



Article

Mechanistic Insights into Glycerol Electro-Oxidation in Alkaline Medium on M@Pt/C Catalysts Revealed by In Situ FTIR

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Abstract

The development of efficient catalysts for the glycerol oxidation reaction (GOR) is crucial for advancing direct glycerol fuel cells. This study provides mechanistic insights into the glycerol electro-oxidation reaction (GOR) on Co@Pt/C, Ni@Pt/C, and Sn@Pt/C catalysts using in situ FTIR spectroscopy. While the structural and electrochemical properties of these materials have been previously reported, their reaction pathways and product selectivity under alkaline conditions remain unclear. Electrochemical performance was evaluated through cyclic voltammetry (CV) and chronoamperometry (1.0 M KOH + 1.0 M glycerol), revealing that the bimetallic catalysts exhibited superior catalytic activity compared to Pt/C. Co@Pt/C demonstrated the highest performance, with a 7.5-fold increase in current density relative to Pt/C, followed by Sn@Pt/C (3.4-fold) and Ni@Pt/C (2.8-fold). In situ FTIR analysis identified key oxidation products, including C3, C2, and C1 species, with evidence of both partial and complete oxidation. These findings demonstrate that the core metal plays a key role in governing reaction pathways and C–C bond cleavage, providing important insights for the rational design of anode materials in direct glycerol fuel cells.

Keywords: electrocatalysis; glycerol oxidation reaction (GOR); platinum-based materials; in situ FTIR analysis



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1. Introduction

At present, the technological, economic, and social development of any society hinges on increasing energy consumption, which imposes significant socio-environmental costs. Consequently, it is crucial to foster initiatives that exploit renewable energy sources with higher efficiency and lower environmental impact.

In this context, fuel cells emerge as a promising clean energy-generating alternative, operating with renewable sources, producing virtually no pollutants, and exhibiting high theoretical efficiency. They can be used as sources of electrical energy for stationary, mobile, and portable systems. Among these technologies, Polymer Electrolyte Membrane Fuel Cells (PEMFCs) stand out due to their versatile applications. Essentially, their operation relies on the oxidation of fuel at the anode (particularly gaseous hydrogen) and the reduction

of oxygen at the cathode. In some models, H_2 can be replaced by low-molecular-weight alcohols, leading to Direct Alcohol Fuel Cells (DAFCs) [1].

The utilization of glycerol as a fuel in DAFCs has garnered increasing research interest, becoming a focal point of study in recent years. Glycerol is an alcohol commonly produced through more cost-effective methods compared to hydrogen. Its low toxicity, high boiling point, elevated specific energy, and potential for biomass-derived production are significant attributes that enhance its applicability [2].

The complete oxidation of glycerol releases 14 electrons; however, the challenge of cleaving C–C bonds represents a significant obstacle that must be overcome to enable its application. Consequently, several catalysts have been evaluated to facilitate bond cleavage and mitigate the poisoning effects that frequently occur when conventional catalysts are employed [3].

Currently, Pt-based materials have demonstrated remarkable efficiency in catalyzing various electrochemical reactions, including the glycerol oxidation reaction (GOR). Nevertheless, the catalytic activity of Pt is hindered by the strong adsorption of certain intermediates onto active sites, reducing its performance. To counteract these effects, Pt is often combined with other transition metals (nickel, cobalt, and copper, among others) [3].

In general, GOR leads to the formation of C3, C2, and C1 products. The oxidation of a primary hydroxyl (OH) group converts glycerol into glyceraldehyde (GALD), while oxidation of the secondary hydroxyl group forms dihydroxyacetone (DHA). From these initial steps, glycerol can undergo further electro-oxidation, producing C3 products such as glyceric acid (GLA), tartronic acid (TA), mesoxalic acid (MA), and hydroxypyruvic acid (HPA). C2 products, including glycolic acid (GA), glyoxylic acid (GLOA), lactic acid (LA), and oxalic acid (OA), may also be generated. The most commonly observed C1 compound in GOR is formic acid (FA). Ultimately, the GOR can lead to the formation of carbonate (CO_3^{2-}) in an alkaline medium or CO_2 in an acidic medium. The reaction pathways and the preferred formation of byproducts are influenced by catalyst selectivity as well as the experimental conditions [3,4].

To illustrate these points, Ottoni et al. [5] investigated the application of PdAu for GOR catalysis in an alkaline medium. The authors observed that the addition of Au significantly enhanced Pd's activity, with the $Pd_{50}Au_{50}/C$ catalyst exhibiting twice the activity of Pd/C. Fourier Transform Infrared Spectroscopy (FTIR) identified GALD, DHA, TA, GA, OA, FA, and CO_3^{2-} as the main byproducts. Similarly, Wang et al. [6] evaluated PtBi/C for GOR under alkaline conditions, concluding that the addition of Bi promoted C–C bond cleavage and reduced catalyst poisoning. PtBi/C exhibited a peak current density of approximately 9 A mg_{Pt}^{-1} , more than 10 times higher than Pt/C. FTIR analysis revealed the formation of TA, GA, GLA, OA, FA, and carbonate.

Garcia et al. [7] developed PtAg/C and PtAg/MnO/C catalysts for GOR. In single-cell tests, PtAg/MnO/C exhibited a power density of 102.8 mW cm^{-2} , compared to 59.4 mW cm^{-2} for Pt/C. Through FTIR, the main products identified were GALD, DHA, TA, GLA, GLOA, GA, HPA, FA, and CO_3^{2-} .

Luo et al. [8] studied Pt-Ni catalysts in different proportions for GOR in an alkaline medium (KOH). The authors observed that PtNi₂ demonstrated superior C–C cleavage efficiency and lower poisoning by C=O species. Through combined FTIR and high-performance liquid chromatography (HPLC) techniques, TA, GA, GLA, OA, FA, and carbonate were identified as the principal byproducts.

Pereira et al. [9] also employed in situ FTIR and demonstrated that GOR in a NaOH electrolyte resulted in the formation of GALD, GLA, TA, DHA, HPA, OA, FA, and CO_3^{2-} . The authors concluded that PtSb/C favored GOR initiated by the oxidation of the secondary OH group, leading to increased DHA formation.

The combination of Pt with other metals in a core–shell structure has attracted growing attention in recent years. Core–shell electrocatalysts are able to enhance catalytic activity in oxidation reactions of organic molecules, benefiting from both structural and electronic effects. The presence of a secondary metal in the core influences the Pt surface electronically, which plays a key role in catalytic performance [10].

For instance, Maya-Cornejo et al. [11] synthesized Cu@Pd/C and Cu@Pt/C core–shell catalysts and tested them in GOR using crude glycerol from biodiesel production. Both catalysts exhibited superior activity compared to Pt/C and Pd/C, with Cu@Pd/C and Cu@Pt/C demonstrating greater tolerance to impurities in crude glycerol.

Another example comes from Zhou et al. [12], who developed trimetallic nanoparticles with core–shell structures, where various combinations of Pt and Au coated @Ag core for GOR applications. The Pt_xAu_y@Ag nanoparticles exhibited enhanced GOR reactivity and higher selectivity for C3 products compared to commercial Pt/C. Notably, Pt₄@Ag demonstrated a current density 2.6 times higher than Pt/C in an acidic electrolyte, while Pt₄Au₆@Ag reached a current density 4.7 times higher.

Although Co@Pt/C, Ni@Pt/C, and Sn@Pt/C nanoparticles were previously synthesized by our group for alcohol electro-oxidation under distinct reaction environments [13], their mechanistic behavior in the alkaline glycerol oxidation reaction (GOR) has not yet been investigated. GOR involves different adsorption characteristics, dehydrogenation steps, and potential-dependent C–C cleavage pathways compared to other small organic molecules, requiring a dedicated mechanistic study. Moreover, no comparative evaluation of these three metal-core architectures under identical electrochemical conditions has been reported to date, particularly involving in situ FTIR spectroscopy. This gap motivates the present work, which aims to correlate structural features with activity, stability, and product selectivity during GOR on Pt-based core–shell catalysts.

Herein, we address these gaps by synthesizing and systematically comparing Co@Pt/C, Ni@Pt/C, and Sn@Pt/C nanocatalysts prepared through a controlled sequential reduction method designed to promote core–shell-type architectures. Structural, morphological, and compositional analyses previously reported in [13] support the formation of Pt-enriched surface features and distinct core metal identities. Electrochemical evaluation demonstrates substantial improvements in activity, long-term stability, and onset potential relative to Pt/C. Finally, in situ FTIR spectroscopy is employed to elucidate the evolution of C1, C2, and C3 intermediates, providing insight into how the core metal influences early reaction pathways and C–C bond scission under alkaline conditions.

2. Materials and Methods

2.1. Synthesis of Catalysts

The synthesis procedure of the Co@Pt/C, Ni@Pt/C and Sn@Pt/C catalysts follows our previously reported methodology [13]. Briefly, the synthesis involved two main steps. The first one consisted of the formation of nanoparticle cores composed of Co, Ni, and Sn. The second step consisted of depositing a Pt layer onto the previously formed metallic cores, followed by supporting the resulting nanoparticles on carbon powder. This procedure was carried out to obtain catalysts with a metal loading of 20%. The Pt-to-metal ratio was kept at 1:1 for each synthesis.

Initially, precursor salts of Co, Ni, or Sn (CoCl₂·2H₂O–Sigma-Aldrich–Merck KGaA, Darmstadt, Germany; NiCl₂·6H₂O–Sigma-Aldrich–Merck KGaA, Darmstadt, Germany; or SnCl₂·2H₂O–Sigma-Aldrich–Merck KGaA, Darmstadt, Germany) were added along with sodium citrate (Synth) in 50.0 mL of ultrapure water (18.2 MΩ cm at 25 °C/Milli-Q–Merck KGaA, Darmstadt, Germany). The citrate-to-precursor ratio was 1:1. The mixture was then heated to 90 °C under stirring, with a continuous N₂ flow throughout the solution.

Once the desired temperature was reached, an excess of NaBH_4 (Fluka Analytical–Merck KGaA, Darmstadt, Germany) was introduced as the reducing agent for the metal precursor salts. The solution was stirred for approximately 30 min. Subsequently, the N_2 flow was interrupted, and 25.0 mL of ultrapure water was added to the suspension containing Co, Ni, or Sn nanoparticles. Then, an aqueous solution (5%) of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich) was introduced.

Next, ascorbic acid (Chimie Test, São Paulo, SP, Brazil) was added in excess to reduce the Pt precursor, and this solution was stirred for 2 h. Vulcan XC-72 (Cabot Corporation, Boston, MA, USA, ~30 nm particle size and $250 \text{ m}^2 \text{ g}^{-1}$ surface area) was added to obtain supported catalysts with a 20% metal loading. The suspension was stirred at room temperature for 24 h. Subsequently, the suspended catalysts were vacuum filtered, washed with ultrapure water, and dried for 2 h at 70°C . Finally, the samples were ground and subjected to thermal treatment at 300°C under an N_2 atmosphere for 1 h in a tubular furnace.

2.2. Electrochemical Characterization

Electrochemical characterization was performed using cyclic voltammetry (CV) and chronoamperometry, with a Pine Research Wave Driver 40 DC potentiostat/galvanostat (Pine Research Instrumentation Inc. – Durham, NC, USA) interfaced with a computer. A 1.0 mol L^{-1} KOH (Sigma-Aldrich) aqueous solution was used as the electrolyte for all experiments. CVs were performed within a potential range of 0.05 to 1.1 V, with a scan rate of 50 mV s^{-1} . A platinum plate was used as the counter electrode, while a reversible hydrogen electrode (RHE) served as the reference electrode. A glassy carbon electrode (5 mm diameter) was employed as the working electrode. Before each experiment, the glassy carbon electrode was polished using alumina with particle sizes of $3.0 \mu\text{m}$, $1.0 \mu\text{m}$, and $0.3 \mu\text{m}$ (in this order).

Next, catalyst inks were prepared with the following composition: 1 mg of catalyst, $200 \mu\text{L}$ of isopropyl alcohol, and $10 \mu\text{L}$ of a 5% (mass/volume) Nafion solution. The suspension was sonicated for 30 min, after which $15 \mu\text{L}$ of the ink was applied to fully cover the surface of the glassy carbon electrode. After the complete evaporation of isopropyl alcohol (approximately 2 min), the electrochemical analyses began.

Subsequently, CV experiments were carried out in the presence of 1.0 mol L^{-1} glycerol (Sigma-Aldrich–Merck KGaA, Darmstadt, Germany). Chronoamperometry was performed by applying a potential of 0.6 V for 1 h [13,14].

All electrochemical results were normalized by the electroactive surface area (ECSA, expressed in cm^2 of Pt) of the catalysts, which was determined based on the charge related to the hydrogen desorption region (measured in μC) divided by the charge density required to reduce a monolayer of protons on a polycrystalline Pt surface ($210 \mu\text{C cm}^{-2}$ of Pt) [15].

2.3. In Situ FTIR Experiments

In situ FTIR experiments were performed using a Shimadzu IRTracer-100 spectrophotometer (Shimadzu Corporation, Kyoto, Japan) equipped with a liquid nitrogen-cooled mercury–cadmium–telluride (MCT) detector. The reflectance accessory was a VeeMax III platform (Pike Technologies, Fitchburg, WI, USA) set at a 60° incidence angle. The spectroelectrochemical cell was sealed with a planar CaF_2 window at its bottom.

The cell (Figure 1) contained three electrodes: a gold disc working electrode, a reversible hydrogen electrode, and a platinum wire counter electrode surrounding the working electrode. The gold disc was chosen as the working electrode due to its reflective properties, which enhance spectral resolution [16]. Prior to the FTIR experiments, catalyst inks were prepared following the same procedure described for the electrochemical measurements. An aliquot of the catalyst ink was deposited onto the gold disc electrode

by drop-casting and dried at room temperature, forming the catalyst layer used for the spectroelectrochemical measurements. Spectra were collected within the range of 3000 to 1000 cm^{-1} and expressed as a percentage of the reflectance. Each spectrum is calculated as $I = (R - R_0) \times 100$, where R represents the spectrum collected at a specific potential, while R_0 is the reference one, collected at 0.05 V. This configuration implies that species containing active IR functional groups, formed during the potential scan, will absorb some of the radiation at their characteristic wavenumbers, resulting in downward-pointing bands. Conversely, absorbing species eventually consumed during the reaction will cause an increase in signal intensity at the corresponding wavenumbers (since they are no longer present). The result is upward-pointing bands. Spectra were averaged from 50 interferograms, with a resolution of 8 cm^{-1} , over a potential range of 0.1 to 1.1 V at a scan rate of 5 mV s^{-1} [17,18]. The potential was stopped at steps of 0.1 V during spectral collection.

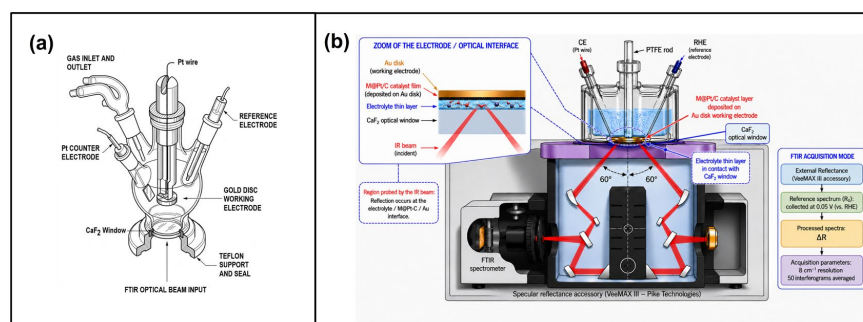


Figure 1. Schematic representation of the in situ FTIR spectroelectrochemical cell and external reflectance configuration employed for glycerol electro-oxidation studies. (a) Cross-sectional view of the electrochemical cell showing the gold disc working electrode, platinum counter electrode, reversible hydrogen reference electrode (RHE), gas inlet/outlet system, and CaF_2 optical window. (b) Illustration of the experimental arrangement mounted on the specular reflectance accessory, including the optical path of the incident and reflected infrared beams, the electrode/optical interface, and the thin electrolyte layer formed between the catalyst-coated gold electrode and the CaF_2 window. Reflectance spectra were collected using an external reflectance configuration and expressed as relative reflectance (%). The schematic illustration was created by the authors based on photographs of the experimental setup and refined with the assistance of artificial intelligence tools for graphical rendering.

3. Results and Discussion

3.1. Physical Characterization

The structural and morphological characterization of these materials has been previously reported in detail [13] and is briefly summarized here to support the discussion of the electrochemical and spectroscopic results (Table 1).

Table 1. Crystallite size (D), lattice parameter (a), Pt-Pt Interatomic Distance ($d_{\text{Pt-Pt}}$), and particle size from TEM (D_{TEM}) for Pt/C, Co@Pt/C, Ni@Pt/C, and Sn@Pt/C [19–22]. Adapted from Silva et al., *Energies* 2025 [13].

	XRD			TEM
	D (nm)	a (nm)	$d_{\text{Pt-Pt}}$ (nm)	D_{TEM} (nm)
Pt/C	8.0	0.391	0.277	*
Co@Pt/C	12.0	0.391	0.277	11.2 ± 4.1
Ni@Pt/C	12.0	0.391	0.277	13.9 ± 5.9
Sn@Pt/C	8.0	0.392	0.277	8.7 ± 4.9

* TEM measurements were not performed for this sample.

In Figure 2, TEM micrographs for Co@Pt/C, Ni@Pt/C, and Sn@Pt/C reveal that the particles exhibit a largely spherical shape, with good dispersion of the catalysts over the carbon support, although regions of particle aggregation were also observed [23]. For Co@Pt/C and Ni@Pt/C, the observed particle sizes are consistent with the XRD results, suggesting the formation of core-shell-type structures, in which Co and Ni may remain preferentially confined in the core while Pt-rich domains are located at the outer surface. SEM micrographs and EDS mapping, previously reported [13], also show largely globular morphological structures, with a relatively uniform and homogeneous particle size distribution. EDS analysis highlights that Pt is the predominant element detected at the particle surface regions, which is consistent with the proposed core-shell-type structural organization reported previously [13]. If Co and Ni were homogeneously distributed in the catalyst, their signals would likely be more pronounced in surface-sensitive techniques. This observation is in line with previous studies [24,25].

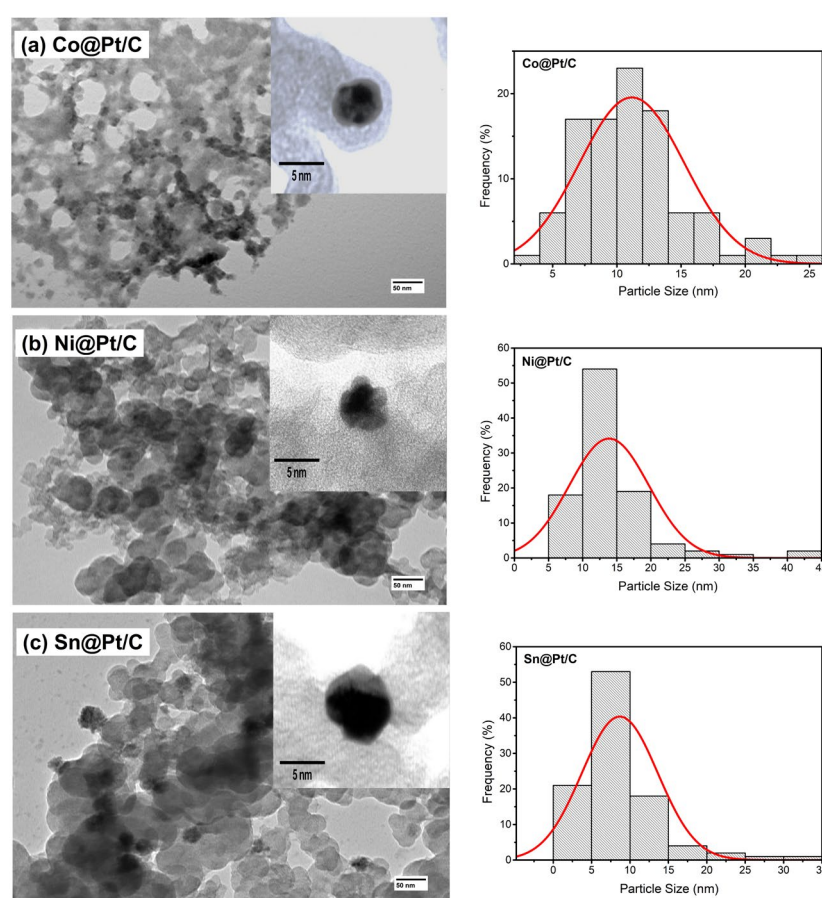


Figure 2. TEM micrographs and particle size distributions of Co@Pt/C, Ni@Pt/C and Sn@Pt/C catalysts. Adapted from Silva et al., *Energies* 2025, 18, 305, under the Creative Commons Attribution (CC BY 4.0) license [13].

3.2. Electrochemical Features of Catalysts

In Figure 3a, the CV profiles for Co@Pt/C, Ni@Pt/C, and Sn@Pt/C are presented. The voltammograms exhibit the typical features of Pt-based materials. Specifically, three regions can be identified, though they are poorly defined: (i) from 0.05 to 0.45 V vs. RHE, the hydrogen adsorption/desorption region is observed, arising from processes that precede H₂ evolution; (ii) from 0.45 to 0.8 V vs. RHE, a potential range associated with non-faradaic processes is present, originating from double-layer charging; and (iii) from 0.8 to 1.1 V vs. RHE, the oxygen region is identified, corresponding to the formation of OH[−] adsorption.

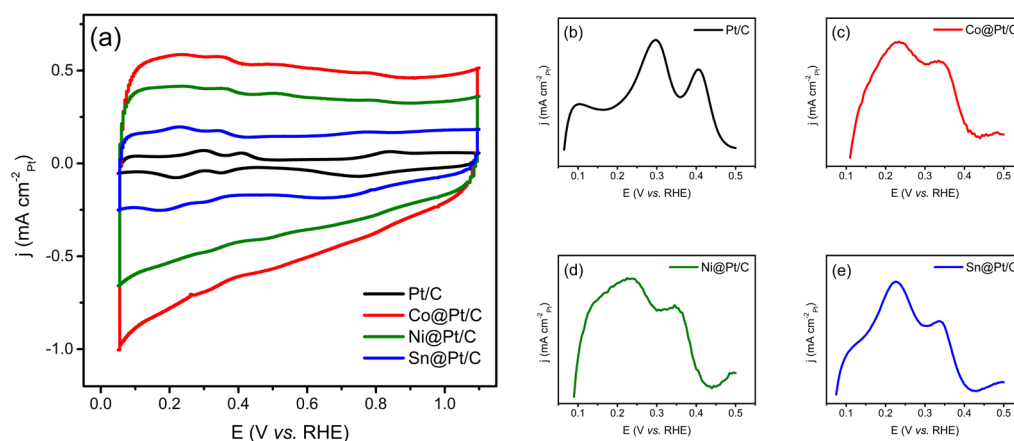


Figure 3. Cyclic voltammograms in 1.0 M KOH at 50 mV s⁻¹: (a) comparison among Co@Pt/C, Ni@Pt/C, and Sn@Pt/C; (b) hydrogen desorption region of Pt/C; (c) hydrogen desorption region of Co@Pt/C; (d) hydrogen desorption region of Ni@Pt/C; (e) hydrogen desorption region of Sn@Pt/C.

In the cathodic scan, broad cathodic waves around 0.75 V vs. RHE are detected, which corresponds to the reduction of oxides formed during the anodic scan. Figure 3b–e highlights the hydrogen desorption regions for comparison, demonstrating that the presence of Co, Ni, and Sn substantially modifies the adsorption parameters of chemical species on Pt [26–31].

3.3. Electro-Oxidation of Glycerol

The voltammograms acquired in the presence of 1.0 M glycerol (Figure 4) exhibit the characteristic profile of glycerol electro-oxidation in alkaline media, showing well-defined oxidation peaks during both the anodic scan and the reverse (cathodic) scan. Notably, the hydrogen adsorption/desorption peaks, typically observed between 0.05 and 0.45 V (vs. RHE), disappear in the presence of glycerol, suggesting a strong interaction between the catalyst surface and the adsorbed glycerol molecules [32,33].

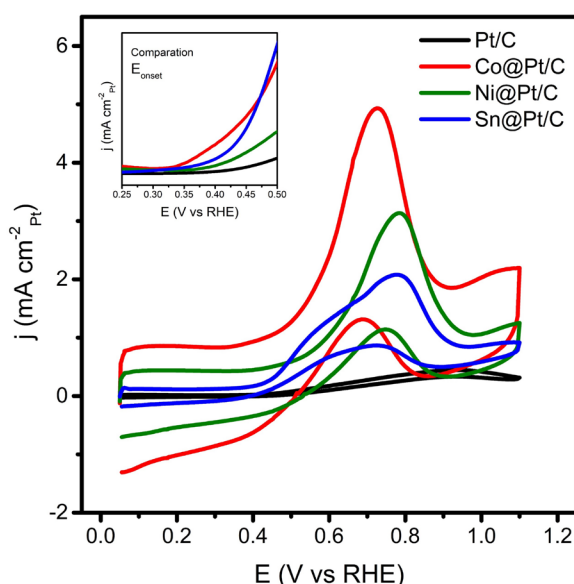


Figure 4. Voltammograms of Pt/C, Co@Pt/C, Ni@Pt/C, and Sn@Pt/C in 1.0 M KOH + 1.0 M glycerol compared to Pt/C. Scan rate: 50 mV s⁻¹. The inset highlights the comparison of onset oxidation potentials (E_{onset}).

As shown in Figure 4, Co@Pt/C, Ni@Pt/C, and Sn@Pt/C catalysts exhibit significantly higher current densities compared to Pt/C, demonstrating superior catalytic activity. The oxidation onset potential (E_{onset}) is shifted to lower values for all modified catalysts relative to Pt/C (inset of Figure 4), indicating a reduction in activation energy. Among the tested materials, Co@Pt/C exhibits the highest peak current density in the anodic scan ($\sim 4.93 \text{ mA cm}^{-2}$), followed by Ni@Pt/C ($\sim 3.12 \text{ mA cm}^{-2}$) and Sn@Pt/C ($\sim 2.08 \text{ mA cm}^{-2}$), compared to only $\sim 0.45 \text{ mA cm}^{-2}$ for Pt/C.

The potentials at which the maximum current densities (j_{peak}) occur are also significantly shifted. Specifically, $j_{\text{peak/anod}}$ and $j_{\text{peak/cat}}$ are observed at 0.72 and 0.69 V for Co@Pt/C, 0.78 and 0.75 V for Ni@Pt/C, and 0.78 and 0.72 V for Sn@Pt/C, compared to 0.93 V in both scans for Pt/C. The higher current response and lower E_{onset} values suggest that Co, Ni, and Sn promote the oxidation process.

After reaching $j_{\text{peak/anod}}$, a drop in current density is observed, particularly at higher potentials, due to the formation of oxides on the Pt surface at potentials above 0.9 V vs. RHE, leading to inhibition of active sites [4]. The presence of Co, Ni, and Sn in the core-shell structures may influence the oxidation behavior of the Pt shell by modifying its electronic properties and altering the adsorption of oxygen-containing species at the catalyst surface. These effects may facilitate the formation of reactive oxygenated species at lower potentials, contributing to the lower onset potentials observed for Co@Pt/C, Ni@Pt/C, and Sn@Pt/C compared to Pt/C. At higher potentials, however, progressive Pt oxidation likely minimizes these effects, leading to a reduction in the availability of active sites for glycerol electro-oxidation [3,8,10]. The chronoamperometric results (Table 2) further confirm the superior catalytic stability of Co@Pt/C, which maintains the highest steady-state current density after 3600 s.

Table 2. Electro-oxidation parameters of glycerol on Pt/C, Co@Pt/C, Ni@Pt/C, and Sn@Pt/C: onset oxidation potential (E_{onset}); peak current density in the anodic scan ($j_{\text{peak/anod}}$); peak current density in the cathodic scan ($j_{\text{peak/cat}}$); and current densities obtained from chronoamperometry after 3600 s (j_{crono}).

	E_{onset} (V vs. RHE)	$j_{\text{peak/anod}}$ (mA cm^{-2})	$j_{\text{peak/cat}}$ (mA cm^{-2})	$j_{\text{peak/anod}}/j_{\text{peak/cat}}$	j_{crono} (mA cm^{-2}) (3600 s)
Pt/C	0.42	0.45	0.33	1.36	0.094 ± 0.008
Co@Pt/C	0.34	4.93	1.31	3.76	0.707 ± 0.051
Ni@Pt/C	0.39	3.12	1.13	2.76	0.266 ± 0.027
Sn@Pt/C	0.38	2.08	0.86	2.42	0.318 ± 0.031

The long-term stability of a catalyst is crucial for its practical large-scale application. Therefore, Co@Pt/C, Ni@Pt/C, and Sn@Pt/C were evaluated for GOR catalysis over 100 CV cycles (electrolyte: 1.0 M KOH + 1.0 M glycerol, scan rate: 50 mV s^{-1}). Figure 5 presents the voltammetric profiles at selected cycles (left panels) and the corresponding anodic peaks (expressed in current densities) as a function of the number of cycles (right panels).

Distinct behaviors were observed for each catalyst. Pt/C (Figure 5a,e) exhibits its highest current density in the first cycle, followed by a sharp decrease within the first 10 cycles. Afterward, a slight increase in the peak current is observed, though it does not return to its initial value. In contrast, Co@Pt/C (Figure 5b,f) displays a significant enhancement in catalytic activity up to the 20th cycle. Additionally, a noticeable shift in the E_{onset} is observed, indicating improved oxidation efficiency of glycerol and its intermediates

over time. After 20 cycles, the anodic peak current stabilizes, and by the 100th cycle, Co@Pt/C maintains a much higher catalytic performance than in the initial cycle.

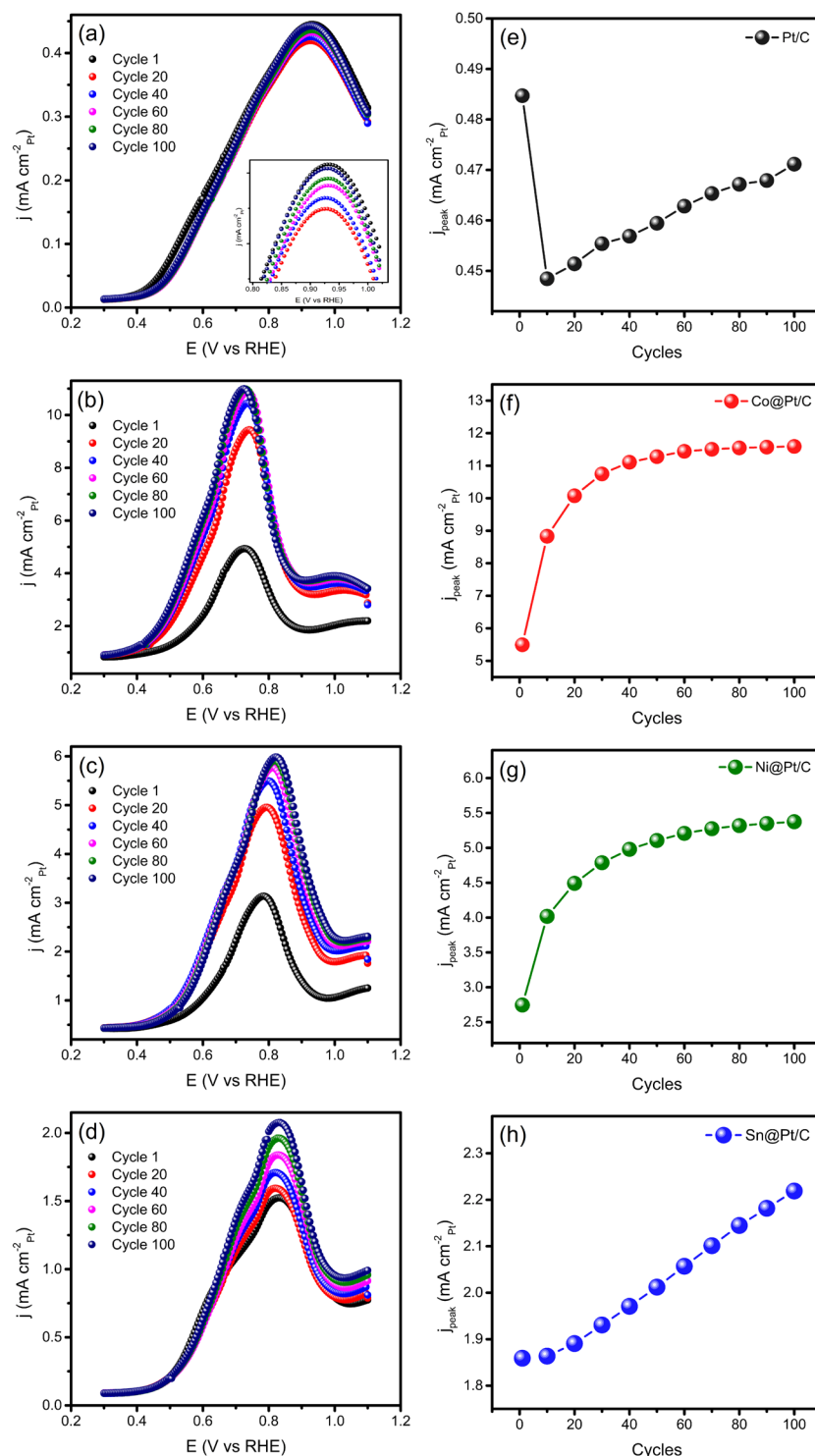


Figure 5. Voltammetric profiles (a–d) and peak current density (e–h) for GOR over 100 cycles (1.0 M KOH + 1.0 M glycerol, scan rate: 50 mV s^{-1}) for Pt/C (a,e), Co@Pt/C (b,f), Ni@Pt/C (c,g) and Sn@Pt/C (d,h).

A similar trend is observed for Ni@Pt/C (Figure 5c,g), where current density steadily increases up to approximately the 60th cycle before stabilizing. Sn@Pt/C (Figure 5d,h) exhibits a distinct behavior, showing no significant shift in E_{onset} . However, a continuous

increase in the oxidation peak currents is observed throughout the 100 cycles, suggesting a progressive activation process of the catalyst.

After 100 cycles, the addition of Co, Ni, and Sn significantly improves the catalytic stability of Pt. The presence of these metals in the core of the nanostructure likely enhances Pt's resistance to poisoning by intermediate species formed during the GOR [34]. Additionally, Co@Pt/C continues to display the highest anodic peak current density compared to other catalysts (Figure 6).

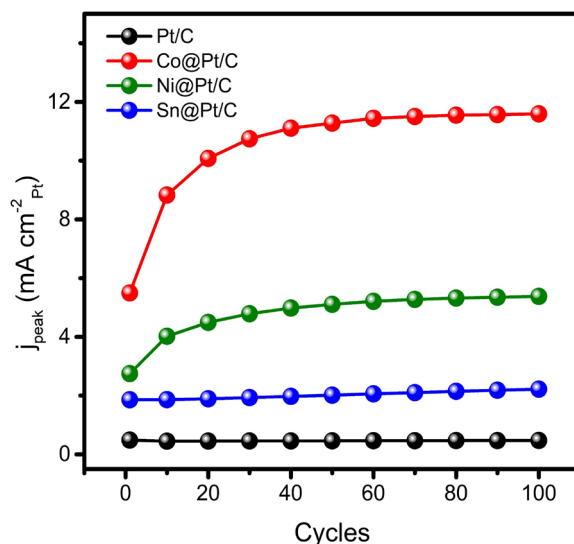


Figure 6. Anodic peak current density as a function of the number of voltammetric cycles for each material.

To observe the behavior of the catalysts over extended operational periods, Figure 7 presents the results of chronoamperometry tests. The applied potential (0.6 V vs. RHE) was selected at a level where the catalysts were already active (above their onset potentials) yet not excessively high to exceed the practical operating window of the fuel cell [17,19].

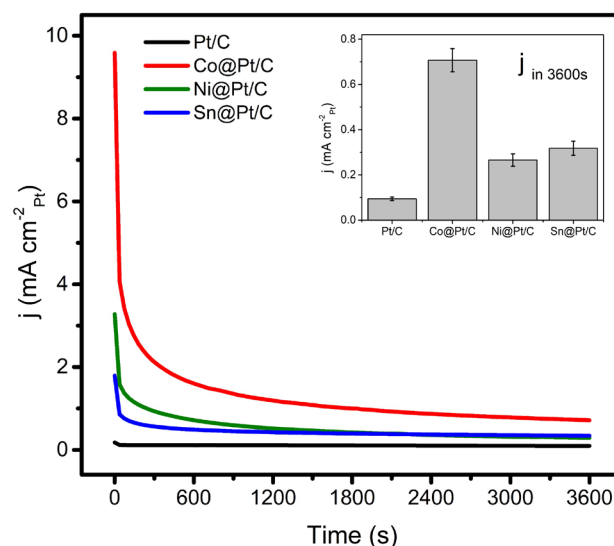


Figure 7. Chronoamperometry at 0.6 V (vs. RHE) over 3600 s for Pt/C, Co@Pt/C, Ni@Pt/C, and Sn@Pt/C (indicated in the figure). Electrolyte: 1.0 M KOH + 1.0 M glycerol.

In Figure 7, Co@Pt/C, Ni@Pt/C, and Sn@Pt/C exhibit an initial sharp decay in current density within the first 100 s, a behavior attributed to the rapid consumption and

subsequent decrease in the concentration of chemical species in the diffusion-limited layer near the electrode surface. This initial decay may also be influenced by surface restructuring effects, particularly in core-shell catalysts, where the interaction between the core metal and the Pt shell can alter the stabilization of active sites, impacting the initial reaction kinetics. After this initial phase, a gradual but continuous decay is observed until reaching a stability zone, which can be explained by the progressive occupation of active sites by products from the glycerol oxidation reaction [17,35].

After 3600 s, the current densities recorded for Co@Pt/C, Sn@Pt/C, and Ni@Pt/C are 707, 318, and 266 $\mu\text{A cm}^{-2}$, respectively. These values represent an increase of 7.4, 3.4, and 2.8 times compared to Pt/C, respectively. Therefore, it can be concluded that the incorporation of Co, Ni, and Sn into the core-shell structure enhances the catalytic performance of Pt in GOR under fixed potential conditions over an extended period. The activity of the catalysts, in descending order, is: Co@Pt/C > Sn@Pt/C > Ni@Pt/C.

3.4. In Situ FTIR

Figure 8 shows the FTIR spectral series collected in the potential range from 0.1 to 1.1 V vs. RHE at a scan rate of 5 mV s^{-1} . The series reveals the growth of bands associated with the main products of the glycerol oxidation reaction for all catalysts. Since some bands at higher potentials become very intense, Figure 9 provides an expanded view of the spectra recorded at lower potentials (from 0.1 to 0.6 V vs. RHE), allowing for a more detailed analysis.

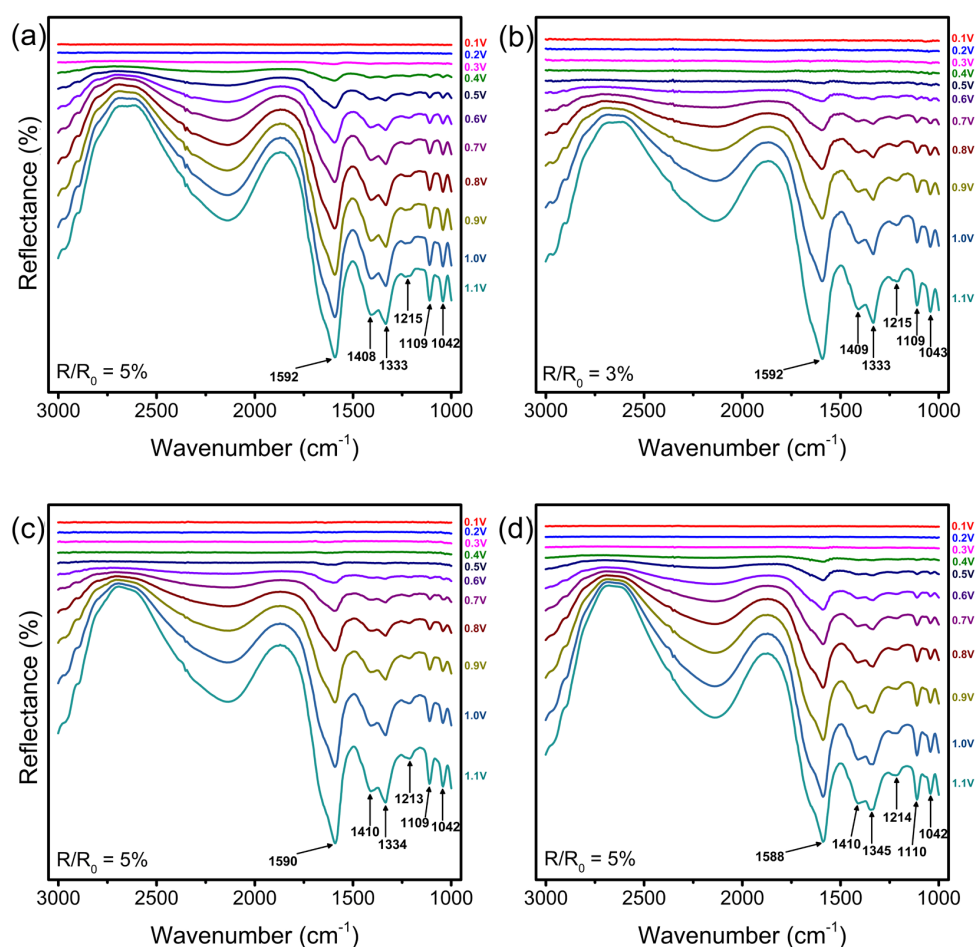


Figure 8. FTIR spectra for glycerol oxidation (electrolyte: 1.0 M KOH + 1.0 M glycerol; scan rate: 5 mV s^{-1}) collected between 0.1 and 1.1 V vs. RHE: (a) Pt/C; (b) Co@Pt/C; (c) Ni@Pt/C; and (d) Sn@Pt/C. For clarity, spectra were vertically shifted to avoid overlap.

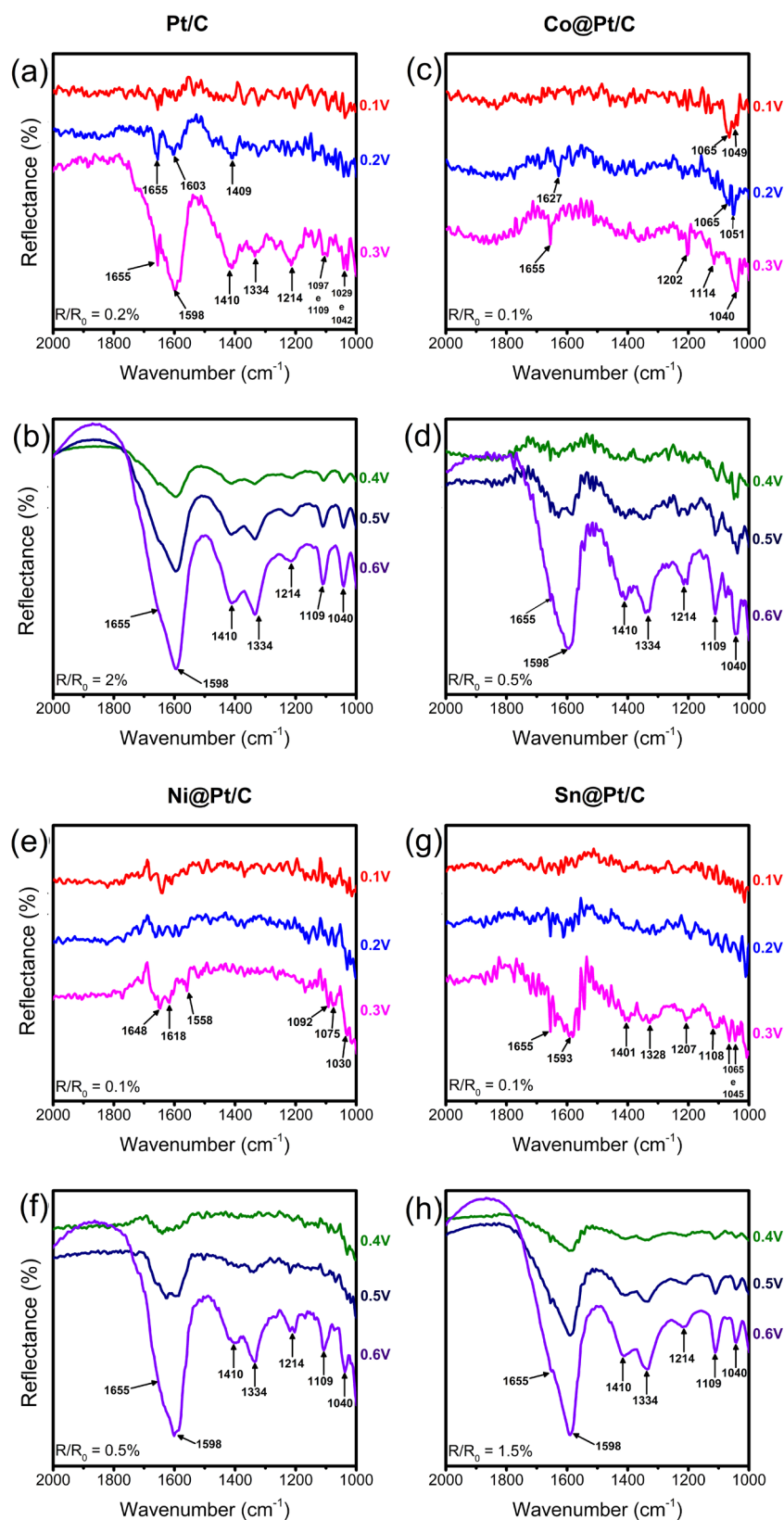


Figure 9. Expanded view of the FTIR spectra collected between 0.1 and 0.6 V vs. RHE for Pt/C (a,b); Co@Pt/C (c,d), Ni@Pt/C (e,f), and Sn@Pt/C (g,h). Extracted from Figure 8. Spectra retain the same vertical offset applied in Figure 8.

The FTIR analysis presented in this work was employed primarily as a qualitative spectroelectrochemical approach to identify possible reaction intermediates and oxidation products based on characteristic band assignments reported in the literature.

In summary, between 0.5 V and 1.1 V, the catalysts exhibit the following main bands: 1042 cm^{-1} , corresponding to the adsorption of alcoholic species on the catalytic surface [6,36], 1110 cm^{-1} , related to the formation of glyceraldehyde [37], 1215 cm^{-1} , associated with the presence of formate ion [5,38], 1334 cm^{-1} , linked to a combined effect of 1,3-dihydroxy-2-propanone and tartronate [5,6,38], and 1410 cm^{-1} , relating to carbonate [8,36,39].

An intense band is observed around 1590 cm^{-1} , which can be attributed to the combined effects of the bending mode of water and bands related to the appearance of carbonyl and carboxyl ions from various chemical species (such as glycolate, glyoxylate, glycerate, oxalate, and ketones, among others) [5,7,8,36]. Table 3 summarizes the main bands observed in the present study. Additionally, from 0.6 V to 1.1 V, a broad band between 3000 and 2500 cm^{-1} , associated with the consumption of C–H and OH– groups, is commonly observed in the catalysts [40].

Table 3. Attribution of the main bands observed by in situ FTIR during glycerol electro-oxidation on Pt/C, Co@Pt/C, Ni@Pt/C, and Sn@Pt/C (Electrolyte: 1.0 M KOH + 1.0 M glycerol; Potential range: 0.1–1.1 V vs. RHE).

Wavenumber (cm^{-1})	Functional Groups/Compounds	Reference
1590	H–O–H bending and asymmetric stretching of COO^-	[5,7,8,36]
1410	Symmetric stretching of O–C–O (possible formation of carbonate)	[8,36,39]
1334	Symmetric stretching of O–C–O (possible formation of 1,3-dihydroxy-2-propanone and tartronate)	[5,6,38]
1215	Symmetric stretching of C–O (relating to carboxylic acid)	[5,38]
1110	Symmetric stretching of C–O (relating to alcohol and/or aldehyde)	[37]
1042	Symmetric stretching of C–O (relating to alcohol and/or aldehyde)	[6,36]

Observing the enlarged spectra described in Figure 9, different profiles can be noted for the glycerol oxidation reaction at low potentials. Specifically, Pt/C (Figure 9a,b) demonstrates the formation of bands starting at 0.2 V vs. RHE: 1655 cm^{-1} (H–O–H bending), 1603 cm^{-1} (carbonyl species), and 1409 cm^{-1} (carbonate-related signal). At 0.3 V, additional (and more prominent) bands appear at 1655, 1598, 1410, 1334, 1214, 1110, 1042 and 1029 cm^{-1} . From 0.6 V onwards, the band at 1655 cm^{-1} diminishes and merges into a broad band centered at 1598 cm^{-1} .

The spectral series of Sn@Pt/C (Figure 9g,h) indicates that this catalyst exhibits a performance similar to Pt/C, with activities starting at 0.2 V and maintaining the same by-product formation pattern [36,38,41].

In Figure 9c,d, bands at 1049 and 1065 cm^{-1} for Co@Pt/C are already present at 0.1 V, suggesting early alcohol adsorption, along with possible glycolate formation at this potential. Between 0.2 and 0.5 V, Co@Pt/C displays minor bands, corresponding to an increasing population of adsorbates from alcohol and by-product formation (aldehyde, ketone, and glycerate ion). From 0.6 V onwards, a more prominent development of bands is observed at 1655, 1598, 1410, 1334, 1214, 1109 and 1040 cm^{-1} , persisting until the end of the series at 1.1 V [5,42–44].

In contrast, spectra collected for Ni@Pt/C (Figure 9e,f) show several small bands at 0.3 V. Up to 0.5 V, the bands suggest that this catalyst favors reaction pathways leading to

species containing C–O groups to a greater extent than the previous ones. Specifically, from 0.6 V onwards, prominent bands develop at 1598, 1410, 1334, 1214, 1109, and 1040 cm^{-1} .

The intensities of the main bands shown in Figure 8 (at approximately 1100 cm^{-1} , 1215 cm^{-1} , 1335 cm^{-1} , and 1410 cm^{-1}) were calculated by integrating their respective areas and are plotted in Figure 10. It can be observed that, throughout the spectral series, the Pt/C and Sn@Pt/C catalysts exhibited the highest intensities for the formation of glyceraldehyde, 1,3-dihydroxy-2-propanone and carbonate. Additionally, Sn@Pt/C also exhibited higher intensities associated with formate formation. It is important to note that higher FTIR band intensities do not necessarily indicate superior catalytic activity or higher product selectivity, since the spectral response may also be influenced by differences in adsorption strength, surface coverage, and accumulation of intermediate species at the catalyst interface.

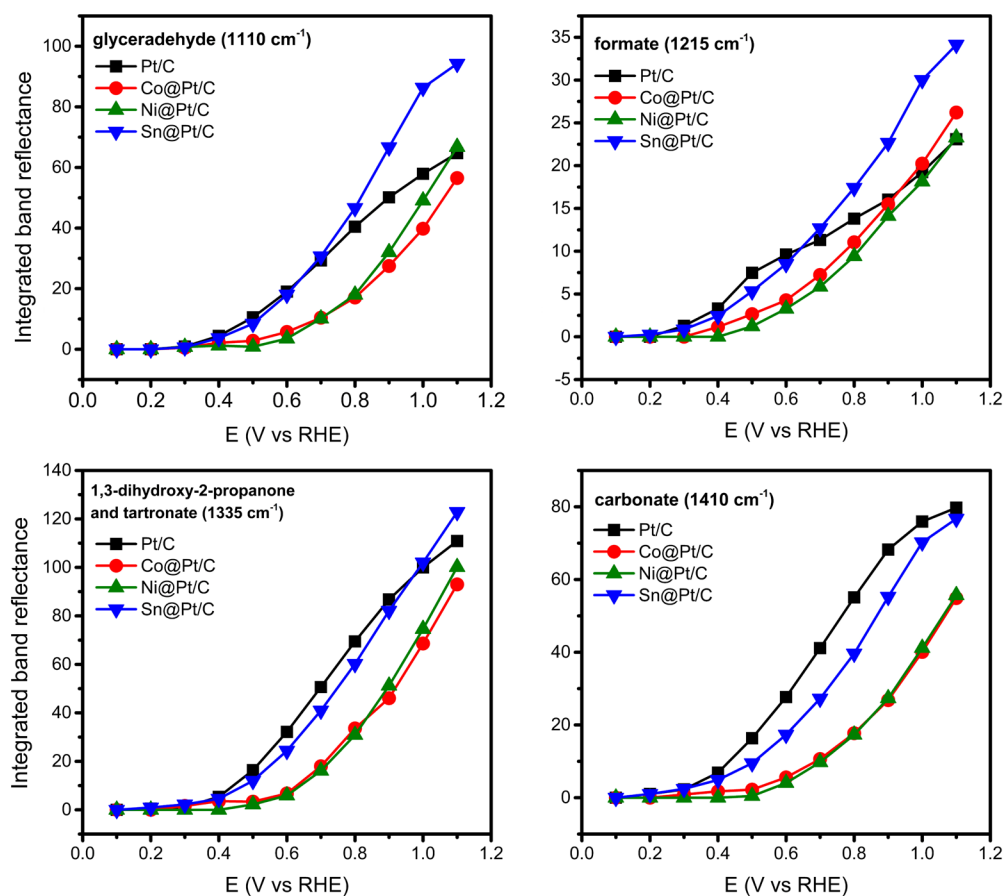


Figure 10. Intensity of reflectance bands for the byproducts observed in the spectral series of the in situ FTIR. Extracted from Figure 8.

When comparing the spectral series observed at the lowest potentials (Figure 9), it is evident that the Co@Pt/C and Ni@Pt/C catalysts promote the formation of other byproducts, suggesting a significant change in the reaction mechanism when compared to Pt/C [5]. The behavior of these catalysts resembles that of Pt/C only from 0.5 V vs. RHE onwards, which is reflected in the intensities of the bands corresponding to glyceraldehyde, 1,3-dihydroxy-2-propanone, formate, and carbonate, as shown in Figure 10. It is also worth noting that the estimation of band areas for those vibrational modes detected at lower potentials for Co@Pt/C and Ni@Pt/C is not feasible, as these signals are likely suppressed by the byproduct bands that become more prominent from 0.5 V onwards.

In contrast, Sn@Pt/C exhibits a by-product formation profile similar to that of Pt/C. The higher intensities of bands corresponding to glyceraldehyde, 1,3-dihydroxy-

2-propanone, formate and carbonate compared to Pt/C are likely due to the synergistic effect of Sn on the active Pt sites at the material's surface without significantly altering the reaction mechanism.

The loss of a steep slope observed in Pt/C for formate formation from 0.6 V and for the other byproducts from 0.9 V may indicate a decline in the material's catalytic activity. On the other hand, Co@Pt/C, Ni@Pt/C and Sn@Pt/C do not exhibit this loss of slope, suggesting a more sustained catalytic performance for GOR under the tested conditions.

Overall, the emergence of bands associated with the formation of C1 species, such as formate and carbonate, suggests that all the catalysts possess at least some ability to cleave C–C–C bonds, thereby promoting the complete oxidation of glycerol molecules to some extent. Furthermore, the spectral series indicates that the catalytic activity of Pt/C, Co@Pt/C, Ni@Pt/C, and Sn@Pt/C for GOR becomes noticeable from 0.2 V vs. RHE. However, it is only from 0.4/0.5 V onwards that this activity becomes significant enough to generate substantial current densities, as confirmed by the CV profiles in the presence of glycerol.

Based on the in situ FTIR results and the band assignments discussed above, Figure 11 presents a schematic representation of the proposed glycerol electro-oxidation pathways in alkaline medium. The scheme summarizes the main C3 intermediates identified during the reaction, as well as the formation of C2 and C1 products associated with C–C bond cleavage. The proposed pathways were constructed as a qualitative mechanistic interpretation based on the FTIR observations and literature reports discussed throughout this work.

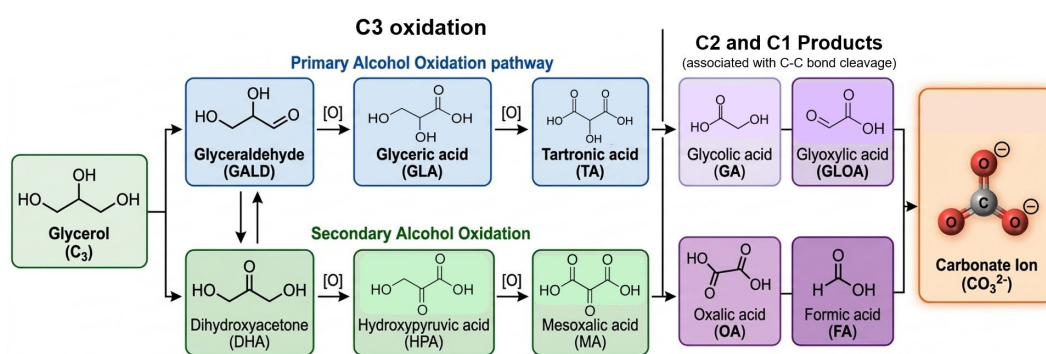


Figure 11. Proposed qualitative reaction pathways for glycerol electro-oxidation in alkaline medium based on in situ FTIR observations and literature band assignments. The scheme summarizes the main C3 intermediates and the formation of C2 and C1 products associated with C–C bond cleavage during glycerol electro-oxidation.

A final observation is that the differences in the spectral features observed for all catalysts investigated in this study are noticeable only at low potentials (Figure 9), while the full spectral series presented in Figure 8 displays virtually the same bands, with similar intensity ratios. These findings suggest that any improvement in electrocatalytic activity for GOR is only observed at potentials where the core–shell structures can be partially oxidized before Pt/C. At high potentials, these differences are minimized (since platinum itself is already oxidized), and the reaction pathways become similar for all materials. These characteristics of core–shell materials are particularly relevant when considering the operating potential windows of glycerol-fed fuel cells, where high electrocatalytic activity at low overpotentials is crucial for a material to be considered an effective catalyst in such devices.

4. Conclusions

Electrochemical tests demonstrated that Co@Pt/C, Ni@Pt/C, and Sn@Pt/C outperform Pt/C in the glycerol oxidation reaction (GOR). In cyclic voltammetry (CV) with glycerol (1.0 M KOH + 1.0 M glycerol), these catalysts exhibited a shift toward more negative E_{onset} values and higher current density peaks, indicating enhanced catalytic activity. After 100 CV cycles, the presence of a second metal improved stability and resistance to poisoning effects. Chronoamperometry at 0.6 V vs. RHE further confirmed the superior catalytic performance, with Co@Pt/C achieving a 7.5-fold increase over Pt/C, while Ni@Pt/C and Sn@Pt/C showed 2.8- and 3.4-fold improvements, respectively. In situ FTIR analysis revealed the formation of C3, C2, and C1 byproducts, with the appearance of carbonate bands suggesting partial oxidation of glycerol toward highly oxidized carbon-containing species. These findings highlight the potential of Pt-based M@Pt/C catalysts with proposed core-shell-type architectures for improving GOR efficiency and advancing direct glycerol fuel cell applications. The in situ FTIR results reveal that Co and Ni modify reaction pathways at low potentials, while Sn@Pt/C exhibited a reaction profile more similar to Pt/C, consistent with possible bifunctional effects. These findings reinforce the importance of core metal selection in controlling reaction intermediates and influencing catalytic activity and reaction pathways. Further investigations employing complementary analytical techniques may provide additional insights into the distribution of reaction products and the mechanistic pathways involved in glycerol electro-oxidation.

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Abbreviations

The following abbreviations are used in this manuscript:

GOR	Glycerol Oxidation Reaction
PEMFCs	Polymer Electrolyte Membrane Fuel Cells
DAFCs	Direct Alcohol Fuel Cells
C3 products	Three-carbon compounds formed during glycerol oxidation

C2 products	Two-carbon compounds formed during glycerol oxidation
C1 products	One-carbon compounds formed during glycerol oxidation
GALD	Glyceraldehyde
DHA	Dihydroxyacetone
GLA	Glyceric acid
TA	Tartronic acid
MA	Mesoxalic acid
HPA	Hydroxypyruvic acid
GA	Glycolic acid
GLOA	Glyoxylic acid
LA	Lactic acid
OA	Oxalic acid
FA	Formic acid
CO ₃ ^{2−}	Carbonate
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-ray Diffraction
TEM	Transmission Electron Microscopy
D	Crystallite size calculated from XRD
A	Lattice parameter
d _{Pt-Pt}	Pt-Pt Interatomic Distance
D _{TEM}	Particle size from TEM
SEM	Scanning Electron Microscopy
EDS	Energy-Dispersive X-ray Spectroscopy
CV	Cyclic Voltammetry
CA	Chronoamperometry
ECSA	Electrochemically Active Surface Area
RHE	Reversible Hydrogen Electrode
E _{onset}	Onset potential for glycerol oxidation
j _{peak}	Peak current density
j _{crono}	Current density obtained from chronoamperometry

References

- Wang, Y.; Diaz, D.F.R.; Chen, K.S.; Wang, Z.; Adroher, X.C. Materials, technological status, and fundamentals of PEM fuel cells—A review. *Mater. Today* **2020**, *32*, 178–203. [\[CrossRef\]](#)
- Ahmad, M.S.; Rahim, M.H.A.; Alqahtani, T.M.; Witoon, T.; Lim, J.; Cheng, C.K. A review on advances in green treatment of glycerol waste with a focus on electro-oxidation pathway. *Chemosphere* **2021**, *276*, 130128. [\[CrossRef\]](#) [\[PubMed\]](#)
- Fan, L.; Liu, B.; Liu, X.; Senthikumar, N.; Wang, G.; Wen, Z. Recent Progress in Electrocatalytic Glycerol Oxidation. *Energy Technol.* **2021**, *9*, 2000804. [\[CrossRef\]](#)
- Antolini, E. Glycerol electro-oxidation in alkaline media and alkaline direct glycerol fuel cells. *Catalysts* **2019**, *9*, 980. [\[CrossRef\]](#)
- Otoni, C.A.; Da Silva, S.G.; De Souza, R.F.B.; Neto, A.O. Glycerol oxidation reaction using PdAu/C electrocatalysts. *Ionics* **2016**, *22*, 1167–1175. [\[CrossRef\]](#)
- Wang, C.Y.; Yu, Z.Y.; Li, G.; Song, Q.T.; Li, G.; Luo, C.X.; Yin, S.H.; Lu, B.A.; Xiao, C.; Xu, B.B.; et al. Intermetallic PtBi nanoplates with high catalytic activity towards electro-oxidation of formic acid and glycerol. *ChemElectroChem* **2020**, *7*, 239–245. [\[CrossRef\]](#)
- Garcia, A.C.; Ferreira, E.B.; De Barros, V.V.S.; Linares, J.J.; Tremiliosi-Filho, G. PtAg/MnOx/C as a promising electrocatalyst for glycerol electro-oxidation in alkaline medium. *J. Electroanal. Chem.* **2017**, *793*, 188–196. [\[CrossRef\]](#)
- Luo, H.; Yukuhiro, V.Y.; Fernández, P.S.; Feng, J.; Thompson, P.; Rao, R.R.; Cai, R.; Favero, S.; Haigh, S.J.; Durrant, J.R.; et al. Role of Ni in PtNi bimetallic electrocatalysts for hydrogen and value-added chemicals coproduction via glycerol electrooxidation. *ACS Catal.* **2022**, *12*, 14492–14506. [\[CrossRef\]](#)
- Pereira, C.V.; Maia, V.A.; Zambiasi, P.J.; De Souza, R.F.B.; Antolini, E.; Neto, A.O. PtSb/C electrocatalysts for glycerol oxidation in alkaline electrolyte. *Results Chem.* **2022**, *4*, 100375. [\[CrossRef\]](#)
- Ren, X.; Lv, Q.; Liu, L.; Liu, B.; Wang, Y.; Liu, A.; Wu, G. Current progress of Pt and Pt-based electrocatalysts used for fuel cells. *Sustain. Energy Fuels* **2020**, *4*, 15–30. [\[CrossRef\]](#)

11. Maya-Cornejo, J.; Guerra-Balcázar, M.; Arjona, N.; Álvarez-Contreras, L.; Valadez, F.J.R.; Gurrola, M.P.; Ledesma-García, J.; Arriaga, L.G. Electrooxidation of crude glycerol as waste from biodiesel in a nanofluidic fuel cell using Cu@Pd/C and Cu@Pt/C. *Fuel* **2016**, *183*, 195–205. [\[CrossRef\]](#)
12. Zhou, Y.; Shen, Y.; Xi, J. Seed-mediated synthesis of PtAu@Ag electrocatalysts for the selective oxidation of glycerol. *Appl. Catal. B Environ.* **2019**, *245*, 604–612. [\[CrossRef\]](#)
13. Silva, R.N.; Pocrifka, L.A.; Antolini, E.; Passos, R.R. Electro-Oxidation of Glycerol on Core-Shell M@Pt/C (M = Co, Ni, Sn) Catalysts in Alkaline Medium. *Energies* **2025**, *18*, 305. [\[CrossRef\]](#)
14. Ferreira, H.S.; Gocyla, M.; Ferreira, H.S.; Araújo, R.G.O.; Almeida, C.V.S.; Heggen, M.; Dunin-Borkowski, R.E.; Eguiluz, K.I.B.; Strasser, P.; Salazar-Banda, G.R. A comparative study of the catalytic performance of Pt-based bi and trimetallic nanocatalysts towards methanol, ethanol, ethylene glycol, and glycerol electro-oxidation. *J. Nanosci. Nanotechnol.* **2020**, *20*, 6274–6285. [\[CrossRef\]](#)
15. Trasatti, S.; Petrii, O.A. Real surface area measurements in electrochemistry. *Int. Union Pure Appl. Chem.* **1991**, *63*, 711–734. [\[CrossRef\]](#)
16. De Souza, R.F.B.; Teixeira Neto, E.; Calegari, M.L.; Santos, E.A.; Martinho, H.S.; Dos Santos, M.C. Ethanol electro-oxidation on Pt/C electrocatalysts: An “in situ” Raman spectroelectrochemical study. *Electrocatalysis* **2011**, *2*, 28–34. [\[CrossRef\]](#)
17. Marinho, V.L.; Antolini, E.; Giz, M.J.; Camara, G.A.; Pocrifka, L.A.; Passos, R.R. Ethylene glycol oxidation on carbon supported binary PtM (M = Rh, Pd and Ni) electrocatalysts in alkaline media. *J. Electroanal. Chem.* **2021**, *880*, 114859. [\[CrossRef\]](#)
18. Ferreira, D.S.; Gaiotti, A.C.; Araujo, H.R.; Batista, B.C.; Reis, D.D.; Giz, M.J.; Camara, G.A. Electro-oxidation of glycerol over Sb-modified Pt (100) preferentially oriented nanoparticles. *J. Catal.* **2023**, *417*, 445–452. [\[CrossRef\]](#)
19. Frota, E.F., Jr.; Barros, V.V.S.; Araújo, B.R.S.; Purgatto, A.G.; Linares, J.J. Pt/C containing different platinum loadings for use as electrocatalysts in alkaline PBI-based direct glycerol fuel cells. *Int. J. Hydrogen Energy* **2017**, *42*, 23095–23106. [\[CrossRef\]](#)
20. Castagna, R.M.; Sieben, J.M.; Alvarez, A.E.; Duarte, M.M.E. Electrooxidation of ethanol and glycerol on carbon supported PtCu nanoparticles. *Int. J. Hydrogen Energy* **2019**, *44*, 5970–5982. [\[CrossRef\]](#)
21. Ho, V.T.T.; Pham, H.Q.; Anh, T.H.T.; Nguyen, A.V.; Quoc, K.A.N.; Vo, H.T.H.; Nguyen, T.T. Highly stable Pt/ITO catalyst as a promising electrocatalyst for direct methanol fuel cells. *Comptes Rendus Chim.* **2019**, *22*, 838–843. [\[CrossRef\]](#)
22. Barbosa, J.R.; Leon, M.N.; Fernandes, C.M.; Antonias, R.M.; Alves, O.C.; Ponzio, E.A.; Silva, J.C.M. PtSnO₂/C and Pt/C with preferential (100) orientation: High active electrocatalysts for ammonia electro-oxidation reaction. *Appl. Catal. B Environ.* **2020**, *264*, 118458. [\[CrossRef\]](#)
23. Ruiz-Montoya, J.G.; Nunes, L.M.S.; Baena-Moncada, A.M.; Tremiliosi-Filho, G.; Morales-Gomero, J.C. Effect of palladium on gold in core-shell catalyst for electrooxidation of ethanol in alkaline medium. *Int. J. Hydrogen Energy* **2021**, *46*, 23670–23681. [\[CrossRef\]](#)
24. Habibi, B.; Ghaderi, S. Synthesis, characterization and electrocatalytic activity of Co@Pt nanoparticles supported on carbon-ceramic substrate for fuel cell applications. *Int. J. Hydrogen Energy* **2015**, *40*, 5115. [\[CrossRef\]](#)
25. Habibi, B.; Ghaderi, S. Ni@Pt core-shell nanoparticles as an improved electrocatalyst for ethanol electrooxidation in alkaline media. *Iran. J. Hydrog. Fuel Cell* **2015**, *2*, 109. [\[CrossRef\]](#)
26. Silva, J.C.M.; De Souza, R.F.B.; Parreira, L.S.; Teixeira Neto, E.; Calegari, M.L.; Santos, M.C. Ethanol oxidation reactions using SnO₂@Pt/C as an electrocatalyst. *Appl. Catal. B Environ.* **2010**, *99*, 265–271. [\[CrossRef\]](#)
27. Godínez-Salomón, F.; Hallen-López, M.; Solorza-Feria, O. Enhanced electroactivity for the oxygen reduction on Ni@Pt core-shell nanocatalysts. *Int. J. Hydrogen Energy* **2012**, *37*, 14902–14910. [\[CrossRef\]](#)
28. Reyes-Rodríguez, J.L.; Godínez-Salomón, F.; Leyva, M.A.; Solorza-Feria, O. RRDE study on Co@Pt/C core-shell nanocatalysts for the oxygen reduction reaction. *Int. J. Hydrogen Energy* **2013**, *38*, 12634–12639. [\[CrossRef\]](#)
29. Habibi, B.; Ghaderi, S. Ethanol electrooxidation on the Co@Pt core-shell nanoparticles modified carbon-ceramic electrode in acidic and alkaline media. *Iran. J. Hydrog. Fuel Cell* **2016**, *1*, 19–31. [\[CrossRef\]](#)
30. Habibi, B.; Ghaderi, S. A comparative study of electrocatalytic performance of the M@Pt (M = Fe₃O₄, Co and Ni) nanoparticles for direct ethanol fuel cells. *J. Iran. Chem. Soc.* **2017**, *14*, 1633–1642. [\[CrossRef\]](#)
31. Sharma, R.; Gyergyek, S.; Andersen, S.M. Critical thinking on baseline corrections for electrochemical surface area (ECSA) determination of Pt/C through H-adsorption/H-desorption regions of a cyclic voltammogram. *Appl. Catal. B Environ.* **2022**, *311*, 121351. [\[CrossRef\]](#)
32. Zhou, Y.; Shen, Y. Electro-oxidation of glycerol by tetrametallic platinum-gold-palladium-silver nanoparticles. *J. Appl. Electrochem.* **2021**, *51*, 79–86. [\[CrossRef\]](#)
33. Oh, L.S.; Han, J.; Lim, E.; Kim, W.B.; Kim, H.J. PtCu nanoparticle catalyst for electrocatalytic glycerol oxidation: How does the PtCu affect to glycerol oxidation reaction performance by changing pH conditions? *Catalysts* **2023**, *13*, 892. [\[CrossRef\]](#)
34. Ren, F.; Zhang, Z.; Liang, Z.; Shen, Q.; Luan, Y.; Xing, R.; Fei, Z.; Du, Y. Synthesis of PtRu alloy nanofireworks as effective catalysts toward glycerol electro-oxidation in alkaline media. *J. Colloid Interface Sci.* **2022**, *608*, 800–808. [\[CrossRef\]](#)
35. Rezaei, B.; Saeidi-Boroujeni, S.; Havakeshian, E.; Ensafi, A.A. Highly efficient electrocatalytic oxidation of glycerol by Pt-Pd/Cu trimetallic nanostructure electrocatalyst supported on nanoporous stainless steel electrode using galvanic replacement. *Electrochim. Acta* **2016**, *203*, 41–50. [\[CrossRef\]](#)

36. Jeffery, D.Z.; Camara, G.A. The formation of carbon dioxide during glycerol electrooxidation in alkaline media: First spectroscopic evidences. *Electrochem. Commun.* **2010**, *12*, 1129–1132. [[CrossRef](#)]
37. Moreira, T.F.M.; Kokoh, K.B.; Napporn, T.W.; Olivi, P.; Morais, C. Insights on the C2 and C3 electroconversion in alkaline medium on Rh/C catalyst: In situ FTIR spectroscopic and chromatographic studies. *Electrochim. Acta* **2022**, *422*, 140507. [[CrossRef](#)]
38. Simões, M.; Baranton, S.; Coutanceau, C. Electro-oxidation of glycerol at Pd based nano-catalysts for an application in alkaline fuel cells for chemicals and energy cogeneration. *Appl. Catal. B Environ.* **2010**, *93*, 354–362. [[CrossRef](#)]
39. Inoue, H.; Kimura, S.; Teraoka, Y.; Chiku, M.; Higuchi, E.; Lam, B.T.X. Mechanism of glycerol oxidation reaction on silver-modified palladium electrode in alkaline medium. *Int. J. Hydrogen Energy* **2018**, *43*, 18664–18671. [[CrossRef](#)]
40. Ferreira, R.S., Jr.; Giz, M.J.; Camara, G.A. Influence of the local pH on the electrooxidation of glycerol on Palladium–Rhodium electrodeposits. *J. Electroanal. Chem.* **2013**, *697*, 15–20. [[CrossRef](#)]
41. Lima, R.N.S.; Colle, V.D.; Tremisioli-Filho, G.; Angelucci, C.A. Unveiling the effect of Pt addition on Ag/C catalyst for enhanced glycerol electrooxidation. *Electrochim. Acta* **2024**, *489*, 144181. [[CrossRef](#)]
42. Falase, A.; Main, M.; Garcia, K.; Serov, A.; Lau, C.; Atanassov, P. Electrooxidation of ethylene glycol and glycerol by platinum-based binary and ternary nano-structured catalysts. *Electrochim. Acta* **2012**, *66*, 295–301. [[CrossRef](#)]
43. Geraldes, A.N.; Silva, D.F.; Silva, J.C.M.; De Souza, R.F.B.; Spinacé, E.V.; Neto, A.O.; Linardi, M.; Santos, M.C. Glycerol electrooxidation in alkaline medium using Pd/C, Au/C and PdAu/C electrocatalysts prepared by electron beam irradiation. *J. Braz. Chem. Soc.* **2014**, *25*, 831–840. [[CrossRef](#)]
44. Mou, H.; Chang, Q.; Xie, Z.; Hwang, S.; Kattel, S.; Chen, J.G. Enhancing glycerol electrooxidation from synergistic interactions of platinum and transition metal carbides. *Appl. Catal. B Environ.* **2022**, *316*, 121648. [[CrossRef](#)]

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