Letter

Measurement of Surface Diffusion at the Electrochemical Interface by In Situ Linear Optical Diffraction

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ABSTRACT: A new in situ method for measuring the surface diffusion rates of adsorbates on electrode surfaces in electrolyte solution is presented. The method is based on the generation of a periodic spatial modulation of the adsorbate coverage via interfering laser pulses and subsequent monitoring of the diffusion-induced decay of this pattern using the optical diffraction signal of a second laser. Proof-of-principle measurements of the surface diffusion of adsorbed sulfur on Pt(111) electrodes in 0.1 M H_2SO_4 indicate potential- and coverage-dependent diffusion constants that are significantly higher than those of sulfur on Pt(111) under vacuum conditions.

Grating creation — Surface diffusion

Nd:YAG — HeNe — diffraction

KEYWORDS: *surface diffusion, electrochemical interface, linear optical diffraction, in situ LOD, Pt(111) electrode, chemisorbed sulfur*
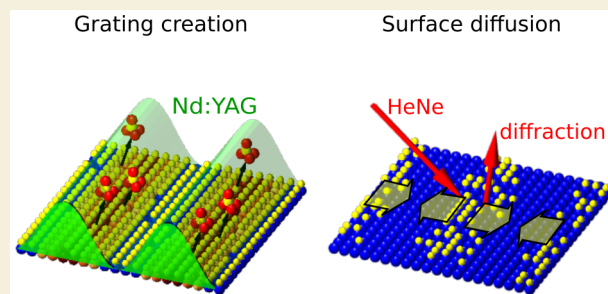
D iffusion of adsorbed species at solid−liquid interfaces plays a major role in many processes, such as crystal growth or electrocatalysis. Quantitative data on such interfacial diffusion are therefore essential for understanding and optimizing these processes. Surface diffusion on solids under vacuum conditions has been extensively studied using field electron[1−3] and field ion microscopy,[2−4] scanning probe microscopy,[2,3,5] or profile evolution techniques, where diffusion can be traced optically[2,3,6−12] or by electron microscopy.[2,3,13] In contrast, only a few studies on surface diffusion at the solid−liquid interface exist, predominantly due to the lack of suitable experimental methods. These studies were based on the direct observation of adsorbate motion by electrochemical video-rate scanning tunneling microscopy (STM),[14,15] on STM measurements of the fluctuations of atomic steps[16−18] or adatom island shapes,[17,19] and on nuclear magnetic resonance spectroscopy.[20] Because these studies are restricted to the temperature window of liquid water, where the adsorbate surface mobility is high, they are often limited to model systems with slow diffusion rates.

To measure faster diffusion rates, we introduce here an in situ profile evolution technique, where diffusion is traced using linear optical diffraction (LOD). This method has been extensively used for studies of adsorbate diffusion under ultrahigh vacuum (UHV) conditions, e.g., of CO and H on Pt(111) and Ni(*hkl*).[6−12] In the LOD, a density grating within an adsorbate layer is formed by localized thermal desorption, induced by a temperature grating that is generated using two interfering beams of a pulsed laser. The subsequent evolution of the adsorbate density distribution is then probed by diffraction of a continuous wave laser beam at the grating. From the exponential decrease of the optical diffraction

intensity, the surface diffusion coefficient can be extracted.[21,22] This way, diffusion rates can be measured over many orders of magnitude $(10^{-7}-10^{-16} \text{ cm}^2/\text{s})$.[21]

We here show that LOD is also suited for in situ studies of adsorbate diffusion at the interface between solid electrodes and liquid electrolytes. The optical setup and electrochemical cell is shown in Figure 1 (for more details, see Supporting Information, section 1). The adsorbate coverage grating is created by the beam of a frequency doubled (532 nm), 10 Hz, s-polarized Nd:YAG laser (Continuum Surelite EX), which is split up and brought to interference at the adsorbate covered sample surface under an angle of θ = 17.9°. The resulting grating has a periodicity of $\Lambda = \lambda/(2 \sin(\theta))$ = 650 nm[23] and is probed via a 5 mW p-polarized He−Ne laser (632 nm, Thorlabs HNL050L-EC) under an incident angle of 46.9°. Its first-order linear diffraction signal, which reflects the modulation amplitude of the adsorbate distribution, is then emitted almost normal to the surface and measured by a PMT detector (Hamamatsu H11901-01). To compensate intensity fluctuations of the laser beam, its incident intensity is monitored using a photodiode (Thorlabs DET36A/M), located directly at the laser output. An identical photodiode is used to monitor the optical reflectance, which provides information about adsorbate coverage changes during the
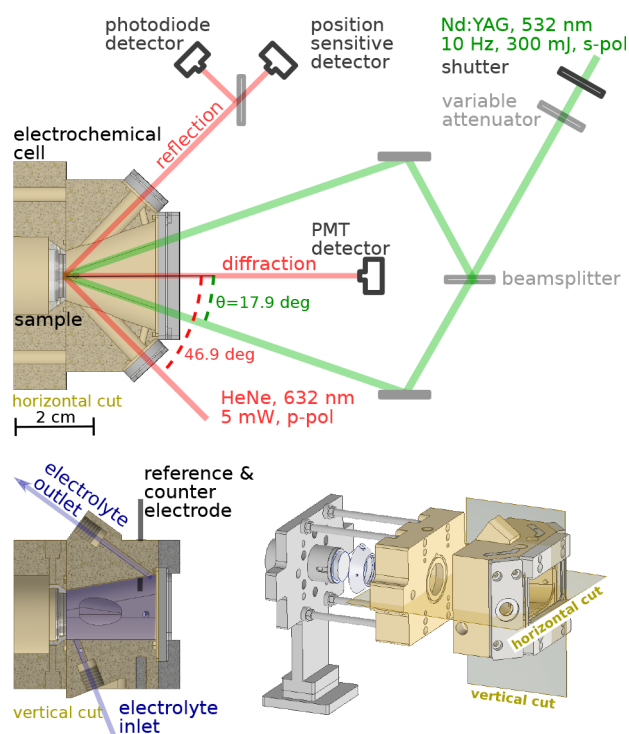
Figure 1. Optical setup and electrochemical cell for in situ LOD measurements of surface diffusion in electrochemical environment.

measurement. An additional position-sensitive detector (Thorlabs PDP90A) allows precise cell alignment and monitoring of the beam pointing stability.

The single crystal sample is located within a newly developed electrochemical cell made of PEEK. An inlet and

outlet allow exchanging the electrolyte volume of 10 mL as well as measurements under electrolyte flow. For the optical measurements, the laser beams pass through fused silica windows. These are arranged perpendicular to the probe beam to allow polarization-dependent studies.

Proof-of-principle in situ LOD studies of adsorbate diffusion were performed for sulfur on Pt(111) in 0.1 M H_2SO_4. Chemisorbed sulfur (S_{ad}) is known as a strong catalyst poison and stable over a wide potential range, up to potentials of about 0.8 V/RHE,[24] where oxidation to SO_4^{2-} commences. The onset of oxidation strongly depends on temperature and shifts to lower potentials with higher temperature.[25,26] Furthermore, multiple oxidation cycles of at least 1.2 V are necessary to completely remove chemisorbed S_{ad}.[26] Despite its high relevance to catalyst and fuel cell poisoning, S_{ad} diffusion at Pt(111) electrodes has not been studied so far, and only a few studies exist under vacuum conditions.[5,27,28]

In the experiments, the Pt(111) single crystal sample was first annealed in an induction oven. Then approximately 1 monolayer (ML) S_{ad} was adsorbed by 5 min immersion into 10 mM Na_2S solution, followed by extensive rinsing with ultrapure water and transfer into the cell filled with deaerated electrolyte solution.

The measurement procedure consisted of four steps, schematically shown in Figure 2A: (I) creation of an adsorbate coverage modulation, (II) further coverage reduction, (III) diffusion-induced decay of the previously created coverage modulation, and (IV) determination of the average adsorbate coverage. Figure 2B,C shows the diffraction signal (blue) and the relative reflectance change $\Delta R/R$ (red) as well as the electrode potential (blue) and current density (red) during these steps.
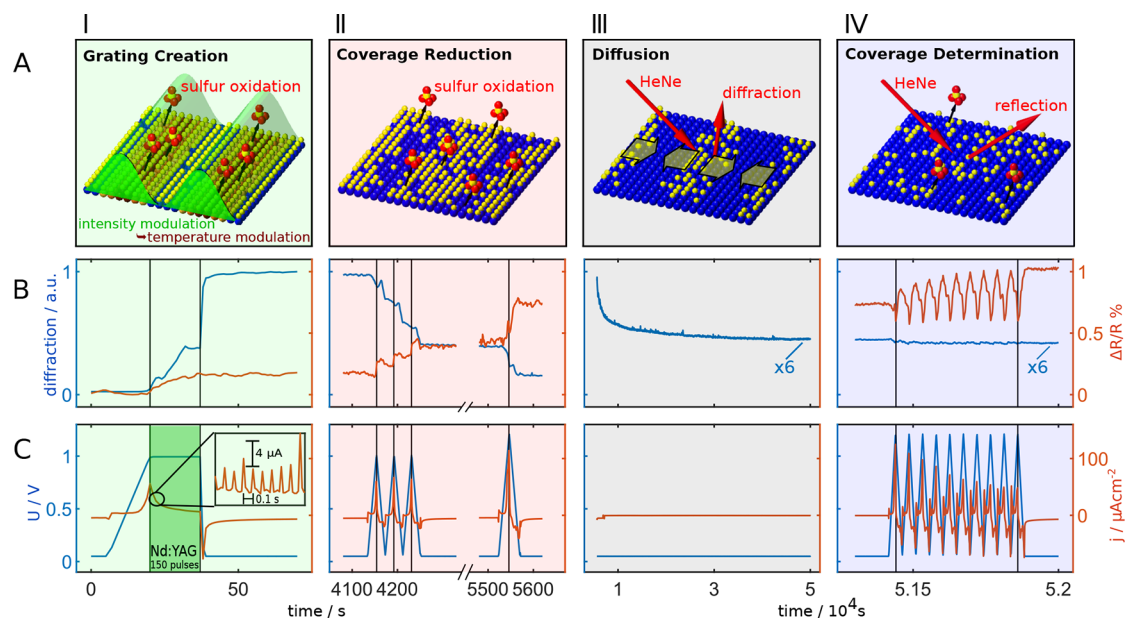

Figure 2. (A) Schematic sketch illustrating the four steps (I–IV) of the in situ LOD measurements, (B) corresponding optical diffraction (blue) and reflectance (red) signal changes, and (C) the potential (blue) and electrochemical current density (red) during a typical measurement. In step I, an adsorbate grating is formed by local sulfur oxidation induced by irradiation with two superimposed beams of the nanosecond Nd:YAG laser. Current spikes due to laser-induced sulfur oxidation are illustrated in the inset. Then, the average adsorbate coverage is further reduced by potential cycles into the sulfur oxidation regime (II), before the actual diffusion measurement by diffraction of the HeNe laser beam at the adsorbate lattice is performed (III). Finally, the average adsorbate coverage in the diffusion measurement is determined by full oxidation of the residual adsorbed sulfur (IV). Note that different time scales in the four sections were used.

In step I, the interference of the Nd:YAG laser beams create a periodic intensity pattern and thus a spatial temperature modulation on the sample. At the same time, the electrode potential is increased to the onset of sulfur oxidation (≈ 1 V). Because S_{ad} oxidation is temperature-dependent,[25,26] its rate is locally increased in the areas of higher temperature and a periodic S_{ad} grating is created. The enhancement of the oxidation rate by the laser manifests as small current spikes that occur simultaneously with the laser pulses (Figure 2C, inset). Quantitative interpretation of these current spikes is difficult, however, because of the highly nonlinear dependence of the current on the laser intensity. As the S_{ad} is oxidized to SO_4^{2-}, no sulfur readsorption from the electrolyte can occur. This is an advantage as compared to thermal desorption of S_{ad} into the liquid, where readsorption may partially refill the formed grating. However, also laser-independent and thus spatially homogeneous sulfur oxidation occurs in this potential range. Potential and laser pulse energies must therefore be chosen carefully to create an adsorbate grating with sufficient modulation depth, without lowering the average S_{ad} coverage too much or damaging the Pt surface (see Supporting Information, section 5).

The formation of the grating can be clearly observed in the diffraction signal, which is continuously increasing during application of the Nd:YAG laser pulses. Sufficiently strongly modulated S_{ad} gratings could only be achieved by multiple (50−300) pulses. Unfortunately, the increase in signal with number of pulses was not fully reproducible, probably because of small positional fluctuations in the interference patterns of the individual pulses. We therefore chose the number of pulses on the basis of the diffraction signal amplitude. After the initial grating formation, the potential is changed back from the oxidative regime to the double layer or hydrogen adsorption region. This potential change results in a pronounced increase of the diffraction signal. We attribute this increase to the desorption of oxygenated species that were previously adsorbed on Pt lattice sites are freed from S_{ad} by the grating creation process. As the optical diffraction signal originates from differences in the local reflectance of the surface and the difference between bare (or SO_4^{2-} covered) and the S_{ad} covered Pt(111) electrode is larger than that between Pt(111) covered by oxygenated species and by S_{ad},[24] the desorption of oxygenated surface species will increase the grating contrast.

In step II, the average sulfur coverage can be further reduced by potential cycling, as evidenced by the increase in $\Delta R/R$ already described in ref 24. This allows studying the S_{ad} diffusion at different coverages. The coverage reduction is controlled by the upper potential limit or the number of cycles and can be directly monitored by the change in $\Delta R/R$. However, the decrease in S_{ad} coverage also leads to a strong decrease of the diffraction signal.

Step III is the actual measurement of the surface diffusion process. The latter results in a gradual decay of the coverage profile until the coverage is uniform. The corresponding decrease in the amplitude of the adsorbate grating is determined from the change in the diffraction signal. If the diffusion constant D is coverage-independent, the diffraction signal intensity I follows an exponential decay (see Supporting Information, section 2):

$$I(t) = I(t=0)\cdot\exp\left(\frac{-8\pi^2 D}{\Lambda^2}t\right) \tag{1}$$

Thus, D can be directly obtained from the decay's time constant. If D is coverage-dependent, there is no simple expression describing the diffraction signal and a multi- or non-exponential decay is expected.[22] However, eq 1 remains a sufficiently good approximation for a grating with a shallow coverage modulation, where D can be assumed to be rather constant.[6,7] This is usually the case after sufficiently long times, when the coverage distribution approaches equilibrium, as can be observed in the example in Figure 2B, III (see Supporting Information, section 4). Here, the diffraction signal can be described by a single exponential decay, after the initially fast decay of the signal has subsided.

In the last step (IV) of the experiment, the average coverage is determined by oxidative stripping of the remaining S_{ad} via potential cycles and analysis of the corresponding changes in the optical reflectance signal (see Supporting Information, section 3). The relation between optical reflectance change and sulfur coverage was already investigated in a previous work[24] and is shown in the inset of Figure 3B. In some experiments, a small diffraction signal remained even after complete removal
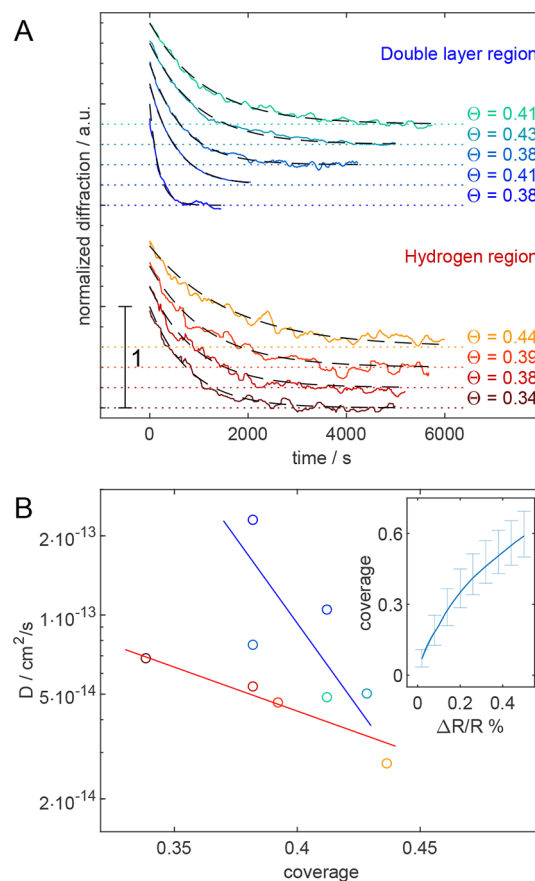

Figure 3. (A) LOD transients of S_{ad} diffusion on Pt(111) in the double layer (blue to green, $U = 0.31$ V) and hydrogen adsorption region (red to yellow, $U = 0.17, 0.12, 0.14, 0.05$ V) and corresponding exponential fits (black dashed line) at various S_{ad} coverages Θ. (B) Resulting diffusion constants as a function of S_{ad} coverage. The coverages were determined from the change in $\Delta R/R$ using the $\Delta R/R$−coverage relation plotted in the inset. Adapted with permission from ref 24. Copyright 2022 Elsevier Ltd.

of the S_{ad} from the surface (see Figure 2B). This is attributed to minor laser-induced Pt surface modification.

Using the described methodology, we studied the coverage and potential dependence of S_{ad} surface diffusion on Pt(111) in 0.1 M H_2SO_4 in the hydrogen adsorption and double layer region. The selected measurements (see Supporting Information, appendix) are performed at coverages between 0.34 and 0.44 ML (error estimation is given in the Supporting Information, section 3). The decay of the diffraction signals (Figure 3A, colored lines) is well described by single exponential fits (dashed black lines), from which the diffusion constants were extracted via eq 1 (for more details, see Supporting Information, section 4).

In Figure 3B, the obtained diffusion constants are plotted against coverage for the two potential regimes. They are in the range of 2×10^{-14} to 2×10^{-13} cm^2/s. The scatter in the data largely results from the limited accuracy of the coverage measurement, which is about ± 0.02 ML. The error in D originating from the exponential fit is smaller than 6% (95% confidence interval) and can thus be neglected. In both potential regions, the S_{ad} diffusion is faster at lower coverages, although the effect is stronger in the double layer than in the hydrogen adsorption region (a factor 20 per 0.1 ML coverage change compared to a factor 2.2 per 0.1 ML, according to a linear regression). Furthermore, diffusion in the double layer region is faster than diffusion in the hydrogen region at least at lower coverages. This suggests that adsorbed hydrogen inhibits the S_{ad} surface diffusion by blocking available surface sites. The measured diffusion rates are about an order of magnitude higher than those found by Renisch et al. for tracer diffusion of S_{ad} on Pt(111) under UHV conditions.[5] Extrapolating the coverage dependence observed in our studies to the tracer diffusion regime, this difference would be even several orders of magnitude larger. Although minor laser-induced modification of the Pt substrate is observed for some measurements in the double layer region (see Supporting Information, section 5), such modification cannot explain these findings because it should increase the density of defects which usually inhibits surface diffusion.[3] Thus, our observations indicate a pronounced influence of the electrochemical environment on the surface diffusion process.

In summary, we introduced in situ linear optical diffraction as a new method for measuring surface diffusion in electrochemical environment and demonstrated its feasibility by measuring the diffusion of S_{ad} on Pt(111) in 0.1 M H_2SO_4. The measured diffusion constants are close to the upper limit of what can be measured by direct microscopic methods, such as video-rate STM. However, in situ LOD, in principle, allows one to measure even much faster diffusion processes. Already the current experimental setup would allow decay constants to be measured in the range of several seconds, which would enable quantitative determination of diffusion constants that are up to 3 orders of magnitude higher than those reported in this work. Several orders of magnitude more are obtainable by increasing the lattice spacing of the adsorbate grating, which would require modification of the incident angles and the electrochemical cell. Therefore, in situ LOD allows the range of surface diffusion measurements in electrochemical environment to be extended from low-mobility model systems to systems of high practical relevance, e.g., in electrocatalysis. Furthermore, the general approach may have applications beyond surface diffusion measurements. For example, the subsequent adsorption of reactive species into an adsorbate grating (e.g., the adsorption of OH in a grating of adsorbed CO) could allow the rate of surface reactions at electrochemical interfaces to be quantitatively measured.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmeasciau.2c00066.

> In situ LOD setup and cell, simple model for the adsorbate grating evolution, sulfur coverage determination from optical reflectance, temporal evolution of the diffraction signal, influence of grating creation on the platinum surface, measurement data (PDF)

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Author Contributions

CRediT: **Lasse Kattwinkel** conceptualization (equal), formal analysis (lead), investigation (lead), methodology (lead), software (lead), visualization (lead), writing-original draft (lead); **Olaf M. Magnussen** conceptualization (equal), funding acquisition (lead), supervision (lead), writing-review & editing (lead).

Notes

The authors declare no competing financial interest.

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