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Less Noble or More Noble: How Strain Affects the Binding of Oxygen on Gold

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Abstract: *Many heterogeneous catalysts exploit strained active layers to modulate reactivity and/or selectivity. It is therefore significant that density functional theory, as well as experimental approaches, find that tensile strain makes the gold surface more binding for oxygen, in other words, less noble. We show that this behavior does not apply when re-structuring of the gold surface is allowed to occur simultaneously with the adsorption of oxygen. In situ cantilever-bending studies show the surface stress to increase when oxygen species adsorb on a (111)-textured gold surface in aqueous H_2SO_4. This implies a positive sign of the electrocapillary coupling parameter and, hence, a trend for weaker oxygen binding in response to tensile strain. These conflicting findings indicate that different electrosorption processes, and specifically oxygen species adsorption on the bulk-terminated surface, exhibit fundamentally different coupling between the chemistry and the mechanics of the surface.*

The coupling of adsorption enthalpies of reactants and intermediate species to the mechanics of the surface is a current topic in surface science and catalysis. As active layers may be strained, for instance by epitaxy with a misfitting substrate crystal, the strong chemo-mechanical coupling that is suggested by theory[1–5] and well-supported by experiments[6–10] affords a tool for tuning the reactivity and selectivity of surfaces in heterogeneous catalysis. Indeed, the mechanical modulation of the reactivity can be directly observed and quantified when hydrogen evolution rates on gold and platinum electrodes vary in phase with elastic strain cycles.[11] The adsorption of oxygen species on gold is of interest in this context, in part because the impact of strain may contribute to the unexpected reactivity of gold surfaces when in the form of small clusters or nanoporous materials.[12–15] Ab initio density functional theory indicates that an increase in the in-plane lattice parameter makes Au surfaces bind oxygen more strongly; in other words, tensile tangential strain makes Au less noble.[16] Experiments have confirmed this prediction, both through a direct measurement of the shift in the electrode potential with strain during oxygen species electrosorption on Au,[17] and more indirectly through the observation that surface stress becomes more negative when oxygen species adsorb on the highly curved surfaces of nanoporous Au.[18]

The link between surface stress measurements and the coupling of adsorption enthalpies to strain emerges from the theory of electrocapillary coupling.[17,19] As its central quantity, the electrocapillary coupling parameter, ς, is alternatively and equivalently defined (and measured) as the variation of surface stress, f, with surface charge density, q, at constant tangential (area) strain, e, and as the variation of electrode potential, E, with e at constant q.[20–22] Cantilever bending experiments measure $\delta f/\delta q$ during the potential scans of cyclic voltammetry,[23–26] whereas dynamic electro-chemomechanical analysis (DECMA) measures $\delta E/\delta e$ from the potential modulation when small strain cycles at typically 2 to 100 Hz are imposed on the electrode.[17,27] Most studies of ς so far have investigated capacitive processes. Different experiments here agree quantitatively between themselves[17,23,24,27] and with ab initio simulation.[28,29]

Beyond capacitive processes, ς is also relevant for adsorption. As the value of E of an electrosorption process measures the free energy of adsorption, Δg^{ad},[30] it is natural to expect a connection between ς and the variation of Δg^{ad} with strain. Provided that the entropy of adsorption is not significantly strain-dependent, this connection takes the form[19]

$$\mathrm{d}\Delta h^{\mathrm{ad}}/\mathrm{d}e = -z_{\mathrm{I}} F \varsigma, \tag{1}$$

where Δh^{ad} is the enthalpy of adsorption, z_{I} is the ionic valency, and F denotes the Faraday constant. Negative ς thus implies that tensile strain makes the surface bind anions such as OH more strongly.

In view of the reports of stronger oxygen binding on Au at tensile strain ($\varsigma < 0$), it is remarkable that previously reported DECMA experiments[17] suggest ς during oxysorption to depend on the strain frequency, with a trend for more positive values at lesser frequency but still with negative sign at the lower limit of frequency. As the electrosorption of oxygen species on the Au surface is known to occur in several steps, the observed frequency dependence suggests that the respective processes may be characterized by different electrocapillary coupling parameters, and that different kinetics might afford a separation of the respective coupling phenomena in time-dependent studies.

Here, we use cantilever bending studies of the surface stress variation to study electrocapillary coupling in the limit of slow oxygen electrosorption on Au. When combined with

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data from the faster strain cycles of DECMA, the results present a picture of coupling during at least two separate adsorption steps. While an initial, fast process is characterized by the previously established $\varsigma < 0$, we find a sign inversion and $\varsigma > 0$ when more time is admitted for the adsorption, suggesting that the surface actually becomes less favorable for oxygen binding when strained in tension.

As a consistency check with previous reports, we first examined capacitive processes with our system. The experimental details are described in the Supporting Information. Figure 1 a shows a 5 mV s^{-1} cyclic voltammogram (CV) within the regime of dominantly double-layer charging. The graph of charge density, Δq, versus electrode potential, E, in Figure 1 b is nearly closed and displays little hysteresis, consistent with capacitive behavior. Figure 1 c shows the change, Δf, in surface stress (relative to an arbitrary reference value) versus E. The coupling coefficient ς is determined from the straight line of best fit to the graph of Δf versus Δq (Figure 1 d). The result, $\varsigma = -1.81 \pm 0.02$ V, is compatible with the previous finding of -1.86 ± 0.1 V,[17,27] suggesting that our electrodes and procedures are in agreement with previous reports.

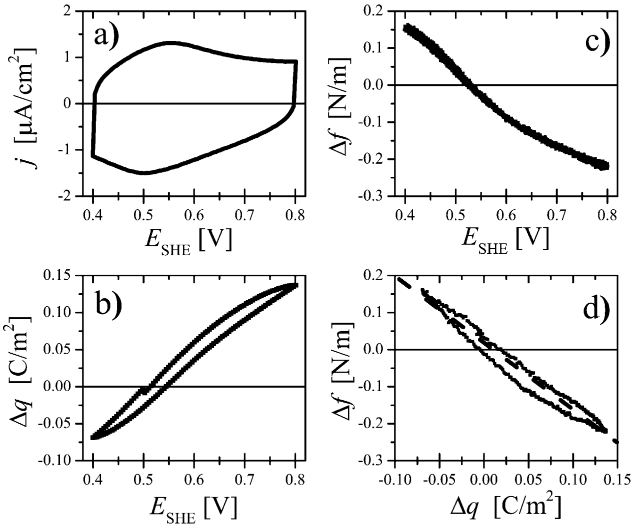

Figure 1. Results for Au in 10 mM H_2SO_4 at 5 mV s^{-1} within the double-layer regime. a) Cyclic voltammogram of current density j versus potential E. b) Charge density Δq versus E. c) Change in surface stress Δf versus E. d) Graph of Δf versus Δq. Dashed line: best fit; slope indicates $\varsigma = -1.81 \pm 0.02$ V.

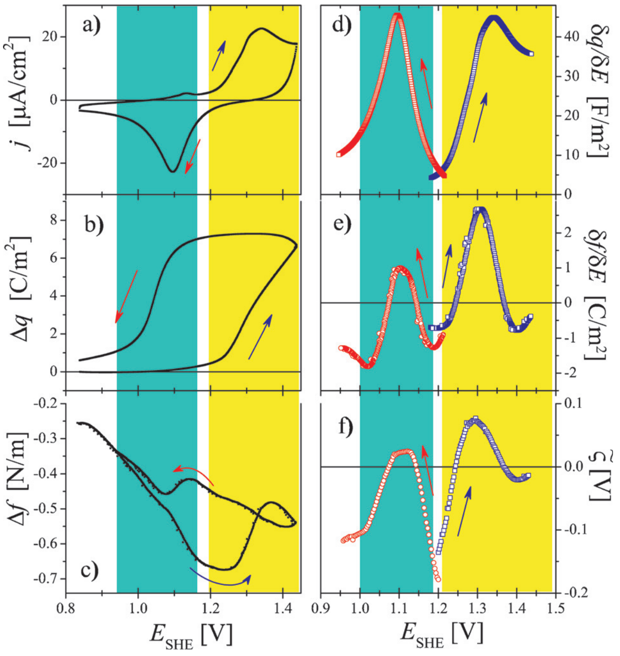

Figure 2. Results for oxygen electrosorption on Au in 10 mM H_2SO_4 at 5 mV s^{-1}. a) Cyclic voltammogram. b) Change in charge density Δq versus E. c) Change in surface stress Δf versus E. d) and e) graphs of the experimental derivatives $\delta q/\delta E$ and $\delta f/\delta E$ versus E. f) The coupling coefficient ς versus E, computed from the derivatives according to Equation (2). Arrows indicate sweep direction; color shades highlight oxygen adsorption (yellow) and desorption (cyan) processes.

The results for oxygen electrosorption are shown in Figure 2. The CV (Figure 2 a) is dominated by oxygen species adsorption and desorption peaks which are substantially displaced from each other on the potential axis. Near the cathodic vertex, the negative current in the anodic scan direction might suggest a Faraday current. Yet, CVs with a more negative lower vertex potential (Supporting Information) are free of that feature, indicating that the oxygen desorption continues for a short while after the inversion of the scan direction in Figure 2 a. The graph of Δq versus E (Figure 2 b) reflects the hysteresis of the CV. A small closure failure is natural in view of the Faraday current associated with the irreversible processes near the positive vertex potential of the CV.[33,34]

We then examined the variation in surface stress during oxygen electrosorption. Starting out in the capacitive regime, the graph of $\Delta f(E)$ (Figure 2 c) initially reproduces the trend of Figure 1, with surface stress decreasing upon anodic scanning. A minimum in Δf is reached near $E \approx 1.25$ V, where the CV indicates the onset of OH adsorption. Throughout the adsorption peak in the CV, Δf increases. Further increase of E then brings a decreasing f again. When the scan direction is inverted, the small current in the CV indicates an essentially capacitive depolarization of the oxygen-covered electrode surface. In this regime, Δf displays a weak linear increase with decreasing potential, terminating in an abrupt drop during oxygen desorption. The cathodic branch of the graph of $\Delta f(E)$ then merges with the anodic branch of the (nominally) capacitively charged surface.

In light of the hysteresis in the CV of Figure 2, the experimental measurables such as E and q are not automatically good state variables in a phenomenological description of the surface. Yet, the microscopic origin of the surface stress variation has been linked to the charge density. It is therefore of interest to explore the effective coupling coefficient $\tilde{\varsigma} = \delta f / \delta q$, where the δ denote the actual changes in f and q during an increment δE of the potential.

We evaluated $\tilde{\varsigma}$ from our experiments by means of Equation (2):

$$\tilde{\varsigma} = \frac{\delta f}{\delta q} = \frac{\delta f}{\delta E}\left(\frac{\delta q}{\delta E}\right)^{-1} \qquad (2)$$

The two terms on the right-hand side of Equation (2) can be computed as the derivative of the experimental $f(E)$ and as $j(E)/\dot{E}$, respectively. $\dot{E}$ and j denote the potential scan rate and the current density, respectively. Figures 2e and d show the respective graphs in the regions of interest, namely for oxygen species adsorption (yellow) and desorption (cyan), along with the corresponding $\tilde{\varsigma}(E)$ (Figure 2f).

The results for $\tilde{\varsigma}(E)$ reflect the sign inversions that are immediately apparent in the graph of $f(E)$, and specifically the positive sign of the electrocapillary coupling parameter in the regions where the CV indicates that the oxygen coverage of the surface varies strongly. It appears natural to interpret the related peaks in $\tilde{\varsigma}(E)$ during the initial adsorption step and during desorption of OH in terms of a transition between the (positive-valued) signal from oxysorption proper and the signatures of the fast electrosorption processes which dominate in the surrounding regions of electrode potential. Within that notion, the peak represents a superposition of signatures from different processes, weighted depending on their relative contribution to the signal. It is then not obvious if the peak value of $\tilde{\varsigma}$ corresponds to the coupling parameter of oxysorption or if that value represents a weighted sum of positive and negative terms from various processes occurring simultaneously.

To suppress signatures from fast pseudo-capacitive processes, we recorded the evolution of q (through chronoamperometry), and of f, with time during potential step experiments. The electrode was first equilibrated in the clean-surface regime (at $E = 0.8$ V) for 20 s and the potential then stepped to 1.3 V, at the adsorption peak of the CV. Subsequently, the potential was stepped back to the value at desorption, 1.1 V, to monitor desorption (Figure 3a). The different kinetics suggests differences in overpotential (over the potential for adsorption at equilibrium) or different activation barrier heights. If a single process dominates, then graphs of Δf versus Δq for each process should be linear with slope ς. The graphs are indeed quite linear (Figure 3b), suggesting that the surface stress-charge behavior associated with a single process is indeed observed in isolation. Linear regression yields $\varsigma = +0.11 \pm 0.01$ V for adsorption and $\varsigma = +0.14 \pm 0.02$ V for desorption. As anticipated above, the coupling is indeed stronger than suggested by the peak values of $\tilde{\varsigma}$ (Figure 2f). The finding of a positive-valued response parameter is confirmed.

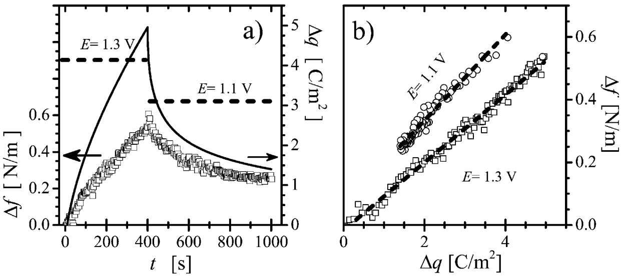

Figure 3. a) Evolution of charge density Δq and of surface stress Δf with time t, measured simultaneously during constant-potential holds after jumping up from 0.8 V to 1.3 V (oxygen species adsorption) and then down to 1.1 V (desorption). b) Graphs Δf versus Δq for data of (a). Electrocapillary coupling coefficients from linear regression are $\varsigma = +0.11 \pm 0.01$ V for adsorption and $\varsigma = +0.14 \pm 0.02$ V for desorption.

The finding of $\varsigma > 0$ is remarkable since we have previously shown[17] that ς measured by DECMA during strain cycles of frequency 20 Hz remains negative-valued, in the range of −2.0 V to −0.5 V, for Au electrodes throughout the oxygen species adsorption and desorption regime, irrespective of the superimposed potential scan rate. The finding from the 20 Hz cycles implies a fast oxysorption process that has $\varsigma < 0$. Consistent with that experimental finding, DFT studies indicate that tensile strain makes bulk-terminated Au surfaces bind oxygen more strongly.[16] The coupling of oxygen adsorption energy, E_{O_2}, to the in-plane change in lattice parameter, a, is found as $\mathrm{d}E_{O_2}/\mathrm{d}\ln a = 13$ eV.[16] Evaluating this with Equation (1), with $z = 4$ for two oxygen atoms, ς of the analogous electrosorption process is estimated at −1.6 V. The consistency between theory and the DECMA experiment therefore includes the magnitude of the coupling.

Besides the agreement during fast cycles, the DECMA experiments[17] also show a pronounced frequency-dependence of ς in a small potential window near oxygen electrosorption. Here, ς becomes significantly more positive as the frequency decreases, a finding that has no obvious explanation in the DFT results. The frequency-dependent trend is further supported by the present finding of $\varsigma > 0$ during part of the oxysorption process, since the surface stress measurement during the CV (Figure 2), as well as the potential jump experiments (Figure 3), probe much slower processes (duration 100 s of seconds, comparable to cycles at frequencies below 10^{-2} Hz). The observations are therefore consistent with a fast initial adsorption step of OH that has $\varsigma < 0$ and with a subsequent, slow reordering process that has $\varsigma > 0$. The fast process is probed by the strain cycles of DECMA, at 2 Hz–20 Hz, whereas the slow process is probed by the potential step experiments of Figure 3.

The slow process has been discussed in terms of surface restructuring.[17] It is widely accepted that increasing the excess of adsorbed OH or O on Au induces the transformation (referred to as the replacement-turnover (RTO) process) from an initial state of adsorbed oxygen species on top of the bulk-terminated surface to a place-exchanged state.[33–35] Such a replacement-turnover process has been monitored in previous experimental studies using scanning tunneling microscopy and atomic force microscopy.[37,38] The successive electrosorption steps are thus: i) $\mathrm{OH_{sol}}^- \rightleftharpoons \mathrm{OH_{ads}} + e^-$, followed by ii) $\mathrm{OH_{ads}} \rightleftharpoons \mathrm{O_{ads}} + H^+ + e^-$, and then iii) $\mathrm{O_{ads}} \rightleftharpoons \mathrm{O_{rto}}$ (Figure 4). Steps (ii) and (iii) are known to be coupled,[35] and during potential scans the three electrode processes are not typically clearly separated. We therefore have to assume that the experimental $\tilde{\varsigma}$ value in Figure 2 may represent a weighted sum of the ς of the individual processes, whereas the potential step experiments of Figure 3 probe the process with $\varsigma > 0$ in isolation.

Since the positive ς is observed only for slow cycles and in the potential windows where the oxygen adsorbate layer is

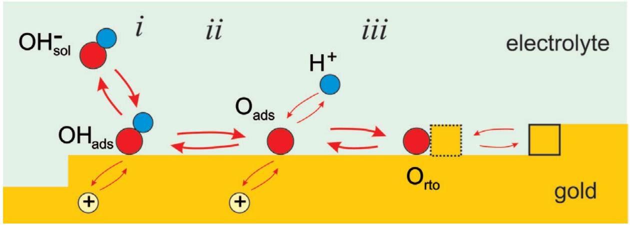

Figure 4. Representation of the oxygen species electrosorption process: step i) $OH_{sol}^- \rightleftharpoons OH_{ads} + e^-$; step ii) by $OH_{ads} \rightleftharpoons O_{ads} + H^+ + e^-$; step iii) by $O_{ads} \rightleftharpoons O_{rto}$.

built or stripped, and as it has been established[34–36] that the RTO step (iii) is considerably slower than the initial OH adsorption in step (i), we conclude that the positive electrocapillary coupling, $\varsigma = +0.11$ to $+0.14$ V, is representative of the RTO process.

To summarize, our findings support the notion that each individual electrode process is characterized by an independent value of ς, that the fast initial adsorption of OH has $\varsigma < 0$ and that the slower RTO has $\varsigma > 0$. More specifically, ς was found with a value of -1.8 V for the initial OH adsorption,[17] in qualitative agreement with theory for O adsorption on bulk-terminated Au. By contrast, the present study suggests $\varsigma = +0.11 \pm 0.01$ V for RTO and $+0.14 \pm 0.02$ V for the stripping of the oxygen which is bound in the RTO configuration. We are unaware of an established microscopic mechanism explaining the sign-inversion of the electrocapillary coupling during RTO. Theory suggests the formation of a mixed adlayer containing 1/3 monolayer (ML) of Au adatoms and 1 ML of O.[39] As the Au–O bond in various bonding surroundings is substantially shorter (by roughly 1/3) than the Au–Au bond,[40] the epitaxy with the crystal could conceivably strain the adlayer in tension, which would be tantamount to a more positive surface stress. For anion adsorption this would imply $\mathrm{d}f/\mathrm{d}q = \varsigma > 0$, in agreement with our observation.

Irrespective of the underlying atomistic mechanism, our results are compatible with the previously reported theory[16] that suggests that tensile strain makes gold surfaces less noble in the sense that the strain suppresses the adsorption of oxygen on top of the bulk-terminated surface. However, when it comes to the formation of a mixed oxygen-gold surface layer that is known as the replacement-turnover process, and that comes closer to a hypothetical process of oxidation, our results show that tensile strain actually has the opposite effect, reducing the bond strength. In the spirit of previous work,[16] this amounts to saying that tensile strain in fact makes the gold surface more noble.

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