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# The performance of structurally well-defined $Ag_xPt_{1-x}$/Pt(111) surface alloys in the oxygen reduction reaction – An atomic-scale picture

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## ABSTRACT

Aiming at a fundamental understanding of the performance of bimetallic electrodes in the oxygen reduction reaction (ORR), on an atomic scale and specifically of the role of Ag surface atoms in bimetallic PtAg electrodes in this reaction, we have investigated the properties of structurally well-defined $Ag_xPt_{1-x}$/Pt(111) surface alloys with increasing Ag surface content in the ORR. Electrode surfaces with a well-known distribution of surface atoms were prepared and characterized by scanning tunneling microscopy under ultrahigh vacuum (UHV) conditions, and transferred in a controlled way, without contact to air, to a newly designed electrochemical flow cell setup. This allows us to determine the potential-dependent activity and selectivity of the ORR towards $H_2O$ or $H_2O_2$ under well-defined reactant mass transport conditions. We find a significant enhancement of the ORR activity for $Ag_xPt_{1-x}$/Pt(111) surface alloys compared to Pt(111). From an analysis of the relative abundance of different types of $Ag_xPt_{3-x}$ trimer ensembles and simulations of the potential dependent activity of the different sites based on their $O_{ad}$ binding energy (*J.K. Nørskov et al., J. Phys. Chem. B 108 (2004) 17886*), the enhanced ORR activity can be related to $AgPt_2$ surface sites, which are identified as most active sites, more active than $Pt_3$ sites. Consequences of the excellent agreement between kinetic measurements and simulations based on calculated changes in the ORR thermodynamics induced by surface Ag on the validity of this approach are discussed.

## 1. Introduction

Bimetallic catalyst have played a dominant role in the search for more efficient catalysts for the oxygen reduction reaction (ORR), driven by the need to reach higher efficiencies in proton exchange membrane fuel cells [1,2]. Nanostructured bimetallic electrocatalysts, e.g., carbon supported PtCo and PtNi catalysts have already shown a substantial enhancement of the ORR activity at low overpotentials compared to pure Pt/C catalysts [3–9]. As part of these efforts, fundamental aspects of the reaction, including the elementary reaction steps have been investigated in model studies, either by studying the reaction on bimetallic planar model electrodes [4,10,11] and/or by computational methods [12–15]. In these model studies it would be particularly interesting to find out correlations between certain structural elements, on an atomic scale, and their ORR activity (structure activity correlations). In combination with theoretical work this would gain detailed insight into the principles underlying the high activity of certain bimetallic catalysts and thus provide a firm basis for the systematic design of improved catalysts. This approach is used in the present study, where we investigated trends in the ORR performance of $Ag_xPt_{1-x}$/Pt(111) monolayer surface alloys with increasing concentration of Ag surface atoms, up to 50%. These surfaces were structurally well defined, with a well-known distribution of the surface atoms based on previous scanning tunneling microscopy (STM) imaging [16,17]. Following our previous studies of the ORR on well-defined $Pt_xAu_{1-x}$/Pt(111) [11] and $Pt_xRu_{1-x}$/Ru(0001) [10] surface alloys, the experimental results will be compared with simulations, where according to a theoretical model developed by Nørskov, Rossmeisl and coworkers [12] we first calculated the activity of individual structural elements from the binding energy of adsorbed oxygen $O_{ad}$, and then, in a next step, the total ORR current by adding over the contributions of different structural elements. On a bimetallic surface, the $O_{ad}$ binding energy, which represents the only descriptor for the ORR activity in the above model, may be modified compared to adsorption on Pt(111) by a number of different effects, including geometric strain effects [18], due to a compressive or tensile strain of the topmost layer compared to its bulk analog, or the interaction of the respective surface atoms with the chemically different substrate (vertical-ligand effects) or with chemically different metal atoms in the surface layer (horizontal ligand effects) [19]. In good agreement with theoretical expectations, such

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effects have also been found experimentally to dramatically influence the ORR [10,11,20,21].

Background for the present study are results of a previous experimental study where it had been shown that in acid electrolyte, higher ORR activities can be obtained on PtAg nanoparticles compared to Pt nanoparticles, if the Pt/Ag ratio was higher than 0.4. In contrast, the ORR activity was below that of Pt for Pt/Ag ratios below 0.2 [22], suggesting a substantial influence of the nominal composition on the ORR performance of PtAg nanoparticles. In another study, a lower ORR activity was found for partly dealloyed PtAg nanoparticles compared to Pt nanoparticles [23]. Finally, after accelerated degradation tests, 'not dealloyed', carbon supported $Pt_3Ag$ nanorods (size 3–5 nm) were found to be more active for the ORR than $Pt_3Au$ and $Pt_3Pd$ [24]. Since these results were obtained on structurally ill-defined electrode materials, and since furthermore also the chemical composition of the surface was modified by partial dissolution of surface Ag upon potential cycling, correlations between the ORR activity of these PtAg bimetallic electrodes and specific structural elements and thus the identification of active sites, on an atomic scale, were hardly possible from these results.

This is the main objective of the present work, where we try to establish a link between theoretical predictions and experimental results by using structurally well-defined $Ag_xPt_{1-x}$/Pt(111) electrodes for the ORR. The $Ag_xPt_{1-x}$/Pt(111) surface alloys were prepared and structurally characterized by scanning tunneling microscopy under ultrahigh vacuum (UHV) conditions (Section 3.1). Based on previous findings that $Ag_xPt_{1-x}$/Pt(111) surface alloys with Ag contents > 50% are instable in the potential range of the ORR in acid electrolyte, the highest Ag surface content investigated was 50%. After transferring the electrode into an electrochemical cell, without contact of the electrode to air, the electrochemical (Section 3.1) as well as the ORR performance (Section 3.2) of these $Ag_xPt_{1-x}$/Pt(111) surface alloys and, for comparison, of a bare Pt(111) electrode, were investigated in 0.5 M $H_2SO_4$ under enforced and well-controlled electrolyte mass transport. The role of the Ag surface atoms for the ORR performance was explored by comparing the measured ORR kinetic current densities with results of the simulations, which are based on the relative abundance of different $Ag_xPt_{3-x}$ trimer atomic ensembles on the bimetallic surface structures and using the theoretical model by Nørskov et al. [12] for determining the activity of the different ensemble types (Section 3.3). These trimer sites are considered as reaction sites and were quantified by STM. The agreement between theoretical predictions based on reaction step thermodynamics and kinetic data measured experimentally as well as consequences for the validity of this general approach are discussed. Finally, the influence of the Ag surface content on the selectivity of the ORR products (towards of $H_2O$ or $H_2O_2$) is quantified and discussed in an atomistic picture (Section 3.4).

## 2. Experimental set-up and procedures

The experiments were performed in a combined ultrahigh vacuum (UHV) – electrochemical flow cell (UHV-EC) system, consisting of a UHV system (base pressure $< 1 \times 10^{-10}$ mbar) for sample preparation and its characterization by structural/spectroscopic techniques, a flow cell system for electrochemical measurements under enforced and controlled electrolyte flow, and a transfer system allowing sample transfer between both systems without contact with air, which had been described in detail previously [25]. The UHV system was equipped with standard facilities for surface preparation, such as an ion gun for $Ar^+$ sputtering (SPECS, IQE 11/35) and a Knudsen cell type evaporator (Tectra, WKC3) for Ag deposition. A home built pocket size scanning tunneling microscope (STM) was employed for structural surface characterization, using a tungsten tip. Typically, bias potentials of 0.2–0.8 V for large scale images or below 100 mV for high resolution detail images were applied at the sample, with tunneling currents of 0.3–3.0 nA (larger scale images) or around 70 nA (high resolution detail images). A quadrupole mass spectrometer (QMS - Balzers, QMG-125) allowed for residual gas analysis of the UHV-system.

Prior to each experiment, the Pt(111) single crystal (Mateck GmbH) was cleaned by $Ar^+$ sputtering ($P_{Ar} = 3 \times 10^{-5}$ mbar; E = 0.6 kV) at room temperature (RT), followed by several heating cycles at a heating rate of 4 K $s^{-1}$ up to 1050 K and cool down to RT at a rate of 2 K $s^{-1}$ in order to prepare atomically flat surfaces [17]. To remove residual impurities (carbon, sulfur) from the surface, oxidation cycles including oxygen adsorption during cool down at 800 K (exposure: $10\,L = 10\,s \times 1.33 \cdot 10^{-6}$ mbar), followed by a final heating step to 1000 K with heating/cooling rates as mentioned above, were carried out. The temperature was controlled by a pyrometer (Impac Infratherm, IGA 140). Controlled amounts of Ag were deposited on the Pt(111) sample being at RT by evaporation from a Knudsen cell (deposition rate $0.10 \pm 0.005$ ML $min^{-1}$). After each Ag deposition, the Ag coverage was determined by STM imaging (4–10 STM images with sizes of at least 200 nm × 200 nm for each Ag amount deposited). Representative STM images can be found in refs. [16,17]. The $Ag_xPt_{1-x}$/Pt(111) surface alloys were prepared following the procedure developed by Rötter [16], by annealing the Ag decorated Pt(111) surfaces to 900 K, using identical heating rates as mentioned above for the preparation of Pt(111) surfaces.

The electrochemical (EC) measurements were performed in a home built dual thin-layer laminar flow cell system, which was located in a mini UHV chamber (base pressure $p_{base} < 1 \times 10^{-8}$ mbar) attached to the main UHV chamber. The cell, which is made of KEL-F, is equipped with two counter electrodes (Au) and a reversible hydrogen reference electrode (RHE) connected by a capillary. For the EC measurements the sample was transferred from the main UHV chamber to the mini UHV chamber, which was then purged with nitrogen (5 N) to prevent surface contamination. In a next step, the electrochemical cell was pressed to the sample surface via transfer rods attached to it. The contact between sample and cell body was sealed by an O-Ring (FPM, Arcuss GmbH) to prevent leaking of the electrolyte into the vacuum chamber during the electrochemical measurements. All potentials in this work are given with respect to the RHE scale, currents and Faradaic charges are normalized to the geometric area of the electrode defined by the inner diameter of the O-ring (6 mm). All EC measurements were performed at room temperature (RT).

The electrode potential was controlled by a computer controlled potentiostat (Pine Instruments, AFCBP1). After passing the first cell compartment with the working electrode, the electrolyte flows to a second compartment, which contains a polycrystalline Pt disc electrode serving as current collector for hydrogen peroxide detection (see below). Electrochemical characterization was performed by cyclic voltammetry in 0.5 M $H_2SO_4$ supporting electrolyte, which was prepared from suprapure $H_2SO_4$ (Merck) and ultra-pure water (18.5 MΩ·cm Millipore) and purged with $N_2$ (6.0, MTI). For the ORR investigations, the electrolyte was saturated with $O_2$ (6.0, MTI). The current collector was held at constant potential (1.20 V) to continuously oxidize the hydrogen peroxide generated at the working electrode. After each ORR experiment, the collection efficiency of the current collector was determined by hydrogen evolution measurements, by the ratio of the hydrogen evolution current at the working electrode and hydrogen oxidation current at the current collector. The hydrogen peroxide yield $\chi_{peroxide}$ was determined following Eq. (1):

$$\chi_{peroxide} = \frac{2\,|I_C|/N}{|I_W| + |I_C|/N} \tag{1}$$

where $N$ denotes the collection efficiency, $I_W$ the current at the working electrode and $I_C$ the current at the electrode collector electrode. The time delay resulting from product mass transport from the first to the second compartment of the flow cell, which depending on the electrolyte flow rate was up to 1.5 s, was corrected for in the hydrogen peroxide oxidation current and in the peroxide formation yield.