ORIGINAL PAPER

Electrochemical surface science: past, present and future

Dieter M. Kolb

Abstract Electrochemical surface science means the search for a truly microscopic understanding of electrochemical reactions and hence, of the place where it happens—the solid/liquid interface. It is described how electrochemists adopted strategies and techniques from their surface science colleagues to develop an atomistic view of electrode surfaces (mostly metals) and of simple reactions occurring thereon. Information about surface structure and chemical composition of the interface as a function of potential played a key role in complementing thermodynamic data derived from classical electrochemical methods. The move from structure to dynamics—on an atomistic level—will be the task which lies ahead of us.

D. M. Kolb (✉)
Institute of Electrochemistry, University of Ulm,
89069 Ulm, Germany
e-mail: dieter.kolb@uni-ulm.de

Introduction

One of the most important tasks of modern, physical electrochemistry is the development of an atomistic picture of the solid–liquid interface and its change with an externally applied electric potential, in order to provide the basis for a mechanistic understanding of electrochemical processes. Electrochemists, in principle, were seeking answers to the very same kind of questions, e.g., electronic and structure properties of surfaces and adlayers, as their surface science colleagues, who splendidly solved their puzzles by studies under ultra-high vacuum (UHV) conditions with electrons as their main tool [1]. Electrochemists, on the other hand, were facing the difficulty of a buried surface, a solid in contact with a condensed phase, the electrolyte, and yet, over the last 40 years, they succeeded to develop an electrochemical surface science by adopting experimental strategies and theoretical concepts from surface physicists.

The past: an emerging electrochemical surface science

The four pillars which built the platform for an emerging electrochemical surface science and which all rooted in classical, i.e., UHV-based surface science, were (1) the use of single crystal electrodes, (2) the development or adoption of new, non-electrochemical, structure- or molecule-specific methods that could be applied in situ and under operating conditions, (3) the implementation of UHV techniques in electrochemistry, and (4) the adoption of theoretical concepts from solid state physics and statistical mechanics for the description of the electrochemical interface. There was indeed a well-received conference series which bridged the gap between physical electrochemistry and surface science.

Fig. 1 Speakers and organizers of the 1986 Berlin conference on "Structure and Dynamics of Solid/Electrolyte Interfaces," held at the Fritz-Haber-Institut in Dahlem

It started in La Colle sur Loop, France in 1977, followed by Snowmass, CO, USA in 1979 (with the programmatic title "Non-traditional approaches to the study of solid/liquid interfaces" [2]); Logan UT, USA in 1982; Telavi, Georgia, UdSSR in 1984; Berlin (West), Germany in 1986; Bologna, Italy in 1988; and Monterey CA, USA in 1990. Special highlights and major breakthroughs were surface-enhanced Raman spectroscopy (1977), in situ infrared (IR) spectroscopy (1979), the emersed electrode (1982), in situ X-ray diffraction (1986), and in situ scanning tunneling microscopy (STM) (1988). Figure 1 shows a group photo of the invited speakers at the 1986 Berlin meeting, with H. Gerischer, R. Parsons, M. Fleischmann, A. Bard, W.N. Hansen, B. Conway, and S. Trasatti on it, just to mention some of the prime movers of the field at that time.

1. Single crystal electrochemistry

   Obviously single crystal surfaces are a prerequisite for atomistic studies of adsorption and deposition processes. The influence of the surface crystallographic orientation on reactions such as hydrogen adsorption, oxide formation, or underpotential deposition of metals, as studied by cyclic voltammetry, indeed was the beginning of single crystal electrochemistry [3–5]. To buy a single crystal was the easiest part; to prepare and characterize structurally well-defined and clean single crystal surfaces, however, was a true challenge. In the beginning, electrochemists had to make use of the classical UHV-techniques like low-energy electron diffraction (LEED) and Auger to check structure and cleanliness of their

electrodes before and after electrochemical experiments. Such a procedure restricted single crystal electrochemistry with reliable results to a few groups, which either underwent the endeavor of building their own vacuum equipment [6–9] or had easy access to equipment of next door surface scientists [10]. It was the so-called flame annealing of Pt single crystal electrodes, introduced by J. Clavilier et al. in the early eighties [11], that really opened the door to an everyday use of single crystal electrodes by the whole community.[1] Initially limited to Pt, flame annealing was soon successfully applied to Au surfaces [13], which led to a wealth of new information like thermally and potential-induced surface reconstruction [14]. An equally important step forward was the change from flame annealing to inductive heating in a controlled atmosphere, which was introduced by L.A. Kibler [15]. The latter technique not only disclosed the seminal importance of the cooling gas in obtaining perfect surfaces, particularly in the case of Pt single crystal disks, where traces of oxygen turned out to be detrimental to terraces [16], it also allowed for a wide variety of reactive metals to produce clean and structurally well-ordered single crystal surfaces to be prepared by a rather simple and cheap method. Examples are Ru, Rh, Pd, Ag, and Cu [15] (see Fig. 2).

---

[1] It cannot be overemphasized that H. Gerischer did electrodeposition studies with single crystal spheres as early as 1963 [12]. He obviously was too far ahead of his time, and his publication was forgotten when single crystal electrochemistry became popular 20 years later.

Fig. 2 **a** STM image of Pt(111) in 0.1 M H$_2$SO$_4$ at +0.35 V vs. SCE, after cooling the sample in H$_2$ (from ref. [16]). **b** STM image of Rh(111) in 0.1 M H$_2$SO$_4$ at −0.1 V vs. SCE

1000 nm × 1000 nm   E$_{SCE}$ = +0.35 V   570 nm × 570 nm   E$_{SCE}$ = -0.1 V
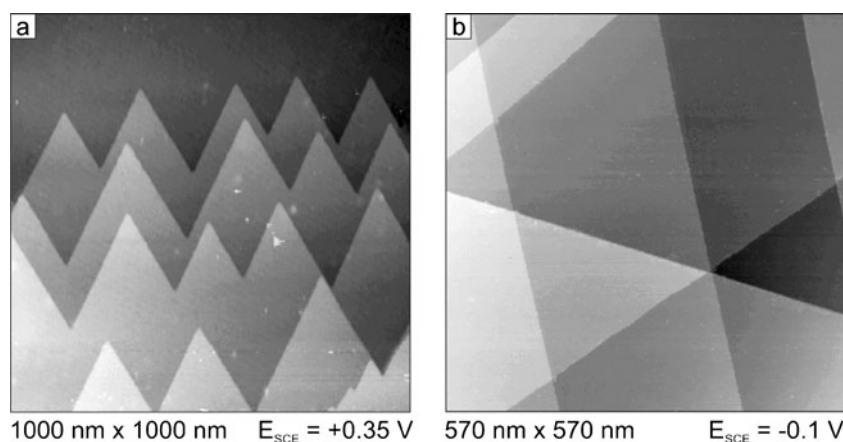
2. New structure- and molecule-specific in situ techniques

Quite early on, it was recognized that classical electrochemical methods should be combined with techniques that were capable of providing information on a molecular basis and were applicable in situ. The obvious choice was optical spectroscopy, preferably in the visible and near-UV wavelength range, where aqueous solutions are transparent. Reflectance spectroscopy, particularly electroreflectance (a modulation technique where the change in reflectance with electrode potential is measured) was among the first so-called non-traditional methods, with which questions of the optical properties of adsorbates, thin metal films, and oxide overlayers were addressed [17]. When later, single crystal surfaces were employed, this method was used to derive surface structure information by determining rotational anisotropies at normal incidence [17] or by involving surface states in the optical transitions [18]. Then came Raman spectroscopy, surface enhanced of course, and despite violent discussions about the origin of the enhancement, vibronic information became accessible [19]. With the development of optical thin layer cells for infrared studies, a major breakthrough was achieved by A. Bewick and S. Pons [20]. By reducing the thickness of the electrolyte film in front of the electrode surface under study down to a few micrometers, in situ IR spectroscopy became possible, yielding important information on reaction intermediates. Since such thin layer cells were also applicable to X-ray studies, with a different window material of course, the whole spectral region—from infrared to X-rays—became accessible to electrochemical studies. X-ray diffraction studies at grazing incidence began to provide structure information of astounding and hitherto unprecedented precision and detail [21]. A second major breakthrough came with the invention of the scanning tunneling microscope by Binnig and Rohrer, which soon after its invention for surface studies under UHV conditions was

adopted to electrochemical needs [22, 23]. This technique has advanced tremendously our knowledge about surface structure effects in electrochemistry, as imaging of electrode surfaces was now possible in situ, in real space, and with atomic-scale resolution.

3. The implementation of UHV techniques in electrochemistry: the ex situ approach

Looking back, the ex situ approach to electrochemical surface science was extremely important for the development of this field. In the beginning, there were no structure-sensitive techniques available for in situ studies. Hence, electrochemists adopted UHV techniques, particularly LEED, to check the quality of their UHV-prepared single crystal surfaces before and after electrochemical
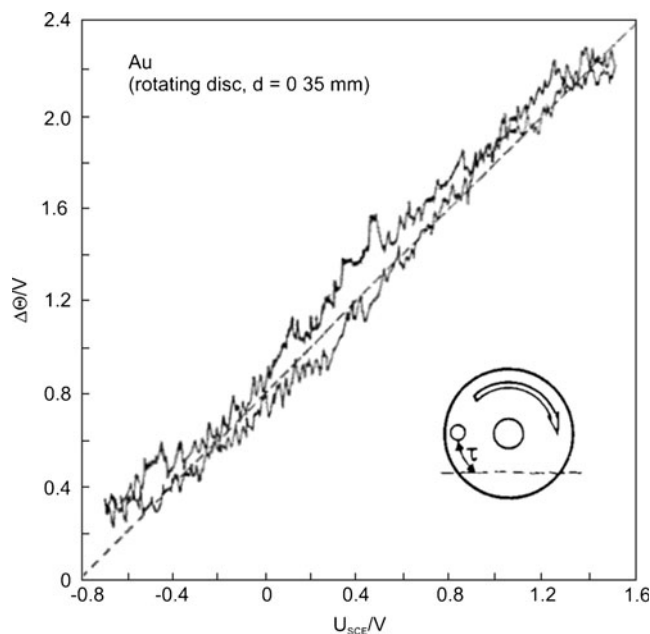
Fig. 3 Continuous work function monitoring for an emersed Au electrode by the Kelvin method. The electrode was a disk, rotating about a horizontal axis, and being in the solution with its lower segment only (from ref. [26])

Fig. 4 Theoretically calculated electrochemical surface phase diagram for the electrooxidation of Pt combining Pt(111) terraces and both {111} and {100} steps. The *upper plot* shows the stability range for each structure (indicated by differently *colored areas*—models are shown in the *lower panel*) as function of the electrode potential Δφ (vs. RHE) and the water chemical potential referenced as $\Delta\mu_{H_2O} = \mu_{H_2O} - E^{tot}_{H_2O}$. The region at which the bulk oxide (PtO₂) is stable is *patterned* (from ref. [32])
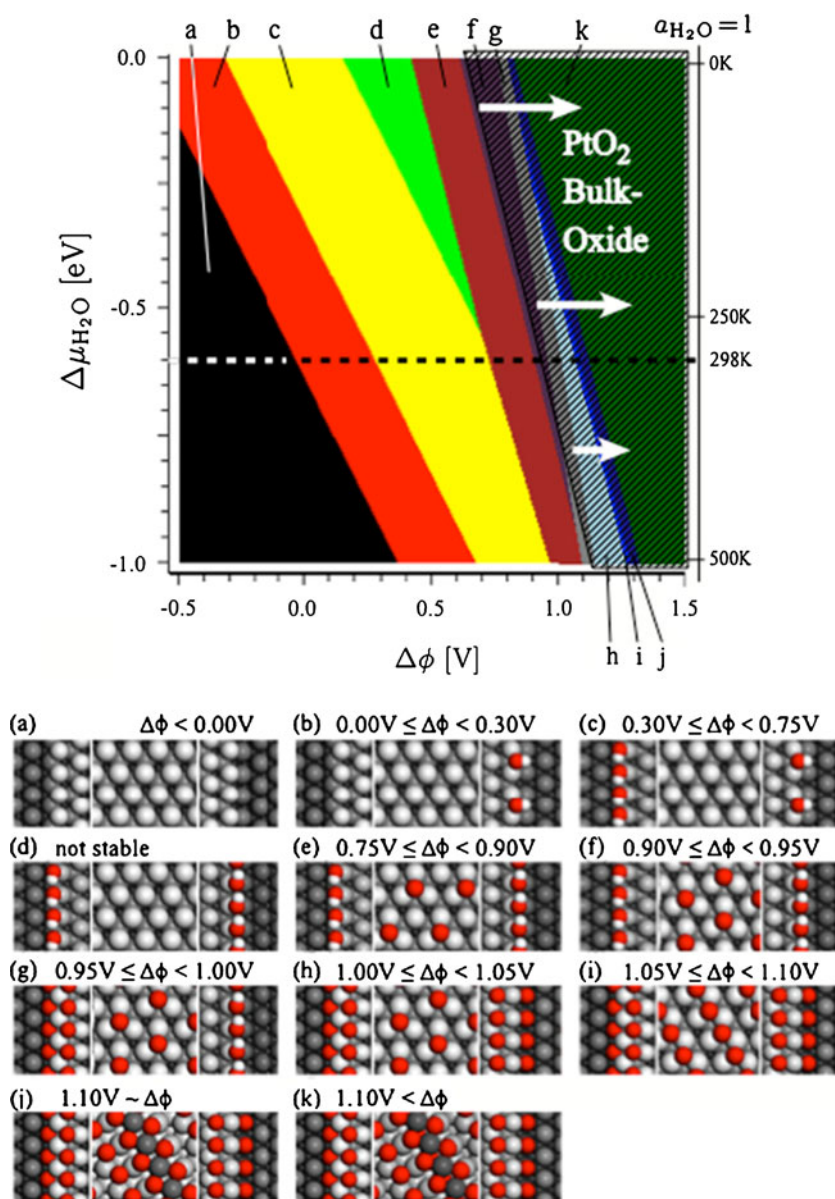
treatment, e.g., after some potential cycles. UHV studies were then extended to strongly bound adsorbates, such as iodide, metal, or oxide overlayers, systems that were believed to survive with little or no changes the transfer into the UHV. An important step forward was achieved by W.N. Hansen, who had the vision that electrodes may be emersed with their electric double layer intact [24]. This was proven, among others, by work function measurements with emersed electrodes as a means of determining the electrode potential in the emersed state [25]. Here, we have to remember that work function and electrode potential represent one and the same quantity (although with different reference points), namely the electrochemical potential of the electrons in the metal. Hence, a 1:1 correlation is expected for the work function of emersed electrodes as a function of emersion

potential, if the potential drop across the interface is retained during and after withdrawal of the electrode from the electrochemical cell. For gold electrodes, such a 1:1 relation has been found in numerous studies, and an example is shown in Fig. 3 [26]. We mention in passing that the work function values for emersed electrodes were often determined from UP spectra by the cutoff of the secondary electron emission. Such values were used to determine the so-called absolute electrode potential, i.e., the potential of the normal hydrogen electrode (NHE) referenced to vacuum (in other words, the work function of NHE) [27].

From studies of emersed electrodes that followed Hansen's discovery, a wealth of information about bare- and adsorbate-covered surfaces was obtained. Examples are the study of surface reconstruction phenomena for

Au(hkl), of ordered adsorption occurring during metal monolayer formation, or the observation of an electrochemical shift in XP spectra [28]. Although in situ STM made ex situ LEED studies obsolete for structure determination, it is the need for chemical information that makes ex situ photoelectron spectroscopy like ESCA still very valuable and indispensible for electrochemical surface science. I noticed an increased interest in recent years in combining again UHV and electrochemistry.

4. New theoretical concepts

The fourth point that contributed in a significant way to the development of modern interfacial electrochemistry was the adoption of theoretical concepts and methods from solid state physics or statistical mechanics. This was particularly important for a better understanding of the electric double layer, or more generally speaking, of the solvent structure near a charged wall. Important results came from computer simulations of the electric double layer, which yielded new information about the spatial distribution of ions and water molecules near the electrode surface [29]. The big step forward, however, came when density functional theory (DFT) entered electrochemistry. This has been demonstrated impressively by the work of J. Nørskov and his group [30, 31]. Their calculation of trends in binding energies and reactivities not only can explain experimental observations (the main task of former theories), but nowadays they can lead the way! This is particularly helpful for the experimentalist, when it comes to complex, multicomponent systems. Although it is still fair to state that the electrochemical interface is too complex to be handled in toto by any current theory (if electric potential, ions, and solvents were included), the overwhelming success of the DFT theory in electrochemistry partly reflects the importance to ask the right questions. The wealth of information that can be obtained by DFT in conjunction with extended ab initio thermodynamics is demonstrated in Fig. 4, which shows the variety of phases that exist for a Pt(111) surface in an aqueous solution on its way to bulk oxide [32].

The present: an atomistic view of the electric double layer and of simple electrochemical reactions

The following case studies exemplify the present situation in electrochemical surface science, albeit the view is very personal, and the examples are mostly from the author's laboratory.

(a) Metal surfaces in contact with an aqueous solution

For many electrochemical reactions, the electrode surface is a genuine reaction partner rather than a mere source or sink of electrons. This is particularly true for reactions, where solution species or reactions intermediates interact chemically with the surface. Hence, a detailed knowledge of the surface structure, geometrical as well as electronic, is important. Information about the geometric structure of electrode surfaces (mainly of single crystalline ones) is now routinely derived from scanning probe microscopy, like in situ STM.

While for many adsorption processes the crystallographic orientation of the terraces is important, surface imperfections like monoatomic high steps, kinks, domain boundaries, or dislocations become reaction centers. Imaging surface defects in situ and under reaction condition is the true virtue of STM, which images surfaces in real space rather than k-space. Such

Fig. 5 STM image of a Au (100) electrode in 0.1 M H$_2$SO$_4$ at −0.25 V vs. SCE, where potential-induced reconstruction proceeds. The initially unreconstructed surface is being gradually transformed into the reconstructed form. The (14×14 nm^2) zoomed image shows a section of the surface, three fourths of which has already been reconstructed; one single reconstruction row on the *left hand side* is seen to grow from the *bottom* to the *top* of the image (from ref. [33])
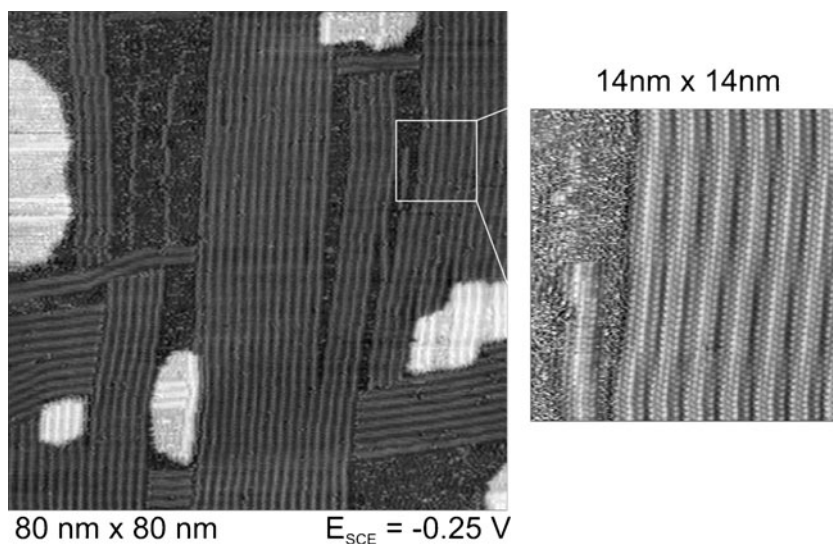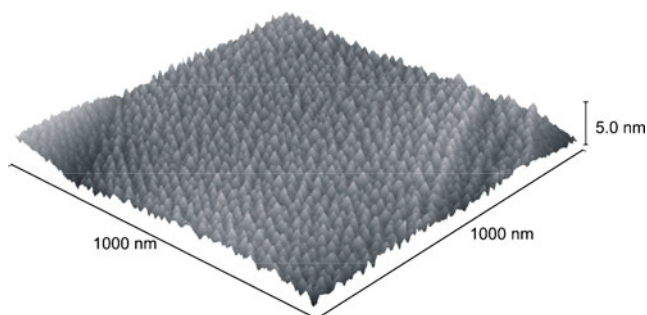
Fig. 6 STM image of a Au(111) electrode, roughened by about 100 oxidation–reduction cycles between 0.7 and 1.3 V vs. SCE at 100 mVs^{-1} in 0.1 M H$_2$SO$_4$. Image taken at +0.05 V vs. SCE (from ref. [34])

an example has been shown in Fig. 2. Another important topic, particularly for studies with gold single crystal electrodes, is surface reconstruction. It is well-known from UHV studies that all three low-index faces of gold reconstruct. Flame-annealed Au (hkl) surfaces are reconstructed, and this state can be preserved in an electrochemical environment under certain conditions, such as avoiding specific adsorption of anions. An interesting feature now is the so-called potential-induced reconstruction: Once the thermally induced reconstruction has been lifted by a potential excursion to positive values, where anions adsorb, the reconstructed surface can be reformed at negative potentials. This is shown in Fig. 5 for Au (100). It demonstrates that the surface structure of a gold single crystal suddenly becomes a function of electrode potential [33].

It has been realized since long that so-called oxidation–reduction cycles (ORCs), which have been employed to clean polycrystalline surfaces, can be detrimental to the single crystallinity of surfaces.

However, ORCs may be used to introduce a surface roughness of a relatively narrow height distribution. Such a technique may be used to produce active surfaces, in analogy to nanostructured ones. An example is given in Fig. 6 [34].
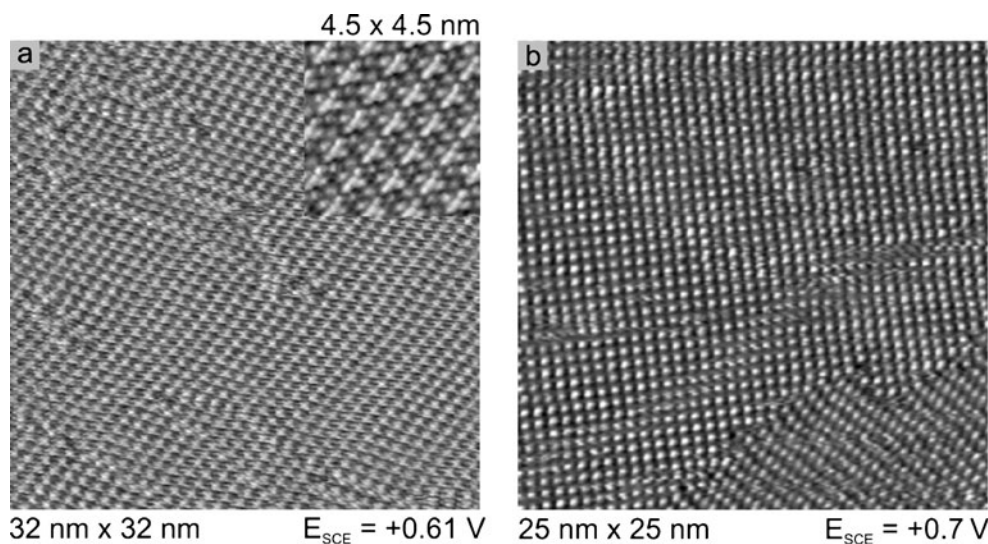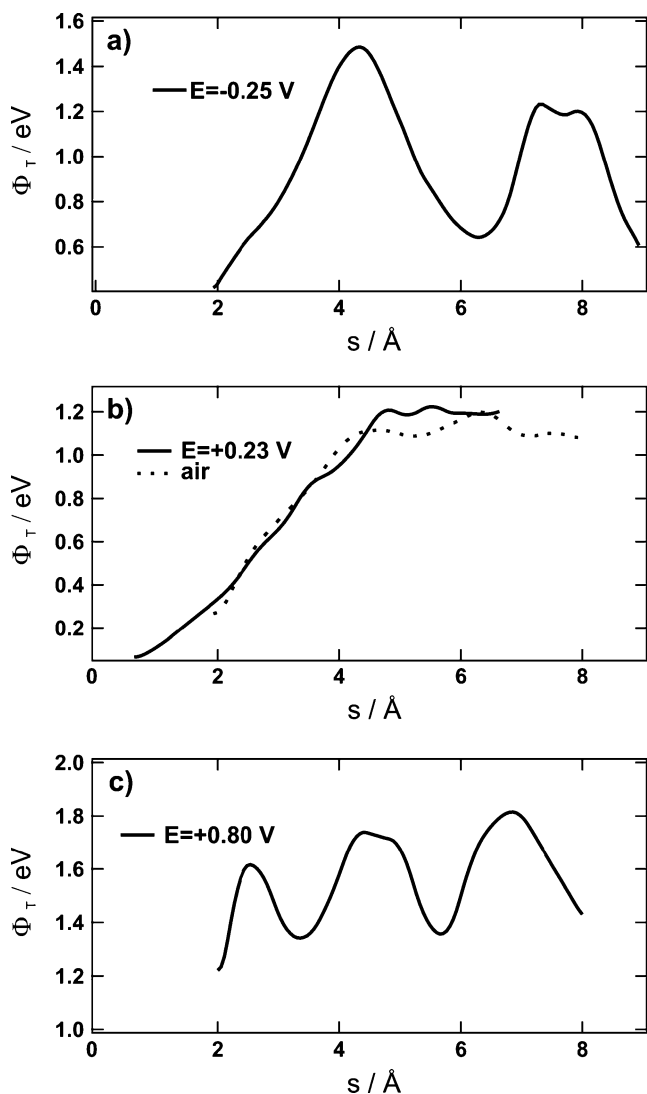
(b) Ordered adlayers of anions

Ordered adlayers have become a playground for STM owners. Generally speaking, an STM can image surface atoms, ions, or molecules only when they are immobile. This is the case for specifically adsorbed anions at rather high coverage, or for self-assembled monolayers, just to give another example. In Fig. 7, ordered adlayers of PdCl$_4^{2-}$ on Au(100) [35] and of PtCl$_4^{2-}$ on Au(100) [36] are shown. Other well-known and intensively studied systems are sulfate adlayers on Au(111) [37], Au(100) [37], and Ag(100) [38].
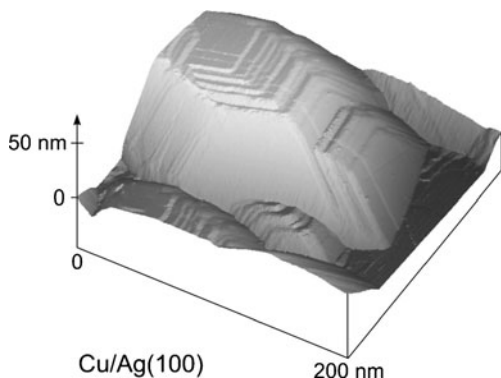
(c) The solution side

While there is a wealth of information from experiments about the interfacial structure parallel to the metal surface, very little is available, when it comes to the direction normal to the surface, into the electrolyte. For the latter case, almost all the information stems from theory, either DFT or statistical mechanics [29]. An experimental attempt to learn more about the electric potential distribution normal to the surface is given in Fig. 8, which makes use of tunneling spectroscopy [39]. It shows the variation of the effective barrier height (EBH) for electron tunneling, as the tip of an STM is moved towards or retracted from the surface at constant speed and constant tunnel voltage. The variation of the EBH for the charged interface has been interpreted as being due to the positive or negative excess charges of the ions in the electric double layer [39, 40]. Interestingly enough, for the uncharged gold/solution interface, i.e., at the

Fig. 7 STM images of ordered anionic adlayers. **a** PdCl$_4^{2-}$ on Au(100) in 0.1 M H$_2$SO$_4$+ 0.1 mM H$_2$PdCl$_4$+0.6 mM HCl [35]; **b** PtCl$_4^{2-}$ on Au(100) in 0.1 M H$_2$SO$_4$+0.1 mM K$_2$PtCl$_4$ [36]. The high-resolution inset of image (**a**) even shows the individual components (atoms) of the square planar PdCl$_4^{2-}$ complex

Fig. 10 Ring of 48 tip-generated Fe clusters on Au(111) in 1-butyl-3-methyl-imidazolium BF_4+50 mM $FeCl_3$ (from ref. [44])
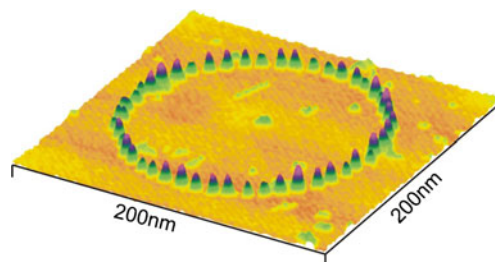

Fig. 8 Tunnel barrier Φ_T as a function of tip–sample distance for Au (111) in 0.1 M H_2SO_4 for three different potentials (vs. SCE): At the pzc (**b**), and negative (**a**), or positive (**c**) of it. $\Phi_T(s)$ for Au(111) in air is also shown for comparison with the curve obtained at the pzc (from refs. [39, 40])

potential of zero charge, a monotonous EBH variation normal to the surface is observed, very similar to the behavior of gold in air.

(d) Metal deposition

Because metal deposition is a nucleation and growth process, surface defects such as monoatomic high steps are known to play a crucial role as nucleation centers. Their density and local arrangement can have a strong influence on the morphology of the deposit, particularly during the initial stages of growth. Because of the ability of STM to image surfaces in real space, this technique is particularly suited to study nucleation at defects and the initial growth of the deposit [41]. A wealth of information has been gathered by the STM community concerning the morphology of metal deposits and its dependence on the overpotential, on the substrate properties and, most important, on the solution composition. The latter refers especially to so-called additives, mostly organic molecules with an ability to influence either the nucleation or the growth behavior of the metal. The common classification of additives into levelers and brighteners reflects their use in achieving flat and shiny surfaces. In Fig. 9, the STM image of a single

Fig. 9 STM image of a single Cu crystallite on Ag(100) in 0.05 M H_2SO_4+1 mM $CuSO_4$. The crystallite was grown at −0.15 V and imaged at −0.05 V vs. Cu/Cu^{2+} (from ref. [41])

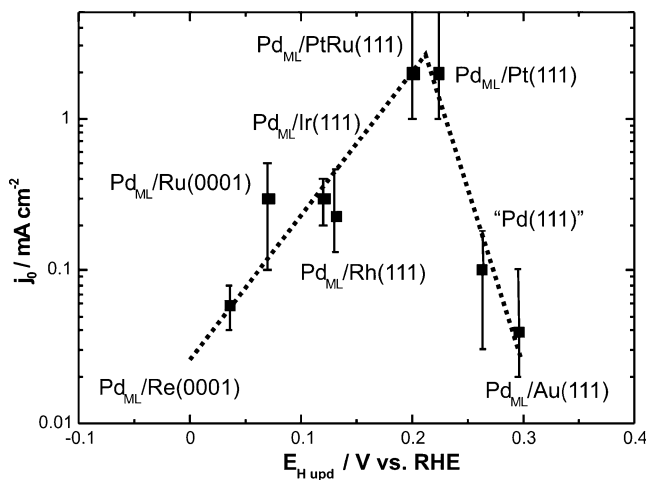Fig. 11 Tuning the catalytic properties of an electrode by surface strain. Volcano plot for the hydrogen evolution reaction on pseudomorphic Pd(111) layers (from ref. [45])

Cu cluster grown on Ag(100) is shown to demonstrate the detailed view this technique is able to provide for a technically most important electrochemical reaction.

For quite some time, STM has been successfully "misused" to manipulate surfaces with the tip, e.g., to position single atoms or molecules by employing the tip–substrate interaction. The most impressive example is the so-called quantum corral of D. Eigler et al. [42], a circle of 48 Fe atoms arranged on a Cu(111) surface with the STM tip, albeit under UHV conditions and at low temperatures. At metal/solution interfaces and at room temperature, such an art work would not be stable. However, by using the so-called jump-to-contact between the tip and the substrate [43], tiny metal clusters can be produced by an STM tip and positioned with high precision, which are stable over a wide potential range. Figure 10 shows a circle of 48 tip-generated Fe clusters on Au(111), about 0.6 nm in height, in an ionic liquid, 1-butyl-3-methyl-imidazolium tetrafluoroborate [44]. As the cluster size can be varied within certain limits by the tip approach, such surfaces may be interesting samples for probing reactivity as a function of particle size.

(e) Tailoring surface properties

The dependence of reaction rates, not only on the chemical nature of the bulk material, but also on surface properties that can be varied at will, is an important aspect of electrocatalysis: tuning the properties for a particular reaction. Such parameters can be the surface chemical composition of an alloy, changing the coverage of metal A on a substrate B, or creating reaction sites by nanostructuring surfaces. More subtle but equally exciting routes involve surface strain for modifying the electronic properties of a certain surface. The deposition of pseudomorphic monolayers on various single crystalline substrate surfaces is a convenient way of changing the lattice parameters of a certain metal. This has been demonstrated convincingly with Pd monolayers on eight different hcp-type substrate surfaces, yielding Pd(111) surfaces with eight different lattice constants, including natural bulk Pd(111). By testing the hydrogen evolution reaction, a clear influence of surface strain on the catalytic properties of the various Pd(111) surfaces was seen (Fig. 11), allowing the electrode to provide optimum reaction conditions [45].

The future

The examples, discussed in the previous section, certainly contain enough open questions to keep the community busy for another decade. The above addressed question of potential-induced surface strain, although being around since the mid-fifties and still of fundamental importance for any charged interface, is only now receiving renewed interest [46], and significant progress can be expected because of more sophisticated experimental tools being now available. Similar tendencies hold for the study of the solution side of the double layer, where theory will continue to be the pace maker. Electrochemical surface science can and hopefully will play a more important role in bioelectrochemistry, where up to now the work of J. Ulstrup and his group stands out as a singular pillar. Metals as electrodes are important and hence, still dominate physical electrochemistry. Metal oxides or other compounds are less intensively studied for obvious reasons; although interesting and technologically important systems, their surfaces are difficult to prepare and often less stable than the electrochemists' drosophilas, gold, platinum, or silver. This area may have to be entered again by an ex situ approach. Solid state electrochemistry, an extremely important field and of great technical relevance, will be addressed by others in this volume. Here, the interfacial region is even more difficult to access by common surface science techniques than in the case of aqueous solutions, and yet, many promising steps in this direction are seen already in the literature. Electrochemistry and material science remain an important combination; new materials are needed in many areas to help electrochemical devices with an economic breakthrough. New electrolytes like air- and water-stable ionic liquids or new electrode materials that work without precious metals will be the basis for future battery systems or for semiconductor devices that can provide solar fuel on a routine basis. I believe that electrochemical surface science will remain the platform for modern electrochemistry, and its highly interdisciplinary character will ensure a constant and beneficial input from neighboring fields like biochemistry, material science, analytic, organic and synthetic chemistry, and many more.

References

1. Ertl G, Küppers J (1985) Low energy electrons and surface chemistry. VCH, Weinheim
2. Furtak TE, Kliewer KL, Lynch DW (eds) (1980) Proceedings of the Snowmass conference on non-traditional approaches to the study of the solid-electrolyte interface, vol. 101
3. Ross PN Jr (1977) J Electroanal Chem 76:139

4. Dickertmann D, Schultze JW, Vetter KJ (1974) J Electroanal Chem 55:429
5. Bewick A, Thomas B (1975) J Electroanal Chem 65:911
6. Hubbard AT (1973) Crit Rev Anal Chem 3:201
7. Hammond JS, Winograd N (1977) J Electroanal Chem 80:123
8. O'Grady WE, Woo MYC, Hagans PL, Yeager E (1977) J Vac Sci Technol 14:365
9. Wagner FT, Ross PN (1983) J Electroanal Chem 150:141
10. Nakai Y, Zei MS, Kolb DM, Lehmpfuhl G (1984) Ber Bunsenges Phys Chem 88:340
11. Clavilier J, Faure R, Guinet G, Durand R (1980) J Electroanal Chem 107:205–211
12. Roe DK, Gerischer H (1963) J Electrochem Soc 110:350
13. Hamelin A (1982) J Electroanal Chem 142:299
14. Kolb DM, Schneider J (1985) Surf Sci 162:764
15. Kibler LA, Preparation and characterization of noble metal single-crystal electrodes. http://www.uni-ulm.de/echem/index.html?id=1023001
16. Kibler LA, Cuesta A, Kleinert M, Kolb DM (2000) J Electroanal Chem 484:73
17. Kolb DM (1988) In: Gale RJ (ed) Spectroelectrochemistry: Theory and practice. Plenum, New York, pp 87–188
18. Kolb DM, Boeck W, Ho KM, Liu SH (1981) Phys Rev Lett 47:1921
19. Jeanmaire DL, VanDuyne RP (1977) J Electroanal Chem 84:1
20. Bewick A, Kunimatsu K, Pons BS (1980) Electrochim Acta 25:465
21. Blum L, Abruña HD et al (1986) J Chem Phys 85:6732
22. Lustenberger P, Rohrer H, Christoph R, Siegenthaler H (1988) J Electroanal Chem 243:225
23. Wiechers J, Twomey T, Kolb DM, Behm RJ (1988) J Electroanal Chem 248:451
24. Hansen WN (1983) J Electroanal Chem 150:133
25. Hansen WN, Kolb DM (1979) J Electroanal Chem 100:493
26. Rath DL, Kolb DM (1981) Surf Sci 109:641
27. Kötz R, Neff H, Müller K (1986) J Electroanal Chem 215:331
28. Zhou WP, Kolb DM (2004) Surf Sci 573:176
29. Spohr E (1999) Advances in electrochemical science and engineering, vol 6. Wiley-VCH, Weinheim, pp 1–75
30. Mavrikakis M, Hammer B, Nørskov JK (1998) Phys Rev Lett 81:2819
31. Ruban A, Hammer B, Stoltze P, Skriver HL, Nørskov JK (1997) J Mol Catal A 115:421
32. T Jacob et al., submitted
33. Kolb DM (2002) Surf Sci 500:722
34. Köntje C, Kolb DM, Jerkiewicz G, to be published
35. Kibler LA, Kleinert M, Kolb DM (2000) Surf Sci 461:155
36. Waibel H-F, Kleinert M, Kibler LA, Kolb DM (2002) Electrochim Acta 47:1461
37. Cuesta A, Kleinert M, Kolb DM (2000) Phys Chem Chem Phys 2:5684
38. Schweizer M, Kolb DM (2003) Surf Sci 544:93
39. Simeone FC, Kolb DM, Venkatachalam S, Jacob T (2007) Angew Chem Int Ed 46:8903
40. Simeone FC, Kolb DM, Venkatachalam S, Jacob T (2008) Surf Sci 602:1401
41. Kolb DM (2002) Advances in electrochemical science and engineering, vol. 7. Wiley-VCH, Weinheim, p 107
42. Crommie MF, Lutz CP, Eigler DM (1992) Science 262:218
43. Kolb DM, Ullmann R, Will T (1997) Science 275:1097
44. Wei YM, Zhou XS, Wang JG, Tang J, Mao BW, Kolb DM (2008) Small 4:1355
45. Kibler LA (2008) Electrochim Acta 53:6824
46. Kramer D, Weissmüller J (2007) Surf Sci 601:3042