor (R$_{ct1}$), and the second semicircle had the remaining four components (CPE$_2$, R$_{ct2}$, W, L$_{hp}$). Thus, the diffusion and adsorption of $NiOH^+$ ions (an intermediate product in the nickel plating process in nickel sulfate solution [9]) onto the electrode surface occurred simultaneously. However, in figure 4, it was difficult to distinguish these two semicircles because the existence of CPE$_1$ and CPE$_2$ flattened the two semicircles; Thus, when joined in series, they appeared to be one semicircle.

Table 1. *Values of components in the equivalent diagram of the studied electrode in the S° solution system at different potentials.*

E (V)	R$_{dd}$ (Ω)	CPE$_1$		R$_{ct1}$ (Ω)	CPE$_2$		R$_{ct2}$ (mΩ)	σ (mΩ.s$^{-1/2}$)	L$_{hp}$ (H)
		(μF)	m		(F)	m			
-0.704	4.323	28.07	0.909	43.47	6.099	0.612	88.53	195.3	22.25
-0.744	4.127	28.31	0.913	24.27	13.75	0.491	42.56	119.4	37.14
-0.834	4.396	25.40	0.919	7.823	61.57	0.333	18.14	52.08	42.70

The findings in table 1 demonstrated that when the sweep potential moved in a more negative direction, the values of Warburg impedance and charge transfer resistance both dramatically dropped. The reason was that just a double layer was generated at the potential of -0.704 V since the Ni^{2+} discharge process had hardly begun. At a potential of -0.744 V, these resistance values had dropped as the Ni discharge process had commenced. The reduction of Ni-H$_{ads}$ on the electrode surface caused a larger release of H_2 gas, particularly at -0.834 V, as did the reduction of $NiOH^+$ ions. Thus, the process of plating Ni from the S° sulfate solution system involved two processes: diffusion and adsorption on the electrode surface.

The diffusion coefficient was calculated by the following equation [10]:

$$D = \frac{2R^2T^2}{n^4F^4A^2C^2\sigma^2}$$

In which: σ was Warburg constant (Ω s$^{-1/2}$); A was electrode surface area (0.5 cm^2); n was the number of electrons exchanged (n = 2); T was the absolute temperature of the plating solution (323 K); R was Bolzman gas constant (8.314 J/mol.K); F was Faraday constant (96500 C/mol); C was the concentration of oxidizing/reducing agent on the electrode (C = 1 mol/cm^3). The values of D during the nickel plating process at potential values of -0.704 V, -0.744 V, and -0.834 V (SCE) were 1.09E-12, 2.92E-12, 1.54E-11 (cm^2/s), respectively. These results demonstrated that the more negative the discharge potential is, the larger the diffusion coefficient is, meaning that the diffusion of ions occurred more easily, so the reaction rate is faster. This is consistent with the results of measuring the cathodic polarization curve of the S° solution (figure 1).

3.2.2. Effect of oxide nanoparticles on electrochemical impedance spectrum in nickel sulfate plating solution

The impedance spectrum of the S°Cu^x, S°Ce^y solution system was used to assess the impact of oxide nanoparticles (CuO, CeO$_2$) on the nickel plating process in the sulfate combination plating solution. Based on the findings of the impedance spectrum assessment in the S° plating solution previously examined, the potential E = - 0.834 V was chosen to measure the impedance spectrum.

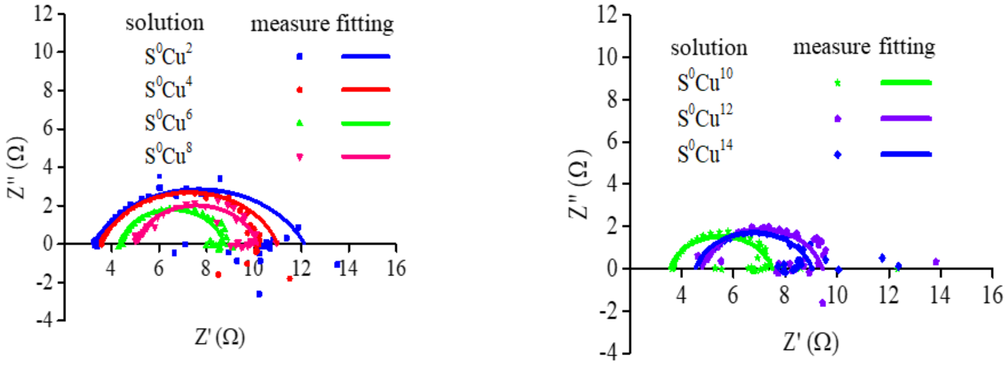

Figure 5. *Nyquist impedance spectra of the studied electrode in S^{0}Cu^x solution (x = 2÷14 g/L) at -0.834 V.*

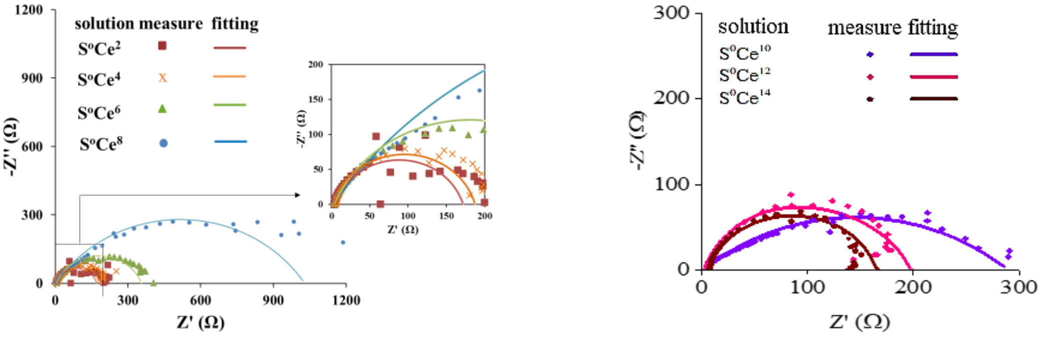

Figure 6. *Nyquist impedance spectra of the studied electrode in S^{o}Ce^y solution (y = 2÷14 g/L) at -0.834V.*

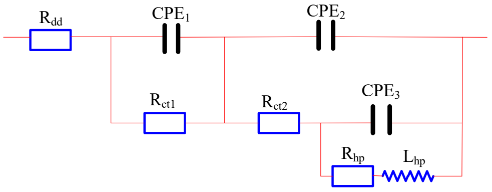

Figure 7. *Equivalent diagram of Nyquist spectra in nickel sulfate solution consisting of CuO/CeO$_2$.*

The results (figure 5, figure 6) showed that the simulation and experimental lines were very similar, so the equivalent circuit in figure 7 was consistent with the nickel discharge process in a nickel sulfate plating solution with added CuO or CeO_2 nano composite particles. The equivalent circuit model in figure comprised R_s, two constant phase elements (CPE_1 and CPE_2), and two charge-transfer resistances (R_{ct1} and R_{ct2}) in parallel branches - indicating that the system's electrochemical response included both double-layer charging and faradaic processes. CPE_1 was associated with the capacitive behavior of the electrical double layer, while CPE_2 and CPE_3 represent non-ideal interfacial capacitance arising from surface roughness and nanoparticle incorporation. The presence of the inductive branch (L_{hp}) reflected the possible adsorption/desorption phenomena during metal nucleation.

When CuO nanoparticles were introduced in the solution, R_{ct1} increased slightly from 3.9 Ω (S^oCu^2) to 8.5 Ω (S^oCu^{14}), suggesting a moderate retardation of electron transfer, yet CuO particles may improve surface uniformity and deposition stability [5]. Conversely, CeO_2-containing baths exhibited significantly larger semicircles, with R_{ct1} ranging from 124 Ω (S^oCe^2) to 354 Ω (S^oCe^{14}), indicating strong inhibition of charge transfer, as CeO_2 particles act as dielectric barriers that restrict Ni^{2+} reduction and promote formation of compact, passivating films [2, 3]. This result was consistent with the polarization measurements (figure 2), where the cathode polarization increased more when the solution had CeO_2 particles than in the case of CuO.

4. CONCLUSIONS

The presence of CuO or CeO_2 oxide nanoparticles in the solution increased cathode polarization in the nickel sulfate plating solution; however, the change was insignificant when the particle content in the plating solution ranged between 2 and 12 g/L, and the shape of the cathode polarization curve remained constant. The EIS results demonstrate that the Ni plating process consisted of diffusion and adsorption processes; When CuO or CeO_2 particles were added to the plating solution, an inductive component appeared with the adsorption process. The incorporation of CeO_2 nanoparticles alters solution conductivity and charge transfer kinetics more significantly than CuO, indicating stronger particle-ion interaction during Ni co-deposition. The impact of CuO and CeO_2 nanoparticles on the nickel layer will be evaluated more clearly in subsequent studies on the morphology, microstructure, corrosion behavior of the coatings.

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TÓM TẮT

Đặc điểm quá trình mạ trong dung dịch niken sunphat khi có mặt các hạt nano oxit CeO_2, CuO

Nghiên cứu này khảo sát tính chất điện hóa của quá trình tạo lớp mạ niken trong dung dịch niken sunphat với các hạt nano oxit CuO và CeO_2 thông qua phương pháp đo đường cong phân cực và phổ tổng trở (EIS). Với hàm lượng các hạt CuO hoặc CeO_2 trong dung dịch trong khoảng 2 đến 12 g/L, độ phân cực catốt của niken tăng không đáng kể. Tuy nhiên kết quả EIS cho thấy, các hạt CuO ít ảnh hưởng đến điện trở dung dịch và quá trình mạ nhưng các hạt CeO_2 lại làm tăng đáng kể điện trở dung dịch, do đó ảnh hưởng đến tốc độ mạ niken. Do điện trở chuyển điện tích của dung dịch sẽ tăng khi nồng độ của các hạt oxit trong dung dịch mạ tăng, điều này sẽ gây bất lợi cho quá trình khử ion của bề mặt điện cực, nên hàm lượng hạt oxit trong dung dịch mạ không nên vượt quá 12 g/L.

Từ khoá: Niken sunphat; CeO_2; CuO; Lớp mạ Ni-CeO_2; Lớp mạ Ni-CuO.