



The origin of high activity of Pt–Au surfaces in the formic acid oxidation

Maja D. Obradović^a, Amalija V. Tripković^a, Snežana Lj. Gojković^{b,*}

^a Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, P.O. Box 473, 11000 Belgrade, Serbia

^b Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P.O. Box 3503, 11000 Belgrade, Serbia

ARTICLE INFO

Article history:

Received 19 May 2009

Received in revised form 20 August 2009

Accepted 21 August 2009

Available online 31 August 2009

Keywords:

Formic acid electrooxidation

Platinum

Gold

Ensemble effect

Fuel cell

ABSTRACT

We have investigated the oxidation of HCOOH on Au-modified Pt (Au@Pt) and Pt-modified Au (Pt@Au) electrodes to establish the role of the ensemble and the electronic effect in the catalysis of this reaction. The surfaces were modified by the electrodeposition of sub-monolayers. Cyclic voltammetry in the supporting electrolyte and CO_{ads} stripping have shown that the electronic Pt–Au interactions are insignificant on Au@Pt, but considerable on Pt@Au. Oxidation of CO_{ads} on Au@Pt commenced at the same potentials as on bare Pt, whereas on Pt@Au the oxidation was delayed for ~0.2 V. Both types of Pt–Au surfaces were found to be more active toward the oxidation of HCOOH compared to bare Pt, exhibiting the maximum activity at Pt fraction between 0.15 and 0.25 with the enhancement factor of more than two orders of magnitude. On bimetallic surfaces the amount of CO_{ads} formed by HCOOH dehydration was low and decreased with decreasing Pt fraction. It was concluded that the high activity of Pt–Au surfaces is caused by the increased selectivity toward the HCOOH dehydrogenation. Similar behavior of Pt–Au surfaces in the HCOOH oxidation, regardless on the Pt–Au electronic interactions, leads to the conclusion that the ensemble effect plays dominant role in the catalysis of HCOOH oxidation.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) using formic acid as a fuel, i.e. direct formic acid fuel cell (DFAFC), has been attracting significant attention since recognition of its advantages over direct methanol fuel cell (DMFC). Crossover of formic acid through the polymer membrane is lower than that of methanol [1] and the equilibrium and the onset potential of the oxidation of HCOOH are less positive than that of CH₃OH [2]. Besides better performance of DFAFC than DMFC at ambient temperature, a somewhat lower toxicity of formic acid than methanol makes DFAFC a promising candidate for power source in portable electronics devices [3].

The mechanism of the formic acid oxidation on Pt involves two reaction paths occurring in parallel [4]. Direct path involves dehydrogenation of HCOOH molecule which produces CO₂, most likely via HCOO as a reactive intermediate [5]. Indirect path is dehydration of HCOOH molecule with the formation of CO_{ads} acting as the poisoning species (at low potentials) or reactive intermediate (at high potentials). Since high activity at low potentials is necessary for high power performance, the presence of CO_{ads} on the electrode surface is to be avoided. This can be achieved on bimetallic surfaces with the second metal that provides oxygen containing species at low potential and thus facilitates oxidative removal of CO_{ads}; the

effect known as the bifunctional effect. Another approach is to favor dehydrogenation path by interrupting large Pt surfaces by foreign atoms, which is known as the third-body or the ensemble effect [6]. This 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, as theoretically predicted by Neurock et al. [7] and experimentally verified by Cuesta et al. [8]. The third possibility is that the second metal modifies the electronic structure of Pt and changes interactions of Pt with CO_{ads} or possibly influences ability of Pt to dehydrate or dehydrogenate HCOOH molecule. This is designated as the electronic effect [6].

While promotion of the methanol oxidation on Pt is most expressed in the presence of Ru and explained by the bifunctional mechanism, the situation with the formic acid oxidation seems to be different. A broad range of metals of rather different character was found to have significant influence on the reaction rate on Pt by shifting the onset potential in the negative direction and increasing the current density, which is generally ascribed to a suppression of the reaction path via CO_{ads}. Adatoms of Pb on polycrystalline Pt [9], Bi on Pt(1 1 1) [10], and Sb on Pt(1 0 0) [11] were found to enhance the reaction rate up to a factor of 70, 40, and 30, respectively. The similar effect was also found on a Pt–Pb alloy [12,13] and Pt–Pb nanoparticles [14], as well as on PtBi alloys [15,16]. The enhancement effect of Pb was proposed to be due to an electronic effect [12], while for Pt–Bi catalysts an electronic effect [10,15], an ensemble effect [15,16], but also a bifunctional mechanism [16] were considered. Adsorbed As [17] and Se [18] on Pt were reported to significantly reduce poisoning, probably through an ensemble

* Corresponding author. Tel.: +381 11 3303 753; fax: +381 11 3370 387.
E-mail address: sgojkovic@tmf.bg.ac.rs (S.Lj. Gojković).

effect. Adatoms of Sn [19] and Pt–Sn alloy [20] also increased the reaction rate with respect to pure Pt, likely through combination of an electronic interactions and a bifunctional mechanism [19]. Pt–Mo bulk alloy [21] and electrodeposited Pt–Co nanoparticles [22] were also investigated and found to be more active than Pt. Pure Pd can oxidize HCOOH and its surface is less poisoned than Pt [23]. Expectably, very high activity was found for Pt–Pd catalysts [23–25], which was firstly ascribed by an electronic effect [23] or recently to the increased resistance to poisoning without any synergistic effects between Pt and Pd [25]. Contrary to Pd, Ru is able to adsorb HCOOH, but through dehydration path producing poisoning CO_{ads} [26]. Thus, Pt–Ru catalyst performed better than Pt only at potentials over 0.45 V [27], where CO_{ads} is oxidized by oxygen containing species on Ru. However, an ensemble effect can reduce CO_{ads} coverage of Pt–Ru surfaces, as shown by the alloys with Pt:Ru ratio of 1:1 [26].

Bimetallic Pt–Au surfaces have been investigated as chemical and electrochemical catalysts since Sachtler et al. [28] reported that cyclohexene dehydrogenation rate was higher at Pt(1 0 0) covered by Au and at Au(1 0 0) covered by Pt, compared to bare Pt(1 0 0). In the last several years Pt–Au surfaces have been extensively studied as the electrocatalyst for the oxidation of formic acid. Pt spontaneously deposited on Au(1 1 1) [29], Pt electrodeposited on Au [30], Pt-decorated Au nanoparticles [31–35] and Pt–Au alloy nanoparticles [31,36,37] were investigated. All the studies agree that Pt–Au surfaces are more active than pure Pt, particularly those with low coverage by Pt. Among three possible mechanisms for the enhancement of Pt activity, the bifunctional effect can be ruled out since the oxidation of Au occurs at the potentials much more positive than the oxidation of Pt. Kristian et al. proposed that the ensemble effect [32] and possibly electronic effect [34] may increase the reactivity of the Pt entities on Au substrate. Park et al. [31] also believe that the ensemble effect is operative, but higher current densities at potentials below 0.2 V ascribe to the electronic modification of Pt atoms which results in the strong interactions of HCOOH with Pt. Obviously, it is difficult to separate the contributions of the ensemble and the electronic effect since both of them can be present in the Pt–Au alloys and on Pt-decorated Au surfaces.

In order to prove which of these effects plays the dominant role in HCOOH oxidation, we investigated two types of Pt–Au surfaces. The first one is polycrystalline Pt decorated by monolayer Au islands (designated as Au@Pt) where the electronic effect in the formic acid oxidation should be minimized. This is because the reaction takes place exclusively at Pt sites (Au is inactive for the oxidation of organic molecules before the oxide region) and only the electronic states of Pt atoms contacting the circumference of Au islands can be altered by the presence of Au. The second surface investigated was polycrystalline Au decorated by Pt islands (designated as Pt@Au) where the conditions for the ensemble effect are similar as on Au@Pt surface, but the electronic effects should be favored since Au atoms are below all deposited Pt atoms.

2. Experimental

Polycrystalline platinum ($A=0.196\text{ cm}^2$) and gold ($A=0.159\text{ cm}^2$) electrodes in the form of rotating disc (Tacusel) were used in this study. The electrodes were polished with an Al_2O_3 suspension (particle size 0.1 and 0.05 μm) and cleaned ultrasonically in high purity water. Before each experiment the electrodes were cleaned by applying at least 10 potential scans in the potential range 0.03–1.60 V vs. RHE at a scan rate 100 mV s^{-1} . Modification of Pt electrode by Au adatoms and Au electrode by Pt adatoms were performed by several cycles in 0.5 M H_2SO_4 containing 0.1 mM HAuCl_4 or H_2PtCl_6 , respectively. HAuCl_4 was dissolved in 0.1 M HCl to avoid hydrolysis [38]. The surface cover-

age by adatoms was varied by the number of potential cycles. After modification the electrode was rinsed with water and transferred into a cell containing 0.5 M H_2SO_4 solution. Then several potential cycles were applied at a rate of 50 mV s^{-1} and the last voltammogram was used for the calculation of the surface coverage by adatoms. Further, in the positive going scan, the potential was held at 0.05 V and HCOOH was added into the electrolyte. After 2 min the scan was continued at the rate of 1 mV s^{-1} (quasi steady-state measurements) or at 50 mV s^{-1} (potentiodynamic measurements). For the CO stripping measurements, pure CO was bubbled through the electrolyte for 20 min while keeping the electrode potential at 0.12 V vs. RHE [31]. After purging the electrolyte by N_2 for 30 min to eliminate the dissolved CO, the adsorbed CO was oxidized in an anodic scan at 20 mV s^{-1} . Two subsequent voltammograms were also recorded to verify the completeness of the CO oxidation.

Real surface area of the Pt electrode before the modification by Au was calculated from the hydrogen desorption charge corrected for the double-layer charging. Assuming a charge of 210 $\mu\text{C cm}^{-2}$ for monolayer hydrogen adsorption, a roughness factor of 2.2 ± 0.1 was estimated. This result was confirmed by the calculation of the charge of CO stripping (assuming 420 $\mu\text{C cm}^{-2}$ for the CO monolayer). In the applied potential range, i.e. with the anodic limit of 1.6 V, and taking into account the roughness factor, the charge for the reduction of platinum oxide monolayer was calculated to be 440 $\mu\text{C cm}^{-2}$. Real surface area of Au electrode was determined from the reduction of the monolayer of gold oxide, which is formed when the anodic limit of the voltammogram is set just before the onset of oxygen evolution, i.e. at the Burshtein's minimum [39]. The charge of the reduction of monolayer gold oxide was 400 $\mu\text{C cm}^{-2}$ and corresponds to the value used by Angerstein-Kozłowska et al. [40]. Approximately the same roughness factor as for Pt electrode was calculated, which is to be expected since both electrodes were polished in the same way. Surface coverage of the modified electrodes was determined by using the charges for the oxide reduction of the pure Pt and Au surfaces.

All the experiments were performed in three-compartment electrochemical glass cells with Pt wires (99.998% purity, Aesar) as the counter electrodes and saturated calomel electrodes (SCE) as the reference electrodes. All the potentials reported in the paper are expressed on the scale of the reversible hydrogen electrode (RHE). The electrolytes were prepared with high purity water (Millipore, 18 $\text{M}\Omega\text{ cm}$ resistivity) and the chemicals provided by Merck. The experiments were conducted at $298 \pm 0.5\text{ K}$. A Pine RDE4 potentiostat and Philips PM 8143 X–Y recorder were employed.

3. Results and discussion

3.1. Preparation and characterization of Pt–Au surfaces

The Au@Pt surfaces were prepared by applying one to eight potential cycles in HAuCl_4 solution, which produced surface coverage of Pt by Au adatoms between 0.13 and 0.86. A typical cyclic voltammogram of an Au@Pt surface is presented in Fig. 1 and compared to the voltammograms of a bare Pt and a bare Au electrode. The voltammogram of the Au@Pt electrode is a superposition of the voltammograms of both metals. It is important to note that irrespectively on the Pt:Au surface ratio, the positions of the peaks for the reduction of Au and Pt oxides on Au@Pt electrodes were approximately the same as the peaks on the pure metals. This result supports the assumption that the electronic states of Pt are not altered by the presence of Au.

The fraction of Pt and Au on the modified surface was estimated by comparing the charges for the Au and Pt oxide reduction with those of the pure metals. The calculated values summed to one within the error of 10%, which implies that 2D Au islands were

Download English Version:

<https://daneshyari.com/en/article/191493>

Download Persian Version:

<https://daneshyari.com/article/191493>

[Daneshyari.com](https://daneshyari.com)