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Tuning Ni-Centered Active Phases with Copper and Cobalt for Ethanol Electrooxidation Reaction

Fatma Nur TİREN¹ Yavuz YAĞIZATLI^{2*} İrfan AR¹

¹ Gazi University, Faculty of Engineering, Department of Chemical Engineering, Eti Mahallesi, Yükseliş Sokak, No:5, Maltepe, Ankara, 06570, Türkiye

Keywords	Abstract
Nickel Copper Cobalt DEFC EOR	Nickel-based bimetallic oxides were synthesized as noble metal free anode catalysts for ethanol electrooxidation. The effects of Cu and Co incorporation into the Ni-centered oxide phase were comparatively examined. Catalysts with different Ni/Cu and Ni/Co compositions were prepared by co-precipitation and evaluated in alkaline ethanol medium to clarify the secondary metal influences phase evolution, bonding features, surface morphology, textural properties, catalytic activity, stability, and interfacial charge-transfer behavior. Among all compositions, Ni ₉₀ Cu ₁₀ exhibited the best electrochemical performance, reaching 3.04 mA cm ⁻² at about 0.75 V and retaining 1.5 mA cm ⁻² after 1000 s, whereas bare Ni delivered about 0.8 mA cm ⁻² . Structural findings indicated that Cu was incorporated into the NiO lattice to form a Ni _{1-x} Cu _x O type solid solution, while the NiCo series showed a stronger tendency toward the formation of NiCo ₂ O ₄ /Co ₃ O ₄ -type spinel domains. The superior response of the NiCu series was also associated with more favorable charge-transfer behavior, whereas the NiCo catalysts exhibited less efficient interfacial kinetics. These results indicate that limited Cu addition strengthens the Ni-centered active phase for ethanol oxidation, while increasing Co content promotes spinel-rich structures that are less favorable for ethanol electrooxidation.

Cite

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0009-0005-2514-1306	Fatma Nur TİREN
0000-0003-4926-3621	Yavuz YAĞIZATLI
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1. INTRODUCTION

Modern societies rely heavily on a continuous supply of energy for activities such as transportation, household operations, agriculture, industrial production, services and the operation of buildings. As the global population grows and technological development and industrialization accelerate, overall energy demand continues to rise. At the same time, dependence on fossil fuels is restricted by their finite reserves and severe environmental consequences. These limitations have made the integration of renewable resources into the energy mix increasingly inevitable. Over the last decade, the global use of energy from renewable sources has increased by roughly a factor of four. Its share now exceeds 20% of total consumption and is still expanding (Maradin, 2021). By providing low-carbon and sustainable options, renewable energies are expected to play a central role in satisfying future energy needs. Wider deployment of these resources can greatly diminish greenhouse-gas emissions and mitigate air pollution, thereby contributing to environmental protection.

*Corresponding Author, e-mail: yavuzyagizatli@gazi.edu.tr



Consequently, broadening the spectrum of renewable energy technologies is essential to secure both long-term sustainability and economic benefits while supplying the energy required by an ever-increasing population. Among clean energy technologies, fuel cells have drawn substantial attention in recent years. They generate electricity from the chemical energy of a fuel by means of electrochemical reactions and are known for their high conversion efficiency (Rayment & Sherwin, 2003). Within the different types of fuel cells, classified according to operating temperature or electrolyte type, direct liquid-fed fuel cells (DLFCs) are particularly attractive because liquid fuels are easy to store and handle, and such systems offer high energy density and good portability (Ong et al., 2017).

Direct Ethanol Fuel Cells (DEFC) can be used in both portable and stationary applications. This increases the potential for use in specialized areas such as military vehicles (Narayana Das, 2016). As a fuel with a high energy density, ethanol has the capacity to produce more energy. This offers the potential to provide longer lasting energy and has a lower impact in terms of carbon emissions. Compared to other alternative fuels ethanol stands out as one of the most efficient liquid fuels for DLFCs. With an energy density of 6307 Wh/kg, ethanol surpasses many traditional and new hydrogen carriers in terms of energy storage capacity (Soloveichik, 2014). In fuel cells using methanol (DMFC), the toxic and flammable properties of methanol raise safety concerns, while ethanol is a safer alternative. Furthermore, Ethanol can be sourced from renewable feedstocks, which makes it a renewable energy carrier (Chang et al., 2023). Furthermore, ethanol's compatibility with existing fuel distribution infrastructure increases the viability of DEFCs and facilitates their large-scale deployment (Kamarudin et al., 2009).

In a DEFC, the anodic process is ethanol oxidation and the cathodic process is oxygen reduction. The anode half-reaction is given by:



At the cathode, oxygen is reduced according to the following half-reaction:



The overall cell reaction:



In studies, platinum (Pt) is widely used in anode catalysts for DEFC due to its high catalytic activity and excellent electrochemical stability (Akhairi & Kamarudin, 2016).

Pt-based catalysts have been extensively investigated for ethanol electrooxidation owing to their high catalytic activity and favorable electrochemical stability (Corradini et al., 2014; 2015; da Silva et al., 2014; Jacob et al., 2015). Despite these advantages, their widespread application remains restricted by high cost, scarcity, and vulnerability to poisoning by adsorbed intermediates generated during the reaction. Consequently,

considerable effort has been devoted to developing non-noble and cost-effective catalyst systems, especially for alkaline ethanol oxidation.

In research, the use of alternative catalysts containing transition metals has been investigated and these metals have attracted attention due to cheap and favorable electrochemical properties (Antolini, 2007; Kamarudin et al., 2009; Zheng et al., 2020). In addition, Fe-N-C, Co-N-C and Mn-N-C doped carbon materials have shown promising results for oxygen reduction reaction (ORR) activity (Osmieri et al., 2018). Ni contributes significantly to ethanol electrooxidation by facilitating C-C bond cleavage and mitigating the accumulation of carbonaceous intermediates on the catalyst surface. Furthermore, Ni-based are commonly modified with metals such as Pd, Cu, Co, and Fe in order to enhance charge-transfer characteristics and improve active site accessibility (Tarasevich et al., 2005; Chen et al., 2017; Mao et al., 2017). Among these, Co markedly tunes the surface acidity and redox behaviour, thus shaping the catalytic response (Sohn & Ozkan, 2016). At the same time, Cu metal facilitates the conversion of intermediates during ethanol oxidation due to its oxygen binding ability. It shows resistance to carbon monoxide (CO) poisoning and enhances catalytic activity by improving electron transfer properties (El-Nagar et al., 2017). In studies, Ni stands out as an effective catalyst for ethanol oxidation and offers a low-cost alternative. Bimetallic catalysts, nickel in combination with cobalt and copper, are expected to increase catalytic activity and provide resistance to carbon deposition. These combinations are thought to improve the efficiency of ethanol fuel cells.

Herein, a series of nickel-based bimetallic oxide anode catalysts for DEFCs was prepared and comprehensively examined. NiCu and NiCo catalysts with Ni/M weight ratios of 90/10, 80/20, 70/30 and 50/50 were synthesized by a co-precipitation route. The resulting powders were dispersed in a suitable medium to form catalyst inks, which were then deposited onto glassy carbon electrodes (GCEs) and used as working electrodes. The ethanol electrooxidation reaction was first evaluated by cyclic voltammetry (CV) to obtain the current-potential response of each catalyst. Chronoamperometry (CA) was employed to monitor the time-dependent stability, while electrochemical impedance spectroscopy (EIS) was used to probe charge-transfer resistance and interfacial properties at the electrode/electrolyte interface. Linear sweep voltammetry (LSV) provided detailed current-density-potential curves for ethanol oxidation. Structurally, phase composition and crystallinity were analyzed by X-ray diffraction (XRD), and surface functional groups were identified by Fourier transform infrared spectroscopy (FTIR). The morphology, particle distribution and elemental composition were investigated using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). Finally, N₂ adsorption-desorption was applied to determine the specific surface area and porosity characteristics of the catalysts, which are directly related to their electrocatalytic performance.

2. MATERIAL AND METHOD

For the preparation of Ni, NiCo, and NiCu catalysts, nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Merck) was used as the nickel source, copper(II) nitrate tetrahydrate (Cu(NO₃)₂·3H₂O, Merck) as the copper source, and cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, Merck) as the cobalt source. In the catalyst ink prepared

for performing electrochemical measurements with the obtained catalysts, ethanol with a purity of 99.8% (EtOH, Sigma) and a Nafion solution (5 wt.%, Sigma) were used as solvents. Sodium hydroxide (NaOH, Merck) was used as the supporting electrolyte in the electrochemical measurements.

2.1. Preparation of Catalysts

NiCo and NiCu bimetallic oxide catalysts were synthesized using the co-precipitation method. For the catalysts with the predetermined weight ratios (90/10, 80/20, 70/30 and 50/50), the required amounts of Ni, Co, and Cu salts were dissolved in ethanol and stirred at room temperature for approximately 48 h using a magnetic stirrer. At the end of this period, in order to remove the solvent, the temperature was increased to 75°C using the heater of the magnetic stirrer, and the solvent was evaporated.

The resulting solid precipitate was calcined in a muffle furnace at 600°C for 8 h in order to stabilize the structure and remove the remaining salts. Explanations regarding the abbreviations and compositions of the synthesized catalysts are provided in Figure 1.

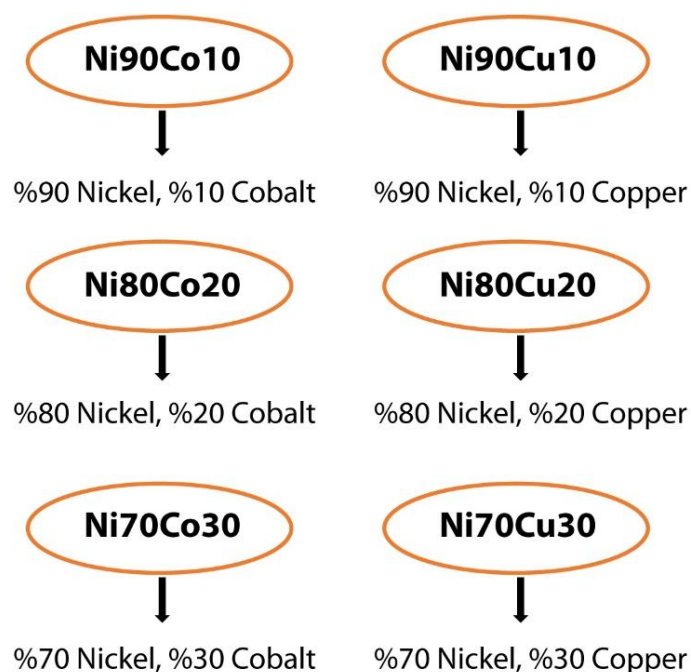


Figure 1. Catalyst abbreviations and their explanations

2.2. Characterization Studies

The crystalline phases of the catalysts were examined by XRD over a 2θ range of 2-90° at a scanning rate of 2°/min. FTIR measurements were then conducted with a Bruker Vertex V70 spectrometer equipped with an ATR unit in the 400-4000 cm^{-1} region to evaluate surface functional groups and metal-oxygen bonding characteristics. Surface morphology was investigated by SEM-EDX using a ZEISS Sigma 300 instrument, and micrographs were recorded at magnifications of 10.000x, 20.000x, and 50.000x. Textural properties, including surface area, pore volume, and pore size distribution, were determined from N_2 adsorption-desorption measurements performed with an AUTOSORB 1C analyzer.

2.3. Electrochemical Activity Studies

Catalyst-coated working electrodes were prepared from inks containing 4 mg of catalyst, 150 μL Nafion solution, and 850 μL ethanol. The mixture was homogenized by vortexing followed by ultrasonication, and 6 μL aliquots were drop cast onto glassy carbon electrodes and dried before use. All electrochemical experiments were conducted in a medium composed of 1 M NaOH and 0.2 M ethanol. CV were recorded from -1.0 to +1.0 V at a scan rate of 50 mV/s, while LSV were obtained over the same range at 10 mV/s. Catalysts from both the NiCu and NiCo series, as well as bare Ni, were tested comparatively. EIS were measured at 0.7 V over frequencies from 10^5 to 0.1 Hz, and chronoamperometric stability was monitored at the same potential for 1000 s.

3. RESULTS AND DISCUSSION

3.1. FTIR

FTIR analysis was used to determine the bonding structure of the catalysts (Figure 2). All NiCo bimetallic oxide catalysts (Ni50Co50, Ni70Co30, Ni80Co20, Ni90Co10) show metal-oxygen vibrations in the 400-800 cm^{-1} range (Figure 2a). A prominent band at $\sim 661 \text{ cm}^{-1}$ appears for every catalyst and is assigned to Ni-O stretching at tetrahedral sites of spinel-type NiCo oxides. The strengthening of this band with increasing Co content indicates the gradual formation of Co-rich spinel sites ($\text{NiCo}_2\text{O}_4/\text{Co}_3\text{O}_4$) in the Ni-rich oxide framework (Wei et al., 2016; Safdar et al., 2024). The low frequency, doublet peak band centered at 563 cm^{-1} with a shoulder at $\sim 513 \text{ cm}^{-1}$ is also a characteristic peak of NiCo structures and is attributed to metal-O stretching at the octahedral sites (Faryabi et al., 2024; Safdar et al., 2024). The presence a shoulder at $\sim 513 \text{ cm}^{-1}$ in the high Ni catalysts is due to the residual NiO-like Ni-O structure. With increasing Co loading, this shoulder gradually disappeared, and the 563 cm^{-1} component became sharper and more intense. This is consistent with the replacement of Ni by Co in the octahedral sublattice and the development of a more ordered spinel skeleton. Conversely, the equimolar Ni50Co50 catalyst exhibits the narrowest and most intense bands at ~ 552 and 652 cm^{-1} , revealing the most pronounced spinel character among the catalysts. In addition, the broad peak appearing around 993 cm^{-1} and 1205 cm^{-1} , which becomes more pronounced as the Co content increases, arises from surface carbonate/bicarbonate species or metal-carbonate complexes $\nu(\text{C-O})$ and $\nu_3(\text{CO}_3^{2-})$ formed by the adsorption of atmospheric CO_2 onto basic hydroxylated NiCo oxide sites (Efremova et al., 2021; Pore et al., 2023). As Co amount rises, the corresponding growth in peak intensity points to greater basicity of Co-rich surfaces and an increased tendency to bind carbonate-like species.

FTIR spectra of bimetallic oxide NiCu catalysts (Ni90Cu10, Ni80Cu20 and Ni70Cu30) show characteristic lattice vibrations of NiCu oxides in the low wavenumber region and additional bands associated with surface carbonate species at higher wavenumbers (Figure 2b). For all catalysts, the peak observed at approximately 480 cm^{-1} originates from Ni-O/Cu-O stretching vibrations in the lattice (Khalaji & Das, 2014; Said et al., 2014). The doublet peak at 534 and 584 cm^{-1} is attributed to Cu-O stretching of monoclinic CuO like structures (Said et al., 2014; Tanvir et al., 2016). This doublet's intensity gradually increases with increasing Cu content,

indicating the growth of CuO rich areas and the increasing contribution of Cu-O vibrations relative to Ni-O in the mixed oxide framework. New bands appeared at 1321 and 1434 cm^{-1} as Cu content in the catalyst increased. This is characteristic of the $\nu(\text{C-O})$ and $\nu_3(\text{CO}_3^{2-})$ modes of surface carbonate and/or basic copper hydroxy-carbonate species formed via adsorption of atmospheric CO_2 onto more basic Cu rich oxide surfaces (Gunasekaran et al., 2006; Al-Amin et al., 2025). The increasing peak intensities with Cu suggest that CuO rich catalysts have a higher density of basic $-\text{OH}/\text{O}^{2-}$ sites capable of binding carbonate species.

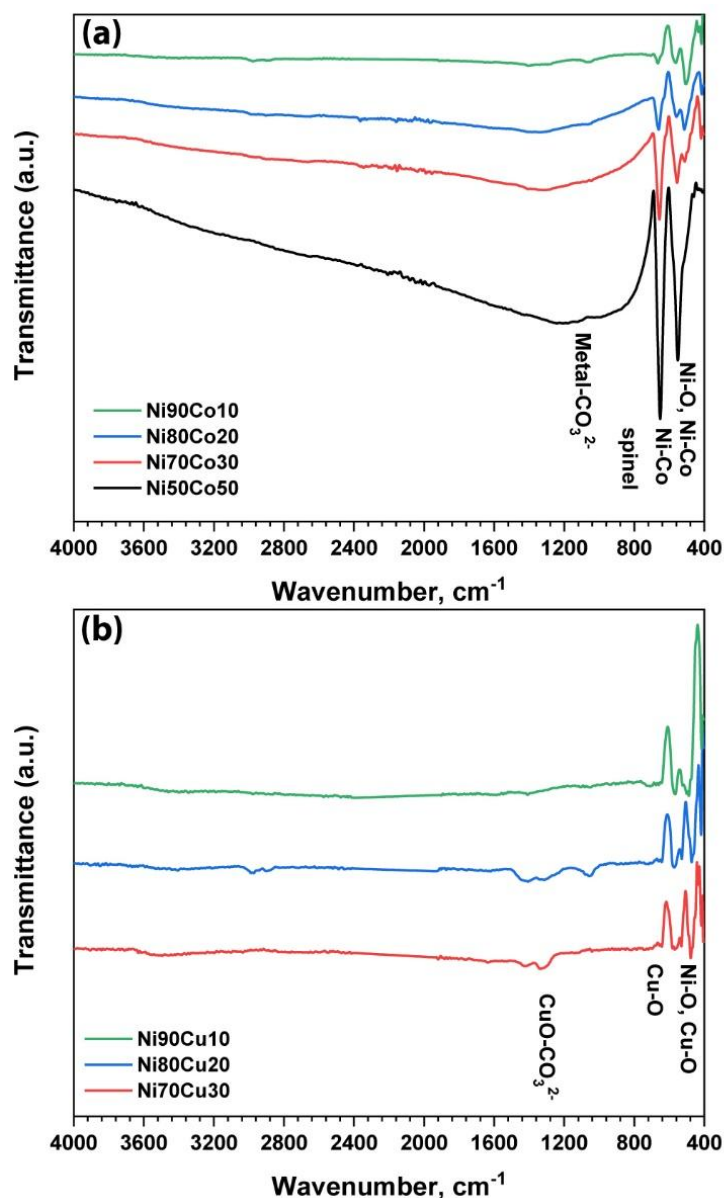


Figure 2. FTIR spectra of synthesized catalysts **a)** NiCo, **b)** NiCu catalysts

3.2. XRD

The phase structure of the synthesized Ni based catalysts was assessed by XRD (Figure 3). All peaks in this pattern correspond well to the cubic bunsenite structure of Cu-doped NiO (JCPDS 47-1049), and no additional CuO/Cu₂O or metallic Cu phase is observed. Therefore, it can be said that the Ni90Cu10 catalyst exhibits a single-phase structure, primarily based on NiO, forming a solid solution with Cu.

At $2\theta \approx 37.25^\circ$, it originates from the (111) plane of cubic NiO (Zhang Y. et al., 2009; Theodoro et al., 2024). Similarly, the peak at 43.29° corresponds to (200) plane of NiO (Theodoro et al., 2024). The $2\theta \approx 62.86^\circ$ peak is associated with the (220) plane of NiO, the $2\theta \approx 75.4^\circ$ peak is associated with the (311) plane, and the $2\theta \approx 79.36^\circ$ peak is associated with the (222) plane (Choi et al., 2014; Alfadhli et al., 2025). These reflections are attributed to the face-centered cubic NiO phase. The dominant phase in the Ni90Cu10 catalyst is highly crystalline cubic NiO. The narrow and symmetric peaks indicate high crystallinity and a relatively narrow distribution of crystallite sizes. Furthermore, no peaks specific to the Cu structure are observed in the XRD spectrum. In many studies on Cu-doped NiO structures, only NiO peaks are observed in the XRD pattern when the Cu content is low. This indicates that Cu^{2+} ions enter the Ni^{2+} sites in the NiO lattice, forming a $\text{Ni}_{1-x}\text{Cu}_x\text{O}$ type solid solution (Hassan E. S. et al., 2016; Benramache et al., 2020). The FTIR spectrum also supports this structure. Compared with Ni90Cu10, the Ni70Cu30 pattern retains the dominant NiO reflections, indicating that the NiO-based framework is preserved. Notably, the main NiO peaks show a slight shift to lower 2θ , consistent with lattice expansion upon Cu^{2+} substitution and the formation of a $\text{Ni}_{1-x}\text{Cu}_x\text{O}$ solid solution at moderate Cu contents (Tangcharoen et al., 2022). Additionally, Ni70Cu30 exhibited accompanying CuO properties showing weak additional reflections around $2\theta \approx 35.5^\circ$ and 38.7° , and characteristic features of monoclinic CuO in the $48\text{--}62^\circ$ region. This suggests partial decomposition of a CuO-rich phase rather than a completely single-phase solid solution at higher Cu loading (Zhang & Xu, 2024; Shishir et al., 2025).

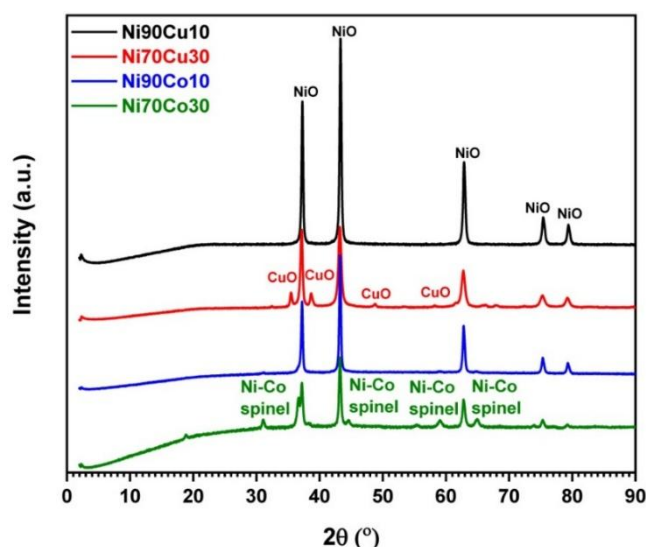


Figure 3. Comparative XRD spectra of Ni based catalysts

Similar to NiCu catalysts, the XRD patterns of Ni90Co10 and Ni70Co30 indicate the presence of the NiO phase at approximately 37.20° , 43.26° , 62.82° , 75.32° , and 79.28° , respectively. Furthermore, additional spinel-type reflections have emerged, particularly in Ni70Co30, around $2\theta \approx 31.1^\circ$, 44.6° , 59.1° , and 65.2° . These reflections are consistent with $\text{NiCo}_2\text{O}_4/\text{Co}_3\text{O}_4$ type spinel oxides (Wen et al., 2018; Zhou et al., 2022). Stronger intensity of these spinel reflections in Ni70Co30 compared to Ni90Co10 supports the increased contribution of spinel domains with increasing Co content and confirms the FTIR-based inference regarding spinel formation in the NiCo series.

3.3. N₂ Adsorption-Desorption

Figure 4 shows the isotherm and porosity values after N₂ adsorption-desorption analysis performed with NiCu and NiCo catalysts.

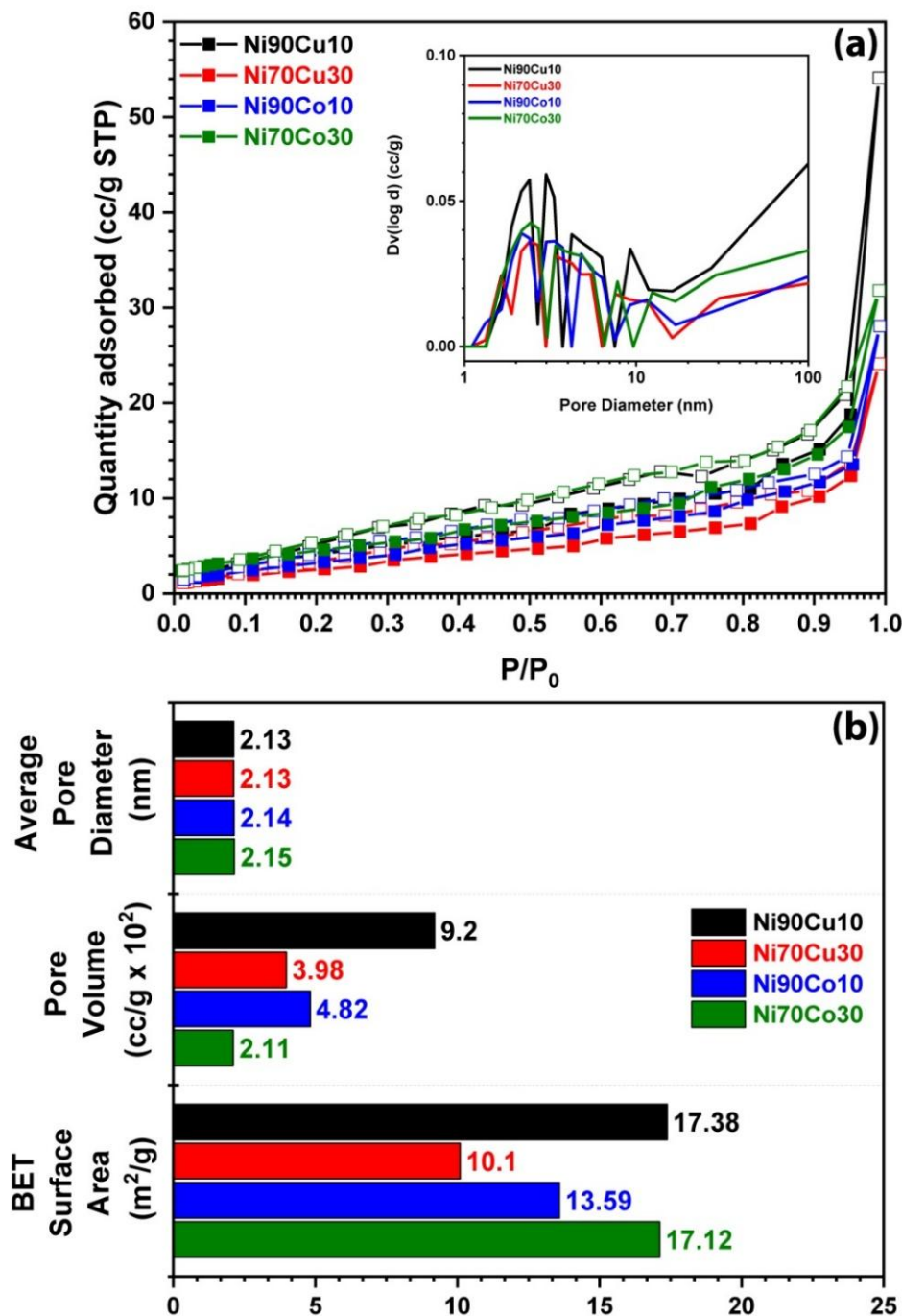


Figure 4. a) BET isotherm, b) porosity and surface area values of NiCu and NiCo catalysts

The isotherm (Figure 4a) of the catalysts exhibits Type IV behavior, as classified by the IUPAC, indicating a mesoporous structure predominantly (Thommes et al., 2015). For Ni90Cu10, suggests that microporosity makes a minor contribution at low relative pressures ($P/P_0 < 0.1$). However, the overall shape of the isotherm confirms that mesopores (2-50 nm) are dominant. A distinct hysteresis loop was observed in the isotherm

starting from $P/P_0 \approx 0.45$. This resembles a Type H3 hysteresis, considering the parallelism of the adsorption and desorption branches and the lack of saturation in the high pressure region ($P/P_0 \rightarrow 1$) (Thommes et al., 2015). Type H3 hysteresis is generally associated with the presence of slit-shaped pores formed by the aggregation of plate-like particles. This suggests that the NiCu bimetallic oxide structure undergoes particle aggregation during synthesis, forming irregular pore networks. The sharp increase in adsorption at $P/P_0 \rightarrow 1$, following near-linear uptake at intermediate pressures, suggests that, in addition to mesopores, interparticle voids or, to a lesser extent, macropores are also present, as is commonly reported for oxide catalysts, which are associated with capillary condensation in large interparticle spaces. Notably, the same Type IV/H3-type structure is also observed for Ni70Cu30, Ni90Co10, and Ni70Co30 (Figure 4a), implying that all compositions share a mesoporous-interparticle pore framework, while the extent of aggregation and void contribution differs among catalysts.

The BJH pore size distribution reveals that the catalyst has a multimodal pore structure (Figure 4a) with the main pore populations concentrated in the narrow mesopore region. The dominant distribution remains centered near the micro/mesopore range (≈ 2 -4 nm). This is consistent with the average pore diameters being nearly constant (≈ 2.13 -2.15 nm) for all four catalysts (Figure 4b). This pore distribution provides a favorable structure for the diffusion of reactant molecules to the active sites. Therefore, composition primarily altered the accessible surface area and pore volume rather than the pore size regime. Ni90Cu10 and Ni70Co30 showed the highest BET surface areas (17.38 and 17.12 m²/g, respectively), while Ni70Cu30 showed a significantly lower surface area (10.10 m²/g) and a reduced pore volume, suggesting a denser structure at higher Cu content. These are consistent with similar Ni based systems in the literature for metallic alloy catalysts without support material (Bikbashev et al., 2024). In NiCo oxides, the formation of spinel-type domains (NiCo₂O₄/Co₃O₄-like), often associated with smaller crystallites and more open pore structures, was observed in XRD and FTIR analysis as the Co content increased. The open porosity of these spinel types also led to an increase in the BET surface area compared to Ni90Co10, a Ni-rich composition. The total pore volume of Ni90Cu10 is 0.092 cm³/g, which is significantly higher than other catalysts (Figure 4b). The average pore diameter, close to 2 nm, suggests that the structure lies at the micropore/mesopore boundary, with mesopores dominant, as confirmed by the distribution plot for all catalysts. As a result, the mesoporous structure and reasonable surface area of the Ni90Cu10 catalyst are capable of overcoming mass transfer resistance during catalytic reactions, enabling effective interaction between the active metal surfaces and the reactants.

3.4. SEM-EDx

SEM-EDx analysis was employed to investigate the morphological structure of the NiCu and NiCo catalysts, with the resulting images and EDx data presented in Figure 5 and Table 1, respectively. SEM images of the Ni90Cu10 catalyst at different magnifications show that the catalyst structure is composed of nanosized particles with a homogeneous distribution but with a pronounced tendency to agglomerate. Particularly in high-magnification images (Figure 5), it was seen that the primary particles have a quasi-spherical form and

aggregate to form irregular, spongy, and porous secondary structures. This aligns with the comparatively low surface area and the high crystallinity indicated by XRD. Compared to Ni90Cu10, Ni70Cu30 exhibited a more compact and denser clustering texture at all magnification ratios, with fewer open spaces between particle clusters. This suggests stronger clustering at higher Cu content. This is consistent with BET results showing that Ni70Cu30 has a lower surface area and smaller pore volume than Ni90Cu10. For the NiCo series, both catalysts maintain the nanoparticle morphology. However, Ni70Co30 showed finer, more fragmented aggregates and a rougher porous texture compared to the relatively more compact Ni90Co10 structures. This is consistent with BET data showing that Ni70Co30 has a higher surface area than Ni90Co10, suggesting that the increased Co content supports a more accessible nanostructure. The increased contribution of spinel-type oxide reflections in the NiCo XRD patterns is consistent with this morphological structure and suggests that spinel-rich areas are associated with the observed finer aggregate texture.

EDx analysis (Table 1) reveals that Ni and Cu are the dominant metallic elements, with 74.37% and 9.95% weight fractions, respectively. Considering only the metallic fraction, this corresponds to a Ni/Cu mass ratio of approximately 88:12 (atomic ratio $\approx$ 89:11%), which is very close to the nominal 90:10 composition targeted during the synthesis confirms the effective integration of Cu into the Ni-based oxide matrix. For Ni70Cu30, the Cu content increases markedly (Cu = 27.19 wt%, Ni = 59.50 wt%), corresponding to a Ni/Cu mass ratio of $\sim$ 69:31 (atomic ratio $\approx$ 70:30), consistent with the intended higher-Cu formulation. The oxygen content (15.21 wt%) reflects the oxidic nature of the $\text{Ni}_{1-x}\text{Cu}_x\text{O}$ solid solution. SEM-EDx results indicate that the Ni90Cu10 catalyst consists of well-crystallized NiCu oxide nanoparticles aggregated into compact secondary particles with a volume composition that is in good agreement with the intended Ni-rich bimetallic oxide formulation. For the NiCo catalysts, EDx confirms the expected incorporation of Co. Ni90Co10 exhibits Ni = 76.62 wt% and Co = 8.24 wt%, whereas Ni70Co30 shows Ni = 59.57 wt% and Co = 24.92 wt% (Table 1). The corresponding atomic fractions further support that the nominal Co loadings were successfully achieved. SEM-EDx results indicate that the catalysts consist of oxide nanoparticles aggregated into porous secondary structures, while the Cu/Co ratio governs both the surface composition and the aggregation density.

Table 1. EDx result of Ni based catalysts

Catalysts		Element			
		O K	Ni K	Cu K	Co K
Ni90Cu10	Weight %	15.68	74.37	9.95	-
	Atomic %	40.76	52.72	6.52	-
Ni70Cu30	Weight %	13.31	59.50	27.19	-
	Atomic %	41.08	41.43	17.49	-
Ni90Co10	Weight %	15.13	76.62	-	8.24
	Atomic %	39.55	54.60	-	5.85
Ni70Co30	Weight %	15.51	59.57	-	24.92
	Atomic %	40.26	42.17	-	17.57

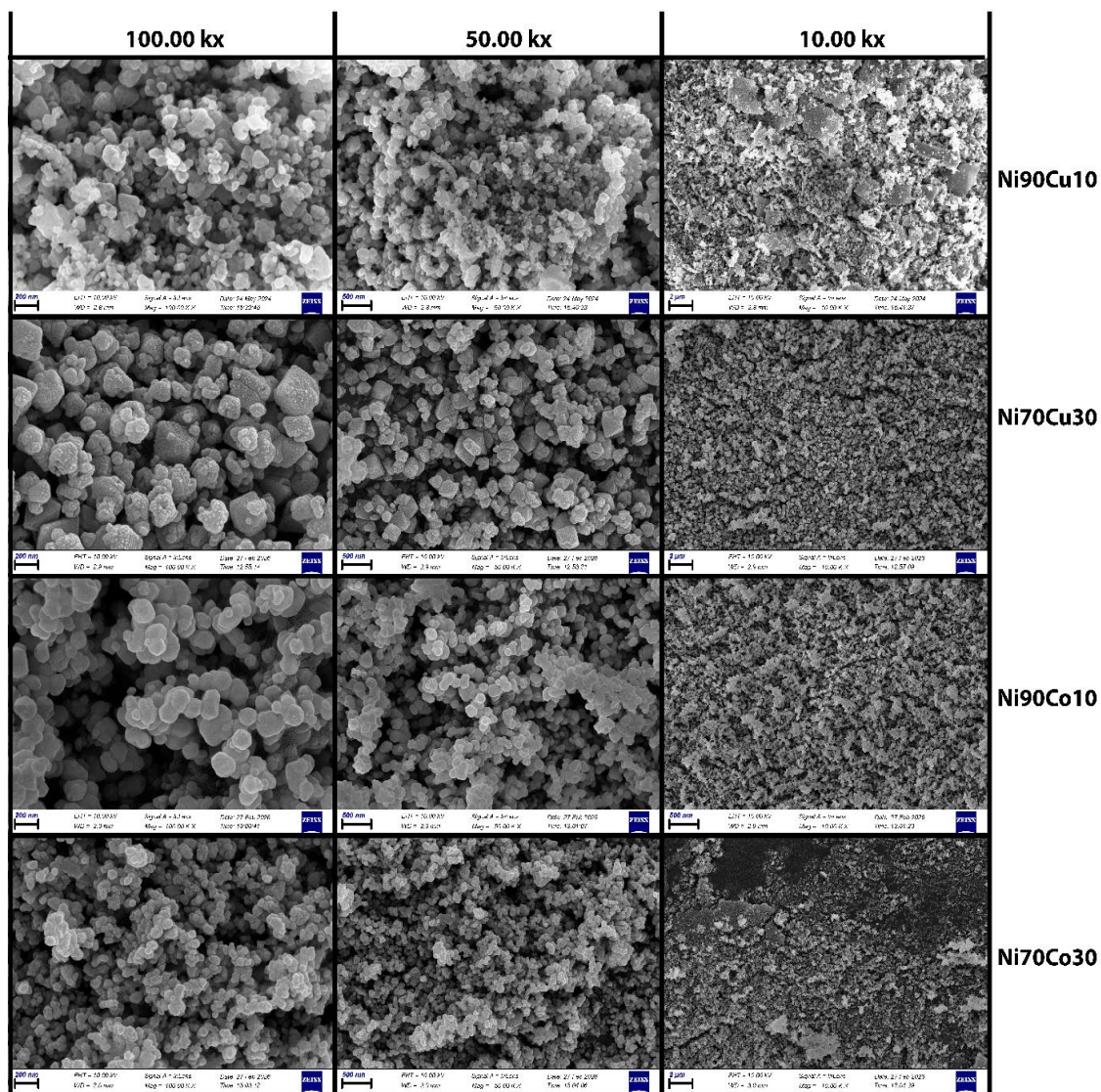


Figure 5. SEM images of Ni based catalysts

3.5. CV

The current density (C_{Density}) versus potential curves obtained from the CV analyses performed with the synthesized catalysts are comparatively presented in Figure 6. Furthermore, double layer capacitance (C_{dl}) and ECSA values obtained from CV measurements performed in a 1 M NaOH support electrolyte at different scan rates in the non-faradic region to determine the ECSA of the catalysts exhibiting the highest activity in the NiCu and NiCo series are given in Figure 6c, 6d.

Based on the CV measurements, Ni90Cu10 delivered the maximum C_{Density} , reaching 3.04 mA cm^{-2} at approximately 0.75 V (Figure 6a). Since this pronounced activity may partly reflect Ni content, CV experiments were also conducted with a pure Ni catalyst for comparison. Under identical conditions, the pure Ni catalyst produced about 0.8 mA cm^{-2} at around 0.70 V. Overall, pure Ni outperformed all NiCo compositions under the investigated conditions. Nevertheless, within the NiCo series, the current response improved with increasing Co content up to 30 wt% (with Ni70Co30 being the best-performing NiCo composition), although it still remained inferior to pure Ni (Figure 6b). When the Co content was increased

above 30 wt%, the activity decreased. In contrast, introducing low Cu contents (10 and 20 wt%) clearly enhanced the activity relative to pure Ni, as evident from Figure 6a. This non-monotonic behavior suggests that Cu and Co may influence surface chemistry of the Ni-centered active phase through different mechanisms. In Ni-based catalysts, the main active species in the oxidation of alcohols, urea, and similar compounds are Ni^{3+} species belonging to the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox couple formed in alkaline media (Liu C. et al., 2023). When Cu incorporated the NiO lattice, it facilitates the conversion of Ni^{2+} to Ni^{3+} by increasing lattice defects and oxygen vacancies and by modifying the Ni 3d band center (Hu et al., 2019). In this way, the NiOOH phase is formed at lower potentials with a higher surface coverage. At the same time, Cu incorporation can facilitate interfacial charge transport and accelerate the Ni-centered oxidation kinetics, which is commonly reflected as a decrease in the apparent charge-transfer resistance and faster electron-transfer processes in NiCu environments (Kang et al., 2024). In the literature, it has been reported that NiCu bimetallic oxides and hydroxides exhibit lower onset potentials (E_{onset}) and higher peak currents compared to pure NiO, which is indicative of the synergistic effect of the NiOOH/CuOOH couple and to the facilitation of the adsorption-desorption steps by Cu (Yin et al., 2024). The presence of the $\text{Ni}_{1-x}\text{Cu}_x\text{O}$ phase in the XRD pattern of the Ni90Cu10 catalyst is consistent with the pronounced increase in activity observed in the CV measurements. Cu acts as an additive that electronically “promotes” the NiOOH-centered active phase without disrupting it. In addition, the separation between the forward and reverse scans for the Ni90Cu10 catalyst indicates that the formed NiOOH species are stable and readily participate in the reaction.

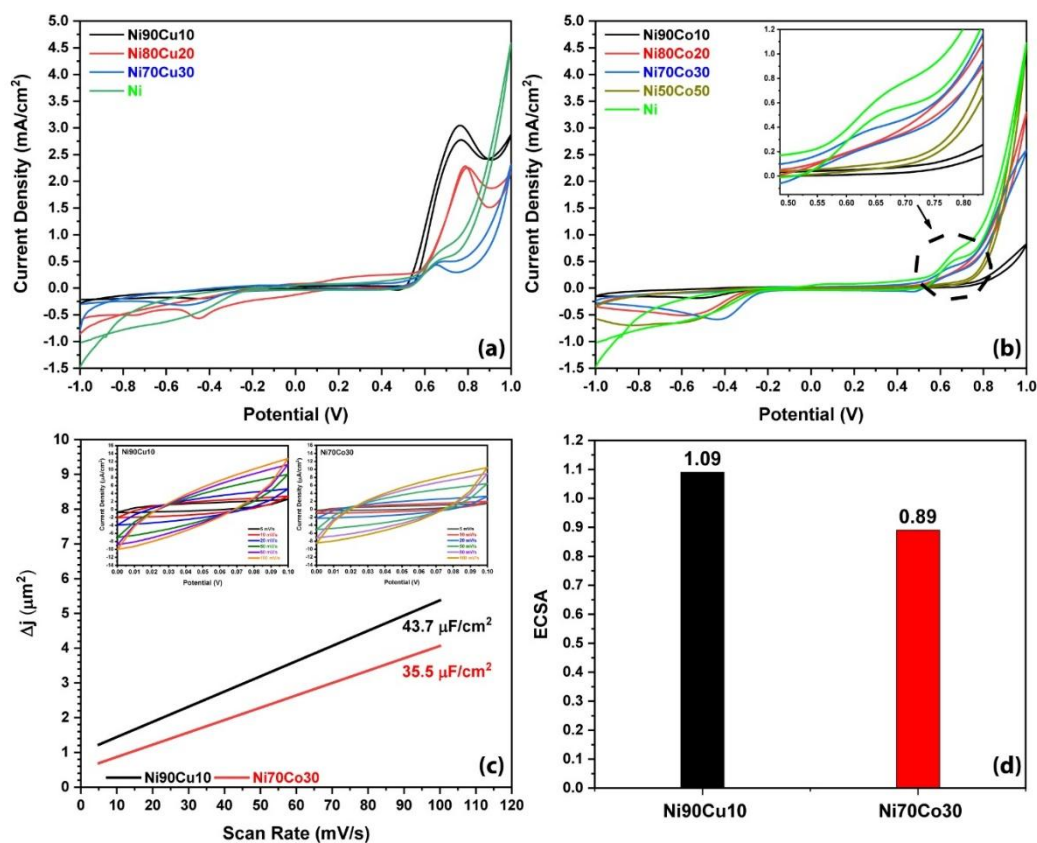


Figure 6. CV curves of *a)* NiCu, and *b)* NiCo bimetallic oxide catalysts (50 mV/s scan rate), *c)* Cdl, and *d)* ECSA values of Ni90Cu10 and Ni70Co30 catalysts

The addition of Co, however, did not perform the same function. FTIR results showed that, instead of a NiO-like environment, spinel Co-Ni oxide phases with $\text{NiCo}_2\text{O}_4/\text{Co}_3\text{O}_4$ developed in the NiCo catalysts. Although these spinel structures can be highly active in oxygen evolution reactions (OER), under the organic oxidation conditions investigated in this study it is considered that a $\text{Ni}(\text{OH})_2/\text{NiOOH}$ -centered mechanism is predominant and that Co decreases both the number and effectiveness of the electrocatalytic centers on Ni. Therefore, the NiCo bimetallic oxide catalysts generally exhibited lower C_{Density} compared to pure Ni. On the other side, although increasing the Co content from 10% to 30% among the NiCo bimetallic oxide catalysts leads to a relative increase in C_{Density} , all NiCo catalysts are observed to display lower activity than pure Ni. This suggests that, overall, the addition of Co dilutes the Ni-centered active phase and exerts an activity-lowering effect, whereas a limited Co content can partially compensate for this detrimental effect by promoting OH^- adsorption and improving interfacial charge transfer kinetics to some extent. When the Co content is increased above 30%, however, the spinel Co-Ni oxide phase becomes dominant on the surface, NiOOH formation and the proper adsorption of the organic molecule are further hindered, and consequently the activity decreases again markedly.

To understand the surface-area contribution from the apparent C_{Density} , the electrochemically active surface area (ECSA) was determined from the C_{dl} measured in ethanol free 1 M NaOH within a non-faradaic potential window (0-0.1 V) at various scan rates. As shown in Figure 6c, Ni90Cu10 exhibits a higher C_{dl} ($43.7 \mu\text{F}/\text{cm}^2$) than Ni70Co30 ($35.5 \mu\text{F}/\text{cm}^2$). Using a commonly adopted specific capacitance value of $C_s = 40 \mu\text{F}/\text{cm}^2$ in alkaline media, the corresponding ECSA values were calculated as 1.09 for Ni90Cu10 and 0.89 for Ni70Co30 (Figure 6d). Notably, the ECSA difference between the two best-performing compositions is modest (~22%). This showed that the difference in catalytic currents is substantially larger, indicating that the superior CV response of Ni90Cu10 cannot be explained solely by a larger accessible surface area and should be mainly attributed to composition dependent effects.

Figure 7 presents the scan-rate dependence of ethanol electrooxidation, including cyclic voltammograms recorded at various scan rates for Ni90Cu10 and Ni70Co30, together with the corresponding plots of C_{Density} versus the $(\text{scan rate})^{1/2}$ derived from these voltammograms. To evaluate the dominant mechanism in catalysts during ethanol electrooxidation, scan-rate dependent CV measurements were performed for the best-performing catalysts from the NiCu and NiCo series (Ni90Cu10 and Ni70Co30). As the scan rate increases, the anode C_{Density} increases systematically for both catalysts (Figure 7a, 7c). This behavior suggests that the overall response is not entirely kinetically limited under the conditions studied, and that transport-related contributions become increasingly significant at higher scan rates. A common diagnostic method for diffusion-driven voltammetric behavior is that the current is proportional to the square root of the scan rate (i vs $v^{1/2}$), as predicted by the Randles-Sevcik framework for diffusion-controlled processes, whereas surface-bound/adsorption-controlled processes typically exhibit i vs v scaling (Batchelor-McAuley et al., 2015; Trachioti et al., 2023).

Accordingly, the C_{Density} obtained at a constant potential is plotted against $v^{1/2}$ (Figure 7b, 7d). For Ni90Cu10, a nearly linear j - $v^{1/2}$ relationship was obtained with j taken at ~ 0.76 V and $R^2 \sim 0.92$. For Ni70Co30, an even stronger linearity ($R^2 \sim 0.98$) was obtained with j taken at ~ 0.66 V. The approximately linear j - $v^{1/2}$ scaling for both catalysts supports a significant diffusion/mass transfer contribution to the measured currents, and the higher linearity for Ni70Co30 points to a relatively stronger diffusion effect compared to Ni90Cu10. The electrooxidation response in the current cell configuration can be interpreted as mixed control (kinetic + mass transfer) rather than a strictly kinetically limited regime. Combined CV-scan rate, ECSA, and XRD results consistently show the presence of diffusional effects, and composition-dependent phase effects still play a dominant role in determining the observed activity trends.

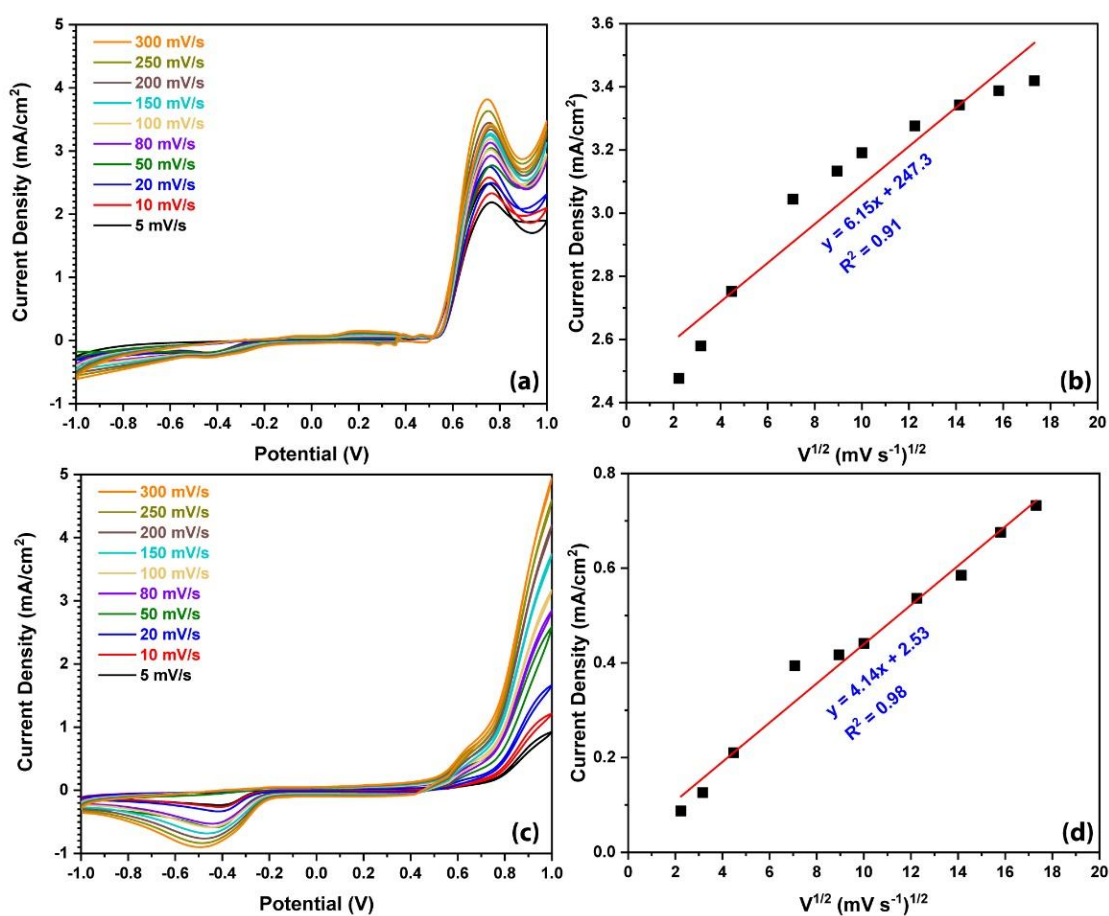


Figure 7. CVs at different scan rates in a 1 M NaOH + 0.2 M ethanol solution and plots of C_{Density} versus the square root of the scan rate: **a), b)** Ni90Cu10, and **c), d)** Ni70Co30

The parameters derived from the CV measurements at 50 mV/s for ethanol oxidation are summarized in Table 2. The NiCu series clearly exhibited higher activity. The Ni90Cu10 catalyst has the highest C_{Density} (3.04 mA/cm^2) and the highest mass activity (MA) (8.95 mA/mg) with the lowest E_{onset} (0.528 V). For Ni80Cu20, although the E_{onset} was higher (0.649 V), the high C_{Density} (2.26 mA/cm^2) and MA (6.66 mA/mg) were maintained. In contrast, for Ni70Cu30, despite having the same E_{onset} as Ni80Cu20 (0.649 V), the C_{Density} (0.52 mA/cm^2) and bulk activity (1.53 mA/mg) were significantly lower. This indicates that increasing the Cu content negatively impacts performance under the selected conditions.

In the NiCo series, only the Ni80Co20 and Ni70Co30 samples produced a significant current response. Ni70Co30 provided higher C_{Density} (0.39 vs. 0.28 mA/cm²) and MA (1.15 vs. 0.83 mA/mg) compared to Ni80Co20 (0.609 V) with a lower E_{onset} (0.559 V). For Ni90Co10 and Ni50Co50, no “significant activity” was observed under the selected conditions. The reference Ni electrode yielded a C_{Density} of 0.80 mA/cm² and a MA of 2.36 mA/mg with an E_{onset} of 0.578 V, thus demonstrating that Ni70Co30 and Ni80Co20 offer lower performance compared to Ni, while the NiCu series offers significantly higher performance.

Table 2. Comparative CV results for the synthesized Ni-based catalysts in ethanol oxidation

Catalysts	E_{onset} (V)	C_{Density} (mA/cm ²)	MA (mA/mg)	C_{dl} ($\mu\text{F}/\text{cm}^2$) / ECSA
Ni/Cu				
90/10	0.528	3.04	8.95	43.7 / 1.09
80/20	0.649	2.26	6.66	-
70/30	0.649	0.52	1.53	-
Ni/Co				
90/10	No significant activity			
80/20	0.609	0.28	0.83	-
70/30	0.559	0.39	1.15	35.5 / 0.89
50/50	No significant activity			
100/0	0.578	0.8	2.36	-

3.6. LSV

Figure 8 shows the LSV curve of bimetallic oxide catalysts, which are the catalysts with the best electrocatalytic activity according to the CV results. The LSV polarization profiles are in correlate well with CV trends and underline the enhancement induced by Cu and the performance suppression associated with Co on the Ni-centered active phase. Among all catalysts, Ni90Cu10 shows the highest anodic C_{Density} and the steepest post-onset rise (~ 4.7 mA/cm² at ~ 0.75 V). This value is approximately six times greater than the response of pure Ni at an identical potential. In addition, the onset of the anodic peak for Ni90Cu10 and Ni80Cu20 shifts to lower potentials compared to pure Ni. This shows that NiOOH formation and the subsequent organic oxidation start more easily on NiCu surfaces. Similar trends have been widely reported for the electrooxidation of urea and alcohols on NiCu alloys and NiCu oxides/hydroxides, and these have been attributed to the synergistic NiOOH/CuOOH redox couple and to the increase in interfacial charge transfer and oxygen vacancy concentration induced by Cu (Li Y. et al., 2023; Mohamed et al., 2024). In contrast, the NiCo bimetallic oxide catalysts exhibit slower LSV responses. Both the E_{onset} shift slightly to more positive values

and the currents at 0.75-1.0 V remain below those of pure Ni. This behavior supports the FTIR and XRD interpretation that Co promotes the formation of spinel-like Co-Ni oxides. The increase in Co content and the predominance of spinel phases appear to have resulted in the suppression of the NiOOH-centered EOR pathway and enhanced competition with the OER at high potentials. Their behaviour consistent with the delayed E_{onset} and lower C_{Density} observed in the LSV curves. In this context, the LSV data confirm that Cu acts as an effective electronic promoter of the NiOOH-centered active phase, whereas Co, under the present synthesis conditions, primarily dilutes and restructures the Ni environment, leading overall to lower electrocatalytic performance.

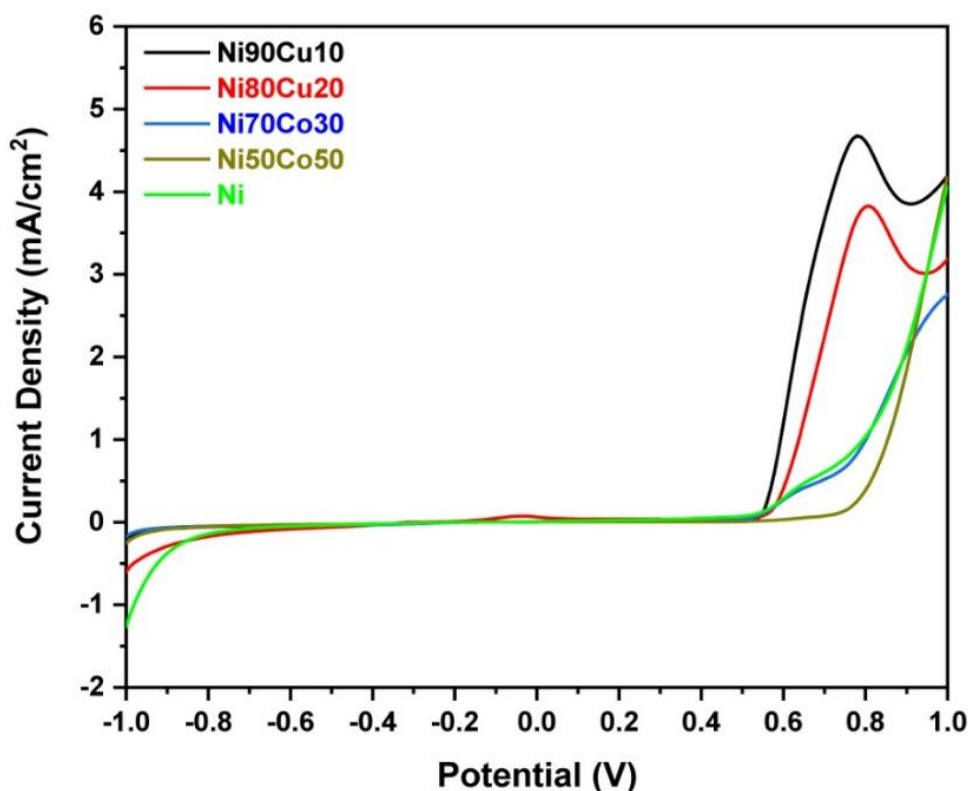


Figure 8. LSV curves of Ni based bimetallic oxide catalysts with the highest electrochemical activity and pure Ni (50 mV/s scan rate at 0.7 V)

3.7. CA

The CA results obtained for 1000 s to assess stability of catalysts and their resistance to poisoning/intermediate accumulation are presented in Figure 9. The sharp current decay observed in the first few seconds for all catalysts is mainly associated with double-layer charging, very rapid ethanol adsorption on the electrode surface, and the fast consumption of fuel in the region close to the surface. After all curves initially exhibit this typical “initial drop” behavior, they transition to a more gently sloping, quasi-steady region from about 100-150 s onward and show a gradual but limited decrease up to 1000 s. Ni90Cu10 is clearly superior to all other catalysts in terms of both the initial C_{Density} and the value reached at 1000 s. The current, which initially rises to approximately 3.3 mA.cm⁻², is maintained at around 1.5 mA.cm⁻² at about 1000 s. The Ni80Cu20 and Ni70Cu30 catalysts also exhibit similar behavior: they generate lower initial currents but yield curves that

decay relatively slowly over time and provide a higher current level than pure Ni at 1000 s. This means that Cu addition enhances initial activity and current retention over time. The NiOOH-centered active phase formed on the surface is more stable and more resistant to poisoning. Indeed, for NiCu-based catalysts in the electrooxidation of ethanol and other small organic molecules, the observation of higher residual currents and lower relative current losses in the CA curves has been associated with the synergy of the NiOOH/CuOOH couple and with the facilitation of the removal of poisoning species via the reduction in charge-transfer resistance induced by Cu addition (Gamal et al., 2024).

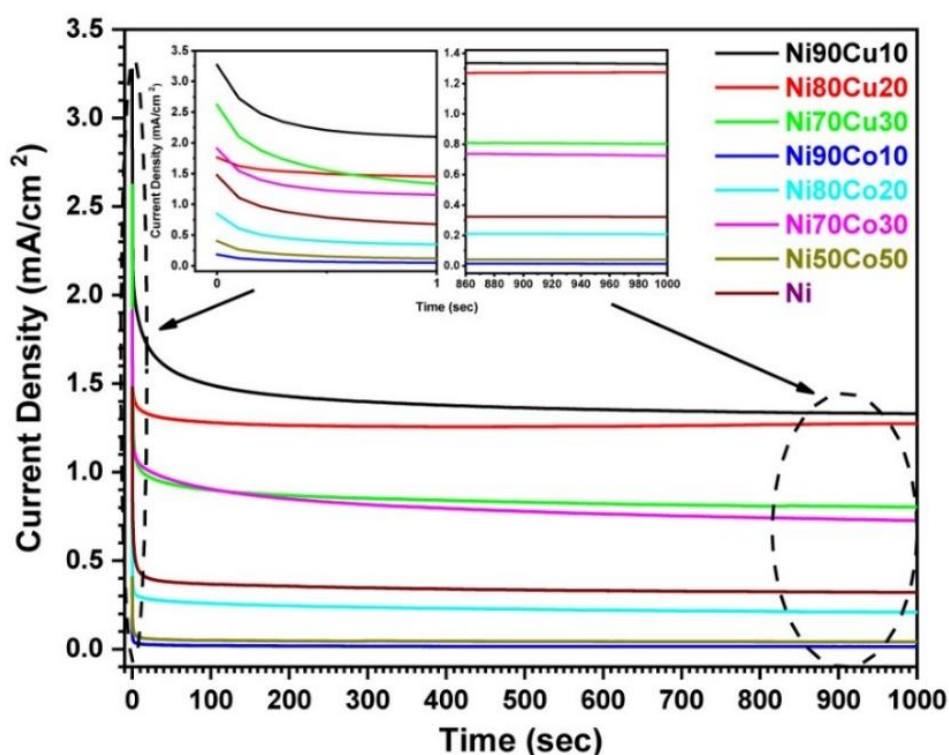


Figure 9. CA curves of NiCu and NiCo bimetallic oxide catalysts, and pure Ni (0.7 V, 20 mV/s scan rate)

For the NiCo bimetallic oxide catalysts, the CA results show that increasing the Co content up to a certain range improves the stability for ethanol electrooxidation. Going from Ni90Co10 to Ni70Co30, the quasi-steady current values reached after the initial rapid current decay are observed to increase gradually. This suggests that Co addition “supports” the NiOOH-centered active phase to some extent by enhancing electron transfer kinetics in the Ni-based phase and facilitating the Ni^{2+} to Ni^{3+} transformation (Yu et al., 2023). In contrast, in the Ni50Co50 catalyst, where the Co content is increased to 50%, both the initial current and the residual current at 1000 s decrease markedly, and the curve exhibits a more steeply decaying profile. This behavior is consistent with the literature reporting that, in Co-rich compositions, Co-rich spinel structures become dominant at the surface instead of NiOOH-like phases, and that these phases preferentially promote the oxygen evolution reaction rather than ethanol oxidation (Anuratha et al., 2022). It has thus been determined that Co addition up to a certain proportion can enhance the Ni-centered active phase and improve stability, whereas when the Co content is increased excessively, the dilution of Ni active centers and the dominance of spinel phases lead to a renewed decrease in performance.

3.8. EIS

The Nyquist responses of the synthesized catalysts are compared in Figure 10, and the corresponding EIS-derived parameters are presented in Table 3. For all catalysts, the spectra consist of a depressed semicircle in the high-frequency region together with an inclined tail at lower frequencies, which is characteristic of diffusion/adsorption-related contributions. This behavior indicates an ethanol electrooxidation process controlled by charge transfer and mass transfer, which can be described by a classical Randles type equivalent circuit (R_s - R_{ct} //CPE-W) for catalysts exhibiting a discernible semicircle. In the enlarged inset graph, when the region closest to the Z' axis is examined in detail, it is seen that, for all catalysts, the value of solution resistance (R_s), corresponding to the high-frequency intercept, lies in the range of approximately 0.077-0.083 $k\Omega$ and is very close to each other (Table 3). Accordingly, the differences can be mainly attributed to kinetic and diffusion-related processes at the electrode-electrolyte interface, with only a minimal contribution from changes in solution resistance. Similarly, for $NiCo_2O_4/WO_3/ACWH$ and similar Ni-based electrocatalysts developed for alcohol oxidation, it has been reported that the high-frequency intercept in the Nyquist diagram gives similar R_s values for all electrodes, whereas the performance differences arise from the semicircle diameter (R_{ct}) (Askari et al., 2024).

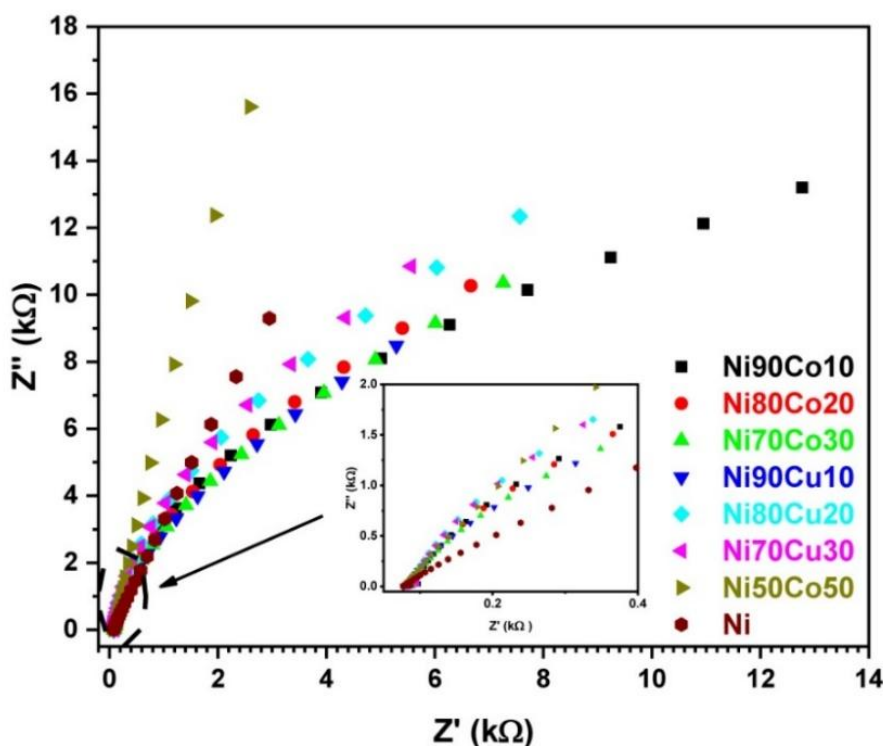


Figure 10. Nyquist diagrams of the synthesized catalysts (10^5 -0.1 Hz, 0.7 V)

Considering the arc widths of the semicircles along the horizontal axis (Table 3), it is clearly seen that Ni90Co10 forms the largest arc (12.69 $k\Omega$), whereas the Ni90Cu10 catalyst exhibit comparatively narrower semicircles (5.21 $k\Omega$). Ni80Co20 and Ni70Co30 display intermediate arc widths (6.58 and 7.18 $k\Omega$, respectively). These trends indicate that the NiCu possess more favorable interfacial charge-transfer characteristics for ethanol electrooxidation than the NiCo. In the literature, for Ni-based oxide/hydroxide

electrodes, it has been stated that, as the semicircle diameter in the Nyquist diagram decreases, both the EOR C_{Density} increase and the overpotential decreases, and that this is due to the Cu addition facilitating the transformation of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ couple and thereby accelerating charge transfer (Li Z. et al., 2022; Askari et al., 2024). In this study as well, the fact that the Ni90Cu10 catalyst provides the highest C_{Density} in CV and LSV and the highest residual current in CA is consistent with its exhibiting smaller semicircles, and thus lower R_{ct} , in the Nyquist diagram compared to the NiCo. In the NiCo, however, the fact that, especially for Ni90Co10 and Ni80Co20, the semicircles form the largest arcs both in the overall diagram and in the enlarged region reveals that, as the Co content increases, the charge-transfer step for ethanol electrooxidation becomes more difficult and the pseudocapacitive/diffusion control at the interface is strengthened. In EIS studies performed for NiCo_2O_4 and similar spinel NiCo oxides, larger semicircles and pronounced Warburg tails have also been observed under alcohol oxidation conditions compared to NiO. It has been reported that, when the composition deviates from the optimum, the predominance of Co phases slows down electron transfer (Zhang C. et al., 2021; Askari et al., 2024). Pure Ni and Ni50Co50 electrodes, on the other hand, display a long and almost linear profile with an inclination of approximately 45° immediately after the Z' axis both in the overall diagram and in the inset, and do not contain a distinct and closed semicircle. This type of behavior is defined in the literature as “Warburg dominant” behavior for systems in which the charge-transfer resistance cannot be reliably separated with a single R_{ct} value and mass transfer or high pseudocapacitance dominates in most of the response. Therefore, the EIS results show that the NiCu catalysts provide the highest activity and stability in ethanol electrooxidation owing to their lower charge-transfer resistance and faster electrode kinetics, whereas, in the NiCo catalysts with high Co content, the predominance of spinel Co-Ni phases leads to an enhance in R_{ct} and activity loss observed in CV, LSV and CA measurements is consistent with the impedance data.

Table 3. Key EIS metrics extracted from Nyquist plots

Catalysts	R_s (k Ω)	Arc width (k Ω)	R_{ct} (k Ω)	Equivalent Circuit Model
Ni90Cu10	0.077	5.21	32.35	$R_s - (R_{\text{ct}} \parallel \text{CPE}) - W$
Ni80Cu20	0.079	7.48	42.43	
Ni70Cu30	0.081	5.48	42.68	
Ni90Co10	0.083	12.69	38.76	
Ni80Co20	0.081	6.58	36.94	
Ni70Co30	0.081	7.18	37.34	

The performance of the catalyst synthesized in this study is compared with representative Ni-based and precious metal based catalysts reported for the electrooxidation of ethanol in alkaline medium, as shown in Table 4. In this study, Ni90Cu10 exhibits an E_{onset} of 0.528 V at 50 mV/s and a C_{Density} of 3.04 mA/cm².

Compared with Ni-based systems, the observed specific activity falls within the wide range reported in the literature. Current outputs range from relatively modest (Ni/ZNC@rGO: 2.07 mA/cm²) to significantly higher values for highly porous oxides (Porous Ni: 55 mA/cm² and NiCo₂O₄/WO₃/ACWH: 27.98 mA/cm²). These are typically measured under varying ethanol concentrations and electrolyte compositions. These comparisons acknowledge that absolute C_{Density} are primarily influenced by test conditions (electrolyte/fuel concentration, catalyst loading, and potential reference). Therefore, the table could be interpreted as a quantitative comparison rather than a strictly normalized ranking.

Electrodes containing Pd or Pt generally exhibited higher mass-normalized activity and lower initial potentials under comparable alkaline conditions. This naturally reflects faster electron transfer kinetics on noble metal surfaces. However, the Ni₉₀Cu₁₀ catalyst shows measurable activity in a low ethanol (0.2 M) alkaline environment, providing a practical non-noble reference point. This supports the conclusion that Cu addition promotes a Ni-centric active phase (Ni(OH)₂/NiOOH) while maintaining a Ni-rich oxide framework.

Table 4. Quantitative benchmarking of ethanol electrooxidation performance for Ni-based and noble-metal-based electrocatalysts in alkaline media

Catalysts	Electrolyte	Scan Rate (mV/s)	Ethanol Molarity (M)	E _{onset} (V)	Specific Activity (mA/cm ²)	MA (mA/mg metal)
Ni ₉₀ Cu ₁₀ (This work)	1 M NaOH	50	0.2	0.528	3.04	8.95
NiCo ₂ O ₄ /WO ₃ /ACWH (Askari et al., 2024)	0.5 M KOH	20	0.5	0.67	27.98	n.a.
Porous Ni (Kutyła et al., 2023)	1 M NaOH	50	1	1.62	55	n.a.
NiCuGO composite (Wala-Kapica et al., 2024)	1 M KOH	50	1	0.66	8.61	n.a.
Ni/ZNC@rGO (Gamal et al., 2024)	1 M NaOH	50	1	0.42	2.07	~5
Pd/p1,8-DAN/GC (Hassan K. M. et al., 2018)	0.5 M NaOH	50	0.7	0.53	1.02	28
Pd@CeO ₂ (Çelebi, 2025)	0.5 M NaOH	50	1	~ -0.5	~9	n.a.
PtCu NCs/CB (Liu D. et al., 2022)	1 M KOH	50	1	0.343	n.a.	4.96

4. CONCLUSION

This study focused on the development of noble metal free Ni-based bimetallic oxide anode catalysts for ethanol electrooxidation in alkaline medium and on clarifying the distinct effects of Cu and Co incorporation into the Ni-centered oxide phase. The comparative structural results showed that the Ni90Cu10 catalyst predominantly preserved a NiO-based single-phase $\text{Ni}_{1-x}\text{Cu}_x\text{O}$ solid solution, where Cu^{2+} ions were incorporated into the NiO lattice, whereas the NiCo series, particularly Ni50Co50, was characterized by a stronger contribution from $\text{NiCo}_2\text{O}_4/\text{Co}_3\text{O}_4$ -type spinel phases, as reflected by the more pronounced metal oxygen vibration bands associated with tetrahedral and octahedral environments. Electrochemical evaluation revealed that the NiCu catalysts were clearly superior to the NiCo series in both ethanol oxidation activity and stability. Among all compositions, Ni90Cu10 delivered the best performance, giving a CV peak C_{Density} of 3.04 mA/cm^2 at about 0.75 V and an LSV current of about 4.7 mA/cm^2 , corresponding to an activity roughly 3-6 times higher than that of pure Ni. These results suggest that ethanol oxidation mainly proceeds through a $\text{Ni}(\text{OH})_2/\text{NiOOH}$ -centered pathway and that Cu promotes the $\text{Ni}^{2+}/\text{Ni}^{3+}$ transition by increasing oxygen-vacancy concentration and lattice defect density in the NiO framework, thereby enabling NiOOH formation at lower potentials and with higher surface coverage. Cu incorporation also improves interfacial charge-transfer properties, which contributes to the lower charge-transfer resistance and faster kinetics observed for the NiCu catalysts. In the Co series, a limited increase in Co content provided some stabilization in the CA response, but further Co addition diluted the Ni-centered active phase and led to lower overall activity. EIS results further confirmed that the main performance differences among the catalysts were governed primarily by charge-transfer resistance rather than by solution resistance. In addition, pure Ni and Ni50Co50 displayed a nearly linear low-frequency response with a slope close to 45° , indicating a Warburg-dominant behavior that could not be adequately represented by a single R_{ct} contribution. The combined structural and electrochemical findings demonstrate that Ni90Cu10 is effective low-cost and Pt-free anode candidates for ethanol electrooxidation in alkaline medium because they provide high activity, good stability, and relatively low charge-transfer resistance.

AUTHOR CONTRIBUTIONS

Conceptualization, Y.Y. and I.A.; methodology, Y.Y., F.N.T. and I. A.; laboratory work, Y.Y., and F.N.T.; validation, Y.Y. and I.A.; formal analysis, F.N.T., Y.Y.; data curation, F.N.T.; manuscript–original draft, Y.Y.; manuscript–review and editing, I.A, and Y.Y.; visualization, Y.Y.; supervision, Y.Y. and I.A.

AI Exclusion: AI tools are strictly prohibited from being listed as authors.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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