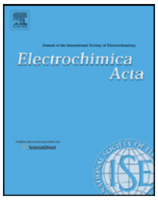
Electrochimica Acta 55 (2010) 3312–3323

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta



Hydrogen oxidation kinetics on model Pd/C electrodes: Electrochemical impedance spectroscopy and rotating disk electrode study

Sergey N. Pronkin[a,*,1,2], Antoine Bonnefont[b], Pavel S. Ruvinskiy[a,1,2], Elena R. Savinova[a,1,2]

[a] Laboratory of Materials, Surfaces and Catalytic Processes, UMR 7515 of CNRS-UdS-ECPM, 25 rue Becquerel, 67087 Strasbourg, France
[b] Institut de Chimie de Strasbourg, UMR 7177, CNRS-Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg, France

ARTICLE INFO

Article history:
Received 1 September 2009
Received in revised form 14 January 2010
Accepted 16 January 2010
Available online 25 January 2010

Keywords:
Hydrogen oxidation reaction (HOR)
Palladium catalysts
Supported nanoparticles
Computational modeling

ABSTRACT

This work reports on the kinetics of the hydrogen oxidation reaction (HOR) on model Pd nanoparticles supported on a low surface area carbon substrate. Two Pd/C samples, with the average particle size 2.6 and 4.0 nm were used. The structure of the catalysts was characterized with the *ex situ* (electron microscopy) and *in situ* (electrochemical) methods. We utilized the electrochemical impedance spectroscopy (EIS) and the rotating disk electrode (RDE) voltammetry to study the kinetics of the HOR on Pd/C. The relevance of these techniques for elucidating the kinetics and the mechanism of the HOR on Pd/C was explored. The experimental results suggest that the catalytic activity of Pd in the HOR is more than 2 orders of magnitude lower than that of Pt, and does not depend on the particle size in the range from 2.6 to 4.0 nm. Computational modeling of the experimental steady-state (RDE) and non-steady-state (EIS) data shows that the reaction kinetics can be adequately described within Heyrovsky–Volmer mechanism, with the rate constants $\upsilon_{0H} = (8.8 \pm 1.5) \times 10^{-10}$ mol cm^{-2} s^{-1} and $\upsilon_{0V} = (1.0 \pm 0.3) \times 10^{-8}$ mol cm^{-2} s^{-1}. The model suggests that underpotentially deposited hydrogen H_{UPD} is unlikely to be the active intermediate H_{ad} of the HOR. It is concluded that the surface coverage of H_{ad} deviates from that of H_{UPD} with increasing overpotential, and the lateral interactions within H_{ad} adlayer are weak.

1. Introduction

Reactions occurring at the hydrogen electrode, the hydrogen oxidation (HOR) and the hydrogen evolution reactions (HER), are among the most extensively studied electrocatalytic processes [1,2]. This is due to the relatively simple reaction mechanisms and to the practical importance of the HOR/HER. The HER is relevant to the water electrolysis, while the HOR is important for the polymer electrolyte membrane fuel cells (PEMFC) [3]. The cathodic hydrogen evolution reaction (HER) has been studied more extensively compared to its anodic counterpart. The investigation of the HOR is complicated by the interference of mass transport, due to the low solubility of H_2 in aqueous electrolytes. For more comprehensive information on the HOR/HER the reader is referred to the recent reviews [4–8].

High activity of Pt in the HOR allows decreasing the noble metal loading at the PEMFC anode fed with clean hydrogen to the level acceptable for commercialization [9,10]. However, stationary applications often rely on the reformate hydrogen, which, even after purification, contains CO impurities in the range 10–100 ppm. To this end, Pt–Ru are considered as the state-of-the-art CO tolerant catalysts, however, one should understand that Pt and Ru are expensive and scarce materials. Therefore, there is still a need to develop less expensive catalysts with the catalytic activity in the HOR comparable to that of Pt (or Pt–Ru), but higher CO-tolerance.

Being currently five times cheaper than Pt, Pd is considered as a promising material for the PEMFC anodes. Pd-based catalysts have shown stronger CO-tolerance than either Pt or Pt–Ru. For example, Schmidt et al. [11] reported on the higher tolerance of Pd–Au (8:2 atomic ratio) as compared to Pt–Ru in the oxidation of H_2/CO mixtures (100–1000 ppm CO). Our recent study on bimetallic Pd–Au/C catalysts also demonstrated that HOR rates on CO-covered surface is significantly higher in comparison with Pt electrodes [12]. These findings triggered the interest in the kinetics of the HOR on mono- and bimetallic Pd electrodes [11–14]. However, before switching to the discussion of the HOR on Pd, it is instructive to briefly summarize the state of the art understanding of the reaction kinetics on Pt, by far the most studied electrode for the HER/HOR.

The studies of the HER/HOR kinetics on Pt resulted in the following generally accepted scheme of the hydrogen electrode reactions:

$$H_2 + 2* \leftrightarrow 2H_{ad} \qquad \text{Tafel reaction} \qquad (1)$$

---

[*] Corresponding author. Tel.: +33 (0)3 68 85 27 56.
E-mail address: sergey.pronkin@unistra.fr (S.N. Pronkin).
[1] ISE member.
[2] Former address: Boreskov Institute of Catalysis, Lavrentieva pr. 5, 630090 Novosibirsk, Russia.

0013-4686/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2010.01.060

$$H_2 + * \leftrightarrow H_{ad} + H^+ + e^- \qquad \text{Heyrovsky reaction} \tag{2}$$

$$H_{ad} \leftrightarrow * + H^+ + e^- \qquad \text{Volmer reaction} \tag{3}$$

where * is a free surface site. The overall process occurs either via Tafel–Volmer (T–V) or Heyrovsky–Volmer (H–V) pathway, or a combination of the two [2,7,8]. Despite numerous studies, the details of the mechanism are still debated [5–7,15–19]. The controversy arises over (i) the magnitude of the exchange current density j_0, (ii) the predominant T–V, H–V or dual-path T–V + H–V mechanism, (iii) the nature and the coverage of the reactive intermediate H_{ad}, and (iv) the lateral interactions within the H_{ad} adlayer.

Chen and Kucernak [15] have recently demonstrated that the application of the rotation disk electrode RDE, a conventionally used method to study the HOR kinetics [20,21], may lead to a strong underestimation of j_0 on Pt and to erroneous conclusions on the reaction mechanism, due to the very rapid reaction kinetics and the ensuing difficulties in separating the kinetic and the mass transport effects. The utilization of ultra-microelectrodes (down to 0.036 μm size) enabled the authors [15] to investigate the HOR in the absence of mass transport limitations, and resulted in *ca.* 20 times higher value of the exchange current density ($j_0 \approx 20$–$23\,\mathrm{mA\,cm^{-2}}$) than reported previously [16–19,22]. The value of Chen and Kucernak is in agreement with an estimation of Gasteiger et al. [10] (*ca.* $27\,\mathrm{mA\,cm^{-2}}$) derived from the dependence of a PEMFC anode overvoltage on the Pt loading. Facile mass transport toward the surface of the ultramicroelectrode made it possible to detect kinetic limiting current plateau ascribed to the Tafel reaction.

A kinetic limiting current has been predicted within T–V mechanism [2], but has not been experimentally observed before the work of Chen and Kucernak [15] because of the slow diffusion rates achievable with conventional RDE. The authors [15] suggested a kinetic model, assuming two types of H_{UPD} as the intermediates in the T–V mechanism of the HOR. The model described the experimental polarization curves *qualitatively*, while *quantitative* agreement has only been achieved for overpotentials below 0.2 V. Later, Chialvo et al. [23–25] and Wang et al. [26,27] suggested a dual-path T–V + H–V mechanism, and developed the kinetic models which provided *quantitative* description of the data from Ref. [15]. According to these models, a sharp increase of the HOR current in the low overpotential region is due to the T–V pathway, while the gradual current increase in the high overpotential region is explained by the H–V pathway. The polarization curves may show two current plateaus rather than one, the first corresponding to the kinetic/adsorption (Tafel) while the second – to the diffusion limitation.

Contrary to the model of Chen and Kucernak [15], the models developed in Refs. [25–27] assumed lower coverage of the HOR intermediate H_{ad} compared to H_{UPD}. Wang et al. [26,27] assumed that the HOR intermediate occupies the on-top site, while H_{UPD} is believed to adsorb in threefold and fourfold hollow sites [5,28]. The assumption of Wang et al. is supported by the recent SEIRAS data from Kunimatsu et al. [29], who detected a spectroscopic band during the HOR on Pt at potentials below 0.1 V RHE, and assigned it to the *on-top* adsorbed reactive H_{ad} intermediate.

Studies of the HOR kinetics on Pd electrodes are scarce. This is in part due to the fact that HOR currents on bulk Pd are superimposed with the currents of the hydrogen *ab*sorption. An RDE study by Maximov and Petrii [30] suggests that the catalytic activity of polycrystalline Pd is several times lower than that of Pt. Unfortunately, the uncertainties in the estimation of the active surface area prevented the authors from determining the value of the exchange current density. Recently, Rau et al. [14] reported an RDE study of the HOR on thick (*ca.* 300 nm) Pd overlayers electrodeposited on Au. Kinetic modeling was performed within the dual-path model previously developed for Pt [25]. The authors concluded that the rate constant of the Volmer step on Pd is *ca.* 2 orders of magnitude smaller than that on Pt, while the rate constants of the Tafel and Heyrovsky steps are comparable to those on Pt. It is, however, difficult either to refer the reported kinetic constants to the unit surface area of Pd, or draw conclusions on the structural sensitivity of the HOR, since the information on the exact structure of the Pd layer and its active surface area is lacking.

Schmidt et al. [13] studied the HOR kinetics on Pd–Au(1 1 1) surface alloys and demonstrated that the exchange current density referred to Pd surface area increases from $j_0 = 0.12\,\mathrm{mA\,cm^{-2}}$ (Pd) for the atomic Pd content $x_{Pd} \approx 0.65$ to $j_0 = 0.16\,\mathrm{mA\,cm^{-2}}$ (Pd) for $x_{Pd} \approx 0.38$. Our recent study of the HOR on bimetallic Pd–Au/C model catalysts [12] supports increase of j_0 with the decrease of Pd overlayer thickness. On the other hand, Markovic and Ross [31] reported on the higher HOR activity of Pd monolayer on Pt(1 1 1) compared to the bare Pt(1 1 1) substrate. According to Kibler et al. [32], the HOR/HER activity of Pd in bimetallic catalysts depends strongly on the nature of the second component.

Considering the practical relevance of Pd anodes for the PEMFCs, and insufficient understanding of the HOR kinetics on Pd, we see an actual need to investigate the kinetics of the HOR on monometallic well-characterized Pd catalysts.

In our previous [33] work we demonstrated that Pd supported on a low surface area carbon substrate is a suitable model for electrocatalysis, *e.g.* in electro-reduction of nitrates. The objective of this work is to study the HOR kinetics on the model Pd/C catalysts with well defined structure. The latter was characterized *ex situ* by the high resolution transmission electron microscopy (HR-TEM) and *in situ* by the hydrogen *ad-*/*ab*sorption and underpotential deposition of Cu. The kinetics of the HOR was investigated using RDE, EIS, and computational modeling.

2. Experimental

2.1. Catalyst preparation and characterization

Pd/C catalysts were prepared by the chemical deposition from H_2PdCl_4 solution [34] on non-activated carbon material of the Sibunit family. This low surface area ($S_{BET} = 6\,\mathrm{m^2\,g^{-1}}$) carbon material had been chosen to avoid the influence of H_2 diffusion in the pores on the HOR kinetics. For the preparation and properties of Sibunit carbons the reader is referred to Ref. [35], and for the details of the catalyst preparation to the Ref. [33].

Two Pd/C samples were prepared with 5 wt.% Pd (S1) and 3 wt.% Pd (S2). Low Pd percentage was chosen to minimize the metal particle coalescence. The size and the structure of carbon-supported Pd particles were characterized by transmission electron (TEM) and high resolution transmission electron microscopy (HR-TEM) with *JEM-2010* microscope (JEOL, Japan) with a lattice resolution of 0.14 nm at the accelerating voltage of 200 kV. The samples for TEM analysis were prepared on a perforated carbon film deposited on a copper grid. TEM images were utilized to estimate the average $\bar{d}_N = \sum_i N_i d_i / \sum_i N_i$ and the surface average $\bar{d}_S = \sum_i N_i d_i^3 / \sum_i N_i d_i^2$ particle diameter.

2.2. Electrochemical measurements

The electrochemical measurements were performed with *Autolab PGSTAT 30* potentiostat equipped with Scangen and FRA modules, in a three-electrode configuration. The cell comprised individual compartments for each electrode. The counter electrode (Pt foil) and the reference electrode (mercury sulfate or trapped hydrogen electrode) compartments were connected to the working electrode compartment via a glass frit and a Luggin capillary, respectively. Electrode potentials are reported *vs.* a reversible hydrogen electrode (RHE), unless otherwise stated. As