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# New Catalysts for Formic Acid Fuel Cells

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**Abstract:** Thallium adatoms deposited at under-potentials have shown the catalytic effect during the electrooxidation of formic acid on platinum ruthenium alloys. At Pt/Ru with an optimal coverage degree with adatoms Tl, HCOOH is oxidized at nearly 180 mV more negative potential than at Pt/Ru electrodes. The catalytic effect of modified Pt/Ru electrodes is plausibly caused by interaction of the Tl adatoms, located at Pt atoms with OH species of adjacent Ru atoms. These interactions stabilize Ru-OH species and allows for their formation at more negative potentials than at the Pt/Ru electrodes. The Ru-OH species oxidize firmly bound intermediates $CO_{ad}$ and thus release the Pt atoms for the oxidation of subsequent HCOOH molecules. The catalytic effect is probably caused by the third-body effect.

**Keywords:** Formic acid, Thallium, Catalyst, Electrochemistry, Bifunctional mechanism.

## 1 Introduction

The fuel cells are very attractive way to cleanly and efficiently produce energy. A fuel cell produces electricity using hydrogen or other fuels. If hydrogen is fuel of choice, there is no waste and only water and electricity are produced. Fuel cells can be used anywhere, ranging from large facilities such as utility power station and small objects such as laptop computer. Furthermore, they can provide power for a various applications such as transport, buildings, industrial processes and long-term energy storage for the grid in reversible systems.

The main advantage of the fuel cells compared to conventional combustion-based technologies is high efficiency. Namely, the fuel cells highly efficiently (>60%) transform chemical energy to electricity. Second advantage of fuel cells is clean production which is reflected in very low or zero emission of pollutants. Thus, fuel cells are excellent way to address ever rising climate challenges.

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However, the $H_2$ usage in fuel cells has encountered many problems such as expensiveness of small hydrogen storage reservoirs, a low gas-phase energy density of $H_2$ and possible accidents during the hydrogen exploitation and transport [1]. One of the possible alternatives is liquid methanol which has very high energy density. But methanol exhibits one relevant drawback which is low rate of electrochemical oxidation. Additionally, it is a toxic volatile organic compound [2]. Aforementioned obstacles related to use of hydrogen and methanol in the fuel cells have guided the latest research towards the application of formic acid (FA) for this purpose [3 – 24]. Benefits of FA relay on its non-toxicity and lower potential than that of either $H_2$ or methanol [2]. The use of FA as a fuel suffers from low volumetric energy density (2104 Wh/dm$^3$), which is substantially lesser compared to neat methanol. However, if FA is employed in high concentration this obstacle can be overcame. The fuel cells where FA is used as fuel are good alternatives for light portable items, for instance mobiles, laptops, digital recorders, etc. [1].

The mechanism of FA electrooxidation:

$$\mathrm{HCOOH} \rightarrow \mathrm{CO_2} + 2\mathrm{H^+} + 2\mathrm{e^-}, E^{\theta} = 0.243\,\mathrm{V} \tag{1}$$

has been extensively studied [25 – 30]. Currently, it is generally accepted a parallel dual-path mechanism [29]. Path 1 refers to direct oxidation, which occurs through dehydrogenation:

$$\text{Path 1}\; \mathrm{HCOOH} \rightarrow \mathrm{CO} + 2\mathrm{H^+} + 2\mathrm{e^-}\,. \tag{2}$$

In the second path the reaction of dehydration occurs:

$$\text{Path 2}\; \mathrm{HCOOH} \rightarrow \mathrm{CO_{ad}} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + 2\mathrm{H^+} + 2\mathrm{e^-}\,. \tag{3}$$

As shown in (3), the intermediate CO is created in this path, and is strongly bound to the electrodes. Its oxidation to the final product, carbon dioxide, is very slow. The first reaction path is favored for the fuel cells. The dehydration reaction is undesirable, since the strongly bound intermediate occupies the Pt atoms and thus hinders the direct oxidation. Adzić *et al.* have formed the catalyst by the under-potential deposition of foreign metals adatoms on electrodes of noble metals, which has shown a great activity in the electrooxidation of FA [31, 32]. The catalytic activity was explained by the third-body effect. Many research groups have studied the catalysts efficiency for the FA oxidation, where catalysts are obtained by alloying Pt with various metals [4 – 49]. Rice and coworkers catalyzed the electrooxidation of FA with the alloy of Pt and Pd. They assumed that this catalyst favored the pathway 1 reaction (dehydrogenation) [4]. Other study found that that the presence of Pd in Pt-Pd catalyst lowered the energy barrier of the FA decomposition [33]. Other studies showed that the Pd suppressed the $CO_{ad}$ species formation. This suppression enables higher rates of FA oxidation [7, 11, 12]. The catalytic performance of Pt has been improved by alloying with Au, owning to several effects (electronic, ensemble and/or synergistic effect) [8, 13, 17, 19, 34 – 37]. In the Pt/Bi alloys, the activity of Bi was ascribed to the third-body effect [40]. However, the synergy between the electronic effect and third-body effect is shown to be responsible for the activity of Bi in Pt/Bi alloys [42]. Electronic interactions between Pt and Pb in Pt/Pb alloys have been responsible for the activity of Pb in these alloys [41]. In the past two decades development of Pt/Ru and Pt/$RuO_2$ catalysts was main focus of many research groups. It has been shown that these alloys have shown the best electrochemical properties in the electrooxidation of simple organic compounds [4, 9, 14, 20, 24, 25, 43 – 55]. The activity of the aforementioned catalysts has been ascribed to both the electronic effect and bifunctional mechanism. Firstly, the amount of adsorbed CO is lowered due to the electronic effect, which is explained by the d-band center shift of Pt in the Pt/Ru alloys away from the Fermi level. Secondly, the “oxy” species oxidize the adsorbed CO in the bifunctional mechanism of the bimetallic catalysts. This species was previously generated on Ru atoms. This furthermore accelerates the FA electrooxidation by both paths.

This study aimed to examine an effect of the surface modification of the alloy composed of platinum and ruthenium with adatoms of thallium on the rate of the electrooxidation of FA.

## 2 Materials and Methods

A standard electrochemical glass cell with separate compartments for the saturated mercury sulphate electrode and Luggin capillary was used in the experiment. The working electrode was a platinum-ruthenium bulk alloy plate (surface area 2.5 $cm^2$), which was polished to obtain a mirror finish. The bulk composition of Pt/Ru alloys was evaluated by X-ray fluorescence spectroscopy. X-ray diffraction showed that all Pt/Ru alloys are solid solutions of Pt and Ru (face-centered cubic) [26]. The counter electrode was a platinum plate. The surface area of platinum plate was 16 $cm^2$ (40×40 mm). It was positioned parallel to the working electrode. Temperature of the cell was maintained by thermostat (25±0.3°C). Used solutions were made of p.a. chemicals (Merck) and demineralized water. FA was added to the electrolyte to the concentration of 0.25M. The ions of thallium were introduced as perchlorates in the concentration range between $10^{-7}$ and $10^{-2}$ M. Before all measurements the oxygen was removed from the reaction mixture by purging with nitrogen. The voltammetry curves were measured with sweep rate of 100 mV $s^-$. The standard electronic circuitry consisted of a programmer (Potentiostat-Galvanostat model 173, EGG Princeton), an X-Y recorder (Hewlett Packard 7035 B) and digital voltmeter (Pros’ Kit 03-9303 C). All presented potentials were shown relative to the SHE.

## 3 Results and Discussion

The catalytic effect of Tl adatoms on HCOOH oxidation is investigated by using Pt/Ru alloys made up of 79 mol% Pt, 21 mol% Ru and 34 mol% Pt, 66 mol% Ru. The alloys were a single phase solution of Pt and Ru (face-centered cubic) [26]. Under-potential deposition of Tl on pure metals Pt and Ru and an effect of the Tl adatoms on these metals on the HCOOH oxidation has already been studied [31]. Therefore, the results of this previous research are not presented in this paper. Under-potential deposition of Tl on the Pt/Ru alloys and an effect of this deposition on electrodes' surface structure were studied by recording voltammetric curves from a solution 1.0 mol dm$^{-3}$ $HClO_4$ in the absence and presence of the $Tl^+$ ion. Figs. 1 and 2 show the voltammetric curves of the electrodes made up of 79 mol% Pt, 21 mol% Ru and 34 mol% Pt, 66 mol% Ru in the solution 1.0 M $HClO_4$ with and without $Tl^+$ ion.

Voltammetry curves were recorded from 0.05 V during android sweep during the third cyclization with an anode border lower than 1.2 V. Recording in such manner minimizes change in the surface composition of the electrode, caused by more rapid dissolution of Ru than Pt. The voltammetry curves of Pt/ Ru electrodes (dashed line in Fig.1. and Fig. 2.) recorded in the absence of $Tl^+$ ions, show clear, distinct peaks corresponding to adsorption and desorption of hydrogen. These peaks are shown between 0.0 and 0.35 V. Potentials of minimum and maximum of these peaks do not differ from those in the voltammetric curve of pure Pt. This indicates that the energy state of hydrogen atoms adsorbed on Pt is not substantially affected by the adjacent Ru atoms. Thus, the adjacent Ru atoms do not considerably alter the Pt atoms energetic state as well. The voltammetry curve of pure Pt shows the presence of double-layer region at the potentials from 0.35 to 0.65 V. However, in this potential region higher current densities are observed in the voltammetry curves of both examined alloys. Greater increase in the current density is more evident in the curve of alloy with the higher Ru content, as a result of formation of oxy species of the Ru atoms. The effect of $Tl^+$ ions in the solution on the shape of the voltammetry curves is presented by the solid lines in Figs. 1 and 2. As seen in these figures, Tl deposits on the Pt/Ru alloys just after reduction of Pt oxide. The voltammetry curves of pure Ru in 1.0 M $HClO_4$ with or without $Tl^+$ ions in the solution are very similar. This indicates that distinct occurrence of under-potential deposition of Tl on the Ru atoms is not observed. Figs. 1 and 2 also show desorption of Tl from the Pt atoms at potentials higher than 0.7 V. A considerably higher peak of Tl desorption from the alloy 79 mol% Pt, 21 mol% Ru than that from the alloy 34 mol% Pt, 66 mol% Ru confirms the Tl adsorption solely on the Pt atoms. The potential of the adsorption beginning and potential of the peak maximum of Tl desorption shift to more positive values with increasing the Ru content in the Pt/Ru alloy. Since the electronic state of Pt is not considerably affected by the adjacent Ru atoms, the change in the electronic state does not alter the potential of desorption of Tl atoms towards more positive values. Tl adatoms plausibly interact with the oxy species on the adjacent Ru atoms. This interaction stabilizes both the Tl atoms and oxy species on the Ru atoms. Therefore, the oxy species are reduced at lower potentials in the presence of Tl adatoms (Figs. 1. and 2.)

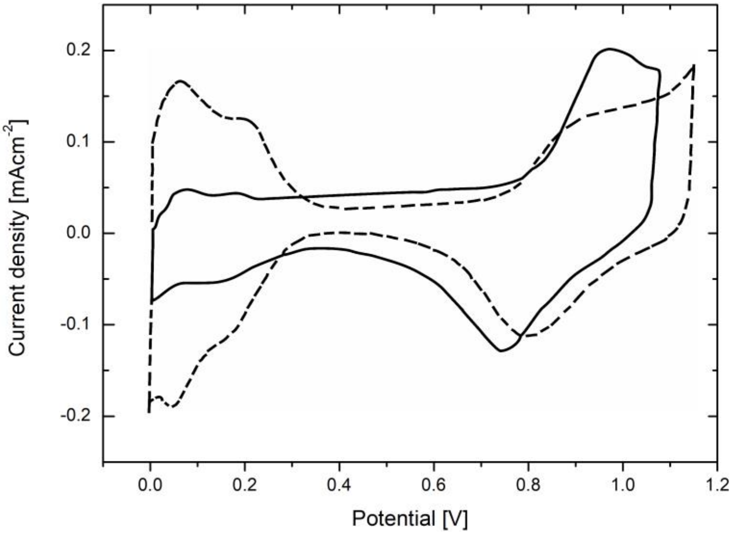

**Fig. 1** – *Voltammetry curves of 79 mol% Pt, 21 mol% Ru electrodes in 1.0 M HClO4 with (—) and without (- - -) 10-4 M Tl+.*

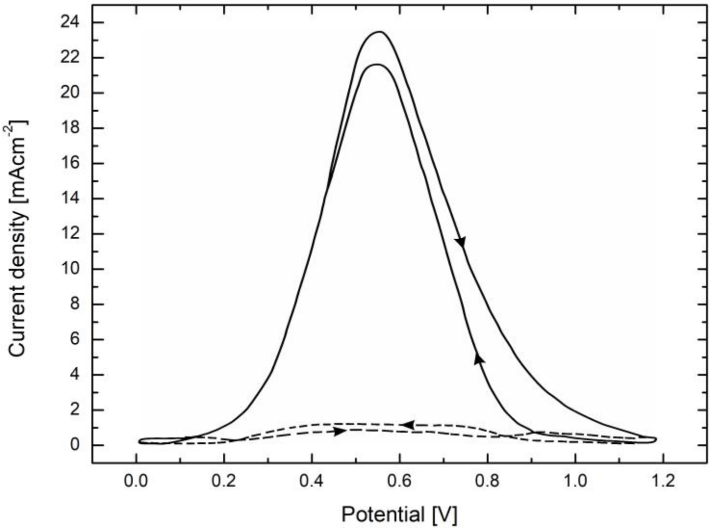

**Fig. 2** – *Voltammetry curves of 34 mol% Pt, 66 mol% Ru electrodes in 1.0 M HClO4 with (—) and without (- - -) 3·10-4 M Tl+.*

An influence of the Tl adatoms on the Pt/Ru alloys on kinetics of electrooxidation of HCOOH is examined by recording voltammetry and polarization curves.

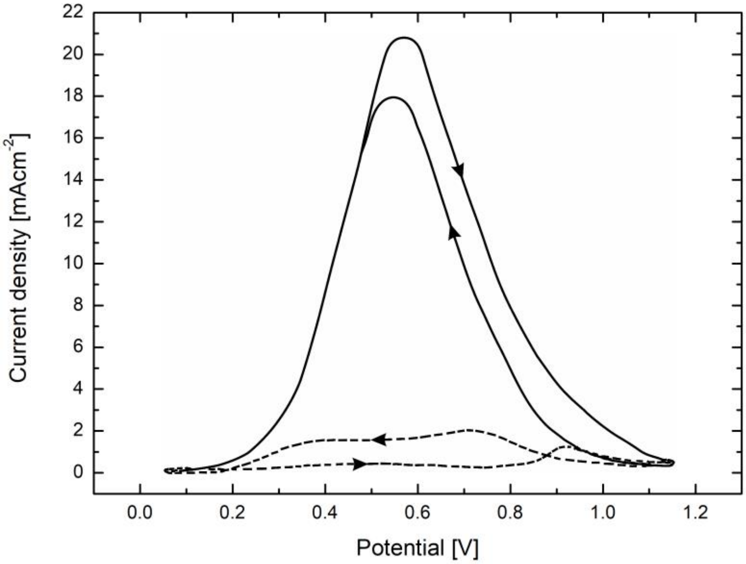

**Fig. 3** – *Voltammetry curves of 79 mol% Pt, 21 mol% Ru electrode in 1.0 M HClO4 containing 0.25 M HCOOH with (—) and without (- - -) 10-4 M Tl+.*

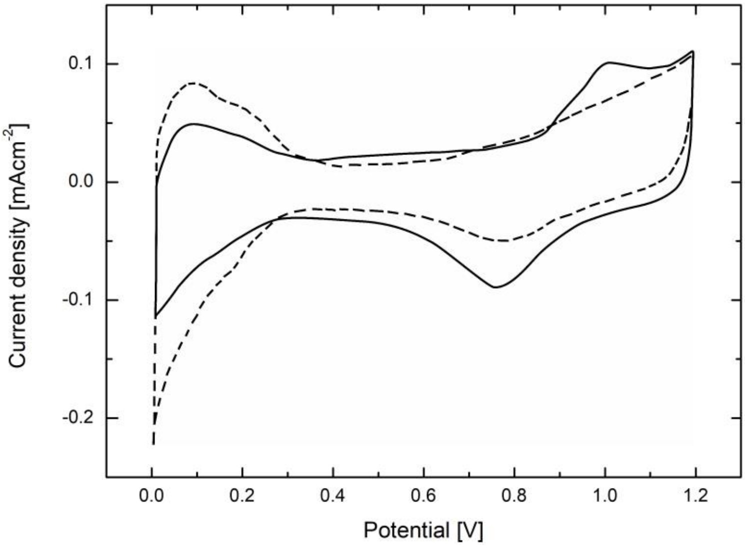

**Fig. 4** – *Voltammetry curves of 34 mol% Pt, 66 mol% Ru electrode in 1.0 M HClO4 containing 0.25 M HCOOH with (—) and without (- - -) 3·10-4 M Tl+.*

The voltammetry curves were recorded during the third cycle. Both Pt/Ru electrodes in the absence of Tl adatoms, during the potential change to anodic or cathodic position, show two anodic peaks in their voltammograms (dashed lines in Figs. 3 and 4.). However, the voltammetry curves of Pt/Ru electrodes modified with Tl adatoms, during the potential change to the anodic or cathodic position have only one anodic peak (solid lines in Figs. 3 and 4.). This finding indicates substantially higher activity of the electrodes with Tl adatoms for the HCOOH oxidation. Also, it is found that around 200 mV more negative potential is needed to start the oxidation using these catalysts.

The reaction of HCOOH oxidation begins with adsorption of its molecules on unoccupied Pt or Ru atoms:

$$\mathrm{HCOOH + Pt(Ru) \rightarrow Pt(Ru)(HCOOH_{ad})}\,. \tag{4}$$

HCOOH cannot be adsorbed on the Pt and Ru atoms occupied with oxy species $\mathrm{Pt(Ru)O_xH_y}$.

Subsequently, the adsorbed molecules are rapidly dehydrogenated:

$$\mathrm{Pt(Ru)(HCOOH_{ad}) \rightarrow Pt(Ru)(\text{-}COOH_{ad}) + H^+ + e^-}\,. \tag{5}$$

A formed “ad” radical, $\mathrm{\text{-}COOH_{ad}}$, exhibits weak bounding to Pt and Ru atoms. It is very reactive and quickly reacts as follows [24, 25]:

$$\mathrm{Pt(Ru)(\text{-}COOH_{ad}) \rightarrow Pt(Ru) + CO_2 + H^+ + e^-} \tag{6}$$

$$\mathrm{Pt(Ru)(\text{-}COOH_{ad}) + Pt(Ru)(H_{ad}) \rightarrow Pt(Ru)(\text{-}CO_{ad}) + H_2O} \tag{7}$$

$$\begin{gathered}\mathrm{Pt(Ru)(\text{-}COOH_{ad}) + Pt(Ru)(HCOOH_{ad}) \rightarrow}\\ \mathrm{Pt(Ru)(\text{-}CO_{ad}) + Pt(Ru)(\text{-}COOH_{ad}) + H_2O}\end{gathered} \tag{8}$$

$$\begin{gathered}\mathrm{Pt(Ru)(\text{-}COOH_{ad}) + Pt(Ru)(\text{-}COOH_{ad}) \rightarrow}\\ \mathrm{Pt(Ru)(\text{-}CO_{ad}) + CO_2 + H_2O}\end{gathered} \tag{9}$$

$$\begin{gathered}\mathrm{Pt(Ru)(\text{-}COOH_{ad}) + Pt(Ru)(HCOOH_{ad}) \rightarrow}\\ \mathrm{Pt\left(Ru\right)(= C(OH)_{2,ad}) + Pt(Ru)(\text{-}COOH_{ad})}\end{gathered} \tag{10}$$

$$\begin{gathered}\mathrm{Pt(Ru)(\text{-}COOH_{ad}) + Pt(Ru)(\text{-}COOH_{ad}) \rightarrow}\\ \mathrm{Pt(Ru)(= C(OH)_{2,ad}) + CO_2 + Pt(Ru)}.\end{gathered} \tag{11}$$

An “ad” radical, $\mathrm{=C(OH)_{2,ad}}$ is weakly bound to the Pt and Ru atoms. It decomposes relatively easy:

$$\mathrm{Pt(Ru)(= C(OH)_{2,ad}) \rightarrow Pt(Ru)(\text{-}CO_{ad}) + H_2O}. \tag{12}$$

Reactions (4 – 6) compose the main reaction pathway of HCOOH oxidation. The slowest step is reaction (5).

The firmly adsorbed intermediate, $CO_{ad}$, is formed in the reactions (7 – 12). In the hydrogen region of potential, the intermediate $CO_{ad}$ emerges mainly relatively rapid in the reaction (7). However, in a double-layer region $CO_{ad}$ is formed considerably slower in the reactions (8 – 12) [24]. Spectrochemical researchers found out that $CO_{ad}$ can be linearly (-$CO_{ad}$) and bridge (=$CO_{ad}$) adsorbed [23, 25]. They have also indicated that during the HCOOH oxidation, bridge-bonded adsorbed formate moieties were created on Pt surface [23, 25]:

$$\mathrm{Pt}\left(\mathrm{HCOOH_{ad}}\right) \rightarrow \mathrm{Pt}\left(\mathrm{HCOO} =_{\mathrm{ad}}\right) + \mathrm{H^+} + \mathrm{e^-}\,. \tag{13}$$

Created Pt(HCOO=$_{ad}$) is oxidized more rapidly compared to $CO_{ad}$:

$$\mathrm{Pt}\left(\mathrm{HCOO} =_{\mathrm{ad}}\right) \rightarrow \mathrm{Pt} + \mathrm{CO_2} + \mathrm{H^+} + \mathrm{e^-}\,. \tag{14}$$

Only, at potentials higher than 0.50 V the firmly adsorbed species $CO_{ad}$ on pure Pt are oxidized. Thus, at potentials lower than 0.50 V, the existence of $CO_{ad}$ intermediate prevents adsorption and electrooxidation of subsequent HCOOH molecules via the main reaction pathway. At higher potentials (>0.50 V), oxy species are formed. These species are most probably Pt-OH and they oxidize the intermediate $CO_{ad}$:

$$\mathrm{Pt} + \mathrm{H_2O} \rightarrow \mathrm{Pt\text{-}OH} + \mathrm{H^+} + \mathrm{e^-} \tag{15}$$

$$\mathrm{Pt(\text{-}CO_{ad})} + \mathrm{Pt\text{-}OH} \rightarrow 2\,\mathrm{Pt} + \mathrm{CO_2} + \mathrm{H^+} + \mathrm{e^-}\,. \tag{16}$$

However, on Ru atoms of Pt/Ru alloy the oxy species are created at about 300 mV lower potential compared to Pt [1, 4, 9, 14, 24, 25,41 – 53]. These Ru-OH species oxidize $CO_{ad}$ intermediates which are strong bounded and placed at adjacent Pt atoms at higher potentials (>0.50 V):

$$\mathrm{Ru} + \mathrm{H_2O} \rightarrow \mathrm{Ru\text{-}OH} + \mathrm{H^+} + \mathrm{e^-} \tag{17}$$

$$\mathrm{Pt(\text{-}CO_{ad})} + \mathrm{Ru\text{-}OH} \rightarrow \mathrm{Pt} + \mathrm{Ru} + \mathrm{CO_2} + \mathrm{H^+} + \mathrm{e^-}\,. \tag{18}$$

New HCOOH molecules are then oxidized on discharged Pt atoms.

In a previous study it is reported that the oxidation HCOOH on Pt mainly follows direct path [22]. It was found that formate mechanism makes fewer than 25% of total current. On the other hand, the indirect path was found to contribute less than 0.1%.

The above shown chemical reactions determine the shape of the voltametric curves of HCOOH electrooxidation at Pt and Pt/Ru anodes. In hydrogen region of potential, the $CO_{ad}$ intermediates are strongly bounded and are made in the reactions (7 – 12). This intermediate blocks most of the Pt surface and thus omits the adsorption and dehydrogenation of HCOOH, as well as oxidation of weakly-bound intermediates on this surface. The HCOOH oxidation via direct pathway occurs on Pt surface with no adsorbed $CO_{ad}$ species. This results in the appearance of the first anodic peak at 0.50 V during the anodic sweep. Decline in the current of HCOOH oxidation after the maximum of the first current peak is a consequence of rapid formation of weakly bound intermediate $=C(OH)_2$. The oxidation of the $CO_{ad}$ species and HCOOH via direct pathway results in the second anodic peak, which emerges in the potential region where Pt-OH and Ru-OH were created on discharged surface of Pt. During potential shift to cathodic side, reduction of oxide releases the Pt atoms which facilitates further HCOOH electrooxidation, which results in rapid current increase. Current first reach the maximum value and then declines owning to both formation of intermediates $CO_{ad}$, $=C(OH)_{2,ad}$ and lowering the potential to more negative values. The appearance of a shoulder after the swift decrease of current is a consequence of the slow formation of intermediate $=C(OH)_{2,ad,}$ resulting from the potential decline to more negative values.

Creation of oxy particles on the Ru atoms at lower potentials than on Pt affects the shape of voltammetry curves of the HCOOH electrooxidation at Pt/Ru alloys. The voltammograms show that increase in the Ru content up to 60% shifts the starting potential of HCOOH electrooxidation to lower potentials and also decreases difference in intensities of maximum of the first peak during the cyclization in the anodic side and in the cathodic side (Figs. 3 and 4.). This indicates the decrease in the coverage degree of the Pt/Ru electrodes by the intermediate COad with increasing the Ru content in the alloy.

The presence of Tl adatoms on the Pt/Ru anodes substantially affects the shape of the voltammetry curves of HCOOH oxidation (Figs. 3 and 4.). Only one peak is observed during the cyclization in both anodic and cathodic side. The peaks maximum of the Pt/Ru electrodes with the Tl adatoms are ten to forty-fold higher than those of Pt/Ru anodes without Tl. Starting potentials of HCOOH oxidation at the electrodes modified with the Tl adatoms are around 200 mV lower compared to those at the unmodified Pt/RuO2 electrodes. This indicates the higher activity of the modified than unmodified Pt/RuO2 anodes for HCOOH electrooxidation. The greater catalytic activity is also observed in the polarization curves (Figs. 5 and 6.). The current densities were measured after the anode was kept for 90 seconds at a particular potential.

Fig 5. and 6 shows the polarization curves of HCOOH electrooxidation at neat Pt and Pt/Ru anodes. These polarization curves indicate higher activity of the Pt/Ru anodes than of neat Pt. The greater activity of Pt/Ru anodes is due to bifunctional mechanism. However, Pt/Ru electrodes with Tl adatoms showed higher activity compared to unmodified Pt/Ru. The coverage degree of the Pt/Ru surface with the Tl adatoms is shown to highly influence activity of modified anodes. The coverage degree is determined by the concentration of $Tl^+$ ions. The increase in the concentration of $Tl^+$, leads to the increase in the activity which reaches the highest value at the concentration of $10^{-3}$ M $Tl^+$ and $3 \cdot 10^{-4}$ M $Ti^+$ for the electrodes 79 mol% Pt, 21 mol% Ru and 34 mol% Pt, 66 mol% Ru, respectively. Further increase in the concentration of $Tl^+$ ions results in decrease of the catalytic activity.

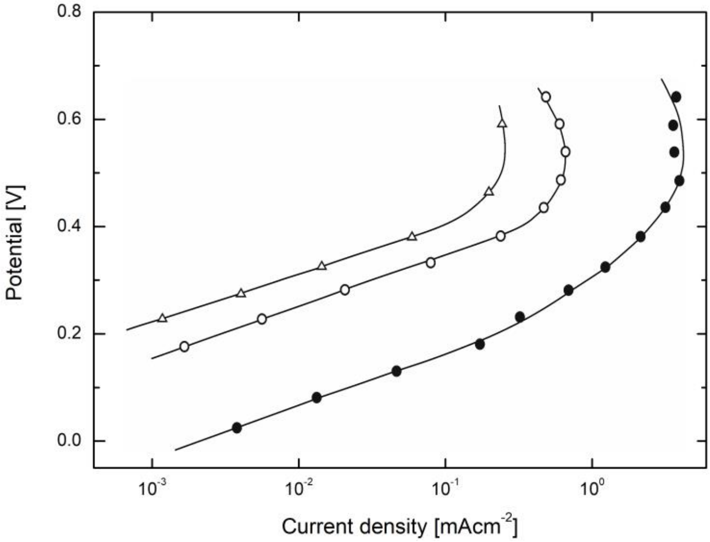

**Fig. 5** – *Steady state polarization curves for the FA electrooxidation at the:* Δ – Pt *and* 79 mol% Pt, 21 mol% Ru*; without* (○) *and with* (●) 10-3 M Tl + *in the solution* 1.0 M HClO4 + 0.25 M HCOOH *at* 25°C.

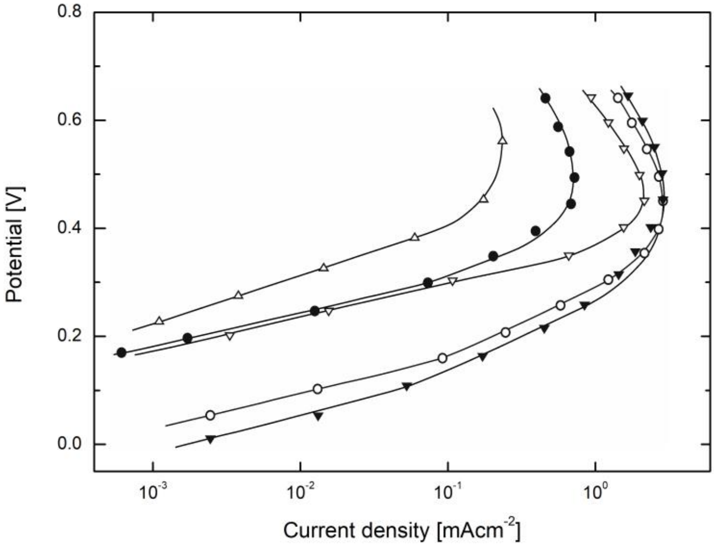

**Fig. 6** – *Steady state polarization curves for the FA electrooxidation at the:* Δ – Pt *and* 34 mol% Pt, 66 mol% Ru; *without* (●) *and with* (▽) $10^{-5}$ M $Tl^+$; ○ – $10^{-4}$ M $Tl^+$ *and* ▼– $3 \cdot 10^{-4}$ M $Tl^+$ *in the solution* 1.0 M $HClO_4$ + 0.25 M HCOOH *at* 25°C.

The catalytic effect of the modified Pt/Ru electrodes is plausibly a result of the change in stability of $OH_{ad}$ caused by the presence of Tl adatoms. The Tl adatoms, placed on the Pt atoms probably interact with the OH species of the adjacent Ru atoms. A bond formed between Tl and OH particles increases the enthalpy of the bond between the OH species and the anode surface. This causes formation of Ru-OH species at these anodes at lower potentials compared to Pt/Ru anodes.

It is also possible that the catalytic effect of the Tl adatoms is partly caused by the third-body effect. Owing to the steric hindrance and lower number of assemblies of free, adjacent Pt atoms, the Tl adatoms prevent adsorption of the intermediates, which require more adjacent Pt atoms for their adsorption.

The above presented results related to the catalytic effect of the HCOOH oxidation at Pt/Ru alloys modified with Tl adatoms indicate the great perspective of these catalysts in the fuel cell application

## 4 Conclusions

The catalytic effect of thallium adatoms deposited at underpotential is found for the electrooxidation of FA on platinum-ruthenium alloys.

The voltammetry curves show deposition of the $Tl^+$ ions on polycrystalline solid solution of the Pt and Ru alloy at underpotential. Tl is desorbed from the Pt/Ru electrodes only at potentials of 0.8 V and higher. The voltammetry and polarization curves demonstrate that the Tl adatoms catalyze the HCOOH oxidation in an acid environment. The catalytic effect depends on the coverage degree of the electrode with adatoms. The modified Pt/Ru electrodes with an optimal degree of coverage with Tl adatoms allow for the HCOOH oxidation at 180 mV more negative potentials than unmodified Pt/Ru electrodes. The catalytic effect is plausibly consequence due to the interactions between the Tl adatoms, placed on Pt atoms, and the OH species of adjacent Ru atoms. These interactions stabilize the RuOH species and allow for their formation at lower potentials compared to the Pt/Ru electrodes. The RuOH species electrooxidize the adsorbed intermediates $-CO_{ad}$ and $=C(OH)_{2,ad}$ and thus release Pt atoms for the oxidation of subsequent HCOOH. To a lesser extent, the catalytic effect is caused by the third body effect. Due to the steric hindrance and lower number of assembles of free adjacent Pt atoms, the Tl adatoms prevent the adsorption of intermediates that require more free adjacent Pt atoms for their adsorption.

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