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Stability and ORR performance of a well-defined bimetallic $Ag_{70}Pt_{30}$/Pt(111) monolayer surface alloy electrode – Probing the de-alloying at an atomic scale

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ABSTRACT

Aiming at a better understanding of surface de-alloying processes on an atomic scale and its impact on the electrocatalytic properties of bimetallic electrodes in the oxygen reduction reaction (ORR), we have investigated the electrochemical de-alloying of a $Ag_{70}Pt_{30}$ monolayer surface alloy on Pt(111), in electrochemical potential step measurements and the performance of the resulting electrodes in the ORR. Structurally well-defined electrode surfaces were prepared and characterized by scanning tunneling microscopy (STM) before and after the electrochemical (EC) measurements under ultrahigh vacuum (UHV) conditions. Potential step experiments were performed in a dual thin-layer flow cell in 0.5 M H_2SO_4 supporting electrolyte, using a UHV-EC transfer system which allowed electrode transfer without intermediate contact to air. STM imaging reveals an increasing, selective removal of Ag from the surface layer in the potential range 0.95–1.05 V_{RHE}, resulting in the formation of monolayer vacancy islands. The last 10% of Ag were removed only at the onset of Pt corrosion and 3D surface restructuring at 1.10 V_{RHE}. Correlating these findings with the total amount of dissolved Ag determined in electrochemical measurements we propose a possible corrosion mechanism. The corroded surfaces, in particular the more strongly corroded surfaces, showed an improved ORR performance, with a lower overpotential, by up to 100 mV, and a lower H_2O_2 yield than Pt(111). The higher stability of the surface alloys compared to a Ag(111) as well as the ORR activity are discussed in terms of electronic ligand and strain effects, for the latter structural effect have to be considered as well.

1. Introduction

Electrochemical de-alloying of metal alloys has attracted considerable interest over the last decades, both from application oriented reasons, *e.g.*, the corrosive de-alloying of technical materials such as steels [1] or the preparation of nanoporous metals [2], or from fundamental reasons [3,4]. In recent years, interest in electrochemical corrosion and de-alloying increased because of potential applications of bimetallic catalysts in the O_2 reduction reaction (ORR) in polymer electrolyte fuel cells [5,6], where de-alloying was used as a means for catalyst preparation on the one hand, *e.g.*, for core-shell catalysts [7,8], but also limited the lifetime of these catalysts due to corrosive de-alloying during operation [9–11]. In general, previous studies of electrochemical corrosion were limited to a macroscopic description, *i.e.*, descriptions based on macroscopic properties such as the metal dissolution rate [12–15]. Atomistic details were addressed so far only in few studies. Magnussen et al. investigated the electrochemical corrosion of Cu(100) by *in situ* scanning tunneling microscopy (STM), showing that this is strongly affected by adsorbates such as Cl anions, but also by corrosion inhibitors such as benzotriazole (BTA) [16]. Also corrosion and de-alloying of bimetallic systems such as Au_3Cu or AuAg alloys was investigated by *in situ* STM, *e.g.*, by Moffat et al. [17], Newman and Sieradzki [18–20], and the groups around Dosch and Stratmann [21–23], providing quantitative information on the corrosion induced changes in surface structure and morphology. Furthermore, *in situ* STM was also employed to study the selective dissolution of a metal in a two-dimensional film, *e.g.* the growth and dissolution of Ni on a Pd/Au(111) bimetallic surface [24,25] or the dissolution of Ni from a NiPd monoatomic layer electrodeposited on Au(111) [26].

Here we report results of a combined *ex situ* STM and

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electrochemistry study on the electrochemical de-alloying of $Ag_{70}Pt_{30}$/Pt(111) monolayer surface alloys, which can be considered as model systems for bimetallic AgPt electrodes. The latter have been demonstrated as promising catalysts for the ORR [27,28]. The preparation of Ag_xPt_{1-x}/Pt(111) monolayer surface alloys, their structure, thermal stability and electrochemical behavior as well as their interaction with CO under UHV conditions have been investigated recently in our group [29–32], following earlier studies on the growth of thin films of Ag on Pt(111) [33,34] and the formation of AgPt surface alloys [35–37]. First results of this study, focusing on the electrochemical properties and the electrochemical stability of the surface alloys in 0.5 M H_2SO_4 supporting electrolyte as function of the Ag surface content, were reported in Ref. [32]. There we could show that that the Ag surface atoms in Ag_xPt_{1-x}/Pt(111) surface alloys are significantly stabilized against corrosive dissolution compared to Ag(111), which we attributed to the interaction with underlying Pt substrate atoms ('vertical ligand effects') and, mainly at lower Ag surface concentrations, with neighboring Pt surface atoms ('lateral ligand effects'). Furthermore, for Ag contents up to 50% in the surface layer, we could not detect any significant Ag dissolution at potentials up to 0.95 V. In the present communication, we focus on the mechanistic understanding of the corrosion process and its potential dependence, including also a quantification of the Ag atoms dissolved during the corrosion process.

Here we present our results on the corrosion of Ag surface atoms and the stability of structurally well-defined bimetallic $Ag_{70}Pt_{30}$/Pt(111) surface alloys, which were prepared and structurally characterized by STM under ultra-high vacuum (UHV) conditions. The dissolution of Ag atoms, induced by potential steps above the stability limit of the surface alloy, on the surface structure and surface composition was studied on an atomic scale using an electrochemical flow cell including a collector electrode for detection of the dissolved Ag atoms. The observations made are discussed in a atomistic picture and a possible corrosive dissolution mechanism is presented.

In the following we will, after describing the experimental setup and procedures, first present results of potential step corrosion measurements on $Ag_{70}Pt_{30}$/Pt(111) surface alloys (section 3.1), followed by the structural characterization of the resulting surfaces by STM (section 3.2). A possible mechanism for the corrosion of Ag_xPt_{1-x}/Pt(111) surface alloys, including in particular the effect of the corrosion potential ('upper potential') is presented in section 3.3. Finally we test the effects of the corrosive surface restructuring on the O_2 reduction reaction (section 3.4).

2. Experimental setup and procedures

The experiments were performed in a combined ultrahigh vacuum (UHV) – electrochemical flow cell (UHV-EC) system, consisting of a UHV system 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 [38]. The UHV system (base pressure < 1×10^{-10} mbar) is equipped with standard facilities for sample preparation and characterization such as an ion sputter gun (Specs, IQE 11–35) for Ar^+ sputtering and a Knudsen cell type evaporator (Tectra, WKC3) for Ag evaporation. Structural characterization of the sample surfaces was performed by STM imaging, using a home-built pocket-size STM. Typical tunneling voltages and currents were 0.2–0.8 V/0.3–3.0 nA for large scale images or <100 mV/around 70 nA for high resolution detail images, applied at the tungsten tip. A quadrupole mass spectrometer (QMS, Balzers, QME-125-1) served for residual gas analysis.

The Pt(111) surface was prepared by 15 min Ar^+ ion sputtering ($p_{Ar} = 3 \times 10^{-5}$ mbar; E = 0.6 kV) at room temperature (RT), followed by heating cycles up to 1050 K at a rate of 4 K s^{-1} and cooling to RT at a rate of 2 K s^{-1}. The temperature was controlled by a pyrometer (Impac Infratherm, IGA 140). Residual impurities (carbon, sulfur) accumulated in the topmost layers were removed by oxidation cycles, including adsorption of oxygen during cooling down (at about 800 K; 10 L = $10 \times 1.33 \times 10^{-6}$ mbar s) followed by a final heating cycle to 1000 K (heating/cooling rates see above). For preparing the $Ag_{70}Pt_{30}$/Pt(111) monolayer surface alloys we first evaporated Ag from a Knudsen cell at a rate of 0.1 ± 0.005 ML min^{-1} with the sample held at room temperature [32]. Next the Ag coverage was determined by STM, evaluating 4–10 STM images (size at least 200 nm × 200 nm). In a last step the Ag covered Pt(111) surface was annealed to 900 K, using the same heating/cooling rates as employed for the preparation of clean Pt(111) surfaces. This procedure had been shown earlier to result in monolayer surface alloys by comparison of the Ag surface coverages derived from quantitative evaluation of STM images before and after intermixing [29]. The evaluation of the surface composition and the determination of the distribution of surface atoms after intermixing by STM are possible because of the different appearance of two types of metal atoms in high resolution STM images ('atomic resolution imaging with chemical contrast'), due to their different electronic properties [39,40].

For the electrochemical (EC) measurements the sample was transferred to an electrochemical flow cell system, located in a transfer UHV chamber (base pressure < 1×10^{-8} mbar), which is attached to the main UHV system via a gate valve. This setup allows for a sample transfer from UHV to the electrochemical cell under well-defined, clean conditions. The home-built laminar flow cell (made of KEL-F) is equipped with two counter electrodes (Au), one close to the working electrode and one at the electrolyte outlet capillary, and connected by a capillary to a reversible hydrogen electrode (RHE). All potentials in this work are given with respect to the RHE scale. The potential was controlled by a computer-controlled bi-potentiostat (AFCBP1, Pine Instruments). For detection of the dissolved Ag the flow cell setup is equipped with a second compartment containing a polycrystalline Au foil (geometric area = 0.95 cm^2) serving as a collector electrode (see cell design in Ref. [38]). Applying a constant potential of 0.45 V to the collector electrode caused re-deposition of the dissolved Ag from the supporting electrolyte. The collection efficiencies of the current collector were determined from the ratio of the currents resulting from hydrogen evolution at the working electrode and hydrogen oxidation at the current collector. This was done both after the corrosion measurements, using a polycrystalline Au collector electrode, and after the ORR measurements where a polycrystalline Pt collector was used.

The electrochemical measurements were performed at room temperature (RT) in 0.5 M H_2SO_4 supporting electrolyte, prepared from ultrapure water (18.5 MΩ cm Millipore) and suprapure H_2SO_4 (Merck) and purged with nitrogen (6.0, MTI), at electrolyte flow rates between 0.6 and 0.9 ml min^{-1}. For each potential step experiment, a fresh surface with a $Ag_{70}Pt_{30}$/Pt(111) composition (deviation ± 4% absolute) was prepared. The geometric area of the electrode is 0.38 cm^2. The resulting surface alloy samples were electrochemically characterized by cyclic voltammetry (CV) before and after the potential step (PS) experiment. For potential step experiments, the potential was stepped from 0.50 V, a potential were the $Ag_{70}Pt_{30}$/Pt(111) surface alloy is not affected by irreversible surface corrosion [32], to the respective upper potential limit, held there for 5 min and then stepped back to 0.50 V. After the EC measurements the cell was flushed with pure water to remove anions and then the electrode was emersed from the electrolyte at