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The impact of platinum loading on Pt-modified Bi catalysts for the electrooxidation of formic acid

ABSTRACT

Herein, a comparison between Pt and Pt-modified Bi catalysts has been studied. The Pt-on-Bi catalysts were prepared by electrodeposition of Pt on the pre-prepared Bi using chronopotentiometry. The quantity of Bi was kept constant, while the amount of Pt was adjusted to establish molar ratio of Pt to Bi of 0.1: 1, or 1:1 or 10: 1.To ensure accurate comparison, a Pt electrode was constructed using the same electrochemical method and quantity as the Pt-modified Bi electrode.The electrochemical properties of the Pt and Pt-on-Bi catalysts were evaluated with the aid of cyclic voltammetry (CV) and chronoamperometry (CA) recorded in 0.1 M H_2SO_4. All Pt-on-Bi catalysts were found to be more active toward formic acid (FA) electrooxidation compared to pure Pt, exhibiting maximum activity on the Pt-on-Bi catalyst with a Pt to Bi atomic ratio of 1:1 (Pt1@Bi). Moreover, the Pt/Bi atomic ratio is associated with the oxidation pathway of FA indicating that the selectivity of Pt-on-Bi electrocatalysts was affected by Pt loading and hence surface morphology. It was shown that the presence of Bi in the structure of the bimetallic catalyst provides a lower susceptibility to the poisoning regarding the Pt catalyst. The accomplished electrochemical performance of the Pt1@Bi electrocatalyst in FA electrooxidation is due to improved utilization of Pt and a balanced Pt/Bi composition.

Keywords:*Bismuth, electrodeposition,catalyst composition, selectivity*

INTRODUCTION

Formic acid plays a dual role in electro catalysis, acting primarily as a renewable fuel in Direct Formic Acid Fuel Cells (DFAFCs) for anodic electro-oxidation to CO_2 [1], and as a structural agent in catalyst synthesis [2]. Direct Formic Acid Fuel Cells (DFAFCs) represent a promising alternative for power supply. Compared to hydrogen-fed fuel cells, DFAFCs offer significant advantages in terms of energy density, storage capacity, and safety. This is primarily due to formic acid's high volumetric capacity of approximately 2 kWh L^{-1}, its low toxicity, and its low flammability [3,4]. Nevertheless, the theoretical volumetric capacity of a direct methanol fuel cell (DMFC) is ~ 4kWh L^{-1}, and it is higher than that of a DFAFC [4]. Despite this, DFAFCs are often considered superior for small, portable applications because their actual performance often overcomes this disadvantage. Besides the role as fuel, FA is used as additive in electrodeposition baths to optimize the composition and microstructure of electrocatalysts [2]. It was shown that the incorporation of FA transforms the catalyst morphology from irregular bimetallic phosphide spheres into a uniform, cauliflower-like structure [5]. Another example is that the addition of FA to plating baths increases the deposition efficiency of Zn–Ni alloys and improves their corrosion resistance [6].

Platinum is acknowledged as the most effective element for the oxidation of FA [3]. However, it faces challenges such as poisoning from intermediate CO and low mass activity, which hinder its practical use in DFAFC. Therefore, developing highly active electrocatalysts that are resistant to poisoning is essential for the commercial viability of DFAFCs. To improve the performance of Pt electrocatalysts in FA oxidation, extensive efforts have been devoted to the synthesis of various Pt-based alloys [1, *3*]. Among these catalysts, the PtBi binary system has attracted considerable attention due to the high activity and inhibition of CO poisoning. The Pt-Bi intermetallic catalysts such as Pt_2Bi with different

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phases,significantly affect the catalytic performance of FA showing mass activity which is 30-fold higher than that of commercial Pt/C catalysts [7].The reported studies of order structures such as intermetallic PtBi Nanoplates could isolate catalyst atoms and limit the formation of the CO intermediate in FA oxidation notably enhancing the activity and stability of the catalyst [8].

In this work, a bimetallic Pt-on-Bi catalysts were synthesized by electrodeposition of Pt on pre-prepared Bi nanoparticles using chronopotentiometry. The deposition technique enabled the creation of catalyst system with different Pt loadings on Bi. The electrocatalytic behaviour of Pt-on-Bi catalysts, with varying Pt/Bi ratios, was systematically investigated toward formic acid oxidation using cyclic voltammetry and chronoamperometry, allowing for a clear comparison with the performance of pure Pt.

EXPERIMENTAL

Materials

All p.a. grade chemicals were provided by Merck. The electrolytes were prepared with high purity water (Millipore,18 MΩ cm resistivity).

Apparatus

The electrochemical experiments were carried out in a conventional three-electrode cell using a VoltaLab PGZ 402 (Radiometer Analytical, Lyon, France). A glassy carbon electrode (GCE, 5 mm in diameter) was used as the working electrode. Before use, GCE surface was prepared according to the method outlined in other source [9]. The counter electrode and the reference electrode were platinum wire and saturated calomel electrode, respectively. Electrolyte solutions were deaerated by a nitrogen stream. All of the electrochemical measurements were carried out at room temperature.

Preparation of the catalysts

The Pt-on-Bi (designated as Pt@Bi/GCE) nanoparticles were synthesized using a two-step electrodeposition method as was previously described [9]. The Pt@Bi/GCE catalysts with different atomic ratios on the surface of catalysts was obtained by controlling the deposited charge of Pt while the amount of Bi was constant as is presented in Table 1. The electrocatalysts are designated as Pt1@Bi/GCE, Pt0.1@Bi/GCE and Pt10@Bi/GCE. For accurate comparison, a Pt electrode was constructed utilizing the same electrochemical method and quantity as the Pt@Bi/GCE bimetallic electrode.

Table 1. Experimental conditions and composition of Pt and Pt-on-Bi catalysts

catalyst	Q_{dep}/mC		m /µg		Atomic ratio
	Bi	Pt	Bi	Pt	Pt/ Bi
Pt1@Bi/GCE	3	4	2.16	2	1/1
Pt0.1@Bi/GCE	3	0.4	2.16	0.2	0.1/1
Pt10@Bi/GCE	3	40	2.16	20	10/1
Pt1/GCE	/	4	/	2	/
Pt01/GCE	/	0.4	/	0.2	/
Pt10/GCE	/	40	/	20	/

Pt or Bi loading was evaluated by the charge integrated during the deposition process (Q_{dep}) according to Eq. (1):

$$m = \eta\, Q_{dep} M / zF \qquad (1)$$

Here, m is the mass of deposited Pt or Bi, η is current efficiency (assuming 100 % current efficiency here), Q_{dep} is the total charge passed through the electrodes during the deposition process, M is the molecular weight, F is the Faraday constant (96,485 C mol^{-1}), and z is the number of electrons transferred (taken as four for the Pt and three for the Bi formation).

Electrochemical characterization

The samples were subjected to electrochemical potential scanning for 50 cyclesata scan rate of 50 mV s^{-1}between hydrogen and oxygen evolution in 0.1 M H_2SO_4 solution to achieve to quasi-steady state voltammograms.The rotating speed of the disc electrode was 1500 rpm.

The electrochemically active surface area of the electrodes (ECSA) was estimated by the$H_{ads/des}$ method in 0.1 M H_2SO_4. The ECSA was calculated from the ratio of the charge measured from the integration of the hydrogen desorption peaks of Pt in a specific potential range and charge required to form a monolayer of hydrogen adsorbed on the Pt surface per unit area and that is 210 µC/cm^2 [10]. Current densities were normalized by the electrochemically active surface area as j / mA cm_R^{-2}, or if they are not normalised then they are designate as j / mA cm_G^{-2}.

RESULTS

Voltammetric analysis

Figure 1 shows the cyclic voltammograms (CVs) of pure Pt, and Pt-on-Bi catalystsof quasi-steady state voltammograms in deaerated 0.1 M H_2SO_4 solution. For Pt/GCE, the curve presents a well-defined hydrogen adsorption/desorption ($H_{ads/des}$), the broad double layer, and the region of oxide formation/reduction.The CVs of Pt-on-Bi show the shapes similar to the pure Pt (Fig. 1a) in hydrogen adsorption/desorption region while the charge of oxide formation/reduction for investigated Pt-on-Bi catalysts is larger in regard to pure Pt. This behaviour highlights the interplay of Bi's redox properties with Pt oxide formation and reduction [11]. Likewise, there is no shift of the surface oxide reduction peak between Pt-on-Bi catalysts and Pt catalysts with the amount of electrodeposited Pt corresponding to one for bimetallic electrode (Fig. 1a).The profilesof Pt-on-Bi catalysts in $H_{ads/des}$ region show an increase in current with higher Pt loading (Fig. 1b). Further, as the Pt loading decreases, the reduction peaks of Pt oxide on Pt@Bi catalysts shift to a lower potential, which is attributed to the different surface morphology i.e size effect of Pt islands [12].

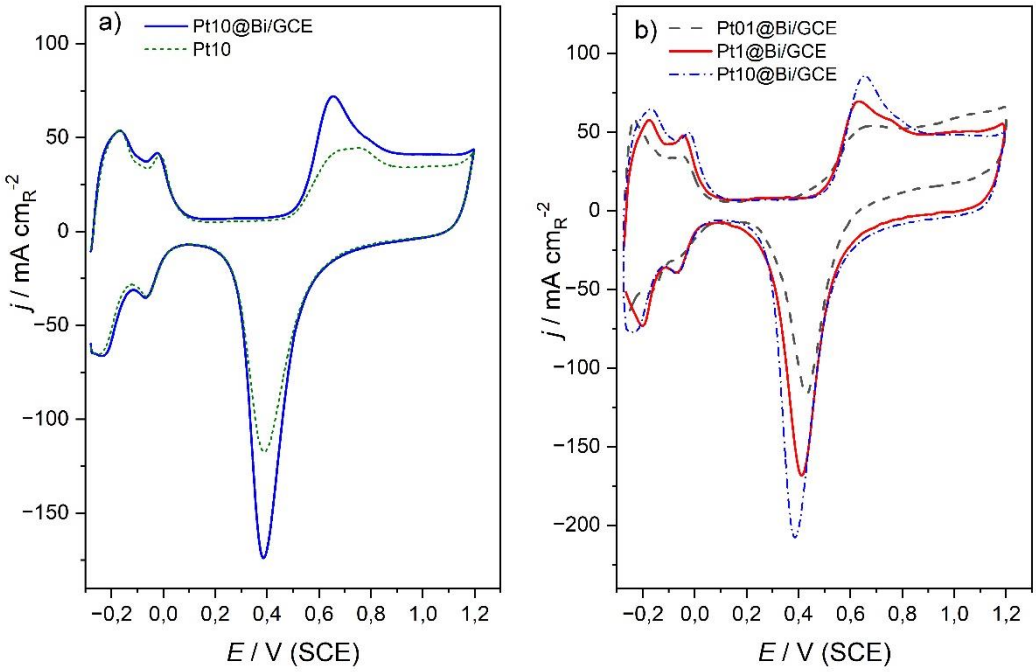


Figure 1. CVs of Pt10/GCE and Pt10@Bi/GCE (a) and of Pt1@Bi/GCE, Pt01@Bi/GCE and Pt10@Bi/GCE electrodes (b) in 0.1 M H_2SO_4 at ω = 1500 rpm and v = 50 mV s^{-1}.

All electrodeposited catalysts were subjected to electrochemical potential scanning for 50 cycles to achieve quasi-steady state, as was shown on Fig. 2 for Pt1@Bi/GCE. Figure 2a shows the first 15 cycles, with arrows indicating the trend of changes during cycling. Slightly smaller changes in the shapes of voltammograms are observed from cycles 10 to 50, as depicted in Fig. 2b.Based on the charge ratio in the anodic (*Q*a) and cathodic (*Q*c) parts of the hydrogen region, it was concluded that after 50 cycles, the ratio (*Q*a/*Q*c) approached 1, indicating a stable electrode (Fig. 2c). According to the ICP–MS analysis it was revealed that after 50 cycles in 0.1 M H_2SO_4, Pt-on-Bi electrodes are composed of Bi core occluded by Pt and Bi-oxide surface layers [9].

Electrooxidation of formic acid

Figure 3 presents the CVs of Pt/GCE and Pt-on-Bi catalysts toward FA oxidation in a mixed solution of 0.125 M HCOOH and 0.1 M H_2SO_4. For Pt/GCE, the characteristic of formic acid electro oxidation follows a dual-pathway mechanism, indicating that dehydrogenation is the direct pathway and dehydration serves as the indirect pathway [13]. As can be seen in forward scan, a peak current density (j_{f1}) at ~ 0.3 V is related to the direct oxidation of FA to CO_2, with the simultaneous formation of CO_{ad} through the indirect path.The other peak (j_{f2}) at ~ 0.6 V is due to the oxidation of intermediate CO generated from the dehydration of FA in the presence of oxygenated species formed on Pt [14]. During a backward scan, the reduction of surface oxides occurs, which releases more Pt sites for FA oxidation.

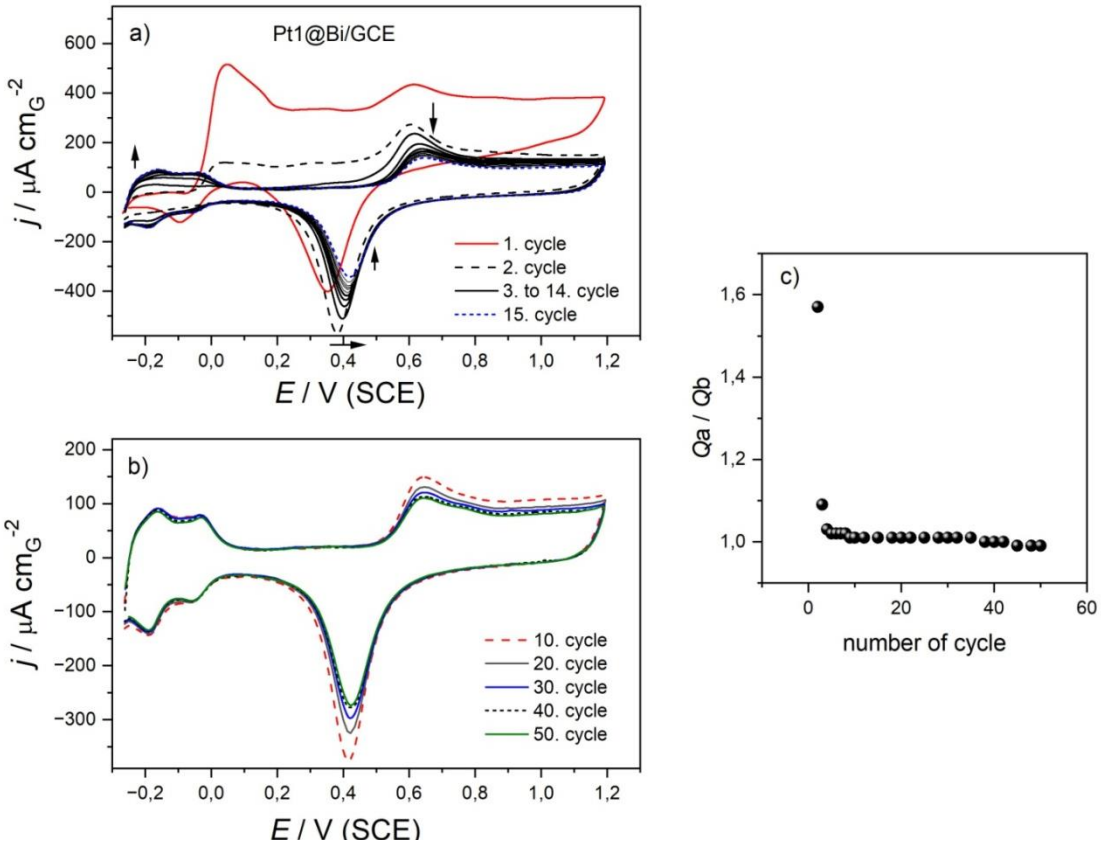


Figure 2. The first 15 cycles of Pt1/GCE (a), 10 to 50 cycles of Pt1@Bi/GCE electrode (b) in 0.1 M H_2SO_4 at ω = 1500 rpm and v = 50 mV s^{-1}, and dependency of Qa/Qc from the number of cycles (c)

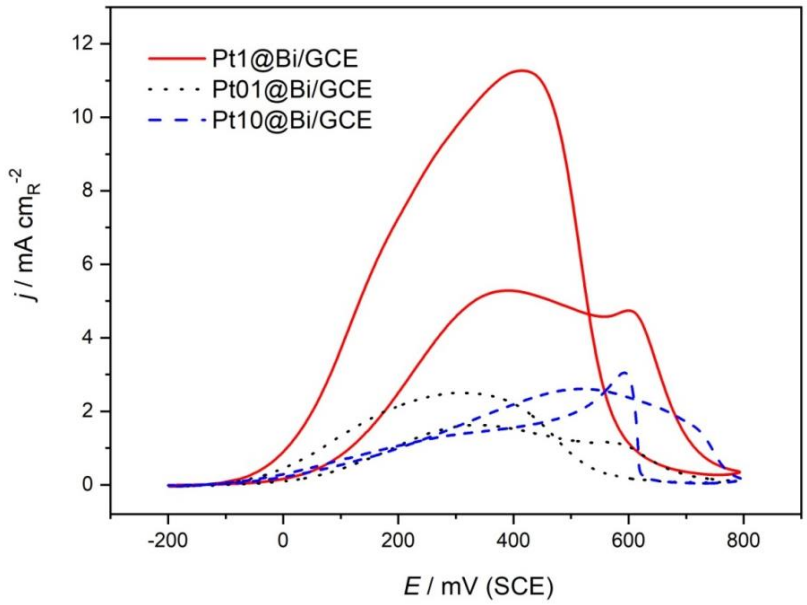


Figure 3. CVs for oxidation of 0.125 M HCOOH in 0.1 M H_2SO_4 recorded on Pt1@Bi/GCE, Pt01@Bi/GCE and Pt10@Bi/GCE electrodes at ω = 1500 rpm and v = 50 mV s^{-1}.

As a result, the reaction current increases, reaching a peak. However, at more negative potentials, the current begins to decrease due to the depletion of oxygenated species essential for the oxidation of CO_{ad}. Notably, the currents are higher than those observed in the forward scan as

the Pt surface is effectively cleared of CO_{ad}, allowing for enhanced catalytic activity. According to Fig. 3 the most active Pt-on-Bi catalyst toward FA electrooxidation is Pt1@Bi/GCE, showing the highest reaction currents in forward and backward direction. In contrast to Pt1@Bi/GCE and Pt01@Bi/GCE, Pt10@Bi/GCE demonstrates a single broad peak, clearly indicating that the predominant pathway for the oxidation of FA is direct. Furthermore, the poorly defined shoulder on the descending slope of the curve suggests the involvement of an indirect pathway in the reaction.

Figure 4 presents the forward scan of CVs of Pt/GCE and two Pt-on-Bi catalysts toward FA oxidation. The ~ 100 mV shift in the initial oxidation potential (E_{in}) along with an increase in current density observed on Pt@Bi/GCE catalyst demonstrates that bimetallic electrodes have higher catalytic activity than Pt/GCE (Table 2).It is clear that the FA activity is affected by the presence of Bi in the structure of Pt-on-Bi catalysts.The observed behaviour is explained by the ensemble effect caused by surface Bi oxides disrupting Pt domains [9].

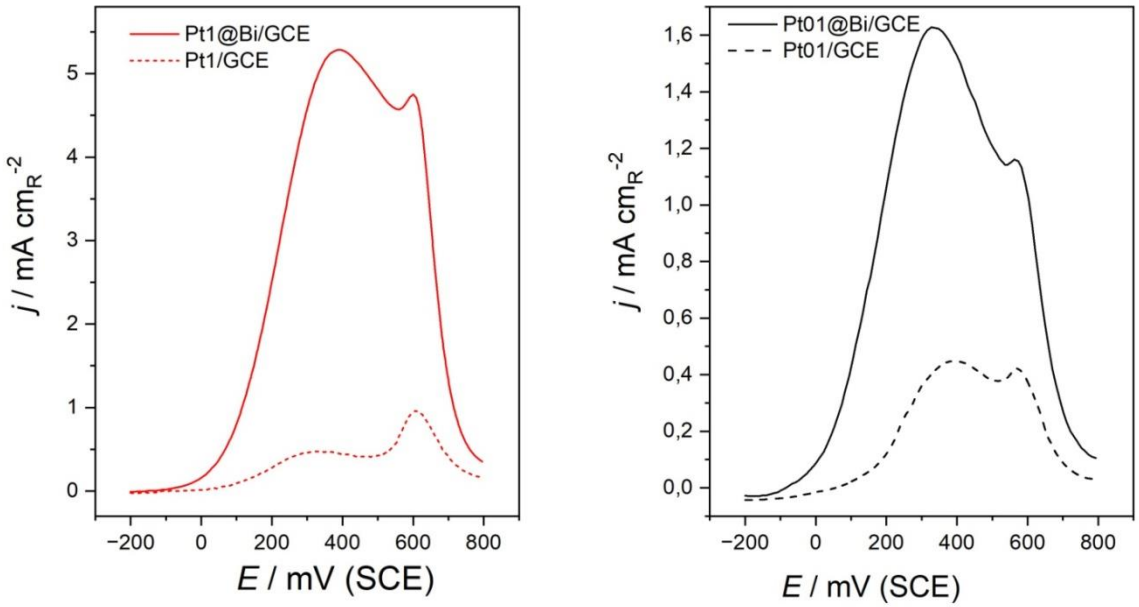


Figure 4. Forward scan of CVs for oxidation of 0.125 M HCOOH in 0.1 M H_2SO_4 recorded on Pt1@Bi/GCE and Pt1/GCE (a) and on Pt01@Bi/GCE and Pt01 /GCE electrodes (b) at ω = 1500 rpm and v = 50 mV s^{-1}.

According to Fig. 4, the peak current density at j_{f1} on Pt-on-Bi is higher, while the peak current density at j_{f2} is comparatively lower than that on pure Pt during FA oxidation. The enhanced activity, illustrated by a higher first peak around ~0.3 V compared to the Pt/GCE, clearly demonstrates that formic acid oxidation on the Pt-on-Bi catalyst is shifting towards a more efficient dehydrogenation pathway. This observation aligns with findings from previous reports [15,16].The ratio of j_{f1}/j_{f2} (Table2) was further used to evaluate the effect of Pt/Bi composition on FA oxidation pathway. The j_{f1}/j_{f2} on Pt-on-Bi is not only larger than that on pure Pt but also exhibits a notable enhancement as the Pt loading on the Bi surface diminishes.

Table 2. Parameters of FA oxidation on Pt-on-Bi and Ptelectrocatalysts

Catalyst	E_{in} / mV	j_{f1} / mA cm^{-2}	j_{f2} / mA cm^{-2}	j_{f1}/j_{f2}
Pt1@Bi/GCE	– 60	5.3	4.7	1.13
Pt1/GCE	50	0.46	0.97	0.47
Pt01@Bi/GCE	– 65	1.65	1.16	1.42
Pt01/GCE	50	0.44	0.44	1

To investigate the long-term electrochemical durability of the examined catalysts, the CA analysis was performed in 0.1 M H_2SO_4 solution with 0.125 M FA at the fixed applied potential of 0.2 V. According to Fig. 5, the current density of the examined catalysts declines sharply in the early stages because of the formation of adsorbed carbonaceous intermediates on the catalytic surface sites during FA electrooxidation. Over time, the current density stabilized and reached a

pseudosteady state. A comparison with the initial current density measured at 0 s, the current density after 1200 s is reduced by 68% for Pt0.1@Bi/GCE, while for the other two Pt-on-Bi catalysts the difference is higher (Fig. 5a). The lower durability of Pt/GCE catalysts compared to the Pt-on-Bi catalyst is clear (Fig. 5b), as shown by the larger difference in initial and stabilized current densities, caused by rapid poisoning of the Pt surface by CO_{ad} intermediates. Apparently, the presence of Bi in the bimetallic catalyst structure provides a lower susceptibility to poisoning by promoting the direct path, and consequently enhances FA electrooxidation performance compared to the Pt catalyst.

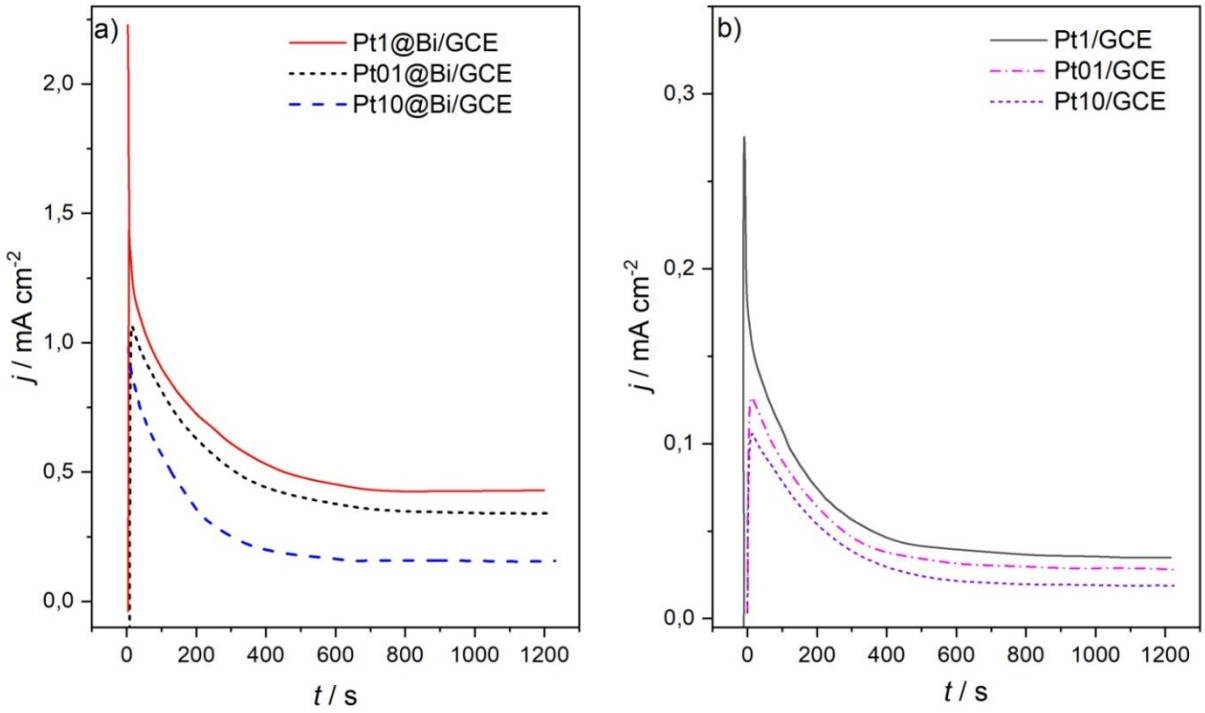


Figure 5. Chronoamperometric curves for the oxidation of 0.125 M HCOOH in 0.1 M H_2SO_4 solution at 0.2 V on Pt@Bi/GCE (a) and Pt /GCE electrodes (b)

DISCUSSION

The electrochemical oxidation of FA proceeds as already mentioned, through duel path mechanism - dehydrogenation (direct path) and dehydration (indirect path).For dehydrogenation, when CO_2 is directly formed, only a small ensemble of Pt atoms is needed [13].In dehydration, adsorbed CO is oxidized by OH at higher potentials,requiringlarger Pt ensembles. Research has demonstrated that the rate of formic acid oxidation improves with a decrease in particle size, specifically in relation to platinum ensembles, and a reduction in the number of defects [17]. According to the literature findings the direct oxidation of FA(dehydrogenation) on Pt surface does not require the presence of continuous neighbouring Pt sites [13], while the dissociative adsorption of formic acid to form CO requires at least two ensemble binding sites [18].Higher reaction currents was observed on Pt1@Bi/GCE in regard to Pt01@Bi/GCE (Figs. 3 and 4) while Pt01@Bi/GCE exhibited higher the ratio of j_{f1}/j_{f2} (Table 2). The heights of peaks j_{f1} and j_{f2}, along with their ratio, indicate which path is more dominant during the electrooxidation of FA on the catalyst surface. As the platinum loading on the bismuth surface decreases, the direct oxidation of formic acid becomes more dominant, as evidenced by the performance of the Pt01@Bi electrocatalyst. Nevertheless, Pt01@Bi electrocatalyst exhibiting lower activity. The explanation is accumulation of stable surface intermediates that block active sites, inhibiting further adsorption and oxidation of new FA molecules. In situ ATR-SEIRAS studies have shown that the dehydrogenation path proceeds via the formation of bridge-bonded adsorbed formate ($HCOO_{ad}$) [19, 20].The rate of formate formation is fast, but its subsequent oxidation to CO_2 is slow, so the overall current density remains low as demonstrated by the Pt01@Bi/GCE in regard to Pt1@Bi/GCE electrocatalyst. The dehydrogenation pathway is

more effective in producing less CO poison than the dehydration pathway, although it is not that fast since the accumulation of formate occurs.

To elucidate the superior activity of Pt1@Bi/GCE among the examined electrocatalysts, it is essential to recognize the significant role of its electroactive surface area.The calculated values of specific activity (current normalized by electrochemical active surface area, ECSA) for Pt01@Bi/GCE, Pi1@Bi/GCE and Pt10@Bi/GCE was 0.11 cm^2, 1.1 cm^2 and 1.35 cm^2, respectively. Among the studied Pt-on-Bi catalysts, Pi10@Bi/GCE catalyst demonstrates the highest specific activity but its activity is lower due to its poor intrinsic activity (activity per site). Although there are many active sites available, they may not all be optimal for the reaction. The electrooxidation of FA is highly sensitive to structure. On Pt nanoparticles, the {100} facets are more effective for the direct pathway, while the {111} facets are better suited for the indirect pathway [17,21]. It was shown that small Pt nanoparticles with high (100) site concentration have the highest activity [22].

For meaningful comparisons of catalytic performance among Pt-based systems, it is crucial to normalize data to account for variations in experimental conditions like electrolyte pH, potential range, catalyst loading, and scan rates. Specifically, current densities must be adjusted based on the mass of Pt. The calculated values of mass activity for Pt01@Bi/GCE, Pi1@Bi/GCE and Pt10@Bi/GCE are 57.5 m^2/g_{Pt}, 53 m^2/g_{Pt}, and 6.75 m^2/g_{Pt} respectively. An increase in Pt loading resulted in a subsequent decrease in mass activity as the platinum surface changed from isolated platinum nanoparticles to platinum agglomerates. Based on Figs. 3 and 4, the achieved mass activity at E = 300 mV is 2475 mA / mg_{Pt}, 862 mA / mg_{Pt}, and 94.5 mA/mg_{Pt}, for Pi1@Bi/GCE, Pt01@Bi/GCE, and Pt10@Bi/GCE respectively. Therefore, Pi1@Bi/GCE exhibited highest mass activity among the investigated electrocatalysts. Testing catalysts at very low loadings, as demonstrated with Pt01@Bi/GCE, can help reduce mass transport limitations. Even when the mass activity of the catalyst is high, the reaction rate may still be constrained by the rate at which reactants reach the active sites. Additionally, it's important to note that active sites can undergo changes such as surface atoms rearrangement during the electro chemical reaction probably causing instability. Therefore the enhanced electrochemical behaviour of the Pt1@Bi/GCE electrocatalyst in FA electrooxidation is attributed to the better utilization of Pt and a well-balanced Pt/Bi composition. Comparison of FA activity of some recently reported electrocatalysts reveal that the electro deposited Pt-on-Bi catalysts are more active than PtBi on carbon cloth [23], but less active than PtBi two-dimensional metal nanowire networks [24], and intermetallic PtBi nanoplates [8]. Based on a comparison with literature data, some improvements in Pt-on-Bi catalysts should be considered, such as the use of supports (CeO_2, or doping carbonaceous supports with B or N) as a strategy to maximize the direct pathway and reduce CO poisoning, thereby effectively changing the selectivity of the catalyst.

CONCLUSION

The catalytic activity towards the FA oxidation reaction was examined on a catalyst system constructed by the electrochemical deposition of Bi on GCE followed by the electrochemical deposition of Pt. According to electrochemical measurements, Pt-on-Bi activity and selectivity in FA electro oxidation is affected by Pt loading and morphology, which control the competitive reaction pathways between direct dehydrogenation (producing CO_2) and indirect dehydration (producing CO poisoning) path of the reaction. It was shown that the presence of Bi in the structure of the bimetallic catalyst provides a lower susceptibility to the poisoning regarding the Pt catalysts. The accomplished electrochemical performance of the Pt1@Bi electrocatalyst in FA electrooxidation is due to improved utilization of Pt and a balanced Pt/Bi composition.

Acknowledgments

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IZVOD

UTICAJ PUNJENJA PLATINOM NA Pt-MODIFIKOVANE Bi KATALIZATORE ZA ELEKTROOKSIDACIJU MRAVLJE KISELINE

U ovom radu proučavano je poređenje između Pt katalizatora i katalizatora na bazi bizmuta (Bi) modifikovanih platinom (Pt). Katalizatori tipa „Pt na Bi" pripremljeni su elektrotaloženjem platine na prethodno pripremljen bizmut, primenom hronopotenciometrije. Količina bizmuta održavana je konstantnom, dok je količina platine podešavana tako da se postignu molarni odnosi Pt prema Bi od 0,1:1, 1:1 ili 10:1. Radi preciznog poređenja, pripremljena je i elektroda od čiste platine, uz korišćenje iste elektrohemijske metode i količine metala kao kod elektroda od bizmuta modifikovanih platinom. Elektrohemijska svojstva Pt katalizatora i katalizatora tipa „Pt na Bi" ispitana su pomoću ciklične voltametrije (CV) i hronoamperometrije (CA) u rastvoru 0,1 M H_2SO_4. Utvrđeno je da su svi katalizatori tipa „Pt na Bi" aktivniji u procesu elektrooksidacije mravlje kiseline (FA) u poređenju sa čistom platinom, pri čemu je najveća aktivnost zabeležena kod katalizatora kod kojeg atomski odnos Pt prema Bi iznosi 1:1 (Pt1@Bi). Štaviše, atomski odnos Pt/Bi utiče na mehanizam oksidacije mravlje kiseline, što ukazuje na to da selektivnost elektrokatalizatora tipa „Pt na Bi" zavisi od količine platine, a time i od morfologije površine. Pokazano je da prisustvo bizmuta u strukturi bimetalnog katalizatora smanjuje njegovu podložnost trovanju u poređenju sa katalizatorom od čiste platine. Visoke elektrohemijske performanse elektrokatalizatora Pt1@Bi u procesu elektrooksidacije mravlje kiseline posledica su efikasnijeg iskorišćenja platine i uravnoteženog sastava Pt/Bi.

Ključne reči: *Bizmut, elektrotaloženje, sastav katalizatora, selektivnost*

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