



High oxygen reduction reaction activity of Pt₅Pr electrodes in acidic media

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ABSTRACT

Advancing understanding of oxygen reduction reaction (ORR) electrocatalysis at platinum and platinum alloy surfaces is of great importance for the energy provision schemes that involve fuel cells. While the activity trends of model single crystal electrocatalysts are well-understood, there are still numerous open questions in the case of polycrystalline and nanostructured catalytic materials. The resulting ORR activity in these systems is frequently governed by so-called strain effects and surface imperfections, which are difficult to predict and interpret. Nevertheless, in some cases ORR activity can be correlated with relatively simple semi-empirical parameters such as the radii of the solute element in platinum alloys. In this work, using a simple radii-related consideration we discover high ORR activity of polycrystalline Pt₅Pr alloy, which demonstrates ~4-fold improvement over pure Pt, overcoming or being similar to that of polycrystalline Pt₃Ni and many other polycrystalline Pt-alloys, respectively. We explain the resulting ORR activity in terms of excessive compressive strains in a thin Pt-rich layer at the surface of Pt₅Pr.

1. Introduction

The oxygen reduction reaction (ORR) is one of the most studied electrochemical reactions in the past few decades due to its significance in energy conversion devices, particularly in fuel cells [1] and metal-air batteries [2]. Among these devices, polymer electrolyte membrane fuel cells (PEMFCs) are particularly attractive for automotive applications [3–5]. To take the next steps in advancing the PEMFCs technology, one of the bottle-necks, namely the slow reaction kinetics of ORR, should be overcome [6–9]. This is particularly difficult as the harsh operating conditions in PEMFCs limit the number of potential catalysts: only few classes of materials display the required stability.

Platinum and platinum-based catalysts are considered state-of-the-art catalysts for the ORR as they show high activities, while meeting the stability requirements. However, due to the scarcity and high price of these precious metal catalysts, further improvements in their activity [4,7,10] and durability [11,12] are necessary. In order to achieve this goal, it is important to improve understanding of the behavior of real-world catalysts, which are usually applied in the form of nanostructured thin films or nanoparticles [13–17].

Pt_nX-type alloys of platinum with transition metals and lanthanides have recently attracted considerable attention [9,15,18–28] due to

their promising electrocatalytic performance. Previously, we showed [29] that the behavior of polycrystalline and nanoparticulate Pt-alloy catalysts during ORR can be described by a semi-empirical approach based on the assessment of the strain effects in these catalysts. Also, similar activity trend for several polycrystalline Pt-lanthanide alloys has been demonstrated by the Chorkendorff group [27]. These alloys have a core-shell structure under ORR conditions in which strains arise in the Pt-rich overlayer due to the difference in atomic radii between Pt and the alloying element. However, the exact mechanism of the development of the resulting compressive strain effect remains unclear. Based on the assessment from our previous work [29], we identified intervals of atomic radii that can be considered “promising” to discover new active oxygen reduction Pt-alloy electrocatalysts. It should be noted that we were particularly interested in extended surfaces, which should bind ORR-intermediates slightly weaker than the optimum, as the activity of the respective Pt-alloy electrocatalysts shows a local optimum while reducing the catalyst particle size. This might be useful in designing nanostructured ORR electrocatalysts: the binding energies towards almost all adsorbates increase with the decrease of the particle size. There are only very few choices, which satisfy the criteria of the atomic radii. One of the viable choices for the active alloy is praseodymium, forming a stable intermetallic compound with platinum,

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namely Pt₅Pr. In order to further validate the approach, we test its predictive power and report the ORR activity of Pt₅Pr alloy. The results demonstrate that the activity of the Pt₅Pr alloy shows a 4-fold improvement in comparison to pure Pt in 0.1 M HClO₄. This result adheres to the trend predicted by the previously proposed model.

2. Material and methods

The Pt₅Pr alloy was characterized by X-ray diffraction (XRD) using a Siemens Diffractometer D5000 and an atomic force microscopy (AFM). The surface of the Pt₅Pr electrode was investigated using a MultiMode EC-STM/EC-AFM instrument (Veeco Instruments Inc.) equipped with a Nanoscope IIIA controller using the Nanoscope 5.31r1 software. The tapping mode was applied (AFM tips, Bruker RTESP-300) at a scan rate of 0.5 Hz.

The electrochemical setup used for the experiments is described in detail elsewhere [30]. For the measurements, a VSP-300 potentiostat (Bio-Logic, France) was used. As working electrodes, a polycrystalline platinum and Pt₅Pr alloy (both samples had diameter 5 mm, Mateck, Jülich, Germany) electrodes were used. The cyclic voltammograms were recorded in Ar-saturated and O₂-saturated (Ar 5.0, O₂ 4.5, respectively, Air Liquide, Germany) 0.1 M HClO₄ (Suprapur, Merck, Germany) with a scan rate of 50 mV/s. As the reference and counter electrodes, a mercury–mercury sulfate electrode (MMS) (SI Analytics, Germany) and a polycrystalline Pt wire were used, respectively. The surface of the electrodes was cleaned by performing cycles between 0 and 1.2 V vs RHE in 0.1 M HClO₄. All electrode potentials are reported versus reversible hydrogen electrode (RHE) scale.

3. Results and discussion

Initially, the Pt₅Pr alloy sample was characterized by XRD. A typical XRD pattern of Pt₅Pr is shown in Fig. 1. The lattice parameters were calculated to be $a = b = 5.353 \text{ \AA}$ and $c = 4.386 \text{ \AA}$, which are consistent with the standard reference values for Pt₅Pr (PDF card number 65-8059). All diffraction maxima match well with the standard reference with a hexagonal symmetry and space group $P6/mmm$ (191).

The surface morphology of the Pt₅Pr alloy was analyzed with AFM before and after electrochemical measurements. Typical AFM images are shown in Fig. 2A. The surface of the electrode appeared to be smooth before and after activity evaluations with a roughness of no more than ca 50 nm. It is important to note that the surface smoothness of Pt₅Pr electrode is conserved after activity measurements under

electrochemical conditions, as it is known that in many cases de-alloying of the electrode material results in increase of the sample roughness [31].

Fig. 2B, C compares cyclic voltammograms of Pt₅Pr and Pt(pc) electrodes in Ar-saturated 0.1 M HClO₄. The voltammogram of the alloy is rather “featureless” compared to that of Pt(pc), with large background currents (the region between 0.0 and 0.4 V), similar to e.g. Pt₃Y and other alloys of Pt and early transition metals or lanthanides. Due to the latter fact, the H-underpotential deposition (UPD) region can't be used for determination of the electroactive surface area. Therefore, the alternative way to assess the amount of the available adsorption sites *in-situ* using Cu-UPD was implemented: a 1:1 pseudomorphic overlayer of Cu was formed at Pt-rich surfaces of different morphologies.

Fig. 2D compares stripping voltammograms of Cu monolayers formed at 0.33 V vs RHE on the Pt₅Pr and Pt electrodes. Integration of the anodic peaks gives approximately the same charge of $\sim 440 \mu\text{C cm}^{-2}$, which is typical for the smooth polycrystalline Pt surfaces. Therefore, as it was observed also from AFM images, the surface of the Pt₅Pr sample did not increase the catalytic surface area during electrochemical experiments. Additionally, these facts confirm that there is no Pr at the electrode surface, as UPD of Cu is not possible on Pr atoms.

Taking into account that the surface area of Pt₅Pr electrodes is similar to the Pt reference, we directly compare the corresponding voltammograms taken in O₂-saturated 0.1 M HClO₄ electrolytes under the rotating disc electrode (RDE) conditions. Fig. 3A shows typical RDE-voltammograms (anodic parts) for Pt and Pt₅Pr samples in O₂-saturated 0.1 M HClO₄ electrolytes taken at a scan rate 50 mV/s and a rotation rate of 1600 rpm. The figure shows that Pt₅Pr is more active than pure polycrystalline Pt. The extracted kinetic current densities presented in Fig. 3B, C quantifies the degree of the activity improvement at 0.9 V (RHE), which is a reference point for the PEMFC applications. The measured ORR activity of Pt₅Pr corresponds to ~ 4 -fold improvement with respect to pure Pt. The slope of the curves shown in Fig. 3C slightly changes with the potential. We hypothesize that these changes are due to adsorbate-adsorbate interactions (e.g. OH-species), influencing the kinetics of the oxygen reduction reaction at Pt-based surfaces.

Fig. 4A shows the dependence of the maximal ORR activity reported in the literature for polycrystalline and nanostructured Pt alloys (measured in 0.1 M HClO₄) as a function of the atomic radii of the “solute”, alloying elements (black symbols). From the figure, it can be seen that there are two prominent activity maxima, which correspond to the radii of Cu and Y. The exact origin of such behavior is not yet clear [29]; however, one can explain this effect semi-quantitatively.

It has been shown that for the majority of polycrystalline and nanostructured platinum alloys, after a relatively short contact with aqueous electrolytes during electrochemical potential cycling, the surface layer (3–5 atomic layers thick) loses almost all atoms of solute elements by surface de-alloying [15,27,32]. The resulting Pt-rich top layer protects most of these electrodes from further de-alloying. Importantly, this process leads to the introduction of exclusively compressive strain into the surface layer, irrespective of the nature of the solute atoms and their radii. The mechanism of such a counterintuitive relaxation of the system is not yet clear. However, the compressive strains statistically weaken the binding of ORR active centres to the reaction intermediates, such as *O, *OH or *OOH (where “*” denotes the adsorption site).

Optimal catalytic sites for the ORR should bind the reaction intermediates slightly weaker than pure Pt(111) surface [9]. Taking this into account, Fig. 4 can be interpreted as following. De-alloying of the Pt-X alloy samples introduces compressive strains that subsequently result in (for the majority of the catalytic centres) their lower affinity towards the ORR intermediates. The optimum is reached if the binding energies for the intermediates are slightly weakened compared to pure Pt (ca 0.1 eV for OH-intermediates) both on the side of the solute element atoms that are bigger (Y) or smaller (Cu) than Pt. For atomic radii much

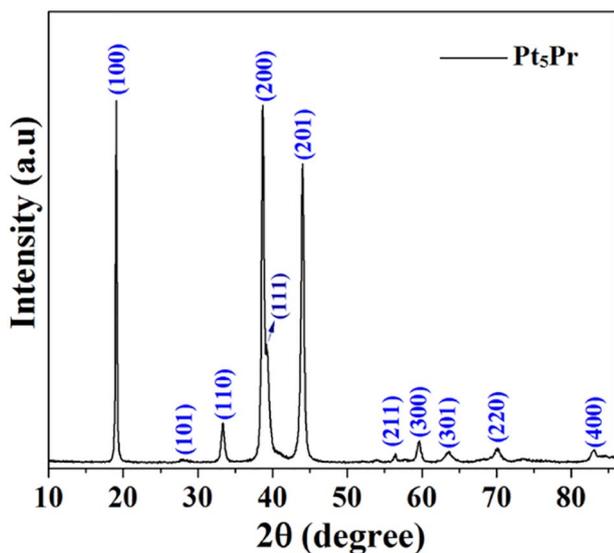


Fig. 1. XRD pattern of the polycrystalline Pt₅Pr sample.

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