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Identification of Non-Faradaic Processes by Measurement of the Electrochemical Peltier Heat during the Silver Underpotential Deposition on Au(111)

*Stefan Frittmann, Vadym Halka, and Rolf Schuster**

Abstract: *We measured the heat which is reversibly exchanged during the course of an electrochemical surface reaction, i.e., the deposition/dissolution of the first two monolayers of Ag on a Au(111) surface in (bi)sulfate and perchlorate containing electrolytes. The reversibly exchanged heat corresponds to the Peltier heat of the reaction and is linearly related to its entropy change, including also non-Faradaic side processes. Hence, the measurement of the Peltier heat provides thermodynamic information on the electrochemical processes which is complementary to the current–potential relations usually obtained by conventional electrochemical methods. From the variation of the molar Peltier heat during the various stages of the deposition reaction we inferred that co-adsorption processes of anions and Ag do not play a prominent role, while we find strong indications for a charge neutral substitution reaction of adsorbed anions by hydroxide, which would not show up in cyclic voltammetry.*

Electrochemical reactions are usually accompanied by various side reactions including co-adsorption of anions, double-layer charging, or restructuring of the solvent layers at the electrode–electrolyte interface. Not all of these processes contribute to the charge which flows in the outer cell circuit, and even if they do, it is often impossible to separate the different contributions solely based on the electrochemical current signal. To obtain complementary information on the electrochemically driven processes, we measured the total reaction entropy of the electrochemically driven processes in parallel to the electric current, flowing in the external cell circuit. The reaction entropy of electrochemical reactions is directly accessible by measuring the heat, which is reversibly exchanged between the electrochemical interface and its surrounding upon the electrochemical reaction.[1] This so called electrochemical Peltier heat is given by the product of the temperature and the reaction entropy, including all side reactions, plus a contribution due to ion and electron transport during the current flow in the electrochemical cell. This ion- and electron-transport contribution is constant in the respective electrolyte and can be estimated by literature data on the Eastman entropy of transfer.[1e] We recently demonstrated that reversible heat effects of single electrodes, which are caused by minute electrochemical conversions, for example, the deposition of a few percent of a monolayer of a metal or even double-layer charging, become measurable.[2]

Herein we study the reversible heat exchange upon the Ag underpotential deposition (UPD) on Au(111) as a prototypical example for the first stages of electrochemical metal deposition. We determine the reaction entropy during the various stages of the deposition or dissolution of the first two monolayers of Ag on Au(111) and compare it to that of pure Ag bulk deposition in order to draw conclusions about possible side reactions.

Silver UPD on Au(111), mostly from acidic sulfate-containing solutions was intensively studied by several groups.[3] A concise summary of the general characteristics of Ag UPD is given for example, in Ref. [3f]. In Figure 1a a typical cyclic voltammogram (CV) is presented, which was recorded in 2.5 mM Ag_2SO_4/0.1 M H_2SO_4 with a flame-annealed (111)-textured Au film as electrode in our calorimeter cell. A typical Ag deposition cycle starts at potentials positive of the UPD I region, where the Au(111) surface is covered with about 0.2 monolayers (ML) of sulfate[4] (ML refers to the topmost Au atoms). When the potential is lowered, Ag deposition proceeds essentially in three steps, marked by UPD I, II, and III in Figure 1a. (It should be noted that on well-prepared Au(111) single crystalline surfaces the peaks in the CV appear slightly sharper than with our (111)-textured Au films). From the charge balance and structural information obtained by STM and other methods[3b,c,f] Esplandiu et al. proposed a Ag coverage of 0.44 ML just negative of the UPD I peak.[3f] Based on the changes in the STM images[3f] and on EQCM measurements[3e] it was concluded that the Ag coverage continuously increased between the UPD I and UPD III peaks. The first (1 × 1) Ag monolayer is completed upon passing the rather wide UPD II wave, while a second Ag layer is deposited during the UPD III current wave, as unequivocally shown by surface X-ray diffraction (SXRD).[3h,i] In contrast to the Ag coverage, the role of anions during the UPD process is under more dispute. Esplandiu et al. proposed co-adsorption of anions and Ag^+ ions in the intermediate potential range.[3f] However, in EQCM measurements[3e] and measurements of the electrosorption valency of Ag in a thin layer cell[5] no significant change of the anion coverage was found. To explicitly study the influence of the anions on the Ag UPD process and its heat effects we performed calorimetric measurements in different electrolytes, exchanging the bisulfate by sulfate or perchlorate. Corresponding CVs are shown in Figure 1b

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[*] S. Frittmann, Dr. V. Halka, Prof. R. Schuster
Institut für Physikalische Chemie
Karlsruhe Institute of Technology
Kaiserstrasse 12, 76131 Karlsruhe (Germany)
E-mail: rolf.schuster@kit.edu

Supporting information (experimental details, estimates of the molar Peltier heat of Ag bulk deposition and a listing of possible charge-neutral side processes and their reaction entropy) and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201600337.

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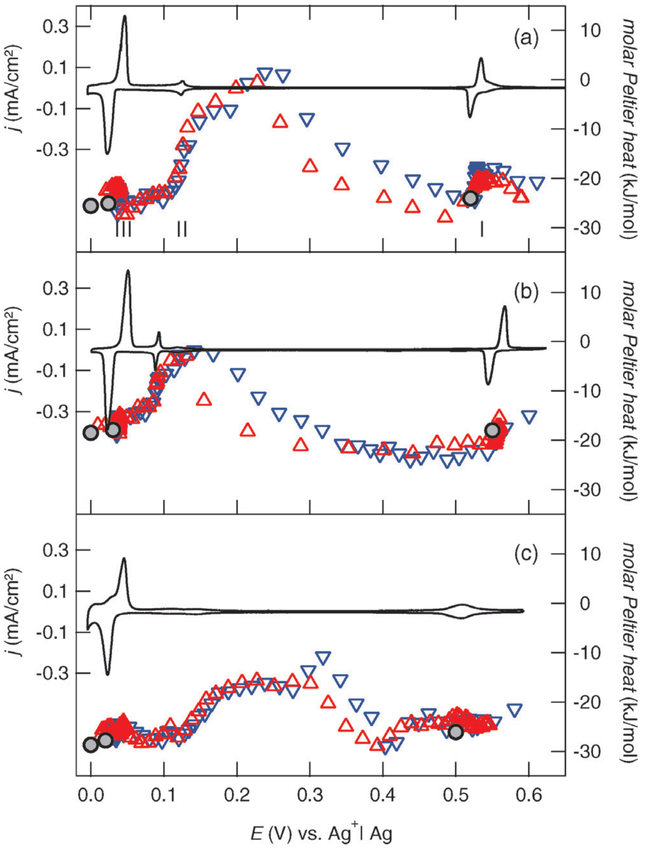

Figure 1. Cyclic voltammograms (left axis) and potential dependent molar Peltier heats (right axis) for Ag UPD from a) 2.5 mM Ag_2SO_4/ 0.1 M H_2SO_4, b) 2.5 mM Ag_2SO_4/ 0.1 M K_2SO_4, 1 mM H_2SO_4, and c) 5 mM $AgClO_4$/0.1 M $HClO_4$. The black, shaded circles give the molar Peltier heat obtained from the extrapolation of the molar heat to zero potential pulse amplitude, the triangles result from series of subsequent 10 ms long galvanostatic pulses with $+0.5\ mA\,cm^{-2}$ (red upward triangles) and $-0.5\ mA\,cm^{-2}$ (blue downward triangles). These pulses correspond to an electrochemical conversion of 0.025 ML of Ag. The experiments were performed at room temperature.

and c. There are only small differences compared with the CV in sulfuric acid solution. In perchloric acid (Figure 1 c) the current waves appear wider than in Figure 1 a and in the UPD II region no pronounced peak can be seen, in accordance with findings in the literature.[3b] In the sulfate solution the UPD II peak is split up into a rather sharp peak at 0.09 V and a hump at about 0.11 V (Figure 1 b).

The heat of the electrochemical Ag UPD process was measured with our electrochemical microcalorimeter.[2b] The key improvements to achieve the required sensitivity were 1) the use of a thin electrode/pyroelectric-sensor assembly of only 125 μm thickness with low heat capacitance and 2) the minimization of the loss of heat from dissipation into the electrolyte by conducting the electrochemical reactions for only 10 ms.[6] From the temperature change of the electrode/sensor assembly during the electrochemical reaction, we can quantitatively determine the heat effects accompanying the reaction. Normalization by the electrochemical conversion, that is, the charge, which flowed in the cell circuit, yields the molar heat. To obtain the reversible contribution to the molar heat effects, that is, the molar Peltier heat, we either have to extrapolate the molar heat values for different potential pulse amplitudes towards zero conversion or, alternatively, apply only very small potential or current pulses to stay close to equilibrium. Both procedures were applied and are described in detail in the Supporting Information.

In Figure 1 the values for the reversibly exchanged molar heat, that is, the molar Peltier heat, are depicted for all three solutions. The black, shaded circles present the molar Peltier heat for the UPD I and III regions, as well as for Ag bulk deposition. The bulk deposition was measured on an approximately 200 ML thick Ag film, which was deposited in situ on the Au surface. The data points were obtained by extrapolation of multiple pulse measurements at the respective equilibrium potentials. Their standard deviation among different experiments was below $\pm 2\ kJ\,mol^{-1}$. In addition in Figure 1 values of the molar Peltier heat are given, which were determined from series of small galvanostatic pulses, causing progressive deposition (blue downward pointing triangles) or dissolution (red upward triangles) of Ag in the Ag UPD region. To obtain the data points for Ag deposition, we started at potentials positive of the Ag UPD I (ca. 0.6 V) and applied subsequent negative current pulses. Each current pulse caused the deposition of about 0.025 ML of Ag (assuming purely Faradaic Ag deposition). In between the current pulses the cell was left at open circuit conditions for about 2 s to allow for the stabilization of the new equilibrium potential. The potential scale presents the potential before applying the respective current pulse. We proceeded to stepwise deposit Ag until the potential approached that of Ag bulk deposition. Then we reversed the polarity of the pulse current and stepwise dissolved the Ag UPD layer. The small scatter of the data stems from the uncertainty, arising from irreversible heat, as well as from the error of the heat measurement.

The datasets for the molar Peltier heat of the Ag UPD processes are strikingly similar for all three electrolytes. In particular, although the absolute values slightly differ between the systems, within one system the molar Peltier heats of UPD I, UPD III, and Ag bulk deposition are essentially the same. At potentials in between the UPD I and III, the molar Peltier heat exhibited a pronounced maximum for all electrolytes. In the acidic solutions (Figure 1 a,c) the maximum was found around 0.25 V, whereas in the sulfate solution the maximum is shifted towards ca. 0.15 V (Figure 1 b).

Since the molar Peltier heats and therefore also the reaction entropies are the same for UPD I, UPD III, and Ag bulk deposition, it is straight forward to assume that Ag bulk deposition, that is, Faradaic Ag deposition is the predominant electrochemical reaction for all these processes. The absolute values of the molar Peltier heat for Ag bulk deposition in the different electrolytes can be well understood from the entropy of Ag, that of Ag^+, and the entropy of transport in the different solutions (see Supporting Information). However, for a definite identification of the electrochemical processes, a more careful analysis of the possible contributions to the Peltier heat is needed. For the following

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discussion we formally split the deposition reaction into two processes, the Faradaic Ag deposition ($Ag^+(aq) + e^- \rightarrow Ag(ad)$) and an accompanying charge neutral process. The possible accompanying charge neutral processes are 1) co-adsorption of Ag^+ together with anions, 2) the substitution of adsorbed anions by other ones, and 3) ordering processes of the solvent at the interface.

In principle the contributions to the reaction entropy of all possible charge-neutral processes had to be considered in detail. However, a comparison of the results of the different electrolyte solutions provides more simple arguments to point out that Faradaic Ag deposition is the predominant process also for UPD I and III. We studied Ag UPD from sulfuric acid solutions, where the predominant ions in solution are hydronium and bisulfate, and from 0.1 M K_2SO_4/ 1 mM H_2SO_4, in which the predominant anionic species is sulfate, while the small amount of hydronium is mostly captured as bisulfate. Hence, the entropy of the solvated ions involved in hypothetical charge-neutral processes would differ considerably between the two solutions. Therefore, dependent on the solution, side processes should contribute fairly differently to the reaction entropy and hence to the molar Peltier heat of UPD I and III. Since, however, in both solutions the molar Peltier heat of UPD I and III is the same as for Ag bulk deposition, charge-neutral processes are negligible for UPD I and III. In particular we can state that the charge, which flowed in the outer cell circuit corresponded to Faradaic deposition of Ag and that the anion coverage did not significantly change during UPD I and III. For a more detailed consideration, the possible processes and estimates of their reaction entropies are listed in the Supporting Information. In particular, from the entropy of co-adsorption processes of sulfate and Ag^+ and the tight error bars for the measured molar Peltier heats, we expect that this co-adsorption process contributed by less than 4% to the overall UPD I and III processes in sulfate and bisulfate containing solutions.

In the intermediate potential region, between UPD I and III, the molar Peltier heat deviates considerably from that for Ag bulk deposition (Figure 1). In all three studied solutions we found a pronounced maximum of the molar Peltier heat in the intermediate potential range, about 15 to 25 $kJ\,mol^{-1}$ more positive than the molar Peltier heats of Ag bulk, UPD I and UPD III. Following the above formal separation of the Ag deposition process into Faradaic Ag deposition and accompanying charge-neutral processes, we have to seek a charge-neutral process with a positive entropy change during the cathodic Ag deposition reaction. The positive reaction entropy of the side process will then partly compensate the negative reaction entropy of the Faradaic Ag deposition process and lead to a more positive net molar Peltier heat. What could be the nature of such an accompanying charge-neutral process with positive entropy? Note that co-adsorption processes of Ag^+ and anions would exhibit negative entropy changes, owing to the immobilization of Ag and anions and their rather small solvation entropy (see Table S3). In principle co-desorption processes, that is, the release of adsorbed Ag and anions into the solution might be candidates. However, such processes would lower the total Ag coverage and hence contradict the electrochemical charge balance: From SXRD measurements it has been unequivocally shown that at potentials just positive of the UPD III peak, one Ag monolayer has been deposited.[3h,i] We measured a total charge for the UPD I and II regions of about 200 $\mu C\,cm^{-2}$, which is close to the Faradaic charge of 220 $\mu C\,cm^{-2}$ for the deposition of one Ag monolayer, in accordance with others.[3b] Furthermore, the point of zero charge (pzc) of the surface shifts negatively during Ag deposition on Au(111) by about 1 V,[3f] which should oppose desorption of anions. Therefore, co-desorption processes are unrealistic in the present case. The negative shift of the pzc also opposes an entropy gain through disordering of the solvent water in the interface. Since the pzc shifts negatively, the electric field in the double layer is expected to increase, which should lead to ordering of the water structure.[7]

Hence the only processes, which may provide an explanation for the Peltier heat maximum, are substitution processes of adsorbed anions, that is, substitution of adsorbed sulfate or perchlorate by oxygen species. Indeed, in alkaline solutions the adsorption of hydroxide on Ag(111) was experimentally found at potentials as low as about 0.4 V (versus reversible hydrogen electrode (RHE)).[8] Considering that the potential for OH adsorption should shift with pH parallel to that of the RHE,[9] in our 5 mM Ag^+ solutions at pH 1 and pH 4 this corresponds to −0.3 V and −0.5 V versus the Ag dissolution potential. It should be noted that DFT calculations found stable OH species on Ag(111) only at potentials above 0.93 V versus RHE, corresponding to 0.2 V and 0.03 V versus Ag/Ag^+ in our solutions. However, both, experimental and theoretical findings strongly suggest that adsorbed hydroxide may be thermodynamically stable on the Ag UPD layer in acidic solutions, at least at potentials slightly above the Ag bulk dissolution potential. For our system this implies that, when the Au surface becomes more Ag-like with increasing Ag coverage, adsorbed sulfate or perchlorate may become partly substituted by hydroxide. By this process bisulfate or perchlorate ions with strongly positive absolute entropy are formed in solution. The entropy gain overcompensates the loss from immobilization of OH, which is formed by decomposition of water. Therefore, the reaction entropy of such a substitution process will become positive. We estimated about 31 $J\,K^{-1}\,mol^{-1}$, 190 $J\,K^{-1}\,mol^{-1}$, and 150 $J\,K^{-1}\,mol^{-1}$ for the entropy gain in the solutions of Figure 1 a, b, and c, respectively. For this estimate we assumed that the entropy contribution of the adsorbed species does not change considerably upon the substitution (see Supporting Information). It should be noted that the substitution of adsorbed sulfate by surface oxide, would lead to similar entropy changes. However, from the surface Pourbaix diagram[9] it can be inferred that oxide formation would only occur at higher potentials. The entropic contribution of the substitution process determines the deviation of the measured molar Peltier heat from that of Faradaic Ag deposition. Thus, from the reaction entropies of the substitution process, the Peltier heat, and the information on the total electrochemical conversion in the CV, we can assess the coverage of OH. As shown in the Supporting Information, we expect of the order of 0.1 ML of OH adsorbed on the Ag UPD layer.

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In conclusion, by measuring the (reversible) heat effects accompanying electrochemical reactions, we obtained the reaction entropy of the complete process, including charge-neutral side processes. For Ag UPD on Au(111) we found that the deposition process is mostly governed by Faradaic Ag deposition without significant changes of the anion coverage. We can safely exclude co-deposition of Ag and anions, since such a process should lead to lowering of the Peltier heat, which contradicts our measurements. On the other hand the maximum of the molar Peltier heat in the intermediate potential range provides strong evidence for a charge-neutral substitution process of part of adsorbed sulfate by hydroxide upon the completion of the first Ag monolayer. Hence, the potential-dependent measurement of the molar Peltier heat allowed electrochemical processes to be unraveled, which are hard if not even impossible to detect by conventional electrochemical methods, such as cyclic voltammetry. The measurement of the Peltier heat is in principle possible for all reversible surface electrochemical processes. Examples include hydrogen or oxygen adsorption processes, co-adsorption of non-covalently interacting anions and cations as well as double-layer charging.

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