

Spontaneous deposition of Pt on the Ru(0001) surface

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Abstract

Spontaneous deposition of Pt on a Ru(0001) single crystal surface has been demonstrated by in situ scanning tunneling microscopy and linear sweep voltammetry techniques. The immersion of a ultra-high vacuum (UHV) prepared Ru single crystal in a platinum-ion-containing solution results in the formation of monolayer-to-multilayer Pt deposits without application of an external potential. The coverage and morphology of the Pt deposit depend on the concentration of platinum ions and the time of immersion. This simple method can be applied to Pt deposition on Ru nanoparticles, which can considerably reduce Pt loading in Pt/Ru electrocatalysts. The electrochemical behavior of such Pt/Ru(0001) bimetallic surfaces depends on the coverage of the Ru electrode and amount and morphology of the Pt deposit, which indicates a pronounced electronic modification of the Pt adlayer due to a strong Pt/Ru interaction. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electrochemical deposition of metal monolayers on noble metal electrodes has attracted considerable interest over the years. This interest stems from the possibility of implementing strictly surface modifications on the electrodes studied, and these modified, bi-metallic surfaces can serve as model systems for studies that can help in the design of new catalysts. Underpotentially deposited metal adlayers have been used most often to modify the catalyst surface [1]. An alternative to this method is the so-called “spontaneous” or “irreversible” adsorption of non-noble metal cations on noble metal substrates. This deposition is accomplished by immersion of a clean noble metal surface in cation-containing solutions, which produces adlayers strongly interacting with the substrate without the application of an external potential [2,3].

Spontaneous deposition also occurs when the noble metal is immersed in a noble metal ion-containing solution, as recently shown by Wieckowski and coworkers [4,5] for the deposition of Ru adlayers on a

Pt(*hkl*) surface. The maximum coverage of the Pt electrode by the Ru deposit was reported to be not higher than 20% as inferred from Auger electron spectroscopy [4,5] and scanning tunneling microscopy (STM) measurements [6]. These surfaces showed considerable catalytic activity for the methanol oxidation reaction [4,7], which indicates that this method can be a promising alternative method of preparation for new catalysts. Spontaneous deposition was also reported for Pd on polycrystalline [2] and single crystal Pt electrodes [8,9]. A Pd deposit of up to a monolayer (ML) was found in Ref. [8], while the amount of deposited Pd in the second case was considerably lower [9].

In this work we describe a study of the spontaneous deposition of Pt on a Ru(0001) single crystal surface studied by voltammetry and in situ STM. Unlike the previously reported spontaneous deposition of noble metals on noble metals [4–6,8,9], multilayer Pt deposits can be obtained. Ruthenium is a component of Pt/Ru fuel cell electrocatalysts for methanol and methanol reformate fuels [10,11], which explains the considerable attention that this system attracts. Spontaneous deposition of Pt on Ru could provide a simple method for well-controlled deposition of desired amounts of Pt on Ru nanoparticles that could lead to improved Pt/Ru electrocatalysts with considerably reduced Pt loadings.

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As is shown below, the morphology, the amount and the uniformity of the Pt deposit depend on the concentration of $[\text{PtCl}_6]^{2-}$ ions in the solution and the time of immersion. Voltammetry curves for such Pt/Ru(0001) bimetallic surfaces depend on the morphology of the Pt deposit and show a distinct difference from the curves for either Ru(0001) or Pt(111).

2. Experimental

The working electrode was a Ru(0001) single crystal $8 \times 3 \text{ mm}^2$ disk polished with diamond paste down to $0.3 \mu\text{m}$, obtained from Metal Crystals and Oxides, Cambridge, UK. The single crystal was additionally oriented to better than 0.1° . The single crystal electrode surface was prepared in ultra-high vacuum (UHV), following the standard procedure for Ru [12]. It consisted of two cycles of argon ion sputtering at room temperature and annealing at 1400°C , followed by five cycles of oxygen adsorption and desorption in an oxygen atmosphere of 10^{-7} Torr at 500 and 1400°C , respectively. A final flash annealing was done in UHV at 1400°C to remove the residual oxygen from the surface. The crystal was allowed to cool down in the vacuum chamber. The chamber was then filled with ultra-pure Ar and the crystal was transferred from the UHV chamber into an Ar-filled glove box and immersed in the PtCl_6^{2-} solution for a certain time. After the immersion in the solution, the crystal was thoroughly rinsed with $0.1 \text{ M H}_2\text{SO}_4$ and ultra pure water and, protected by a water drop, was transferred to an electrochemical or STM cell. Solutions were prepared from Optima* sulfuric acid from Fisher and MilliQ UV-plus water (Millipore). An $\text{Ag}|\text{AgCl}|3 \text{ M KCl}$ electrode was used as a reference electrode and all potentials are quoted with respect to its standard poten-

tial. The in situ STM studies were performed using a Molecular Imaging Pico STM with a 300S scanner and a Molecular Imaging Model 300S Pico bipotentiostat. The cell, made of Teflon, exposed an area of ca. 0.3 cm^2 and had a volume of ca. 1.5 cm^3 . Prior to each experiment, an STM tip was prepared by etching a 80:20 Pt/Ir wire in a CaCl_2 solution and insulating it with Apiezon wax.

3. Results and discussion

The STM investigation of the morphology of Ru(0001) and Ru(0001)/Pt surfaces obtained by the above procedure was carried out in $0.1 \text{ M H}_2\text{SO}_4$ solution. A representative view of the Ru(0001) surface is shown in Fig. 1A. The image was recorded at the potential of $-0.150 \text{ V vs. Ag}|\text{AgCl}|3 \text{ M KCl}$, which is in the double layer region for the Ru(0001) surface [13,14]. The straight and monoatomic steps running in the $\langle 11\bar{2}0 \rangle$ direction are clearly seen. The majority of the steps is equally spaced and is separated by atomically flat terraces giving an overall morphology of a well sputter-annealed Ru surface. The small bright spots visible at the Ru terraces are in the range of a monolayer height and they are probably the nuclei of the oxide formed during the transfer of the crystal from the Ar filled glove box into the STM cell.

The spontaneous deposition of Pt on Ru(0001) was carried out from $x \text{ M}$ ($x = 10^{-2}, 10^{-3}, 10^{-4}$) $[\text{PtCl}_6]^{2-} + 0.1 \text{ M H}_2\text{SO}_4$ solution. The Ru crystal was immersed in the platinum-containing solution immediately after the transfer from the UHV chamber to an Ar-filled glove box. A representative view of the Pt deposit formed during immersion for 30 min in a $10^{-3} \text{ M } [\text{PtCl}_6]^{2-} + 0.1 \text{ M H}_2\text{SO}_4$ solution is shown in Fig. 1B. The Pt deposit mainly consists of 3–10 nm-sized Pt

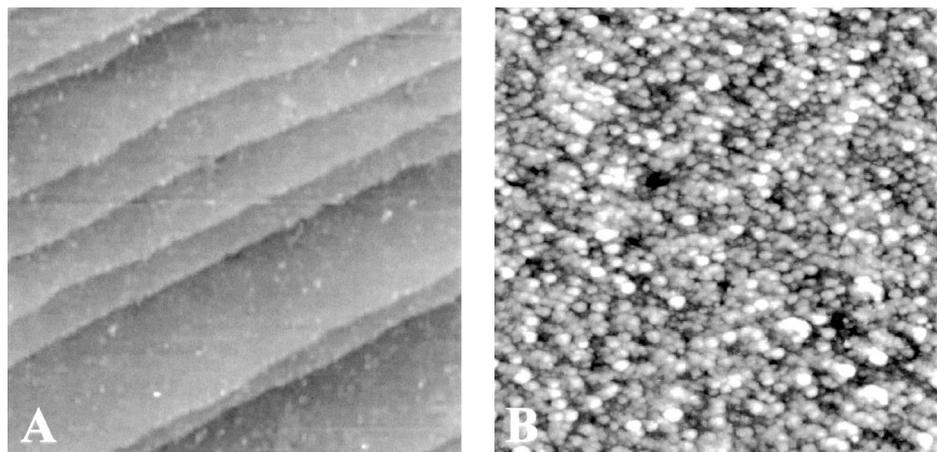


Fig. 1. STM images in H_2SO_4 solution of: (A) the Ru(0001) surface; (B) Pt spontaneously deposited on Ru(0001) in $1 \text{ mM H}_2\text{PtCl}_6 + 0.1 \text{ M H}_2\text{SO}_4$ solution (see text for details). Image (A): $260 \text{ nm} \times 260 \text{ nm}$, recorded at $-0.15 \text{ V vs. Ag}|\text{AgCl}|3 \text{ M KCl}$, Z range 2 nm ; image (B): $230 \text{ nm} \times 230 \text{ nm}$, recorded at open circuit potential, Z range 10 nm .

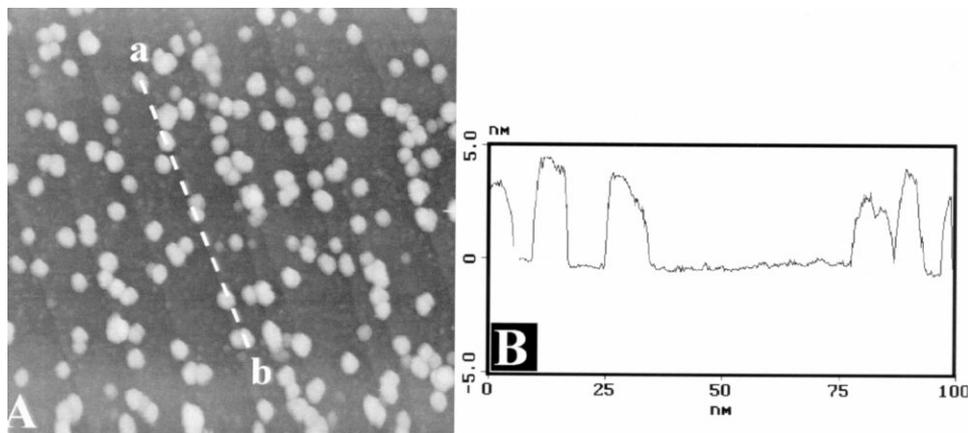


Fig. 2. (A) STM image ($200 \text{ nm} \times 200 \text{ nm}$) of Pt clusters spontaneously deposited on Ru(0001) in $0.1 \text{ mM H}_2\text{PtCl}_6 + 0.1 \text{ M H}_2\text{SO}_4$ solution (see text for details). (B) Cross-section of Pt clusters at the place in image (A) indicated by the dashed lines a and b. Image recorded at open circuit potential in $0.1 \text{ M H}_2\text{SO}_4$, Z range 5 nm .

clusters, which are closely packed and merged into a textured layer (Fig. 1B). In analyzing a number of STM images, no features associated with the Ru(0001) surface could be recognized, indicating that the coverage of the Pt deposit is close to 100%. A roughness analysis of the Pt layer shows that at least 10 Pt monolayers were deposited spontaneously. This result undoubtedly indicates that Pt deposits spontaneously on the Ru(0001) surface forming a multilayer deposit. This is quite different from the results for Ru/Pt(*hkl*) and Pd/Pt(*hkl*) spontaneous deposition systems [4,8,9] where submonolayer amounts of metal were deposited forming a morphology limited to one or two monolayers in height.

In a further study of spontaneous deposition of Pt on Ru(0001) the deposition conditions (concentration of $[\text{PtCl}_6]^{2-}$ and time of immersion) resulting in an uniform Pt deposit were investigated. The goal was to produce a deposit where the average amount of Pt was limited to 2–3 ML. The most representative results are described below.

The morphology of a Pt deposit on a Ru single crystal immersed in a $10^{-4} \text{ M } [\text{PtCl}_6]^{2-} + 0.1 \text{ M H}_2\text{SO}_4$ solution for 2 min is presented in Fig. 2A and B. One can see that the Ru surface is decorated with a great number of Pt clusters with the majority of them nucleated predominantly on the step edges. This is not surprising since the steps are known to be active places where preferential deposition occurs in conventional electrodeposition processes [15]. The Pt clusters have a columnar shape and a relatively uniform size. Their height is in the range of 3–5 nm (10–15 ML) and their diameter is between 6 and 10 nm (Fig. 2). The clusters cover about 35% of the Ru surface, which can be determined from the STM images. By assuming the average height of the clusters to be 4 nm ($\sim 13 \text{ ML}$, Fig. 3B), one can estimate that the total amount of Pt deposited is between 4 and 5 ML. Therefore, depending

on the deposition conditions (Fig. 1B vs. Fig. 2), Pt deposits of vastly different morphologies can be obtained on Ru(0001) surfaces.

A representative STM image of a Pt deposit obtained by immersing a freshly prepared Ru single crystal in the $10^{-2} \text{ M } [\text{PtCl}_6]^{2-} + 0.1 \text{ M H}_2\text{SO}_4$ solution for 1 min is shown in Fig. 3. The concentration of $[\text{PtCl}_6]^{2-}$, larger than that for Fig. 2 by two orders of magnitude, was used to assess clearly its effect on the nucleation density of Pt. The time of exposure was reduced in order to limit the Pt coverage to 1–2 ML. The entire Ru surface is covered with 2–6 nm-sized Pt clusters. There is an indication of a slight preferential deposition of Pt on

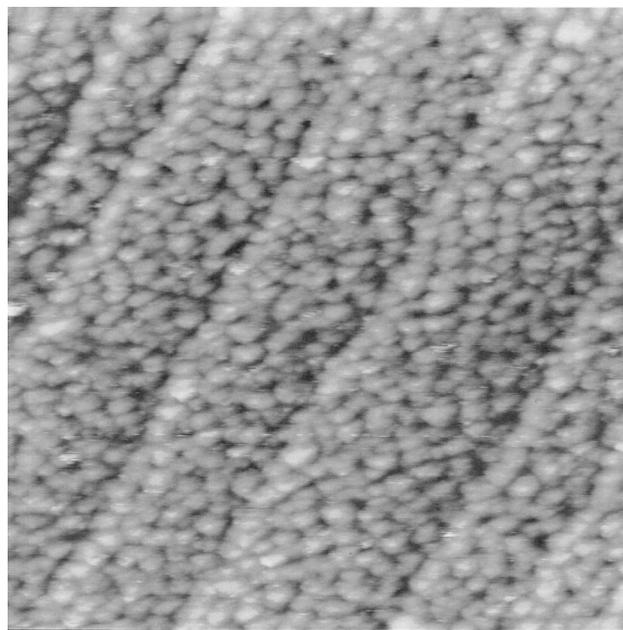


Fig. 3. STM image ($100 \times 100 \text{ nm}$) of a Pt adlayer spontaneously deposited on Ru(0001) in $10 \text{ mM H}_2\text{PtCl}_6 + 0.1 \text{ M H}_2\text{SO}_4$ solution (see text for details). Image recorded at open circuit potential in $0.1 \text{ M H}_2\text{SO}_4$, Z range 2 nm .

step edges. The average height of the Pt clusters deposited on the Ru terraces is 2 ML, while the clusters that are deposited along the step edges are in general one monolayer higher (3 ML). Since the height of the Pt clusters is uniform, the morphology of the underlying Ru(0001) surface (steps and terraces) is easily recognized (Fig. 3). The STM images show that about 92% of the Ru surface is covered and the total amount of deposited Pt is approximately 2 ML.

Although the solution concentration was not the same in these experiments a comparison of the amount of deposited Pt shows that it is related to the time of the crystal immersion. This is evident from a comparison of the amounts of deposited Pt in Fig. 2 (2 ML) and Fig. 3 (5 ML) with the amount of Pt deposited in Fig. 1 (> 10 ML). Furthermore, a close inspection of the morphology of Pt deposits obtained in experiments with a short immersion time (2 min, Fig. 2; and 1 min, Fig. 3) suggests that the nucleation density, i.e. the density of the Pt clusters on the Ru surface is dependent on the concentration of the $[\text{PtCl}_6]^{2-}$ ions. The effect of increasing the concentration of $[\text{PtCl}_6]^{2-}$ ions by two orders of magnitude is the most probable explanation as to why the density of the clusters in Fig. 3 is approximately 25 times higher than in Fig. 2, despite a shorter exposure time.

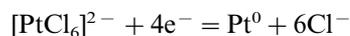
There is no general agreement on the mechanism of spontaneous metal deposition on noble metal substrates. It was ascribed to oxidative dissolution of immersed metal by metal cations from the solution, which is often called a cementation process [16], a chemical reaction with adsorbed hydrogen [2] and to a local cell mechanism involving PtOH formation [17]. The interaction of cations with surface M–OH species is another possible mechanism, since it is known that they can interact strongly with the noble metal oxides formed on the electrode surface [18].

It is interesting that there was no spontaneous deposition of Pt on a Ru(0001) surface, that was immersed in 0.1 M H_2SO_4 , 0.1 M HClO_4 or pure H_2O for some time (more than 1 min) prior to addition of $[\text{PtCl}_6]^{2-}$ ions. The formation of any observable Pt deposit was not detected by in situ STM experiments. This suggests that only a freshly UHV-prepared Ru(0001) surface in contact with a $[\text{PtCl}_6]^{2-}$ containing electrolyte is susceptible to spontaneous Pt deposition. In addition, it suggests that RuOH, which can form in contact with H_2O under such conditions, reduces or prevents spontaneous deposition of Pt. Our in situ surface X-ray scattering (SXS) and STM studies of the Ru(0001) surface in acidified solution [19] show that Ru interacts strongly with H_2O molecules even at open circuit potential and forms an adlayer similar to that of RuOH. The difference between the Ru– H_2O adlayer formed in contact with H_2O at open circuit potential and the RuOH adlayer formed by an applying oxidation poten-

tial is only in the Ru–O interlayer separation [19]. The Ru interaction with H_2O molecules could be enhanced when the immersing electrolyte contains some oxidizing species such as noble metal ions, which can promote oxidation of Ru. This can account for the observed spontaneous deposition of Pt on Ru(0001) from the $[\text{PtCl}_6]^{2-}$ solution. The driving force for this deposition could be the difference between the potential of $[\text{PtCl}_6]^{2-}$ reduction (onset of Pt deposition [20]), and the potential of Ru^0 oxidation (Eq. (1)).

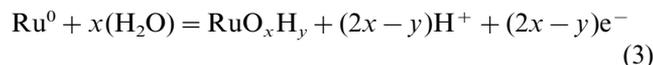
$$\Delta U = \Delta E_{\text{Pt}/\text{PtCl}_6^{2-}} - \Delta E_{\text{Ru}^0/\text{Ru}_{\text{oxidized}}} > 0 \quad (1)$$

Here $\Delta E_{\text{Pt}/\text{PtCl}_6^{2-}}$ stands for the equilibrium potential of reaction defined by Eq. (2)



$$(\Delta E [\text{V}] \sim 0.74 + 0.015 \log[\text{PtCl}_6]^{2-}), \quad (2)$$

while $\Delta E_{\text{Ru}^0/\text{Ru}_{\text{oxidized}}}$ stands for the reaction potential defined by a generalized Eq. (3),



It is not clear what kind of a Ru oxidation reaction might take place during spontaneous deposition of Pt. The oxidative dissolution of Ru can be excluded because it occurs at a potential more positive than the equilibrium potential of $\text{Pt}/[\text{PtCl}_6]^{2-}$ [21]. Ruthenium is well known to form the oxygen-containing RuOH species easily by Reaction (3) with $x, y = 1$. The onset of this reaction on Ru(0001) in non-adsorbing acid solutions is at $E = 0.05$ V vs. $\text{Ag} | \text{AgCl} | 3 \text{ M KCl}$ [13,14]. This is more negative than the equilibrium potential of $\text{Pt}/[\text{PtCl}_6]^{2-}$, and the condition for Pt spontaneous deposition defined by Eq. (1) is satisfied.

If the surface oxidation of Ru were limited to a monolayer range, the amount of Pt deposited would be limited to 1/4 of a monolayer since RuOH formation involves the exchange of one electron per atom, while Pt reduction requires four electrons per atom. The fact that Pt can form a multilayer deposit on a Ru surface indicates that either the oxidation of Ru to Ru(OH) is not limited to strictly one (surface) monolayer or a higher oxidation state of Ru is formed, or some third reaction is taking place. In situ SXS and voltammetry of the oxidation of Ru(0001), however, show that the oxidation beyond a monolayer of RuOH requires very high potentials above 1.2 V [14]. Further work is needed to clarify this question.

The electrochemical behavior of Pt/Ru(0001) bimetallic surfaces formed in previous experiments has been investigated by linear sweep voltammetry in 0.1 M H_2SO_4 . The results are presented in Fig. 4A–C. The voltammetry curve for a multilayer Pt deposit (Fig. 4A) shows a well-defined hydrogen adsorption/desorption region from 0.0 to -0.23 V. This is not observed in the case of the Ru(0001) surface [13,14] indicating that this

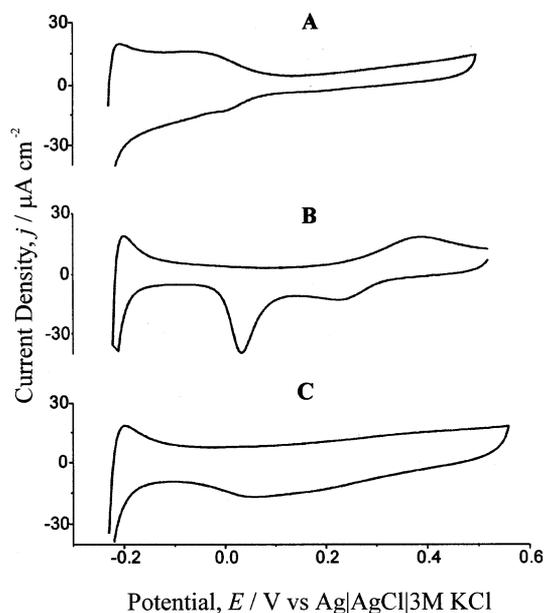


Fig. 4. Voltammetry curves for Pt/Ru(0001) bimetallic surfaces obtained by spontaneous Pt deposition. Sweep rate 20 mV s^{-1} , $0.1 \text{ M H}_2\text{SO}_4$. The curves A, B and C correspond to surfaces in Figs. 1–3, respectively.

behavior reflects the presence of a relatively thick Pt deposit. No features that are characteristic of a Ru surface are observed, which indicates that the Ru surface is completely covered by Pt. This is in agreement with the in situ STM data (Fig. 1). The voltammetry features between 0.0 and -0.23 V have some similarity to those seen for hydrogen adsorption on a Pt(111) surface. This indicates that the Pt clusters have a predominantly (111) orientation which could be expected for epitaxial deposition on a hexagonal Ru(0001) surface.

Fig. 4B shows a voltammetry curve that corresponds to the Pt/Ru(0001) bimetallic surface with large Pt clusters displayed in Fig. 2. The oxidation peak at 0.36 V and two reduction peaks at 0.02 and 0.22 V are associated with the oxidation and reduction of the Ru(0001) surface [13,14]. The hydrogen adsorption/evolution region around -0.23 V differs from the one observed for a multilayer Pt deposit in Fig. 1. The positive peak at -0.23 V can only be due to hydrogen oxidation on Pt clusters. Therefore, the properties of both metals are reflected in the overall behavior of the Pt/Ru(0001) bimetallic surface, and the currents associated with the reaction at each metal surface can be distinguished in the voltammetry curves. The curve in Fig. 4C corresponds to the morphology of the Pt/Ru surface with a uniform 2-ML thick deposit shown in Fig. 3. The positive peak at -0.23 V corresponds to hydrogen oxidation and is broader than in the previous case (Fig. 4B). No clear hydrogen adsorption/desorption is seen and the rest of the voltammogram does not

have features that could be attributed clearly to either a Pt or Ru contribution except for a very broad peak around 0.05 V in a negative scan, which may be due to the Ru oxide reduction. It appears that this voltammetry curve reflects modifications of the electronic properties of the Pt adlayer induced by the interaction with the underlying Ru substrate. Contrary to the case of the isolated large Pt clusters (Fig. 4B), the voltammetry curve is not a linear combination of the contribution of the Pt and Ru surfaces.

4. Summary

The spontaneous deposition of Pt on the Ru(0001) surface described above is a new phenomenon involving a noble metal deposition on a noble metal substrate. This might be a promising alternative approach for preparation of a highly active Pt/Ru bimetallic catalyst. The amount and the morphology of the Pt deposit can be conveniently controlled by controlling the time of crystal immersion and concentration of $[\text{PtCl}_6]^{2-}$ ions. This can provide a simple method for controlled Pt deposition on Ru clusters which can reduce its loading in Pt/Ru electrocatalysts. A local cell mechanism appears responsible for a spontaneous deposition of Pt on Ru where Ru oxidation to RuOH is the cathodic reaction occurring on the crystal surface. This process cannot explain multilayer Pt deposition which remains to be addressed in future work. The electrochemical behavior of Pt/Ru bimetallic surfaces shows a distinct dependence on the thickness and morphology of the Pt deposits, which could be of interest for the design of Pt/Ru catalysts. The electrocatalytic properties of supported Pt/Ru catalyst show enhanced CO tolerance for a considerably lower Pt loading than in commercial Pt/Ru catalysts [22].

Acknowledgements

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