

## Research Article

# Correlation between Formic Acid Oxidation and Oxide Species on Pt(Bi)/GC and Pt/GC Electrode through the Effect of Forward Potential Scan Limit

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Following earlier works from our laboratory, further experiments on electrochemical behavior in formic acid oxidation at electrodeposited Pt(Bi)/GC and Pt/GC electrode were performed in order to examine the effect of successive increase of the forward potential scan limit. Correlation between formic acid oxidation and oxide species on Pt(Bi)/GC electrode with increases of forward potential scan limit is based on the dependency of the backward peak potential from backward peak current. The obtained dependency reveals Bi influence for the scan limits up to 0.8 V. Since the Pt(Bi)/GC electrode is composed of Bi core occluded by Pt and Bi-oxide surface layer, the observed behavior is explained through the influence of surface metal oxide on easier formation of  $\text{OH}_{\text{ad}}$  species. Nevertheless, the influence of electronic modification of Pt surface atoms by underlying Bi is present and leads to the stronger adsorption of OH on Pt. At higher forward potential scan limits (from 0.8 V), Pt has a dominant role in HCOOH oxidation.

## 1. Introduction

Formic acid oxidation (FAO) reaction represents an important reaction in electrocatalysis, since it can be used in fundamental studies and, moreover, formic acid has been proposed as a fuel for direct liquid fuel cells (DLFCs), which can be used as small power supply in electronic devices [1, 2].

FAO on Pt electrodes has been widely studied over the last decades due to the high activity of this metal for the oxidation of different small organic molecules (SOMs) [1, 3, 4]. Since FAO probably has the simplest oxidation mechanism among all different SOMs, understanding of the FAO mechanism on Pt should be very useful for other electrocatalytic oxidation reactions. It is well accepted that FAO on Pt electrodes follows two different reaction pathways [5–7]. The presence of the parallel paths in formic acid oxidation has been confirmed by DEMS, ATR-FTIR, and SEIRAS measurements [8–10]. One of them is known as the direct pathway and implies the formation of an active intermediate, which is immediately oxidized into  $\text{CO}_2$ . The other so-called indirect pathway involves the formation of CO on the electrode surface, which acts as a poison intermediate. Spectroscopic analysis clearly

demonstrated that the poisoning species in the indirect path is adsorbed CO, while the reactive intermediate is a formate species [8–10].

Further improving of Pt electrochemical activity for FAO with addition of metals, such as Pb, Cu, Au, Ni, Ag, Sn, and Co, has been performed [11–15], and, among bimetallic catalysts, Pt-Bi is the most extensively studied. Different types of Pt-Bi catalysts obtained by various methods have been reported, such as the synthesis method capable of producing intermetallic Pt-Bi nanoparticles 1–3 nm in diameter [16] or Pt-Bi intermetallics with a particle size of 20–100 nm with certain preferential surface structures [17], Pt-Bi alloy nanoparticles following the cathodic corrosion method [18], electrochemically codeposited Pt-Bi [19], or Pt modified by Bi either by UPD or by irreversible adsorption [20, 21]. Enhanced activity of Pt in combination with Bi for FAO reaction was referred to as an electronic effect where the modification of the Pt electronic structure due to the presence of Bi enhances the activity of the surface [22], improving tolerance to CO poisoning by steric interference of Bi [23] or to ensemble effect [24, 25]. It is generally considered that the presence of a second metal has an impact on catalyst activity

and stability but can also greatly reduce Pt loading so as to lower the usage of precious metals.

For direct formic acid fuel cell, dehydrogenation is the desired reaction pathway to enhance overall cell efficiency [2]. Bimetallic Pt-Bi catalysts selectively enhance the dehydrogenation reaction rate, thus offering the possibility of overcoming the problem of poisoning the electrode, such as Pt with the intermediate CO [1, 2]. Also, onset potential of FAO is shifted toward less positive potentials on bimetallic Pt-Bi catalysts compared to Pt so that, by reducing the overpotential, a better performance of direct formic acid fuel cell could be fulfilled [2].

Our studies of Pt<sub>2</sub>Bi electrode and Pt-Bi clusters showed high activity and stability for FAO [24, 26]. The main reason for their high stability is the inhibition of dehydration path in the reaction, as well as suppression of Bi leaching in the presence of formic acid. Comparing the results obtained for two types of Pt-Bi catalysts, polycrystalline Pt modified by irreversible adsorbed Bi, and Pt<sub>2</sub>Bi catalyst, the role of the ensemble effect and electronic effect in the oxidation of formic acid was distinguished [27]. The electronic effect contributes to lower onset potential of the reaction, while the high current comes from the ensemble effect.

The aim of the work is to investigate the effect of successive increase of forward potential scan limit on electrochemical behavior of electrodeposited Pt(Bi)/GC and Pt/GC electrodes in formic acid oxidation. In order to reveal the correlation between FAO and oxide species, the dependency of the backward peak potential from backward peak current is performed. The intention is to get some additional insight in examination of the role of Bi on formic acid oxidation.

## 2. Experimental

Platinum-bismuth deposits on glassy carbon (GC) substrate were prepared by a two-step process as described previously [28]. To recapitulate, Bi was deposited onto the GC from 2 mM Bi perchlorate in 0.1 M H<sub>2</sub>SO<sub>4</sub> using chronocoulometry at -0.1 V versus SCE. After the Bi deposition, the electrode was rinsed and transferred to the electrochemical cell containing 1 mM H<sub>2</sub>PtCl<sub>6</sub> solution in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Pt was deposited under the same deposition condition as Bi and the amount of both metals was the same. The bimetallic electrode was denoted as Pt(Bi)/GC. For the sake of comparison, Pt/GC electrode was prepared using the same electrochemical procedure and quantity corresponding to one for bimetallic electrode. Pt(Bi)/GC electrodes were activated by cycling potential with scan rate of 50 mV s<sup>-1</sup> between hydrogen and oxygen evolution in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution 50 times leading to quasi-steady-state cyclic voltammogram (CV). Formic acid oxidation (0.125 M) was investigated in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution after holding the potential for 2 min at -0.2 V by potentiodynamic (scan rate 50 mV s<sup>-1</sup>) measurements. The rotating speed of the disc electrode ( $\omega$ ) was 1500 rpm in all CV experiments. The results are compared to Pt/GC treated in the same manner. Real surface area of the investigated electrodes was calculated from the charge of CO stripping, assuming 420  $\mu\text{Ccm}^{-2}$  for the CO monolayer [28].

All the experiments were performed in standard three-compartment electrochemical glass cells with Pt wire as the counterelectrode and saturated calomel electrode as the reference electrode at room temperature. The potentials reported in the paper are expressed on the scale of the saturated calomel electrode (SCE). The electrolytes were prepared with high purity water (Millipore, 18 M $\Omega$  cm resistivity) and the p.a. chemicals provided by Merck. The experiments were conducted at 295  $\pm$  0.5 K. A VoltaLab PGZ 402 (Radiometer Analytical, Lyon, France) was employed.

## 3. Results and Discussion

*3.1. Effect of Successive Increase of the Forward Potential Scan Limit in Base Voltammograms.* The bimetallic catalyst was prepared by a two-step process using chronocoulometry in a way that controlled the amount of Bi that was electrodeposited onto glassy carbon followed by electrodeposition of Pt layer [28]. Cyclic voltammetry revealed Bi leaching from the electrode surface indicating that Bi was not completely occluded by Pt. Continuous cycling after 50 cycles up to 1.2 V versus SCE in supporting electrolyte assures quasi-steady-state voltammogram. On this way the bimetallic electrode composed of Bi core occluded by Pt and Bi-oxide surface layer was obtained and denoted as Pt(Bi)/GC. For the sake of comparison, Pt/GC electrode was prepared using the same quantity corresponding to one for bimetallic electrode. The base voltammetric profiles of the Pt(Bi)/GC and Pt/GC electrodes in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution are shown in Figure 1. As one can see, the region between -0.25 and 0.2 V versus SCE is associated with the hydrogen adsorption/desorption process [26]. This region is followed by the region of oxide formation/reduction. In the case of the bimetallic catalyst (Figure 1(b)), the base voltammetric profile shows a current contribution in the region of oxide formation/reduction, associated with the redox behavior of Bi at the surface which is superimposed to Pt oxide formation/reduction [18].

In order to investigate the origin of the oxide formation/reduction in the potential region 0.4–1.2 V on Pt(Bi)/GC electrodes, a series of cyclic voltammograms for successive increases of the forward potential scan limit was recorded on this electrodeposited bimetallic electrode and compared with voltammograms obtained on Pt/GC electrode as it was shown in Figure 1(a). Previous analysis concerning the reversibility of various stages of surface oxidation on polycrystalline Pt reveals the presence of irreversible oxygen species below the monolayer of electroadsorbed OH [29]. Concerning Pt/GC, the increase of the forward potential scan limit causes the enhancement of charge for the oxide reduction, indicating that a more extended or thicker oxide film is formed. This finding was proven by nanogravimetry measurements [30] and also by using time-resolved energy dispersive X-ray absorption spectroscopy and time-resolved X-ray diffraction [31]. Besides, it was shown that Pt oxide formation/reduction depends on particle size and film roughness, electrolyte composition, as well as electrode scan rate [32].

Further analysis of base voltammograms obtained by a continuous increase of the forward potential scan limit expressed through the dependency of the charge associated

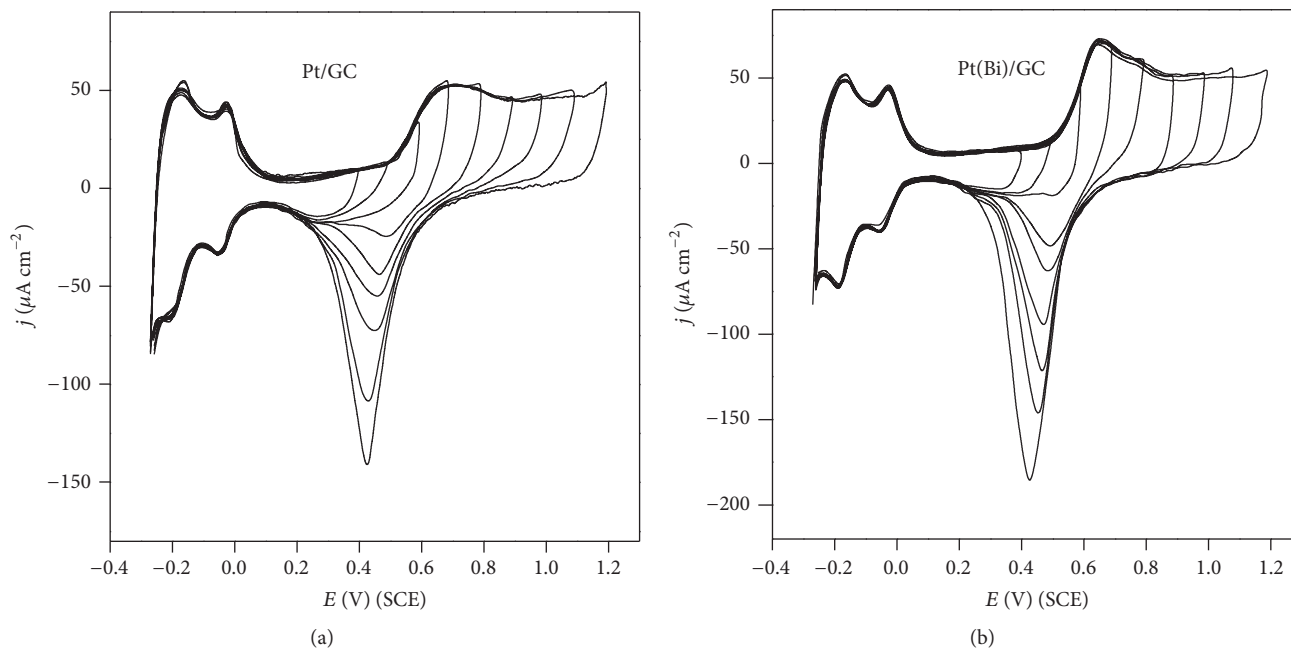


FIGURE 1: CVs on Pt/C (a) and Pt(Bi)/GC (b) electrodes in 0.1 M  $\text{H}_2\text{SO}_4$  at  $50 \text{ mV s}^{-1}$  and  $\omega = 1500 \text{ rpm}$  for successive increases of the forward potential scan limit.

with anodic film formation from the electrode potential is presented in Figure 2. Existences of two slopes on both investigated electrodes signify the presence of different forms of surface oxides. Transition in the region with higher slope (II), that is, the region of irreversibly adsorbed oxygenated species, occurred  $\sim 100 \text{ mV}$  earlier on Pt(Bi)/GC electrode indicating a faster transformation of oxygenated species from reversible to irreversible state. Similar slope in the first region (I) is expected since there is an overlap in CVs up to  $0.6 \text{ V}$  [28]. For higher potentials, larger content of charge on Pt(Bi)/GC in relation to Pt/GC electrode brings about a steeper slope.

The observed behavior could be explained through the electronic model based on the modification of Pt electronic structure in the presence of some other metal [33]. According to the theoretical DFT calculations, Pt overlayer on Bi is under a tensile strain since Bi has a larger lattice constant than Pt. This results in an increase in d-band center of Pt atoms in the out-layer, leading to the stronger adsorption of OH on Pt [33, 34]. In addition, the influence of surface metal oxide is possible since the Pt(Bi)/GC electrode is composed of Bi core occluded by Pt and Bi-oxide surface layer. It is well documented in literature that metal oxide causes an increase in adsorption ability of the hydroxyl ion onto catalyst surface [35]. Therefore, in the case of electrodeposited bimetallic electrode, Bi influences two modes of action contributing to a stronger and enhanced adsorption of OH species.

**3.2. Formic Acid Oxidation with the Increase of the Forward Potential Scan Limit.** Before analyzing the results obtained with the increase of the forward potential scan limit during FOA, it is important to recall some characteristics of Pt electrode in formic acid electrooxidation. In the forward scan direction, taking the Pt/GC electrode into

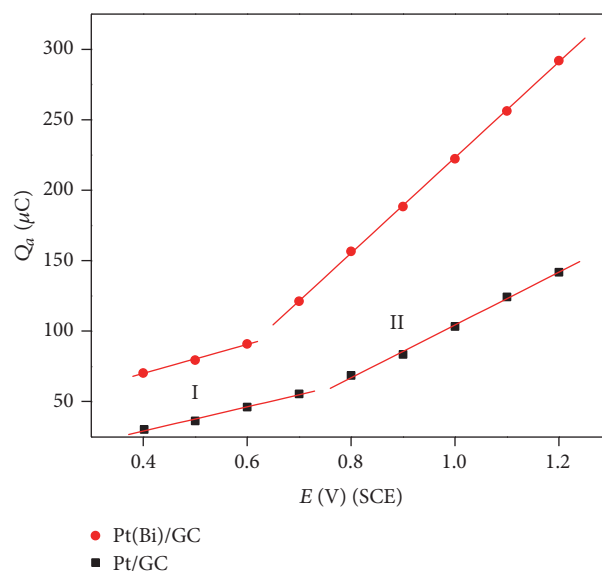


FIGURE 2: Oxide formation charge as a function of the forward potential scan limit (data obtained from Figure 1).

consideration (Figure 3), reaction current slowly increases reaching a plateau at  $\sim 0.25 \text{ V}$  followed by an ascending current starting at  $0.5 \text{ V}$ , attaining a maximum at  $\sim 0.6 \text{ V}$ . Bearing in mind the dual path mechanism, at low potentials, HCOOH oxidizes through the direct path with the simultaneous formation of  $\text{CO}_{\text{ad}}$  through the indirect path. Increased coverage by  $\text{CO}_{\text{ad}}$  reduces the Pt sites available for the direct path and, because of that, current slowly increases reaching a plateau. Subsequent formation of oxygenated species on Pt

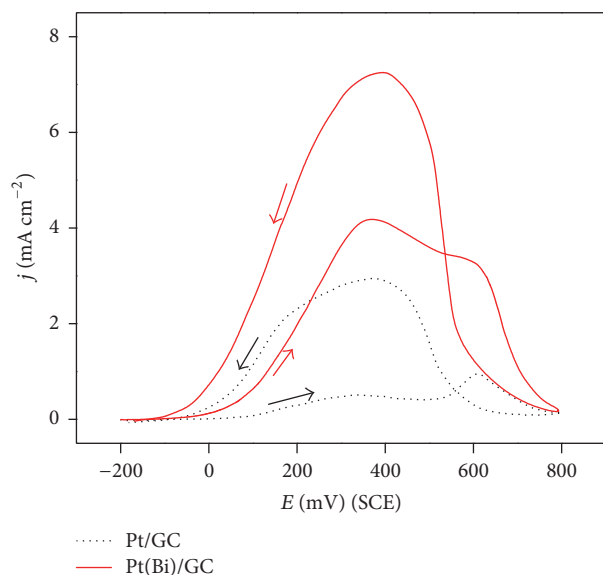


FIGURE 3: CVs for oxidation of 0.125 M HCOOH in 0.1 M H<sub>2</sub>SO<sub>4</sub> on Pt/GC and Pt(Bi)/GC electrode at 50 mV s<sup>-1</sup> and  $\omega = 1500$  rpm.

enables the oxidative removal of CO<sub>ad</sub> and as a result more Pt sites are disposed of for FAO. A reaction current increase until Pt-oxide, inactive for HCOOH oxidation, is formed inducing a peak. In the backward scan after the surface oxide reduction, more Pt sites are released for FAO so the reaction current increases reaching a peak. At more negative potentials, current decreases due to a lack of oxygenated species necessary for CO<sub>ad</sub> oxidation. The currents are much higher than, in the forward scan, because Pt surface is freed of CO<sub>ad</sub>. The polarization curve for electrodeposited bimetallic Pt(Bi)/GC surface indicates different behavior in comparison to Pt/GC. Figure 3 shows that the onset potential for the reaction on Pt(Bi)/GC electrode is about 100 mV less positive in comparison with Pt/GC. In the case of Pt(Bi)/GC electrode, the current rises up to 0.3 V and reaches a peak about 8 times higher than the plateau on Pt/GC. This peak indicates predominant direct oxidation path of HCOOH to CO<sub>2</sub>, occurring on Pt sites that are not blocked by the poisoning CO<sub>ad</sub> species, while the appearance of a poorly defined shoulder on the descending part of the curve signifies some participation of indirect path in the reaction as well. The currents recorded in the backward direction are higher, but the difference between forward and backward scan is not as large as on Pt/GC electrode indicating lower surface poisoning of bimetallic electrodes [36]. It has been shown that a number of neighboring Pt sites on the electrode surface determine the reaction path in the sense that the dehydration path needs an ensemble of at least three adjacent Pt atoms, while the dehydrogenation path is possible on a smaller atomic ensemble [37]. The obtained behavior is explained primarily by the ensemble effect induced by surface Bi oxides interrupting Pt domains but to some extent could also be attributed to the influence of the underlying Bi onto the Pt surface layer, affecting the extent of poison adsorption on the Pt [28].

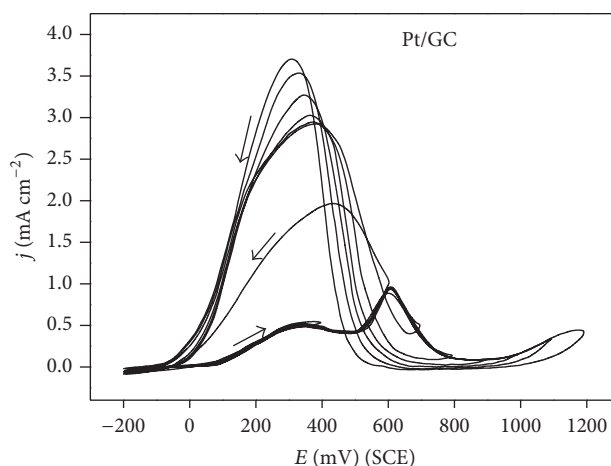


FIGURE 4: CVs for oxidation of 0.125 M HCOOH in 0.1 M H<sub>2</sub>SO<sub>4</sub> on Pt/GC electrode at 50 mV s<sup>-1</sup> and  $\omega = 1500$  rpm for the successive increases of the forward potential scan limit.

The results of the potentiodynamic measurements for HCOOH oxidation support the finding of the quasi-steady-state measurements [28]. Namely, the Tafel slope on Pt(Bi)/GC electrodes is about 120 mV dec<sup>-1</sup>, indicating that the HCOOH oxidation takes place on a surface almost free of CO<sub>ad</sub> through dehydrogenation path. Therefore, the first electron transfer is the rate-determining step, and the slow step that determines the rate of formic acid oxidation on Pt(Bi)/GC electrodes is the C–H bond cleavage and formation of COOH<sub>ad</sub>. The Tafel slope of about 150 mV dec<sup>-1</sup> obtained during formic acid oxidation on Pt/GC electrode indicates that CO was formed and adsorbed on the surface slowing down the reaction rate.

CVs of the FAO on Pt/GC electrode recorded for the successive increases of the forward potential scan limit are shown in Figure 4.

Extension of the forward potential scan limit slightly influences the reaction currents in the forward scan, while the currents recorded in the backward direction become higher and the peak is shifted to a more negative potential. For higher forward potential scan limits, greater amount of surface oxide is formed [30, 31]. Consequently in the backward direction more surface oxide is reduced, releasing more Pt sites for HCOOH oxidation, thus increasing reaction currents.

The polarization curves for FAO obtained for successive increases of the forward potential scan limit from 0.4 V up to 1.2 V on electrodeposited bimetallic Pt(Bi)/GC surface (Figure 5) indicates quite different behavior in comparison to Pt/GC. For the forward potential scan limit 0.4 V there is almost an overlap of reaction currents in forward and backward scan direction suggesting an absence of surface poisoning. It can be noticed that forward reaction currents decrease almost two times at peak potential with further extension of forward potential scan limits. Other contribution of forward potential scan limit extension is obtained in the backward scan direction and it is presented as a dependency of the backward peak potential from backward



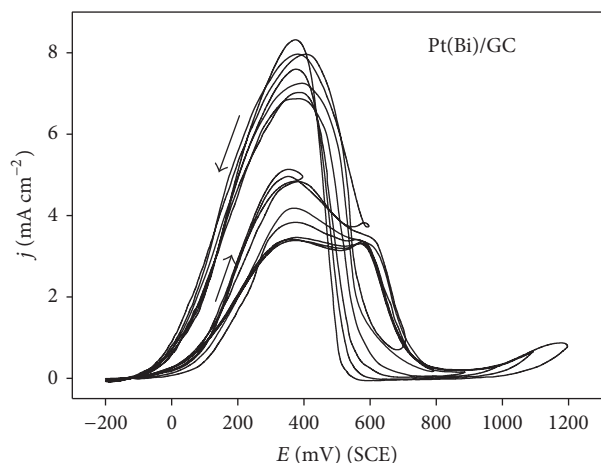


FIGURE 5: CVs for oxidation of 0.125 M HCOOH in 0.1 M H<sub>2</sub>SO<sub>4</sub> on Pt(Bi)/GC electrode at 50 mV s<sup>-1</sup> and  $\omega = 1500$  rpm for successive increases of the forward potential scan limit.

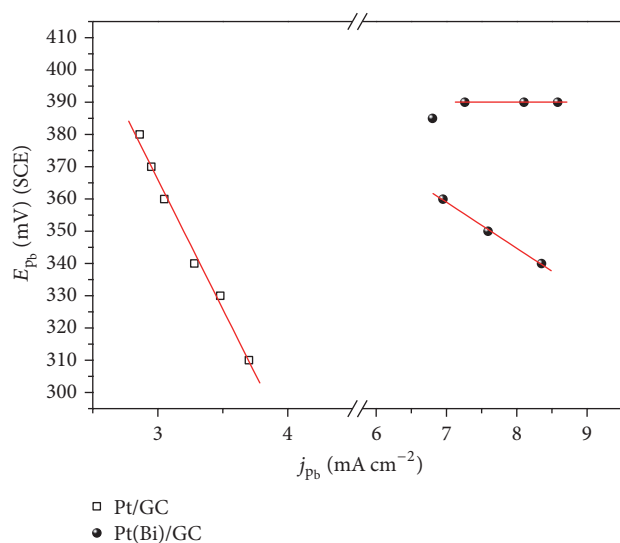


FIGURE 6: Backward peak potential versus backward peak current (data obtained from Figures 4 and 5).

peak current (Figure 6). This dependency on Pt/GC gave one negative slope [30, 38] which means that the increase of the forward potential scan limit enables current enhancement in the backward scan since the reduction of more Pt oxide releases more sites for FAO. However on electrodeposited bimetallic Pt(Bi)/GC surface the dependency of the backward peak potential from backward peak current depicts zero slope for forward potential scan limit 0.6–0.8 V and a small negative slope in potential scan limit 1.0–1.2 V. Zero slope obtained for specified scan limits means that peak potential remained the same while reaction currents decrease indicating the surface blockade. Nevertheless, further increases of forward potential scan limit (1.0–1.2 V) enable some current enhancement since after the reduction of surface oxides, the oxidation of formic acid occurs.

This finding is in accordance with the results presented in Figure 2. So, for the forward potential scan limit 0.4 V,

enhanced adsorption of OH species participates in the oxidation of CO<sub>ad</sub> species, suggesting an absence of surface poisoning. Stronger adsorption of OH species for forward potential scan limit 0.6–0.8 V causes surface blockade. At higher forward potential scan limits (from 0.8 V) Pt has a dominant role in HCOOH oxidation. Besides, the overlap of base voltammograms confirms that observation [28]. To summarize, in the case of electrodeposited bimetallic electrode, it was shown that Bi influences two modes of action affecting the oxidation of surface poisoning (forward potential scan limit 0.4 V) and surface blockade (forward potential scan limit 0.6–0.8 V), whereby potential region of Bi influence in FAO is determined.

It has been reported in literature that the beneficial effect of Bi on Pt on bimetallic Pt-Bi electrodes for HCOOH oxidation reaction followed several different mechanisms as is stated in the introduction part [30–33]. Depending on the fact that the preparation method of the catalysts and their resulting surface composition the contribution of the effects may vary, our previously published results on bimetallic Pt-Bi electrodes confirm the ensemble effect as dominant in HCOOH oxidation [26–28]. Based on the presented electrochemical results, it was possible to offer same additional insight into examination of the role of Bi in formic acid oxidation.

## 4. Conclusion

Successive increase of the forward potential scan limit in base voltammograms of Pt(Bi)/GC and Pt/GC electrodes is expressed through the dependency of the charge associated with anodic film formation from the electrode potential. This dependency shows two slopes on both investigated electrodes due to the presence of different forms of surface oxides. Transition in the region with higher slope occurred ~100 mV earlier on Pt(Bi)/GC electrode indicating the faster transformation of oxygenated species from reversible to irreversible state. The observed behavior is explained through the electronic modification of Pt surface atoms by Bi leading to the stronger adsorption of OH on Pt. Also, the influence of surface metal oxide on easier formation of OH<sub>ad</sub> species is possible. With the increase of the forward potential scan limit, correlation between formic acid oxidation and oxide species on Pt(Bi)/GC electrode reveals Bi influence for scan limits up to 0.8 V. At higher forward potential scan limits Pt has a dominant role in HCOOH oxidation. In this way, potential region of Bi influence in FAO at electrodeposited bimetallic Pt(Bi)/GC electrode is determined.

## Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this paper.

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