



PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

September 22-26, 2014
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ELECTROCHEMICAL OXIDATION OF FORMIC ACID ON Pt- AND Pd-BASED BIMETALLIC CATALYSTS

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ABSTRACT

Electrochemical oxidation of HCOOH was studied on single metal Pt, Pt/C and Pd black catalysts, on bimetallic surfaces of Pt-Au and Pd-Au bulk electrodes as well as on Pt-Co/C, Pt-Au/C and Pt-Pd nanocatalysts. The electrocatalysts were characterized by cyclic voltammetry and CO_{ads} stripping, while the HCOOH oxidation was examined under the potentiodynamic and potentiostatic conditions. The results indicate that the ensemble effect is crucial for high selectivity of Pt-based surfaces toward dehydrogenation path. The enhancement of HCOOH oxidation rate on Pd-based surfaces was reached through electronic modification exhibited by the second metal. Our results also point out that the self-poisoning of the electrocatalyst by CO_{ads} produced by the incomplete CO₂ reduction is related to the strength of the Pt- and Pd-adsorbate bond, which has to be considered in designing of an electrocatalyst for HCOOH oxidation.

INTRODUCTION

Polymer electrolyte membrane fuel cell (PEMFC) using formic acid as a fuel, i.e. direct formic acid fuel cell (DFAFC) is a viable power generator for portable electronic devices [1]. Its advantages over direct methanol fuel cell (DMFC) are higher theoretical open circuit voltage, lower crossover of HCOOH through the polymer membrane compared to CH₃OH and non-toxicity of HCOOH. A problem that still needs to be resolved is the activity and stability of the anode electrocatalyst.

It is generally accepted that on Pt surface HCOOH oxidizes to CO₂ via a dual path mechanism [2,3,4]. Direct path is dehydrogenation of HCOOH molecule without forming of CO_{ads}. Indirect path comprises dehydration of HCOOH molecule with the formation of CO_{ads} and its further oxidation to CO₂. In order to prevent poisoning of the catalyst by CO_{ads}, the dehydrogenation path has to be predominant. This can be achieved by combining Pt with some other metal performing its role through (i) bifunctional mecha-

nism, (ii) electronic effect, or (iii) ensemble effect [5]. Bifunctional mechanism is operative when the second metal is capable to adsorb oxygen-containing species at lower potentials than Pt, thus facilitating the oxidation of CO_{ads} formed on Pt sites. Electronic effect refers to the modification of the electronic structure of Pt atoms, generally resulting in change of the adsorption ability of Pt. If this modification weakens the bond between Pt and CO_{ads} , the electronic effect reduces Pt poisoning. The ensemble effect is based on the fact that the dehydration path requires at least three contiguous Pt atoms, whereas the dehydrogenation path requires at most two Pt atoms [6]. Therefore, when large Pt surface is interrupted by foreign atoms, dehydrogenation path is favored and CO_{ads} formation is suppressed.

Contrary to Pt, investigation of HCOOH oxidation on Pd indicated that the reaction on this metal proceeds exclusively through the dehydrogenation reaction path, since no poisoning CO_{ads} could be detected under the potentiodynamic conditions [7]. Despite this, slow deterioration of the activity of Pd anode during the DFAFC operation was reported [8].

SINGLE METAL Pt AND Pd ELECTROCATALYSTS

Polarization curves of HCOOH oxidation on polycrystalline Pt [9] and Pt/C nanocatalyst [10,11] show well-established feature of this reaction. At low potentials HCOOH oxidizes through the direct path with the simultaneous formation of CO_{ads} in the indirect path [2]. Increasing coverage of CO_{ads} reduces the number of Pt sites available for the direct path, and the current density reaches a plateau. Subsequent formation of oxygen containing species on Pt enables the oxidative removal of CO_{ads} . As more Pt sites are being released, the HCOOH oxidation current increases until Pt-oxide, inactive for HCOOH oxidation, is formed. This results in the current peak. In the backward sweep the sharp raise of HCOOH oxidation current coincides with reduction of Pt oxide. The currents are much higher than in the forward sweep, because Pt surface is freed of CO_{ads} .

Potentiodynamic polarization curves of HCOOH oxidation on Pd black [12,13] showed no significant hysteresis between the anodic and the cathodic direction, thus indicating low poisoning by CO_{ads} . This is in accord with the literature data [7] about the predominance of the dehydrogenation path.

Based on the above mentioned bifunctional, electronic and ensemble effect, various types of bimetallic Pt-Au, Pt-Co, Pd-Au and Pt-Pd catalysts were prepared and investigated [9-13] in order to enhance the activity of Pt and Pd catalysts for HCOOH oxidation.

Pt-Au ELECTROCATALYST

Polycrystalline Pt and Au electrodes were electrochemically modified by sub-monolayers of Au and Pt, respectively [9]. These surfaces served as the model catalysts to establish the role of the ensemble and the electronic effect in the HCOOH oxidation, since Au cannot provide oxygen containing species necessary for the bifunctional effect. It was assumed that electronic modification of Pt by Au atoms will be favoured on Au electrode modified by Pt, because all the Pt atoms are in contact with Au substrate, while on Pt electrode modified by Au only the Pt atoms contacting the circumference of Au islands can be altered by the presence of Au. On both types of the Pt-Au surfaces the surface fraction of Pt was varied between 0.14 and 0.86.

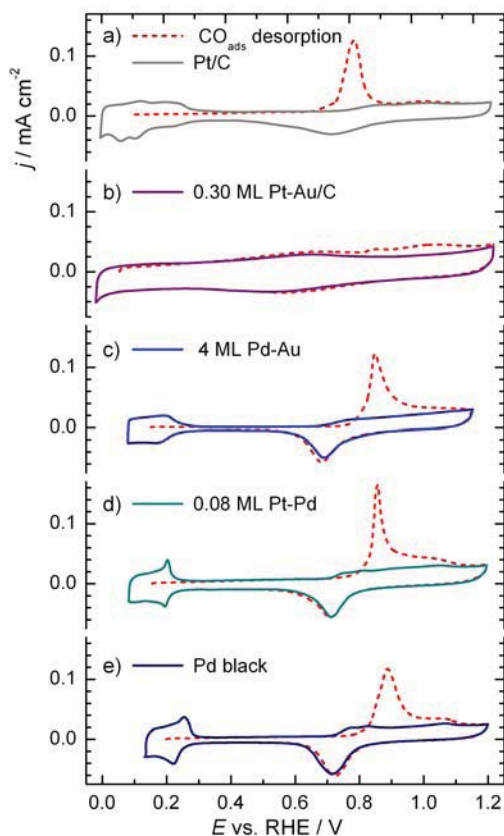


Fig 1. Stripping voltammograms of CO_{ads} and the first subsequent cyclic voltammograms recorded in 0.1 M H_2SO_4 ; $\nu = 20 \text{ mV s}^{-1}$.

on pure Pt was found, which imply that Au substrate exhibits an electronic influence on Pt atoms deposited on it. The same behaviour was also

In addition to the model catalysts, Pt-Au/C nanoparticles were prepared by simultaneous reduction of Au and Pt precursors in the presence of high area carbon and by reduction of Pt precursor on already prepared Au/C nanoparticles [10]. The Pt:Au surface ratio of on the prepared nanoparticles was 0.70:0.30, 0.55:0.45 and 0.30:0.70.

Since the cyclic voltammogram of Pt-Au electrodes show characteristics of both Pt and Au surfaces, the Pt:Au surface ratio was determined by using the charges for the oxide reduction of the pure Pt and Au surfaces. A negative shift in the peak potential for the Pt oxide reduction on Au surfaces modified by Pt with respect to the peak position

observed for the Pt-Au/C nanoparticles. The onset and the peak potentials for the CO_{ads} oxidation on bare Pt and on Au modified Pt electrode are similar. This result as well as the same peak potentials for the Pt oxide reduction on these two surfaces confirms the assumption that the electrochemical behavior of bare Pt and Pt partially covered by Au are similar due to lack of the electronic modification of Pt by Au. The CO_{ads} oxidation on Au modified by Pt and on Pt-Au nanoparticles is delayed with respect to Pt (Fig. 1a and 1b) and the peak potential is as more positive as the Pt surface fraction decreases. Stronger adsorption of CO and OH species on Pt in contact with Au has also been reported for the bulk and surface Pt-Au alloys [14] and ascribed to the electronic interactions.

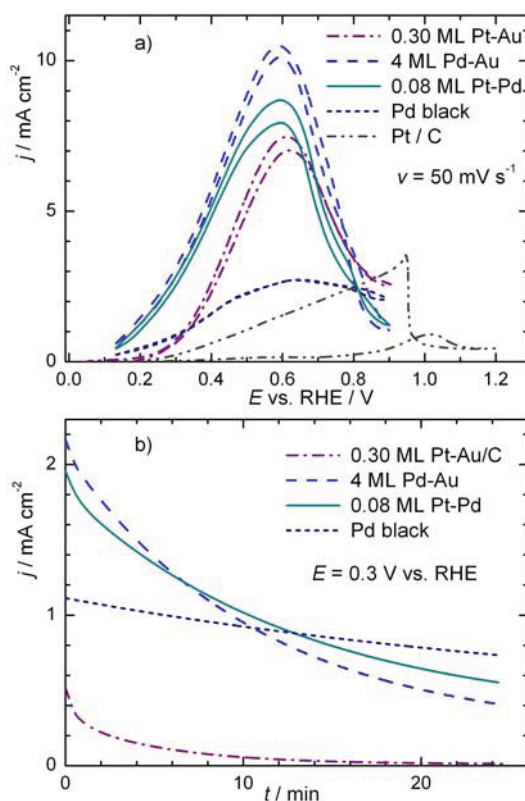


Fig.2 a) Potentiodynamic polarization curves in $0.1 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M HCOOH}$ and b) Decay of the HCOOH oxidation.

dehydration path as the size of Pt domains on the Pt-Au surface decreases (ensemble effect). The HCOOH oxidation rate is similar on Au modified Pt and on Pt modified Au surfaces with a similar Pt fraction, although they

On bimetallic Pt-Au surfaces the HCOOH oxidation takes place exclusively at Pt sites, because Au is inactive for the oxidation of organic molecules before the oxide region. As Pt surface fraction decreases, the plateau corresponding to HCOOH dehydrogenation increases and transforms to peak (Fig.2a). Also, the peak corresponding to the reaction on the Pt sites released after CO_{ads} oxidation decreases and even vanishes on the curve for surfaces with the Pt fraction below 0.3. The backward scan for the same surfaces is almost retraced with the forward one, which shows that Pt is not poisoned by CO_{ads} . This indicates that dehydrogenation path overcomes the

differ in electronic modification of Pt atoms. This leads to a conclusion that the ensemble effect is crucial for high selectivity of Pt-Au surfaces toward dehydrogenation path.

When the activities of Pt-Au surfaces and bare Pt were compared at the potential of 0.4 V, all of them calculated per Pt surface area, it was found that the most active Au electrode modified by Pt sub-monolayer and the most active Pt-Au/C nanocatalyst exhibited about fifty and forty times higher current densities than bulk Pt and Pt/C nanocatalyst, respectively. It is interesting that the Pt-Au/C catalyst with Pt fraction of 0.30, which was found to be the most active under the potentiodynamic conditions, in a chronoamperometric test lost its activity rapidly (Fig.2b). The potentiodynamic curve recorded for this catalyst after the activity loss show a profile typical for dehydrogenation of HCOOH without poisoning by CO_{ads} . Thus, instability of Pt islands on the Au surface is not responsible for the activity loss. However, deactivation by CO_{ads} produced by the CO_2 reduction can not be excluded. The reason for so rapid poisoning of the catalyst with Pt fraction of 0.30 could be the strongest electronic modification of Pt by neighboring Au atoms because in this catalyst the Pt surface fraction is the lowest and consequently the number of Pt atoms in close contact with Au is the highest.

Pt-Co ELECTROCATALYST

Bulk Pt_3Co and $\text{Pt}_3\text{Co}/\text{C}$ and PtCo/C nanocatalysts were investigated for the CO_{ads} and HCOOH oxidation [11]. Pt_3Co alloy with Co electrochemically leached from the surface (“Pt skeleton”) was employed to separate electronic effect from the ensemble and bifunctional effects of Co.

The oxidation of CO_{ads} on Pt_3Co commenced earlier than on Pt. This can be attributed to the weakened bond between Pt and CO_{ads} , but also to the facilitated CO_{ads} oxidation by the oxygen-containing species adsorbed on Co atoms. The CO_{ads} oxidation on Pt_3Co with “Pt skeleton” structure was similar as on Pt surface indicating that bifunctional mechanism is stronger than the electronic modification of Pt by Co.

The onset potentials for the HCOOH oxidation on Pt_3Co alloy and on Pt were similar. CO_{ads} was present on both electrodes, but the coverage was lower on Pt_3Co than on Pt. As a consequence, the HCOOH oxidation current density at 0.4 V was about seven times higher on Pt_3Co . On “Pt skeleton” and bulk Pt the indirect path is predominant over the direct path and the coverage by CO_{ads} is substantial. This suggests that the enhanced activity of Pt_3Co alloy compared to Pt is caused by the ensemble effect. The comparison of CO_{ads} and HCOOH oxidation on $\text{Pt}_3\text{Co}/\text{C}$ and PtCo/C with the same reaction on Pt/C were qualitatively the same as on bulk materials.

Pd-Au ELECTROCATALYST

Polycrystalline Au electrode was modified by electrodeposition of thin Pd films ranging from 1 to 17 monolayer (ML) equivalents [12]. The CO_{ads} stripping charge was used for the determination of the Pd surface area. The cyclic voltammograms of Pd-Au films show that hydrogen adsorption/desorption charge increases with increasing Pd thickness. The potentials of Pd-oxide formation and Pd-oxide reduction on Pd modified Au films are slightly more positive comparing to Pd black (Fig.1c and 1e). Au substrate also influences oxidation of CO_{ads} on Pd. The onset potential of CO_{ads} oxidation on 1 ML Pd-Au is more positive than on Pd black, while with increasing Pd thickness it shifts negatively and approaches the onset potential on Pd black. Stronger bonding of the adsorbates on Pd in contact with Au than on pure Pd originates in the electronic modification of Pd by Au, as predicted by Norskov's group [15].

Potentiodynamic polarization curves of HCOOH oxidation on Pd black and Pd-Au show enlarged activity with increasing Pd thickness, reaching a maximum current density at 4 ML Pd-Au film (Fig.2a). At the thicker Pd layers the activity slowly decreases and the position of the maximum shifts positively reaching a potential of the plateau on Pd black. However, the current densities on the thickest Pd-Au film are still three times higher than on Pd black. The potential of maximum current is well below the potential for Pd-oxide formation, so the water-surface interactions could explain the deactivation of Pd for HCOOH adsorption and oxidation [14]. Bonding of HCOOH molecule with Pd on Pd-Au surfaces is also stronger than on pure Pd, which explains higher HCOOH oxidation rate on Pd-Au.

The results of the chronoamperometric stability test of Pd black and Pd-Au electrodes (Fig.2b) reveal that the least active surface of Pd black exhibits the lowest activity loss of 35 %. The highest activity loss of even 80 % was detected on 4 ML Pd-Au, which is the surface with the highest currents under the potentiodynamic conditions. After the stability test, 4 ML Pd-Au was subjected to the potential cycling. It was shown that the activity increased over cycling suggesting that deactivation at 0.3 V is caused by accumulation of a species that can be oxidatively removed from the surface. It was postulated that this species is CO_{ads} formed in the electrochemical reduction of CO_2 , which is the product of HCOOH oxidation [16]. The experiments with the electrochemical reduction of CO_2 dissolved in the electrolytes supported this assumption.

Pt-Pd ELECTROCATALYST

Pd black was modified by 0.02–0.12 ML of Pt by spontaneous displacement method [13]. The CO_{ads} stripping charge was used for the determination of the electrochemical active surface area. The activity of Pt-Pd catalysts for the CO_{ads} oxidation is similar to Pd black (Fig.1d and 1e). Although the CO_{ads} stripping peaks for pure Pt and Pd are separated by ca. 0.2 V, the CO_{ads} stripping for the Pt-Pd catalysts show a singular peak.

Modification of Pd black by sub-monolayer of Pt significantly enhances its activity for HCOOH oxidation (Fig. 2a). With increasing of Pt coverage from 0.02 to 0.08 ML the maximum current density raises, but further increase in Pt coverage leads to a gradual decrease in the activity. The hysteresis between the forward and backward scans on Pt-Pd catalyst is minor, indicating that direct path in HCOOH oxidation predominates.

The current-time transients presented in Fig.2b show that the initial activity of Pt-Pd is much higher compared with Pd black. However, the activity loss of even 75% was observed for Pt-Pd catalyst over 25 min.

The activity of the most active modified surfaces toward HCOOH oxidation in potentiodynamic and potentiostatic conditions is presented in Fig.2a and 2b. Pt-Au binds the HCOOH molecules too strongly and the poisoning by CO_{ads} formed as the product of CO_2 reduction is more intense than on Pt-Pd and Pd-Au catalysts. Rational synthesis and optimization of catalytic properties of nanoparticles consisting of an Au core, covered by a Pd shell, onto which Pt clusters are deposited is challenge for the future investigation.

CONCLUSION

A high selectivity of Pt-based surfaces toward dehydrogenation path is reached on Au and Pd surfaces modified by a low amount of Pt. Electronic modification of Pd and Pt by Au substrate causes their stronger interactions with HCOOH and CO, thus increasing HCOOH oxidation rate, but also accelerating the poisoning by CO_{ads} formed in the incomplete reduction of CO_2 as the reaction product. Therefore, the activity and the stability of the electrocatalyst have to be balanced.

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