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Ex Situ X-ray Photoelectron Spectroscopy Study of the Interface between a Ag(111) Electrode and an Alkaline Electrolyte. 2. Structure of the Double Layer

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A Ag(111) single-crystal electrode emerged from an alkaline NaF + NaOH electrolyte under various potentials has been studied ex situ by means of X-ray photoelectron spectroscopy. Superequivalent specific adsorption of negatively charged hydroxide and oxide species has been observed at the potentials positive to the point of zero charge (E_{pzc}). The interfacial electroneutrality is provided by the Coulombic attraction of Na^+ cations, which are retained in the emerged double layer. Once the emerged electrode is heated in an ultrahigh vacuum above 370 K, the double layer disintegrates via the decomposition of the adsorbed hydroxide and surface oxide species and likely dissolution of sodium in the Ag(111) bulk. A model of the interface between a Ag(111) electrode and an alkaline electrolyte is discussed.

1. Introduction

Understanding the microscopic structure of the electrode/electrolyte interface is one of the central problems of fundamental electrochemistry. Considerable progress has been achieved in recent years with the help of a constantly increasing number of in situ techniques.^{1,2} Nevertheless, probing the double-layer of emerged electrodes by means of surface science techniques is still urgent and can provide additional information on the nature of the double layer species.^{3–8} In particular, studies on the emerged electrodes provide a possibility to examine nonspecifically adsorbed ions, which cannot be monitored via the in situ vibration spectroscopies. Valuable information can also be obtained upon studying the high-temperature transformations of the adsorbates in an ultrahigh vacuum (UHV).^{9,10}

The electrochemical double layer on the Ag polycrystalline and single-crystal electrodes has been a subject of numerous studies, reviewed in refs 11–15. However, most

of them have been performed in neutral or acidic electrolytes. The information on the state of the Ag/electrolyte interface in alkaline solutions is rather scarce.^{16–19} The present paper continues a series of publications devoted to the study of the interface between a Ag(111) electrode and an alkaline electrolyte under potential variation.^{20–22} In our ex situ X-ray photoelectron spectroscopy (XPS) study a number of surface and bulk oxygen-containing species, including surface (OH_{ads}) and bulk (OH_{bulk}) OH groups and surface oxide-like species ($\text{O}_{\text{ads}}^{\delta-}$), has been observed below the reversible potential of the Ag_2O phase formation.

As recently reported by H.-H. Strehblow et al., a hydroxide adsorbed specifically on a polycrystalline Ag electrode from alkaline NaBr, NaCl, and NaClO_4 electrolytes retains its negative charge.^{23–25} This is a very interesting observation which deserves further investigation. It is desirable to probe the double layer of well-defined single-crystal electrodes by means of surface science techniques. Thus, the aim of the present paper was to clarify the state of the electrochemical double layer between a Ag(111) single-crystal electrode and alkaline electrolyte in the presence of F^- ions, which in contrast to Br^- and Cl^- , do not adsorb strongly on Ag.^{11,26}

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2. Experimental Section

All the experimental details were described elsewhere.^{21,22} The experiments were carried out in a specially designed system which combines a glovebox (Braun) housing an electrochemical cell (EC) connected via a UHV transfer system to the stainless steel chamber of a modified Leybold LHS 12 MCD spectrometer. The Ag(111) working electrode (surface area 0.87 cm²) was immersed under controlled potential for 10 min in a three-electrode three-compartment glass cell filled with a 5×10^{-4} M NaF + 10^{-3} M NaOH aqueous electrolyte (pH 11). Platinum and Hg/HgO/0.5 M NaOH ($E = 0.125$ V vs NHE) were used as counter and reference electrodes, respectively. All the electrode potentials quoted are relative to the Hg/HgO electrode.

The XPS data were obtained using the Mg K α radiation ($h\nu = 1253.6$ eV). The concentrations of the chemical elements in the near-surface region, $C(i)$, were estimated after the subtraction of a Shirley-type background, taking into account the corresponding atomic sensitivity factors.²⁷ Surface concentrations of oxygen species ($N(O)$) have been estimated by measuring the areas (S) of the O 1s and Ag 3d_{5/2} peaks and using eq 1 from ref 28:

$$N(O) = (2.2 \times 10^{16}) \frac{S(O1s)}{S(Ag3d_{5/2})} \text{ atoms} \cdot \text{cm}^{-2} \quad (1)$$

The surface concentration of Na⁺ ($N(Na)$) has been estimated using eq 2:

$$N(Na) = N(O)C(Na)/C(O) \quad (2)$$

Coverage was measured in monolayers (ML) with respect to the number of silver atoms in the topmost layer, which for Ag(111) equals 1.38×10^{15} atoms·cm⁻².²⁹

3. Results and Discussion

3.1. Sodium Adsorption. As discussed in part 1,²² the Ag(111) electrode emerged from the 5×10^{-4} M NaF + 10^{-3} M NaOH aqueous electrolyte (pH 11) was covered with OH_{ads}, OH_{bulk}, and O_{ads}^{δ-}, their concentrations increasing as a function of the emersion potential. Along with the oxygen species, a considerable amount of sodium was observed on the emerged electrode at a potential positive to the point of zero charge (E_{pzc} [E_{pzc} equals -0.69 V vs SCE (that is ca. -0.57 V vs Hg/HgO) for Ag (111) in a NaF electrolyte.¹¹]). Sodium cannot result from the deposition of the electrolyte film, since then one should have expected the presence of fluoride on the emerged electrode with the ratio Na:F = 3:1, corresponding to the composition of the electrolyte solution. However, the amount of fluoride was below 0.5% in the potential interval from -1.2 to +0.2 V. This undoubtedly proves that the presence of Na on the emerged electrode is the result of adsorption.

Figure 1 represents the atomic concentrations of Na, F, total O, OH_{ads}, and O_{ads}^{δ-} vs the emersion potential. The Na⁺ concentration shows a minimum around E_{pzc} , increasing upon both anodic and cathodic polarization. The rise in cation concentration negative to the E_{pzc} reflects its Coulombic attraction to the negatively charged Ag electrode. The increase of the cation concentration in the double layer positive to the E_{pzc} points apparently to superequivalent specific adsorption of some anionic species on the electrode. Recharging an electrode upon specific

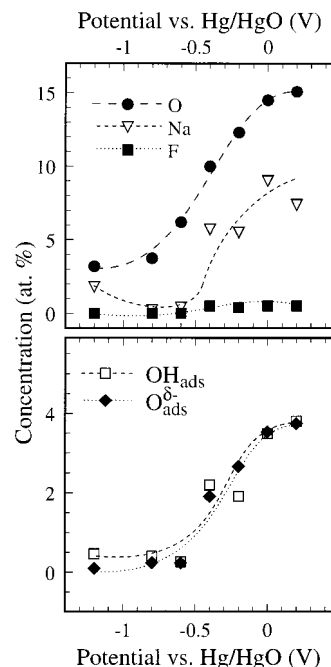


Figure 1. Effect of the potential on the atomic concentrations of Na, F, total O, OH_{ads}, and O_{ads}^{δ-} on the Ag(111) electrode emerged from 0.5 mM NaF + 1 mM NaOH.

adsorption of, e.g., halide anions is well-known for Hg³⁰ and Au.³¹

Note that the total amount of oxygen loaded on the electrode as a result of the immersion into the alkaline electrolyte exceeds considerably the amount of Na⁺ (Figure 1). This is in part due to the fact that only surface oxygen species may contribute to the double-layer charge. The hydroxide species incorporated in the electrode bulk at a potential above -0.6 V²² contributes to the oxygen signal of Figure 1; however, it will not enter into the interfacial charge balance because of the loss of its negative charge.

It is remarkable that the concentration of sodium on the emerged electrode above E_{pzc} follows the same trend as the hydroxide and the oxide species adsorbed on the surface (Figure 1). To account for this observation, it is concluded that OH_{ads} and/or O_{ads}^{δ-} bear a negative charge. This is in line with the conclusion of refs 23 and 24 on the negative charge of the hydroxide species adsorbed on Ag from alkaline NaCl and NaBr electrolytes. Studies on the formation of OH_{ads} on the metal/gas interface prove that hydroxyl behaves as an electron acceptor, acquiring a negative charge.³² This picture is also supported by the calculations of Anderson^{33,34} and Carter and Goddard.³⁵

3.2. High-Temperature Transformations of the Emerged Double Layer. Figure 2 represents the Na 1s core level spectrum and the X-ray excited Na(KLL) spectrum taken from the Ag(111) electrode emerged at 0.0 V from EC and subsequently heated in the stepwise manner in the UHV up to 570 K. Sodium adsorbed on the Ag(111) electrode after the emersion at 0.0 V is characterized by a quite narrow Na 1s line at 1071.5 eV and the X-ray excited Na(KLL) line at 990.6 eV. It should be mentioned that the position of the Na 1s line at 1071.5 eV

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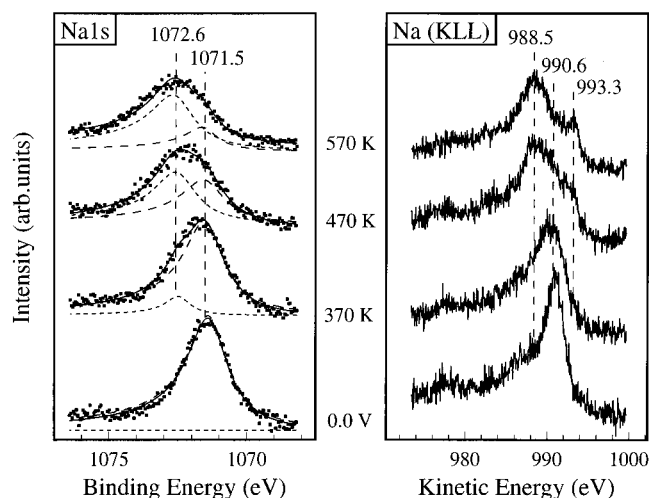


Figure 2. Na 1s XP (left panel) and Na(KLL) (right panel) spectra taken from the Ag(111) electrode after 10 min at 0.0 V in 0.5 mM NaF + 1 mM NaOH and after subsequent heating at 370 K, 470 K, and 570 K. The spectra were registered at the specified temperatures.

Table 1. XPS Data on Na in Reference Compounds

	Na 1s, eV	Na(KLL), eV	α' eV ^a	O 1s, eV	ref
Na ⁺ /Ag(111) ^b	1071.5	990.6	2062.1		this work
Na	1071.5	994.4	2065.9		39
	1071.8	994.5	2066.3		40
NaOH ^c	1071.3	989.8	2061.1	530.7	this work
NaF	1071.1	988.8	2059.9		41

^a The modified Auger parameter α' was calculated as a sum of the BE of the Na 1s line and the kinetic energy of the Na(KLL) line.

^b The Ag(111) electrode emerged from the NaF + NaOH electrolyte at 300 K. ^c NaOH was deposited from a solution of NaOH (5 mM) on the Ag(111) surface. The level of impurities controlled by XPS was less than 1%.

is independent of the emersion potential. The absence of the electrochemical shift in the BE, which was observed in refs 7 and 36 for ions adsorbed on the surface of the emersed electrodes, is apparently due to the fact that Na on the emersed Ag(111) is in electronic equilibrium with the surface (see discussion in ref 37).

The modified Auger parameter α' , which is very characteristic of the chemical state of an element, is calculated using the method of Wagner and Joshi.³⁸ α' for Na on the emersed electrode equals 2062.1 eV and does not shift with the potential. This value is different from the ones for sodium hydroxide and a sodium metal as evidenced by Table 1. Evidently, the state of sodium on the surface of the emersed electrode differs from the ones in the reference compounds. Sodium is most likely to be present on the surface in the form of adsorbed Na⁺ ions.

The heating results in a broadening and shift of the Na 1s peak from 1071.5 to 1072.6 eV and a complication the Na(KLL) spectrum. The curve fit analysis of the Na 1s spectra was performed using Doniach-Sunjić line shapes.⁴² As seen in Figure 2, the curve fit analysis gives a good

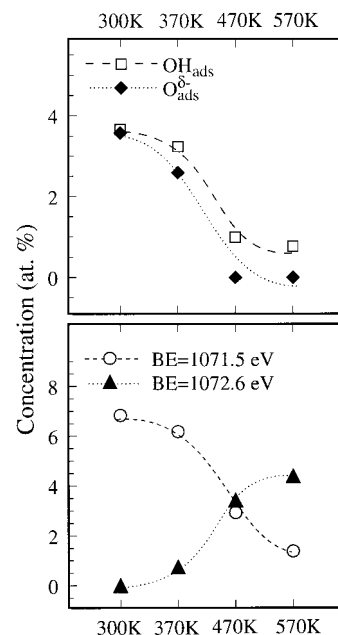


Figure 3. Variation of the atomic concentrations of sodium characterized by Na 1s peaks at 1071.5 and 1072.6 eV following heating in the UHV (bottom) and corresponding concentrations of the surface hydroxide (OH_{ads}) and oxide (O_{ads}^-) species (top) on the Ag(111) electrode emersed from the 0.5 mM NaF + 1 mM NaOH at 0.0 V. See ref 21 for details.

description of the measured Na 1s spectra and demonstrates the appearance of a new peak at 1072.6 eV. Upon heating, the intensity of the peak at 1071.5 eV decreases, whereas the peak at 1072.6 eV becomes more intense. It is quite remarkable that diminishing the 1071.5 eV peak correlates with the decrease of the atomic concentrations of the OH_{ads} and O_{ads}^- species as shown in Figure 3. The drastic change of the sodium lines (Na 1s and Na(KLL)) may be concerned with the high-temperature decomposition of the emersed double layer in an UHV. The 1071.5 eV Na 1s peak is likely due to Na⁺ Coulombically bound to the negatively charged O_{ads}^- and OH_{ads} species. Desorption and/or transformation of the surface oxygen species result in the appearance of a 1072.6 eV Na 1s peak, which is apparently characteristic of sodium in a different electrostatic environment.

The appearance of the two new peaks in the Na(KLL) spectra at 988.5 and 993.3 eV testifies to the formation of two new different states of sodium upon heating (Figure 2). To evaluate α' for these new states, the value of the Na 1s BE at 1072.6 eV was summed up with the Na(KLL) lines at 988.5 and 993.3 eV. The values of α' obtained equal 2061.1 and 2065.9 eV, respectively. The latter can be assigned to metallic sodium (Table 1), which could either form clusters on the surface or/and dissolve in the bulk of silver. Since Ag is known to form intermetallic compounds with Na,^{43,44} the latter explanation seems to be more likely. Diffusion of Na in the subsurface and bulk of Ag(110) has been reported by Lambert et al.,⁴⁵ though at a considerably higher temperature—above 700 K.

The other sodium state, formed upon heating, with α' of 2061.1 eV is characteristic of an ionic compound. Thus, one cannot exclude the formation of some amount of NaOH from Na⁺ and OH_{ads} during the decomposition of the double

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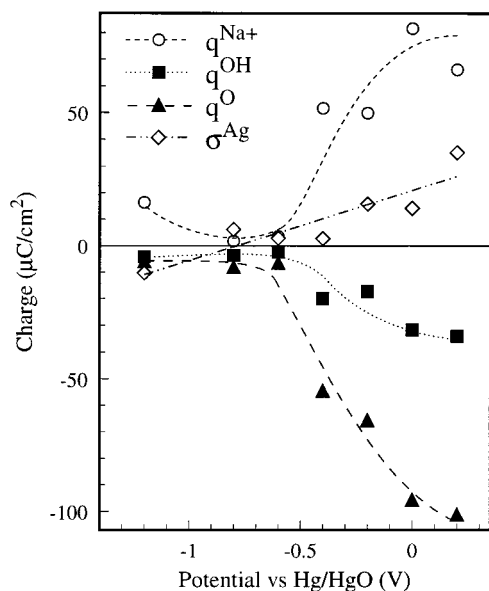


Figure 4. The ionic excess charges of Na^+ ions (q^{Na^+}), OH_{ads} (q^{OH}), surface oxide and hydroxide species (q^{O}), and the excess charge of the Ag(111) electrode calculated as $(-q^{\text{O}} - q^{\text{Na}^+})$ versus the emersion potential. See text for details.

layer upon heating in an UHV. Indeed, heating the emersed electrode, containing both Na^+ and OH_{ads} , in an UHV led to the appearance of the O 1s line at 530.7 eV, which was stable at 570 K and according to our XPS data was characteristic of oxygen in NaOH (Table 1). Meanwhile, when the emersed electrode was rinsed before heating and thus contained OH_{ads} , but not Na^+ , the O 1s peak at 530.7 eV disappeared at ca. 470 K.²¹

3.3. Model of the Double Layer at the Ag(111)/Electrolyte Interface. Figure 4 represents the ionic excess charge q^{Na^+} of Na^+ ions, adsorbed on the Ag(111) electrode and calculated using eq 3, versus the emersion potential:

$$q^{\text{Na}^+} = FN(\text{Na}^+) \quad (3)$$

In the potential region above E_{pzc} the Ag electrode bears an excess positive charge σ^{Ag} . The surface excess charges should satisfy eq 4 to provide the interfacial electroneutrality:

$$\sigma^{\text{Ag}} + q^{\text{Na}^+} = -q^- \quad (4)$$

Here, q^- stands for the anionic excess surface charge. If one assumes that q^- equals the charge associated with the presence of OH_{ads} species in the electrochemical double layer (q^{OH}), then one arrives at the conclusion that at $E > E_{\text{pzc}}$ the value of q^{Na^+} exceeds q^- . This conclusion is unreasonable considering the present understanding of the electric double layer.

$$q^{\text{OH}} = -FN(\text{OH}_{\text{ads}}) \quad (5)$$

We thus infer that the premonolayer surface oxide species have to also be considered for the proper determination of the anionic excess charge, which can be calculated using eq 6:

$$q^- = q^{\text{O}} = -FN(\text{OH}_{\text{ads}}) - \delta FN(\text{O}_{\text{ads}}^{\delta-}) \quad (6)$$

To verify the validity of the calculation of the anionic excess charge, the σ^{Ag} was calculated as a difference between $-q^{\text{O}}$ and q^{Na^+} , using eqs 4 and 6 under the

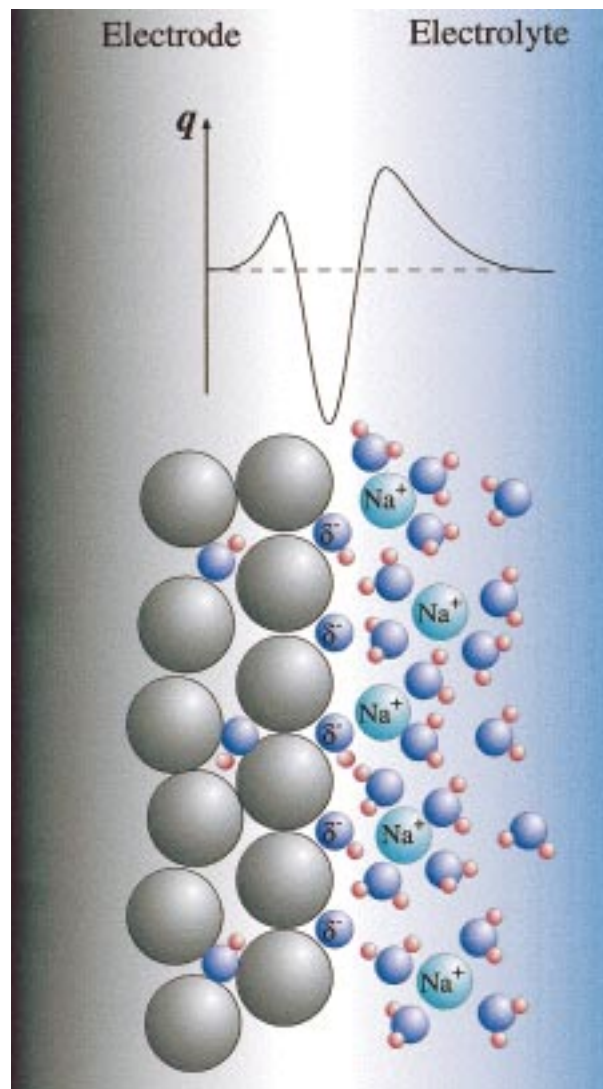


Figure 5. Model of the interface between a Ag(111) and an alkaline electrolyte and schematic distribution of the excess charge density in the interfacial region positive to E_{pzc} .

assumption that δ equals 2, and plotted in Figure 4. The straight line drawn through the calculated σ^{Ag} values demonstrates a reasonable trend of the excess charge on the Ag electrode vs potential. One may see that σ^{Ag} increases monotonically in the potential interval from -1.2 to 0.2 V and reaches zero at ca. -0.8 V, which is ca. 0.2 V negative to the E_{pzc} of Ag(111) in a NaF electrolyte (see section 3.1). Negative shifts of the E_{pzc} are quite typical for the specific adsorption of negatively charged species. Though the exact value of δ cannot be defined, the calculations presented above prove that $\text{O}_{\text{ads}}^{\delta-}$ carries some negative charge and should be considered for the proper calculation of the charge balance in the electric double layer.

We thus conclude that the examination of the emersed Ag(111) electrode with ex situ XPS allows one to reconstruct the structure of the double layer on the immersed electrode. Specific adsorption of the negatively charged hydroxide and oxide species starts at a potential close to the E_{pzc} . The excess charge of the metal electrode is overcompensated by the specifically adsorbed anionic species and an additional adsorption of Na^+ cations is required to provide the interfacial electroneutrality. The emersion of the electrode and its transfer to the UHV result apparently in the retention of the specifically

adsorbed oxygen species and Coulombically attracted counterions. While the ionic composition of the double layer is likely to be preserved, the interfacial water apparently desorbs as evidenced by the present work (see refs 21 and 22). The latter observation is in agreement with refs 7 and 32 but in contrast to refs 23 and 24.

A tentative model of the double layer at the interface between the Ag(111) electrode and alkaline electrolyte above the potential of zero charge is given in Figure 5 (bottom). The distribution of the excess charge density in the interfacial region is shown schematically on the top of Figure 5. It should be stressed that the interfacial region represents a complex entity and penetrates both into the liquid electrolyte and solid Ag electrode. It comprises the silver topmost layers, modified by the incorporation of the OH_{bulk} species, the negatively charged oxide and hydroxide species at the inner Helmholtz plane, and Coulombically attracted Na^+ cations on the outer Helmholtz plane and in the diffuse double layer.

Transformations of the interfacial region upon potential variation would undoubtedly affect the rates of electrocatalytic reactions occurring at the Ag/electrolyte interface. Further studies are in progress to clarify this phenomenon.

4. Conclusions

Adsorption of Na^+ has been observed on the Ag(111) electrode emersed from an alkaline $\text{NaF} + \text{NaOH}$ elec-

trolyte under a potential positive to E_{pzc} by means of the ex situ XPS. The amount of Na^+ in the emersed double layer correlates well with the amount of the hydroxide and oxide species adsorbed on the surface of the Ag(111) electrode. The interfacial electroneutrality is provided if one takes into account the negative charges on the specifically adsorbed hydroxide and oxide species. A model of the interfacial region of the Ag(111)/electrolyte is proposed.

Upon heating in an UHV the decomposition of the double layer is observed resulting in desorption and/or transformation of OH_{ads} and $\text{O}_{\text{ads}}^{\delta-}$ and tentative dissolution of sodium in the Ag bulk.

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