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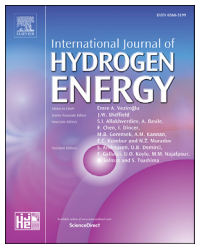

Electrocatalysis of hydrogen evolution reaction on tri-metallic Rh@Pd/Pt(poly) electrode

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ABSTRACT

Hydrogen evolution reaction (HER) was investigated in alkaline solution on tri-metallic Rh@Pd/Pt(poly) electrode, prepared by spontaneous deposition of Rh on top of Pd/Pt(poly) electrode with intermediate Pd coverage of 35%. Characterization of tri-metallic catalyst was performed by electrochemical methods of cyclic voltammetry and CO stripping voltammetry, while its activity for HER was tested by linear sweep voltammetry in 0.1 M NaOH. Rh@Pd/Pt(poly) catalyst has shown superior catalytic activity for HER with respect to initial Pt(poly) and both corresponding bimetallic Pd/Pt(poly) and Rh/Pt(poly) electrodes. This was explained by a strong synergistic electronic interaction between three metals in close contact induced at a number of different active sites across the surface of tri-metallic catalyst, which results with lowering of the binding energy for the adsorption of H intermediate species.

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Introduction

Hydrogen evolution reaction (HER) is one of the most extensively studied electrochemical processes, owing to its involvement in fundamental and applicable aspects of multiple branches of physical chemistry and tight connection with the breaking topic of renewable energy sources [1–5]. HER presents relatively simple, but still not entirely solved technology to obtain high purity hydrogen, labeled as the energy carrier of future [6–9], by electrolysis of aqueous solutions. One of the main obstacles to be tackled in order to make electrolysis more efficient and economically justified for a large scale production is to design more active cathodes for HER [8,10,11]. Despite the high price and low scarcity, noble metals are still preferred over non-noble for the fundamental studies of HER electrocatalysis (and electrocatalysis in general) since they offer higher activity and stability in electrochemical environments and well-defined surface properties [1,2,5]. Traditional Volcano plots [12,13] and their recent reviews [14–16] have confirmed that Pt is the most active electrode material for HER, followed by the other precious metals - Pd, Rh, Ir, Re, while the activities of other metals, some of them even being precious (Au and Ag), are several orders of magnitude lower. Therefore, if considering the activity of Pt as a benchmark for HER electrocatalysis, one of the main research directions is certainly to improve its activity and to decrease the share of Pt in catalysts at the same time. Both of these goals can be achieved by modification of Pt with foreign metal(s) in order to produce bi-metallic or tri-metallic catalysts [17–29] (and references within). Presence of two (or more) metals in close contact will induce the well-known and in electrocatalysis highly appreciated phenomenon of

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electronic effect [30,31]. This effect leads to the changes in the electronic states of the metals, or more precisely in the case of precious metals on the position of the center of the *3d* band, which determines the activity of the catalysts for certain reaction by influencing the adsorption energy of reactants or reaction intermediates [30,31]. Influence of the electronic modification on the reactivity is the most pronounced in the case of low coverage by foreign metal ad-atoms at monolayer or sub-monolayer level and in the case of interaction with simple atoms or molecules [31]. In the case of HER, electronic interaction between constitutive metals should aim to decrease the adsorption energy of H intermediate species, which is the pivotal step in the reaction mechanism. Proper design of the catalysts composition and tuning of this electronic modification can lead to the synergism meaning that the activities of all constituents are surpassed, which is in fact the ultimate goal in electrocatalysis.

Recently, we have successfully modified Pt(poly) with spontaneously deposited Pd and Rh islands at sub-monolayer coverage to improve its activity for HER in alkaline solution [32]. Obtained synergistic effect was explained, in accordance with other studies on different Pd/Pt systems [17–20,33], by the improved overall interaction of bimetallic electrodes with adsorbed H species as a result of the electronic interaction between Pt substrate and deposited Pd or Rh ad-atoms. This electronic interplay results with the shift of the *d*-band center of Pd or Rh deposit, while also the electronic state of Pt substrate is altered, which in overall leads to the lowering of the H intermediate binding energy in the first step in HER mechanism, while at the same time facilitates the displacement of adsorbed inactive H_{upd} species into the subsurface sites. Pd and Rh themselves are also highly active catalysts for HER [12–16], and in fact theoretical study has proposed bimetallic Rh/Pd structures as highly active for HER due to the strong electronic modification that again leads to the shift of the Rh overlayer *d*-band center and promotes energetics of H adsorption [34]. Indeed, we have observed this electronic interaction by X-ray photoelectron spectroscopy through the subtle shift of the characteristic photo-electron lines of both Rh deposit and Pd substrate [35] and experimentally corroborated that it leads to the high activity of Rh/Pd(poly) electrodes for HER [36], which was comparable with the activity of Pt in a certain potential window. Following study has confirmed the high activity of Rh/Pd nanoparticles electrodeposited on the glassy carbon for HER [37].

Relying on previous studies of HER catalysis on bimetallic Pd/Pt(poly), Rh/Pt(poly) [32] and Rh/Pd(poly) electrodes [36], one could project that also corresponding tri-metallic Pt-Pd-Rh electrode with appropriate design should be very active for the same reaction. The origin of this assumption is in fact that even stronger electronic interplay between three constitutive metals in close contact should occur and lead to the additional lowering of the H intermediate adsorption energy with respect to bare Pt and to corresponding bimetallic electrodes. Catalysts based on Pt-Pd-Rh nanoparticles or alloys were explored for the ethanol oxidation [38] and ammonia oxidation [39], where they showed promising activities, but there is a lack of literature data about HER on this tri-metallic system, which could be very active for this reaction.

In this paper, we have prepared tri-metallic electrocatalyst consisting of Pd and Rh nanoislands co-deposited on Pt(poly) and tested its activity for HER in alkaline electrolyte. As a method of preparation, spontaneous deposition was chosen, since this simple, fast and affordable method was already used for successful preparation of related bimetallic Pd/Pt(poly), Rh/Pt(poly) and Rh/Pd(poly) electrodes with enhanced HER activities [32,36]. Having in mind our previous works on these bimetallic electrodes, we have prepared tri-metallic electrode by spontaneous deposition of Rh onto previously prepared Pd/Pt(poly) electrode with intermediate Pd coverage of 35%. In that way, obtained tri-metallic surface, further denoted as Rh@Pd/Pt(poly), will consist of a number of active sites for HER: free Pt surface, Pd islands, Rh islands deposited on Pt, on top of the Pd deposit and on the edges of Pd/Pt islands. Since Pd islands and Pt substrate are under electronic interaction, the positions of their *d* band center, i.e. their electronic states are already altered. Over-deposited Rh islands will thus be under electronic interplay with such electronically "*strained*" Pd islands and Pt substrate, which in overall should lead to the unique position of the Rh *d* band center that is different than in the cases when Rh is deposited on bare Pt(poly) or Pd(poly). Vice versa, the electronic states of Pd islands and Pt substrate will also be different due to the presence of over-deposited Rh. Consequently, we expect that Rh@Pd/Pt(poly) electrode will be highly active for HER, since the adsorption of H intermediate species, as the initial step in HER mechanism, should be energetically promoted due to the unique electronic properties of various active sites present on the tri-metallic catalyst. Electrochemical characterization of prepared Rh@Pd/Pt(poly) electrode by CO striping voltammetry and cyclic voltammetry, as well as HER investigations by linear sweep voltammetry, were performed in alkaline solution and its characteristics and activity were compared with the activities of bare Pt and of corresponding bimetallic Pd/Pt(poly) and Rh/Pt(poly) electrodes.

Experimental

Chemicals

Carrying electrolyte solution for electrochemical measurements was prepared daily fresh by using NaOH pellets (Merck), while depositing solutions were prepared using $PdCl_2$ (Alfa Aesar), $RhCl_3 \cdot xH_2O$ (MaTeck) and suprapure H_2SO_4 (Merck). All solutions were diluted with Milli-pure water. High purity CO (Messer, 99.999%) was used for CO stripping voltammetry, while deaeration of the electrolyte during electrochemical measurements was achieved by the constant flow of the high purity nitrogen (99.999%, Messer) in or over the solution.

Preparation of tri-metallic catalyst

Pt(poly) rotating disc electrode of 5 mm in diameter (Pine Instruments) was used as the substrate for electrochemical experiments. Before each measurement, it was cleaned by electrochemical polishing [40] and its purity was confirmed by cyclic voltammetry in basic electrolyte solution. Preparation

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