Potential Induced Structural Deformation at Electrode Surfaces

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Abstract

The atomic structure on the metal side of the electrochemical interface depends on the applied electric potential and the nature of the adsorbing species in the electrolyte solution. In this short article we review some recent results probing surface stress and surface relaxation effects in single crystal metal electrodes that are driven by potential changes. Both the potential and the structure in the electrolyte layers at the interface alter the metal electronic structure so that the surface in the electrochemical environment is strongly modified from the UHV counterpart. A methodology for linking experimental and theoretical approaches for a fundamental understanding of electrochemical reactions is proposed.

Introduction

Changes in the atomic structure at the electrochemical interface that are induced by changes in the applied electric field strongly correlate both with activity and stability. Although electrochemical reactions always involve charge transfer processes, the applied potential can also induce structural rearrangement without charge transfer. Examples include processes such as metal surface relaxation and surface reconstruction but also double layer charging which leads to rearrangement in the electrolyte side of the interface. Figure 1(a) shows a schematic illustration of the restructuring effects. In ultra-high vacuum (UHV) the relaxation of the surface can be explained within a free electron gas model by the electron overspill which appears due to the sharp termination of the bulk and the resulting surface dipole. The magnitude of the overspill and surface dipole depend on the chemical characteristics and the surface termination and structure. In the electrochemical environment this surface dipole can be tuned by the electrode potential, thus a variation of the relaxation is expected which depends on the applied potential. The effect is often masked by adsorption of species from the electrolyte and also affected by the double layer forming a counter charge to the created dipole. This simple model only accounts for the charge distribution due to the free electrons (s and p-type) and cannot be fully applied to transition metals, which have a strong contribution from the d-bands to the electron distribution and bond formation. For a fundamental understanding of the structural rearrangements at the interface insight into the electron density distribution is required. This is of particular interest as the activity for electrochemical reactions depends on the electron density. In this short article we focus on atomic structure changes that are driven by the applied electric field. A methodology is then suggested that may link together recent advances both in experimental and theoretical understanding [1].

Experimental methodologies

Experimental measurements of atomic structure changes at the electrochemical interface require techniques that offer high resolution, in order to detect changes at the pm level, but also the ability to be performed in the working electrochemical environment. Although imaging methods, such as atomic force microscopy (AFM) and scanning tunnelling microscopy (STM), give a wealth of structural information they are not sensitive to sub-surface structure changes and sensitivity to small atomic displacements is usually poor. Surface stress and surface x-ray diffraction measurements are the principle techniques that give high structural resolution combined with the ability to operate in the electrochemical environment. Surface stress measurements, using different experimental configurations, enable a variety of electrochemical processes to be monitored and can be understood on the basis of thermodynamic relations [2]. In this respect it has been shown that for metal electrodes the surface stress changes originate from a modification of the metallic bonding by the excess charge in the case of weakly adsorbing electrolytes [3]. Measurements have been supported by density functional theory (DFT) calculations of metal surfaces in vacuum [4,5].

Due to the high reciprocal space resolution, surface x-ray diffraction (SXRD) enables a three dimensional picture of the surface structure of metal single crystal electrodes to be obtained [6,7]. In the case of surface reconstruction, for example of Au(*hkl*) electrodes, the x-ray signal from the reconstructed layer is separate from the scattering due to the bulk of the crystal and can be accurately measured. Furthermore, by measurement of the extended specular x-ray reflectivity, information regarding the layering in the electrolyte side of the interface can also be obtained [8]. We note here that development in specialist cell designs may also soon open up new opportunities in electron microscopy [9].

Surface Relaxation and Surface Stress

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Modern surface crystallographic studies have shown that on the atomic scale most clean metals tend to minimize their surface energy by two kinds of surface atom rearrangements; relaxation and reconstruction [10]. Relaxation of metal surfaces is usually defined as small changes in the interlayer spacing (normal to the surface) relative to the ideal bulk lattice [10]. Focusing on electrochemical interfaces, the atomic structure changes of the unreconstructed Au(111) electrode surface were previously studied by a combination of SXRD and surface stress measurements [11]. The surface stress and surface relaxation as a function of surface charge are shown in Figure 1(b) and 1(c) respectively. For potentials positive of the potential of zero charge (*pzc*), where the surface is unreconstructed, increasing positive surface charge causes a decrease in the tensile stress, a result that can be understood on the basis of a simple jellium model [12]. Correspondingly one might expect that positive surface charge would lead to an increase in the surface expansion due to the apparent weakening of the surface bonds but it was found that the opposite was true. Adsorption-strain coupling at solid surfaces has recently been reviewed by Weismüller where the fundamental relationship between adsorption or electric charging and surface stress is shown to be complimentary to the changes in adsorption energies caused by straining a surface [13]. The results that link surface strain and surface expansion on Au surfaces (shown in Figure 1(b) and (c)) have been reproduced by DFT calculations [4,14]. However, recent efforts to develop simple models that are capable of describing the effect of excess surface charge on surface stress and relaxation have been less successful, highlighting the difficulty in generalizing the interplay between electric field and a metal's electronic structure [5]. In this recent work the authors concluded that the "simple charge rearrangement picture that underlies the Ibach model [15]….cannot be transferred to charged surfaces."

There have been numerous experimental and theoretical studies of the relaxation of metal surfaces in UHV and on unreconstructed clean low-index single crystal surfaces it is

often found that the outermost layer of atoms is *contracted* toward the second atomic layer. The tendency for surface contraction has been explained by Finnis and Heine using the Hellman-Feynman theorem, which states that the force on an ion is just the electrostatic force from the other ions and the self-consistent electron density [16]. In the electrochemical environment the experimental data is sparser, partly because it is difficult to successfully prepare and transfer clean reactive metal surfaces into the electrochemical environment. In addition the composition of the electrolyte solution determines both (a) specific adsorption processes (typically supporting anion species) and (b) the details of the 'double layer' structure at the interface. Both of these effects are strongly dependent on the applied potential [17]. Due to their importance in electrocatalysis, Pt(*hkl*) electrodes have been studied extensively and attempts have been made to correlate metal surface relaxation with the bonding of adsorbed species [18]. Recently, SXRD results obtained on the Pt(111) electrode surface in acetonitrile-containing solutions were presented [19] and the results were compared to those obtained in a range of basic aqueous electrolytes -the surface relaxation data is summarised in Figure 2. For the aqueous electrolytes it is apparent that the results for 0.1 M KOH and the different concentrations of MeCN are very similar in shape, exhibiting a sharp reversible change in outward expansion at ~0.33 V. This may be linked to reorientation of the water molecules at the interface [20-22] although it has been suggested that the potential of zero free charge (*pzfc*) is close to the onset of surface oxidation in strongly alkaline solutions [23]. The differences in the magnitude of the surface expansion can be linked to the size of the electrochemical double layer; a more compact layer (observed as the concentration of MeCN is increased) creates a stronger counter charge dipole in the electrolyte which increases the outward relaxation [4]. The results obtained in 0.1 M $HClO_4$ and 0.1 M H_2SO_4 are consistent with the data measured in alkaline solution at the most negative potential, when the Pt surface is fully covered by adsorbed hydrogen. The surface

remains expanded in both H_2SO_4 and $HClO_4$ until the adsorption of sulphate and perchlorate anions at around 0.42 V [24] and 0.65 V [25] respectively. The fact that the surface remains expanded up until an adsorption processes (of an anion or oxygenated species), even into the double layer region in the case of $HClO_4$, demonstrates that expansion cannot be just caused by the adsorption/desorption of hydrogen alone and suggests that the relaxation of the surface is an electronic screening effect caused by the ordering and structure of the double layer [26]. Theoretical understanding of the effects of ordering in the electrolyte has recently been advanced by the incorporation of *ab initio* molecular dynamics simulations into first-principles electronic structure calculations [27,28]. The results for water on Pt(111) give insight into the effect of adsorption processes on the electrostatic potential both within the Pt electrode surface and into the aqueous electrolyte [29].

Surface Reconstruction

Surface reconstruction involves large atomic displacements both perpendicular to and parallel to the surface plane leading to re-bonding and a change in the periodicity of the surface with respect to the underlying substrate. It is well known that all of the low-index Au(*hkl*) surfaces exhibit surface reconstruction both in UHV and in the electrochemical environment and that, in the latter, the reconstruction can be lifted at sufficiently anodic potentials. Recently we have examined the hexagonal Au reconstructions that are observed both on the Au(111) and the Au(001) electrode surfaces and examined the potential-dependent behaviour of the reconstructed surface in alkaline electrolyte (0.1 M KOH) [30]. The results were discussed in terms of two potential regions determined by the electrochemistry [31,32]. For potentials E<-0.45 V, there is no specific adsorption onto the Au surfaces. E=-0.45 V correlates with the onset of the adsorption of hydroxide species, OH⁻. Interestingly a broad minimum was observed in differential capacitance measurements close

to this potential [33], although the potential of zero charge (*pzc*) is expected to be at more positive potentials [34]. In the potential region -1.0 V<E<-0.45 V it was observed that the reconstructions both on the Au(111) and Au(001) surfaces show remarkably similar behaviour in terms of the potential-dependent variation in lattice spacing in the reconstructed Au layer-this is shown in Figure 3(a). The change of the in-plane Au-Au spacing in this potential range can be understood as a pure charging effect; in the absence of specific adsorption the excess surface charge determines the Au-Au surface interaction independent of the underlying Au substrate. Similar electrocompressibility has been observed in halide anion adlayers with hexagonal geometry adsorbed onto noble metal surfaces [35-37] and for underpotentially deposited metal adlayers on metal surfaces [38-40]. Assuming a 2D free electron gas model the electrocompressibility κ_T can be deduced [41,42] to be $\kappa_T = \frac{m_e A^2}{\pi \hbar (Z - N_{ion})^2}$ where $(Z - N_{ion})$ denotes the number of electrons contributing to the free electron gas. Obtaining $\left(\frac{dA}{dE}\right)$ and the surface area, A per atom from the experimental data, the charge of the surface gold atoms $e \cdot N_{ion}$ can be obtained by assuming a 2D isothermal compressibility for the electrocompressibility ($\kappa_{2D} = \kappa_T$) and is shown in Figure 3(b) as a function of the applied potential [30]. With these values an electrocompressibility of the order of $1\text{Å}^2/\text{eV}$ is obtained which is of the same order as the values found for electrochemically deposited metal monolayers [38,40,43]. Although the model assumed is based on the free electron model, thus only taking into account the gold $6s^1$ electrons and neglecting any possible influence of the 5d electrons, it shows that the change in electrocompressibility observed can be explained through a change in the charge of the surface atoms. The minimal nearest neighbour distance corresponds in this case to the point where the charge on the surface atom changes sign. Interestingly, in CO-saturated electrolyte, in which CO is adsorbed onto the surface at -1.0 V, the surface compressibility is suppressed and both the Au(111) and Au(001) surfaces are locked into the highly compressed phases

observed at -0.5 V in the CO-free electrolyte [30]. This suggests that the adsorbed CO is able to accommodate the excess surface charge induced by the applied potential and this is the mechanism that underpins the enhancement in electrocatalytic reactivity [44].

Links to Electronic Structure

Above we have described how structural changes can be explained through changes in the electron density induced by the termination of the bulk crystalline structure and the applied potential at the interface. Though these models can explain the structural changes observed, in order to link the structural changes to electrochemical and, specifically, electrocatalytic activity, a better understanding of the charge distribution at the interface is needed in order to underpin the recent theoretical advances. This would provide empirical insights into the interplay between electric field and the electronic surface structure to help to develop models that are capable of describing the effect of surface charge on structural rearrangements [5]. Experimental methods to probe electronic structure at electrochemical interfaces are difficult to employ. There has been recent progress in developing *in-situ* x-ray spectroscopies utilising specially designed liquid cells which minimise the pathway for transmission of the photoelectrons [45]. Such measurements have been linked with DFT calculations to give insight into reactions such as the oxygen reduction reaction on Pt [46], however, it is still the case that the experiment and theory are rather disconnected. Recently we have used resonant x-ray surface scattering methods which allow direct probing of the charge distribution on atoms selected by the diffraction conditions [47]. The data obtained for halide adlayers adsorbed onto Cu(001) and Au(001) electrode surfaces showed that adsorbed anions induced a potential drop that extended into the metal surface and is responsible for buckling in the sub-surface metal layers [48]. Quantitative interpretation of these results can be obtained by first-principles calculations [49] and the calculations are currently being

developed to explicitly include the effects of the electrode potential and electrochemical environment.

The theoretical developments which have shown the link between the d-band centre and reactivity has been incredibly successful in predicting trends that have led to the discovery of new materials for catalytic reactions [50]. Results suggest that in the electrochemical environment the impact of the electrode potential on the free electrons is also of paramount importance. Direct links of experiment and theory through, for example, resonant SXRD, offer opportunities for significant advances in this field.

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Annotated References

**Outstanding interest

Reference [1]

A recent review of the current status of simple and well-defined electrochemical interfaces both from the point of view of experimental *in situ* structural methods and first-principles electronic structure calculations.

Reference [5]

Ab initio calculations of metal surfaces in an external electric field that focuses on 'simple' sp-bonded metals in order to gain insight into the mechanisms underlying electrocapillary coupling. Includes an interesting discussion of charge-induced relaxation.

Reference [13]

An excellent review of the coupling of chemistry or electrochemistry at a solid-vapor interface or solid-electrolyte interface to the mechanics of the solid. The article links together fundamental concepts to recent experimental and theoretical developments.

Reference [30]

A high resolution surface x-ray diffraction study of the hexagonal reconstructions on the Au(001) and Au(111) electrode surfaces which links the compressibility of the surface atomic layer to the charge on the surface Au atoms within a simple free electron model. The relevance to the electrocatalytic reactivity of Au is also discussed.

Reference [47]

A description of polarization-dependent resonant surface x-ray scattering measurements to probe the charge distribution in the metal side of the electrochemical interface in the case of halide adsorbates on Au and Cu electrodes. The experiments have stimulated the development of first principles calculations to directly interpret the experiments in terms of the electron density distribution subject to applied electrode potentials.

*Special interest

Reference [19]

A recent surface x-ray diffraction study of the Pt(111) electrode in non-aqueous electrolytes. This paper includes a discussion of the dependence of surface relaxation effects on both adsorption processes and electrolyte composition.

Reference [23]

Includes a detailed discussion of the potentials of zero charge and zero free charge in

particular with reference to Pt metal electrodes.

Reference [29]

A short review article that describes the concepts underlying the formation of the electric double layer at the electrode-electrolyte interface. The article presents a new model of the electric double layer based on first-principles calculations.

Reference [45]

An overview of recent developments in x-ray spectroscopies that enable experiments to probe the electrode-electrolyte interface. The article illustrates how the methods are adapted from UHV studies and explains both the information that the techniques yield and some of the limitations.
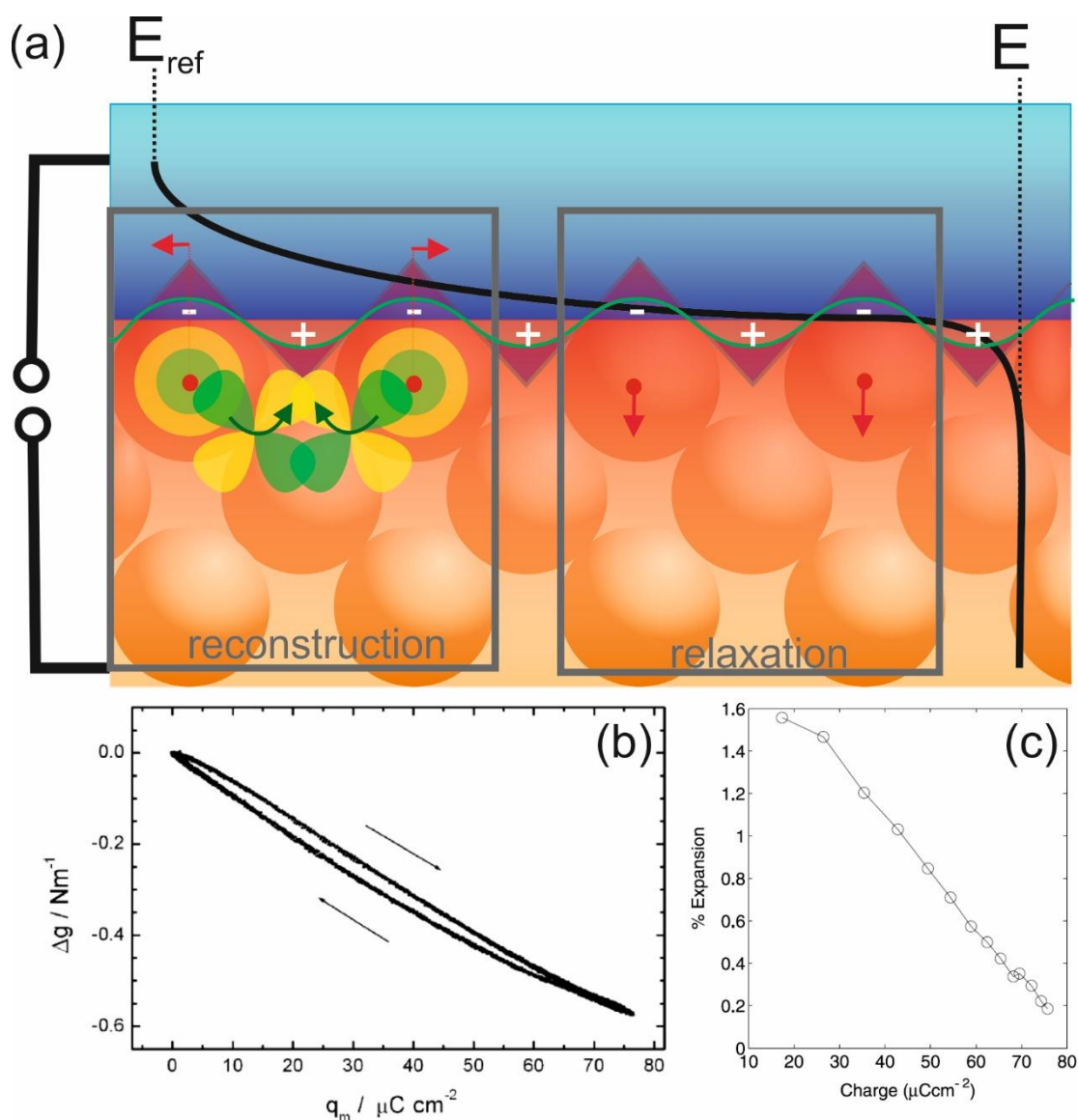
Figure 1. (a) depicts structural rearrangements in form of relaxation and reconstruction at the electrochemical interface. The modification of the electron distribution at the interface due to the termination of the bulk crystal and the applied potential (black line) are depicted. The contour of constant electron density at a surface is shown as the green line, whereas the Wigner-Seitz-Cell is shown as a grey line. In addition the influence of the electronic structure at the surface onto the atomic positions is depicted to show how this can lead to (i) surface stress and/or reconstruction of the top-most atomic layer due to modification of the nearest neighbour bonding and to (ii) changes in the surface relaxation due to the surface dipole

moment.

The response of the Au(111) electrode surface rearrangement in form of **(b)** surface stress and **(c)** surface relaxation to the surface charge are shown . (Adapted from reference [11])
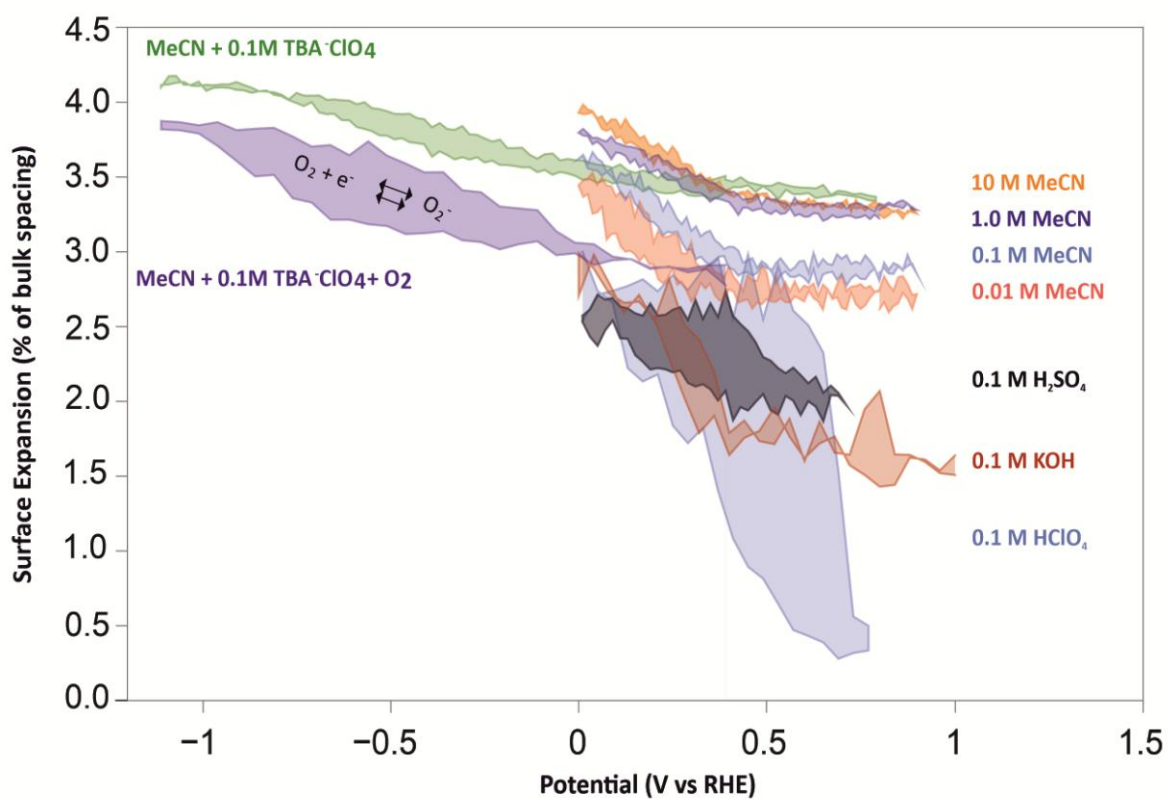
Figure 2. Surface expansion of the Pt(111) electrode in various electrolytes. The measured intensity has been converted to surface expansion using the parameters obtained from fits to SXRD data. The shaded area indicates the amount of hysteresis. (Reproduced with permission from reference [19] with correction to the reference potential)
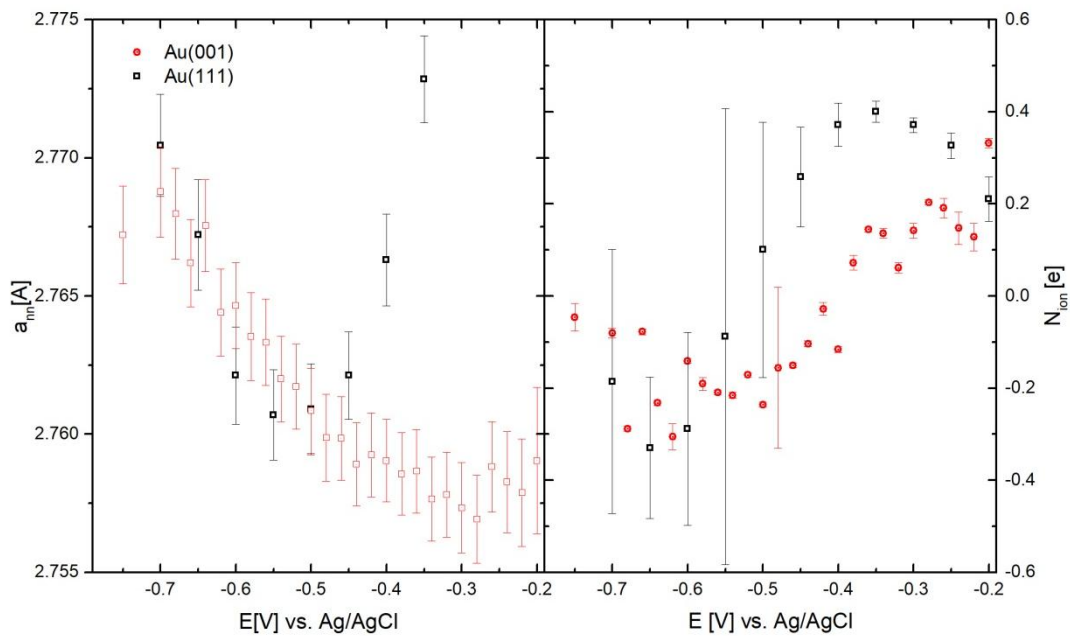
Figure 3. (a) The near-neighbour spacing in the hexagonal reconstructed Au surfaces for both the Au(001) and Au(111) electrodes measured in 0.1 M KOH. **(b)** The potential dependent surface charge per atom obtained for the reconstructed Au(001) and Au(111) surfaces by comparing the experimental electrocompressibility to the compressibility for a 2D layer in the free electron model. (Adapted from reference [30])