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Electroreduction of oxygen on gold-supported nanostructured palladium films in acid solutions

Ave Sarapuu[a], Aarne Kasikov[b], Naomi Wong[c], Chris A. Lucas[c], Gita Sedghi[d], Richard J. Nichols[d], Kaido Tammeveski[a,*]

[a] Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia
[b] Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia
[c] Department of Physics, University of Liverpool, L69 7ZD Liverpool, United Kingdom
[d] Department of Chemistry, University of Liverpool, L69 7ZD Liverpool, United Kingdom

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ABSTRACT

The electrochemical reduction of oxygen on thin Pd films with a nominal thickness of 0.25–10 nm on polycrystalline Au substrate (Pd/Au) was studied. The Pd films were prepared by electron beam evaporation and oxygen reduction was studied in 0.1 M $HClO_4$ and 0.05 M H_2SO_4 solutions using the rotating disk electrode (RDE) method. The surface morphology of Pd overlayers was examined by scanning tunnelling microscopy (STM). O_2 reduction predominantly proceeds through $4e^-$ pathway on all Pd/Au electrodes. The specific activity (SA) of oxygen reduction was lower in H_2SO_4 solution and decreased slightly with decreasing the Pd film thickness. In $HClO_4$, the SA was higher and not significantly dependent on the film thickness. The Tafel slope values close to −60 mV at low current densities and −120 mV at high current densities were found for all electrodes.

1. Introduction

The electrochemical reduction of oxygen is one of the most intensively studied electrocatalytic processes, as this reaction is a primary factor limiting the performance of low-temperature fuel cells. Platinum and its alloys are mostly used as anode and cathode catalysts in these appliances, but the high cost and scarcity of this metal hinders the widespread commercial use of the fuel cells [1]. Therefore, the development of platinum-free catalysts for the fuel cells technologies remains as an important challenge [2].

Among the other metals under consideration palladium has properties most similar to platinum, but it is at least 50 times more abundant on Earth and considerably cheaper [2]. The electrochemical reduction of oxygen on Pd and on its alloys has gained increasing attention in recent years. The electrocatalytic activity of Pd towards oxygen reduction is the second best after Pt amongst the pure metals [3]. Another advantage of Pd and its alloys is their selectivity for oxygen reduction reaction (ORR) in the presence of alcohol in DMFCs [2]. There are many reports that Pd alloys and core-shell nanoparticles may possess a higher electrocatalytic activity for ORR than pure Pd, as reviewed recently by Antolini [2]. In addition, the activity of Pd–Pt and some other Pd-based binary or tertiary systems even surpasses the ORR activity of Pt [2]. The most intensively studied combinations of Pd and non-precious metals are Pd–Co [2,4–7] and Pd–Fe [2,8–10]. For instance, activities comparable or slightly better than that of commercial Pt/C catalyst have been obtained by Manthiram's group for Pd–Co–Mo/C [4] and Pd–Co–Au/C catalysts [5,6]. Shao et al. have achieved catalytic activities close to Pt/C catalysts using Pd_2Co/C nanoparticles [7] and even higher activities with Pd_3Fe/C [8,9] particles. The experimentally found high activity of Pd–Fe alloys is in accordance with the predictions of the DFT calculations, which have shown that the best catalysts have moderately strong metal–oxygen bond and in that case, two competing influences counterbalanced each other: the first factor being the electron transfer or O–O bond-breaking, with the other factor being the removal of O and OH from the surface [9].

Recent attention has been drawn to the strong dependence of the electrocatalytic properties of Pd nanostructures on their surface morphology. The specific activity of palladium nanorods prepared by electrodeposition was found to be close to that of Pt in acid solution, approximately 10 times higher than that of electrodeposited Pd nanoparticles [11]. The higher activity was attributed to the exposure of Pd(1 1 0) surface sites [11]. This is in apparent disagreement with another recent work, where the activity of Pd low index planes increased in the following order:

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* Corresponding author. Tel.: +372 7375168; fax: +372 7375181.
E-mail address: kaido@chem.ut.ee (K. Tammeveski).

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Pd(1 1 0) < Pd(1 1 1) < Pd(1 0 0) and Pd(1 0 0) single crystal plane was even more active than Pt(1 1 0) in 0.1 M $HClO_4$ [12].

There are a number of studies which describe the electrochemical reduction of O_2 on palladium nanoparticles [13–18]. In alkaline solution, nanoparticulate Pd/C catalysts have shown higher activity than Pt/C [14]. The specific activity of the Pd/C catalysts increased by a factor of three when the particle size increased from 3 to 16.7 nm [15]. On the other hand, in acid solution, the activity of Pd nanoparticles incorporated into Nafion film was rather low [16]. Multi-walled carbon nanotubes have also been used as a support of Pd nanoparticles and such catalysts have shown high electrocatalytic activity towards oxygen reduction [17,18].

Gold has been used as a support material for studying the electrocatalytic behaviour of palladium nanostructures, as this metal is rather inactive towards oxygen reduction in acid solution [19–22]. It may also form surface alloys with Pd [23,24]. O_2 reduction has been studied on Pd films on Au prepared by a variety of techniques, including the underpotential deposition (UPD) of copper with subsequent replacement of the copper by palladium [7,25], electrodeposition [11,26–28] and vacuum evaporation [24]. Au single crystals [7,24,26,27], polycrystalline Au [11,28] and nanoporous gold films [25] have been employed as substrates. In acid solution the electrocatalytic activity of Pd/Au(1 1 1) has found to be slightly lower than that of bulk Pd(1 1 1). DFT calculations showed that the d-band centre energy for Pd/Au(1 1 1) surface is higher than that of Pd(1 1 1) leading to the conclusion that it binds oxygen more strongly. This strong binding hinders the subsequent reaction steps, thereby slowing the kinetics of oxygen reduction [7]. Thin Pd layers of various thicknesses on Au(1 1 1) and Au(1 0 0) single crystal surfaces in acid solution were rather active and the activity was higher for a thinner Pd layer (0.9 monolayers) than for a comparatively thick layer (8 monolayers) [26]. In alkaline solution, high electrocatalytic activity was achieved with as little as 18 at.% Pd in the Au(h k l) surface [24]. AuPd alloy nanoparticles supported on nanocrystalline WC showed higher activity towards ORR than Pt/C and Pd/C catalysts [29] and submonolayers of Pd on Au(1 1 1) were more active than bulk Pd [27]. High electrocatalytic activity towards the ORR has been obtained on palladium coated nanoporous gold film electrodes in phosphate buffer solution [25] and on electrodeposited Pd films on bulk Au in KCl solution [28].

In this work, thin films of Pd on polycrystalline Au electrodes were prepared by electron beam evaporation and used as model catalysts for studying the electrochemical reduction of oxygen. The main objective was to evaluate the influence of the Pd film thickness and Au substrate to the specific O_2 reduction activity of Pd. The experiments were conducted in two different acid solutions, in $HClO_4$ and in H_2SO_4, in order to describe the effect of strongly adsorbing (bi)sulphate ions on the kinetics of oxygen reduction on the nanostructured Pd electrodes.

2. Experimental

Bulk polycrystalline gold and palladium electrodes were prepared by mounting Au (99.99%, Alfa Aesar) and Pd (99.95%, Alfa Aesar) disks into Teflon holders. The geometric area of the electrodes (A) was 0.2 cm^2. The electrodes were polished to a mirror finish using 1.0, 0.3 and 0.05 μm alumina powder (Buehler). After polishing, the electrodes were ultrasonically cleaned in Milli-Q (Millipore, Inc.) water for 5 min.

Thin films of Pd having a nominal thickness (h) of 0.25–10 nm were deposited onto the Au substrates by electron beam evaporation from a graphite crucible using Vacuum Service OY evaporation device at a base pressure of around 1×10^{-6} Torr. For preparing the samples for STM measurements, a flat Au film deposited on mica was used as a substrate. After annealing in propane-butane flame the Au film showed a preferential orientation of the (1 1 1) plane.

In situ STM experiments were carried out in 0.05 M H_2SO_4 electrolyte with a Molecular Imaging (Agilent) STM in conjunction with the Picoscan 5.3.3 software. Pt–Ir STM tips were freshly prepared for each experiment by electrochemical etching and coated with Apiezon wax. All STM images were recorded in constant current mode with tunnelling currents ranging from 1.0 to 1.5 nA.

Oxygen reduction was studied in 0.1 M $HClO_4$ and 0.05 M H_2SO_4 solutions using the rotating disk electrode (RDE) method. A reversible hydrogen electrode (RHE) connected to the cell through a Luggin capillary was employed as a reference and all the potentials are referred to this electrode. A Pt wire served as a counter electrode and the counter electrode compartment of the three-electrode cell was separated from the main cell compartment by a glass frit. The potential was applied with an Autolab potentiostat PGSTAT30 (Eco Chemie B.V., The Netherlands) and the experiments were controlled with General Purpose Electrochemical System (GPES) software. The solutions were prepared from 70% $HClO_4$ (Suprapur, Merck) and 96% H_2SO_4 (Suprapur, Merck) and Milli-Q (Millipore, Inc.) water and were saturated with pure O_2 (99.999%, AGA) or deaerated with Ar gas (99.999%, AGA). An EDI101 rotator and a CTV101 speed control unit (Radiometer, Copenhagen) were used for the RDE experiments. All experiments were carried out at room temperature (23 ± 1 °C).

Prior to the O_2 reduction measurements, the electrodes were electrochemically pre-treated in 0.1 M $HClO_4$ or 0.05 M H_2SO_4 by scanning the potential between 0.3 and 1.2 V for 10 cycles at a scan rate of 100 mV s^{-1} and then between 0.3 and 1.4 V for two cycles. The real surface area (A_r) of Pd was determined by charge integration under the oxide reduction peak of the last cycle, assuming the value of 424 μC cm^{-2} as the charge density for the reduction of a monolayer of PdO [30]. After potential cycling the electrodes were immediately transferred to an O_2-saturated solution in another cell in order to avoid surface contamination in air. For O_2 reduction measurements, the potential was held at 1 V for 5 s and scanned between 1 and 0.3 V at 10 mV s^{-1}.

3. Results and discussion

3.1. Surface characterisation by STM

The surface morphology of 0.25–1 nm Pd films prepared by electron beam evaporation onto Au(1 1 1) substrates was characterised by STM measurements and representative images are presented here. The STM images (Fig. 1) reveal that Pd overlayers on Au are not epitaxial, but consist of Pd nanoparticles (nanoislands) that form larger agglomerates. It is evident that even for the 0.25 nm film Pd islands cover most of the Au surface (Fig. 1a). The size of the islands increases with the film thickness, from 3.3 ± 0.9 nm for the thinnest film to 4.6 ± 0.8 nm for 0.5 nm film and 4.8 ± 0.8 nm for 1 nm film. The height profiles suggest that Pd islands are rather flat: their height corresponds only to 1–2 monolayers of Pd for 0.25 nm film. As the film thickness increases, some islands grow in height and the roughness of the film also increases (Fig. 1b and c). An STM image of the Au(1 1 1) substrate is also presented that shows for comparison and contrast a larger surface area with the typical step and terrace structure of well prepared Au(1 1 1) surface, with flat terraces spanning several tens of nanometers (Fig. 1d). The size of the Pd particles is slightly larger than that of Pt films of the same nominal thickness on Au substrate [31]. This is in accordance with other studies, as it has been shown that for carbon supported Pt–Pd catalysts metal particle size increases with increasing Pd content [2,32,33].

3.2. Cyclic voltammetry (CV)

Thin-film Pd electrodes were cycled in Ar-saturated 0.1 M $HClO_4$ or 0.05 M H_2SO_4 solutions prior to the O_2 reduction measurements,