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Variation of the potential of zero charge for a silver monolayer deposited onto various noble metal single crystal surfaces

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Abstract

The potential of zero charge (PZC) of a pseudomorphic silver monolayer electrodeposited onto Au(1 1 1), Pt(1 1 1), Pd(1 1 1), Ir(1 1 1) and Rh(1 1 1) has been determined in diluted perchlorate solution by measuring capacitance–potential curves. The PZC of these Ag overlayers varies in the potential range between −0.8 V and −0.45 V versus SCE depending on the nature of the substrate material and thus reveals significant shifts compared to −0.7 V versus SCE for a massive Ag(1 1 1) electrode. This bulk value for the PZC has also been obtained for two monolayer thick Ag overlayers, demonstrating that mainly the first monolayers are electronically altered by an underlying foreign substrate. In addition, the PZC of thicker deposits has always been found to be identical to the PZC of Ag(1 1 1), showing an epitaxial growth of Ag on the electrodes under study. While no dependence on the lattice constants of the substrates for the PZC of the pseudomorphic Ag monolayers was found, it has been observed that calculated shifts in the d-band centre show the same systematic variation. Work function data for Ag monolayers on Au(1 1 1) and Pt(1 1 1) are in good agreement with the measured PZC values. Consequences of altered double-layer properties on electrocatalytic reactions are briefly addressed.

Keywords: Double-layer capacity; Ag(1 1 1); Ag overlayers; Pseudomorphism; Electrocatalysis

1. Introduction

The potential of zero charge (PZC) has recently been measured for Pd(1 1 1) and for pseudomorphic palladium monolayers electrodeposited onto Au(1 1 1) and Pt(1 1 1) surfaces [1,2]. The significant shifts in the PZC values for these systems reflect alterations in the electronic structure of the metallic monolayers, which impact on binding energies for various adsorbates and thus can be crucial for electrochemical kinetics and electrocatalysis [3–6]. However, an extended systematic study of the PZC for pseudomorphic palladium monolayers by measuring a minimum in the double-layer capacity in dilute solutions can easily be hampered by chemisorption of hydrogen or specific adsorption of anions [2].

We therefore have chosen silver surfaces as model systems, which do not reveal these strong interactions with aqueous solutions. Double-layer properties including the determination of the PZC of Ag single crystal electrodes have thoroughly been examined by the Valette group [7]. The change in PZC with the crystallographic orientation [8,9] and its linear relation to the work function is well known and quantitatively described by Trasatti [10–12]. Langkau and Baltruschat have measured the PZC of Ag deposited onto Pt(1 1 1) and found −0.48 V versus SCE (saturated calomel electrode) and −0.72 V for one Ag monolayer and bulk silver in 0.005 M $NaClO_4$ solution, respectively [13]. These values can be related with the corresponding work function values of 5 eV for a Ag monolayer on Pt(1 1 1) [13] and 4.74 eV for pure Ag(1 1 1) [14].

We assume that alterations in physical and chemical properties of such metallic monolayers, which are often pseudomorphic, are reflected in variations of the PZC depending on the nature of the substrate. We therefore have systematically studied the electrodeposition of Ag monolayers on various fcc(1 1 1) single crystal surfaces (Au, Pd, Pt, Rh, Ir) and measured the respective PZC values as so-called Gouy–Chapman minima after controlled transfer to 0.005 M $KClO_4$ solution. The obtained results are compared with the PZC of a massive

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Ag(1 1 1) electrode and compared with available work function data.

2. Experimental

The electrochemical measurements were performed in a conventional three electrode glass cell. An SCE and a platinum wire were used as reference and counter electrodes, respectively. In order to protect the solution from chloride contaminations, the SCE was placed in a separate compartment. The solutions were prepared from H_2SO_4 (Merck, suprapur), Ag_2SO_4 (Fluka, 99.5%), $KClO_4$ (Fluka, 99.5%, twice-recrystallized) and milli-Q water (18.2 MΩ cm at 25 °C, TOC < 1 ppb). The diameter of the Ag(1 1 1), Au(1 1 1), Pt(1 1 1), Pd(1 1 1) and Ir(1 1 1) crystals used for cyclic voltammetry and capacity measurements were 4 mm, it was 0.07 mm for Rh(1 1 1). The electrodes were annealed by inductive heating in presence of nitrogen (Au, Pd) or a mixture of nitrogen and hydrogen (Ag, Pt, Ir, Rh) for less than 1 min before each measurement, cooled down slowly below 100 °C before contacting with 0.1 M H_2SO_4. After checking for cleanliness and surface quality, the electrodes were transferred to a second cell filled with 0.1 M H_2SO_4 + 0.001 M Ag_2SO_4 for silver deposition. Before measuring in $KClO_4$ solution, the single crystal electrode was rinsed with oxygen-free water to exclude further metal deposition and to remove the sulphuric acid solution. Adsorbed sulphate was desorbed in 0.005 M $KClO_4$ at negative potentials. The capacitance measurements were performed in the perchlorate solution with lock-in amplifier at 20 Hz and a 10 mV peak-to-peak sinusoidal perturbation. Subsequently, the Ag adlayer was stripped in 0.1 M H_2SO_4 to check its coverage and to ensure its stability during the measurement. It shall be pointed out that all electrolytes were purged with nitrogen and all transfers of the electrodes from one cell to the other were done in the absence of oxygen.

3. Results and discussion

All single crystal electrodes could be well-prepared by inductive heating – Ag(1 1 1) [15], Pd(1 1 1) [16], Au(1 1 1), Pt(1 1 1) [17], Rh(1 1 1) and Ir(1 1 1) [18] – yielding high-quality surfaces as well as stable and reproducible voltammograms (not shown here). Since Ag tends to be deposited in the underpotential regime by forming one pseudomorphic (1 × 1) commensurate monolayer, the characterisation of the single crystal surfaces by Ag underpotential deposition (upd) was crucial for the present study. Ag upd voltammograms were used as additional criterion to ensure well-ordered and clean electrode surface structures, because upd of metals is known to belong to very structural sensitive processes.

3.1. Ag deposition and dissolution

In Fig. 1 are shown typical voltammograms for Ag upd on Au(1 1 1), Pt(1 1 1) and Pd(1 1 1). Only in the case of Au(1 1 1), the electrode can be immersed into the Ag solution at a positive potential, where silver deposition does not yet occur without surface oxidation of the substrate taking place. In the other cases, an Ag monolayer was directly formed at 0.5 V for Pd(1 1 1) and Pt(1 1 1) or, as in the case of Rh(1 1 1) and Ir(1 1 1), Ag was stripped close to the Nernst potential after deposition of bulk silver at 0.36 V to yield a monolayer. For the latter electrodes, surface oxidation starts at potentials, which overlap with the Ag upd processes.

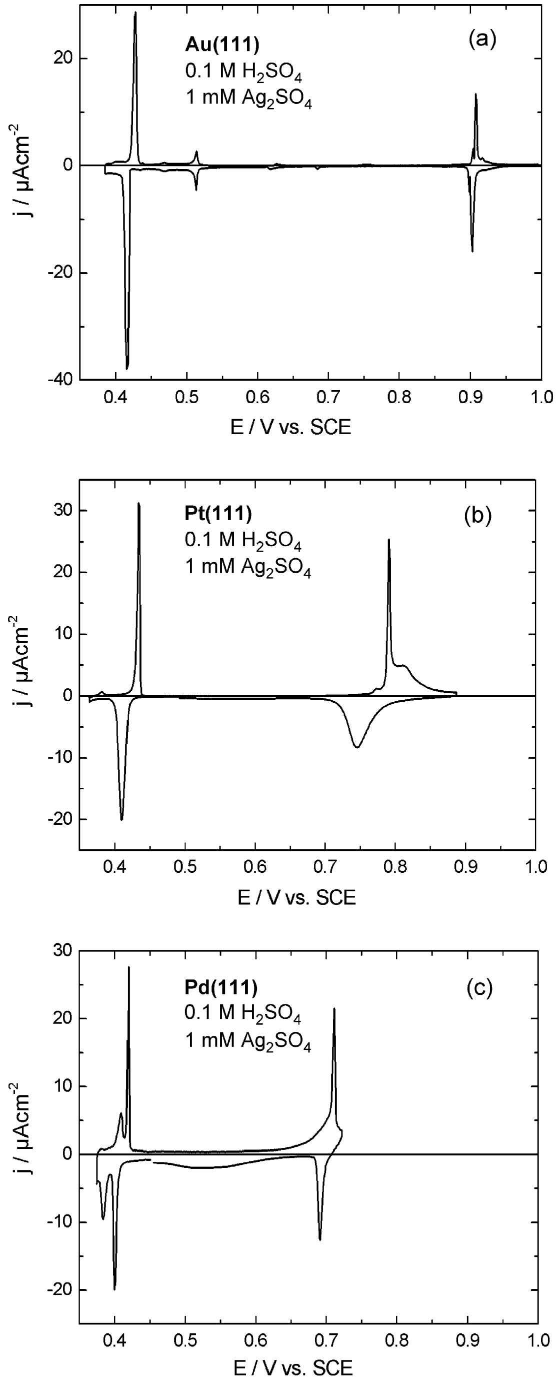

Fig. 1. Cyclic voltammogram of (a) Au(1 1 1), (b) Pt(1 1 1) and (c) Pd(1 1 1) in 0.1 M H_2SO_4 + 1 mM Ag_2SO_4. Scan rate: 1 mV s^{-1}.

Ag upd on Au(1 1 1), Pt(1 1 1) and Pd(1 1 1) involves the deposition of two monolayers taking place in various steps. This has been studied in detail for Ag on Au(1 1 1) by in situ scanning tunnelling microscopy [19] and for Ag on Pt(1 1 1) in situ surface X-ray scattering (SXS) [20]. It is also seen in Fig. 1 that the deposition of a second silver monolayer takes place at rather small underpotential shifts.

Fig. 1a shows the typical voltammogram for the electrochemical Ag deposition onto Au(1 1 1) in 1 mM Ag_2SO_4 + 0.1 M H_2SO_4 [19,21]. The deposition starts with a peak at 0.9 V in the upd region, followed by two current peaks at 0.51 V and 0.42 V. The charge for the first peak was measured to about 112 μC cm^{-2} corresponding to 0.33 monolayers (ML) of Ag [19]. The coverage increases with scanning more negatively until a pseudomorphic Ag_{ML} is formed at 0.44 V [19]. The charge for the peak at 0.42 V was 270 μC cm^{-2} corresponding to the second pseudomorphic ML of Ag, which is in good agreement with published data [19,21]. Esplandiu et al. observed a layer-by-layer growth up to at least 10 monolayers in the overpotential deposition region [19].

For the present study, the electrode was emersed at 0.44 V and 0.40 V, when one or two pseudomorphic Ag monolayers have been deposited, respectively.

Fig. 1b shows a cyclic voltammogram of Pt(1 1 1) in 1 mM Ag_2SO_4 + 0.1 M H_2SO_4, which is also in good agreement with published data [20,22]. We found that the dissolution peak at 0.79 V for the first Ag layer gets sharper with increased surface quality for the Pt(1 1 1) substrate. Marinkovic et al. have studied this system by in situ SXS measurements and suggest that Pt(1 1 1) is free from Ag at 0.85 V, a pseudomorphic Ag monolayer is formed at 0.6 V, and an incommensurate expanded second Ag monolayer is formed at 0.42 V [20].

In Fig. 1c is shown for the first time a voltammogram for Ag upd onto Pd(1 1 1). An anodic peak at 0.75 V (not shown) is a clear indication for oxidation of Pd(1 1 1), which is known to lead to structural transformations of the surface [16]. As in the systems mentioned above, there are current peaks for a first Ag monolayer (around 0.7 V) and a second Ag monolayer close to the Nernst potential. The formation of the second Ag adlayer is related with two peaks, the sharpness of the more positive one being a quality criterion as checked with crystals of different defect density.

The charge densities for deposition of one pseudomorphic Ag monolayer were in good agreement with calculated values (222 μC cm^{-2} for Au(1 1 1), 240 μC cm^{-2} for Pt(1 1 1) and 245 μC cm^{-2} for Pd). In the case of Ag on Rh(1 1 1) and Ir(1 1 1), the charge densities for Ag dissolution in Ag^+-free sulphuric acid were in agreement with 256 μC cm^{-2} and 251 μC cm^{-2}, respectively, though overlapping with the surface oxidation processes of the substrates. We would like to stress that the characteristic hydrogen adsorption peaks for Pt(1 1 1), Pd(1 1 1), Rh(1 1 1) and Ir(1 1 1) in 0.1 M H_2SO_4 are completely masked after formation of an Ag monolayer each. On the other hand, it seems that surface oxidation may take place at more negative overpotentials when a substrate is just freed from the Ag adlayer. This is demonstrated in Fig. 2 for the an Ag monolayer on Rh(1 1 1), where a substantial amount of surface oxidation charge flows already during the Ag dissolution process. This observation shows the well-known fact that sulphate adsorbed on Rh(1 1 1) prevents from surface oxidation and shifts the process to more positive potentials compared to, say, perchloric acid.

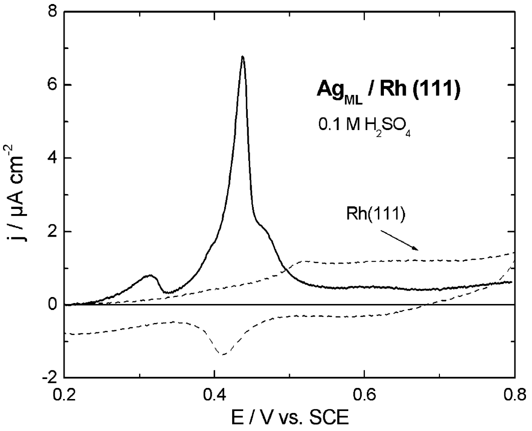

Fig. 2. Current–potential curve for the dissolution of an Ag monolayer from Rh(1 1 1) in 0.1 M H_2SO_4 (solid line). A curve for a blank Rh(1 1 1) electrode is shown for comparison (dashed line). Scan rate: 1 mV s^{-1}.

3.2. PZC measurements

In Fig. 3, a capacitance measurement for massive Ag(1 1 1) in 5 mM $KClO_4$ is shown. According to the Gouy–Chapman theory the capacitance minimum at −0.7 V has to interpreted as the PZC, in excellent agreement with published data from the seminal work of Valette et al., where the PZC for Ag(1 1 1) in 0.005 M NaF and in 0.005 M $NaClO_4$ solution was determined to be −0.69 V and −0.717 V, respectively [7,8].

The PZC for Ag multilayers deposited at 0.35 V (ca. 1000 ML) onto all substrates used in the present study is practically the same as the PZC for a massive Ag(1 1 1). This leads to the conclusion that these thick Ag layers are still well-ordered and behaves like massive Ag(1 1 1). When it was possible to deposit two Ag monolayers in the upd region (on Au, Pt, Pd), again −0.7 V were obtained for the PZC value. This is astonishing, because the atomic structure of the second Ag monolayer may still deviate from the bulk material, as in the case of 2 ML Ag on Pt(1 1 1) [20]. However, it is seen that the second Ag layers are not significantly influenced in their electronic properties by the underlying substrate.

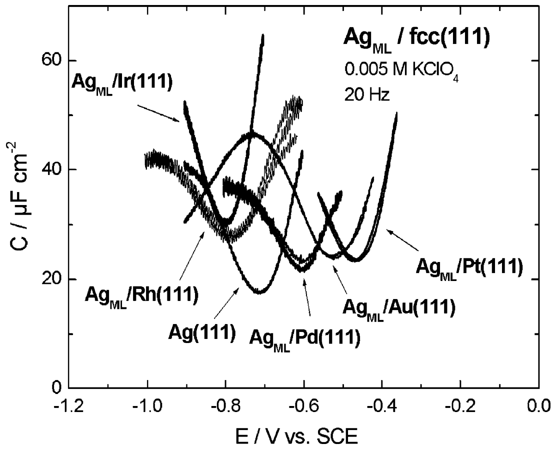

Fig. 3. Capacitance–potential curves of Ag(1 1 1) and pseudomorphic Ag monolayers on Au(1 1 1), Pt(1 1 1), Pd(1 1 1), Rh(1 1 1) and Ir(1 1 1) in 5 mM $KClO_4$ at 20 Hz. Scan rate: 10 mV s^{-1}.

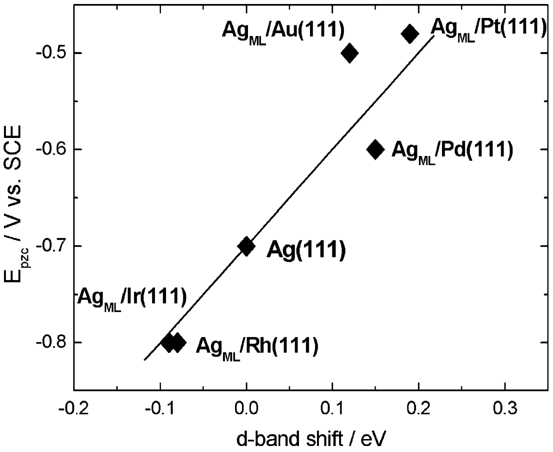

Fig. 4. Comparison of experimentally obtained PZC values for pseudomorphic Ag monolayers with calculated shifts in d-band centre. The latter data are taken from Ref. [3].

The situation clearly changes when inspecting the PZC of a single Ag monolayer deposited onto the different substrates. The corresponding $C(E)$ curves are shown in Fig. 3. For clarity, only the potential regions around the capacitance minima are shown in Fig. 3, however, at negative potentials the double-layer capacitance reaches a value of about 20 μF cm^{-2}, a value which is often observed for a well-defined surface electrodes such as Au(1 1 1) and Ag(1 1 1), where the roughness factor is unity [8]. The most eye-catching point is that the PZC values for the various pseudomorphic Ag monolayers (see Table 1) vary over a broad potential region of more than 0.3 V. This means that variations in chemical and physical properties of metallic monolayers may also be reflected in the location of the PZC.

No capacitance minimum was found for Ag deposited onto Ru(0 0 0 1), even not when a Cu adlayer was displaced by Ag as suggested by Adzic et al. [23]. However, the latter method could be successfully applied for Ag on Pt(1 1 1), for example, where the PZC value could be well reproduced.

At present, unfortunately, there is only limited work function data for pseudomorphic Ag monolayers available (Table 1). However, a linear relation as given by Trasatti [10–12] can also be anticipated for PZC and work function of pseudomorphic monolayers, which is reported here for the first time. There is no systematic dependence of PZC on the lattice constants of the substrates (Table 1), which is supposed to be adopted by the Ag monolayers (see above). While practically all Ag monolayers under study are more or less compressed, the PZC is found to be shifted either towards more positive or more negative values, compared to the properties of bulk silver.

Admittedly, there is no prove for pseudomorphism in the case of Ag monolayers on Pd(1 1 1), Rh(1 1 1) and Ir(1 1 1), although we strongly assume (1 × 1) structures also in these cases. On the other hand, we found that the PZC of an Ag superstructure, corresponding a coverage of 0.33 [19], is identical with the value for a full adlayer. Similarly, it has recently been reported by Jerkiewicz et al. that the pseudomorphic Ag monolayer on Pt(1 1 1) is going to be compressed when a second Ag layer had been deposited and dissolved again [22]. However, we could not detect any change in PZC for Ag on Pt(1 1 1), which might occur after such structural transformation.

Besides the work function, other electronic properties of metallic monolayers are also expected to deviate from bulk values. Donner et al. have recently observed that not only the work function of an Ag monolayer on Au(1 1 1) is increased (Table 1), but also the binding energy for the 3d core levels as measured by XPS is lowered by 0.16 eV [24]. The same authors observe bulk properties already for the second Ag layer on Au(1 1 1) [24], which strongly supports our findings for the PZC. In the same way, it may be useful to compare the PZC values from our work with calculated shifts in the so-called d-band centre for the same pseudomorphic Ag monolayers [3]. Such a comparison is shown in Fig. 4, demonstrating that the observed trends for shift in measured PZC and calculated d-band centre shift are identical. A direct impact of the location of the d-band centre on the work function (and the PZC) of Ag is not expected, since the value of the silver d-band centre is −4.3 eV relative to the Fermi level. However, we strongly believe that both the results of the present experiments and the theoretical calculations for the same systems are related with the same yet unknown physical origin.

Since the d-band model itself predicts a strong dependence of adsorbate (e.g., hydrogen or carbon monoxide) binding energies on the energetic location of the centre of the d-band [3], the observed significant shifts in PCZ values for the Ag monolayers might have a strong impact on electrosorption and electrocatalytic processes. Indeed, it has recently been observed that an Ag monolayer deposited onto Au(1 1 1) reveals a considerable electrocatalytic activity for glucose oxidation, while Ag(1 1 1) itself is completely inactive for this reaction [25]. Such considerations make our study invaluable in exploring basic principles for relations between the electronic structure of bimetallic electrodes and their activity towards certain electrochemical or electrocatalytic reactions.

Table 1
Properties of pseudomorphic Ag monolayers deposited onto various single crystal electrodes

Electrode	PZC vs. SCE (V) [this work]	Lattice constant (nm) [26]	Work function (eV)	Shift in d-band centre (eV) [3]
Ag_{ML}/Au(1 1 1)	−0.50	0.40786	4.87 [24]	0.12
Ag_{ML}/Pt(1 1 1)	−0.48 [13]	0.39231	5 [13]	0.19
Ag_{ML}/Pd(1 1 1)	−0.60	0.38898	–	0.15
Ag_{ML}/Rh(1 1 1)	−0.80	0.38043	–	−0.08
Ag_{ML}/Ir(1 1 1)	−0.80	0.38394	–	−0.09
Ag(1 1 1)	−0.70 (cf. [7])	0.40864	4.74 [14]	0

4. Conclusion

Pseudomorphic Ag monolayers on Au(1 1 1), Pt(1 1 1), Pd(1 1 1), Rh(1 1 1) and Ir(1 1 1) can be obtained by electrochemical deposition in the underpotential regime or after controlled stripping of bulk Ag. These monolayers show significant shifts in PZC to more positive and negative values in a range of 0.35 V with comparison to massive Ag(1 1 1) demonstrating altered electronic properties for the silver surface. The observations are in good agreement with available data on electronic structure and related shifts, which were obtained by various groups both in experiment and by theoretical calculations. Thus, a systematic study on variations of the PZC for a metallic monolayer is presented for the first time.

For the linear correlation with the PZC, a theoretical treatment of the work function for Ag monolayers and related systems has been started. The analysis of basic relations between electronic structure and electrochemical activity for well-defined model electrodes is believed to be of high relevance for electrocatalysis. It is assumed that such fundamental work can also be applied to tailor the properties of real electrocatalysts including nanoparticles. The role of crystallographic orientation and of surface steps has further to be investigated.

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