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The electrode-electrolyte interface in CO₂ reduction and H₂ evolution: a multiscale approach

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3

Mediator-free SECM for pH measurements in the diffusion layer with functionalized gold ultramicroelectrodes

This chapter is based on Monteiro, M. C. O., Jacobse, L., Touzalin, T., Koper, M. T. M. *Anal. Chem.* 92 (2), 2237–2243 (2020)

Abstract

Probing pH gradients during electrochemical reactions is important to better understand reaction mechanisms and to separate the influence of pH and pH gradients from intrinsic electrolyte effects. Here, we develop a pH sensor and measure pH changes in the diffusion layer during hydrogen evolution as a model system. The probe was synthesized by functionalizing a gold ultramicroelectrode with a self-assembled monolayer of 4-nitrothiophenol (4-NTP) and further converting it to form a hydroxylaminothiophenol (4-HATP)/4-nitrosothiophenol (4-NSTP) redox couple. The pH sensing is realized by recording the tip cyclic voltammetry and monitoring the Nernstian shift of the mid-peak potential. We employ a capacitive approach technique in our home-built Scanning Electrochemical Microscope (SECM) setup in which an AC potential is applied to the sample and the capacitive current generated at the tip is recorded as a function of distance. This method allows for an approach of the tip to the electrode that is electrolyte-free and consequently also mediator-free. Hydrogen evolution on gold in a neutral electrolyte was studied. The pH was measured with the probe at constant distance from the electrode (ca. 75 μm) while the electrode potential was varied in time. In the non-buffered electrolyte used (0.1 M Li_2SO_4), even at relatively low current densities, a pH difference of three units is measured between the location of the probe and the bulk electrolyte. The time scale of the diffusion layer transient is captured, due to the high time resolution that can be achieved with this probe. The sensor has high sensitivity, measuring differences of more than 8 pH units with a resolution better than 0.1 pH unit.

3.1 Introduction

The pH affects chemical reactions in a wide variety of systems and pH effects have been studied in the fields of biology^{1,2}, medicine^{3,4}, corrosion^{5,6}, electrocatalysis⁷, among others. For example, during electrochemical reactions that consume or produce either protons or hydroxyl ions, a pH gradient is built up in the diffusion layer. The proton concentration at the electrode-electrolyte interface is known to influence the kinetics and selectivity of various electrochemical reactions such as hydrogen evolution⁸, CO₂ reduction^{9,10}, nitrate reduction¹¹, and oxygen evolution.¹² Measuring the pH near the surface allows to better model these electrocatalytic processes and to understand their mechanism under different reaction conditions and in different electrolytes. In order to probe the diffusion layer, the spatial resolution of the conventional pH glass electrode and other bulk techniques using optical¹³ or colorimetric¹⁴ sensors is not high enough. Instead, local measurements of pH at the micro- and nanoscale can be achieved with Scanning Electrochemical Microscopy (SECM) where miniaturized electrodes are used to probe the local properties of an interface.¹⁵ High spatial and temporal resolution of these measurements can be achieved, which mainly depend on the kind of probe used and the electrochemical signal monitored. Spectroscopic pH measurements at the micro scale have also been reported.^{16–18} However, such measurements do not probe the local proton concentration directly, can only be used for specific electrodes and electrocatalytic reactions, and do not provide spatial resolution. Fluorescence microscopy^{19–21} has also been used to map interfacial pH. Although pH maps can be obtained relatively quickly, the need of adding a fluorophore to the electrolyte is a drawback as it may affect the electrochemical process being studied. Based on the discussion presented here, SECM should be a more suitable technique to measure the interfacial pH during electrocatalytic reactions.

Different probes have been proposed for conducting local pH measurements with SECM. Various transition metal oxides show a super Nernstian open circuit potential (OCP) shift with pH and have been employed as potentiometric pH sensors. Iridium oxide (IrO_x) is the most commonly used²² and several synthesis methods have been reported such as nanoparticles electrodeposition²³, anodic growth²⁴, and sol-gel synthesis.²⁵ The sensing response relies on the porosity of the oxide layer; dense oxide films have a slow response to pH changes, while porous layers show a fast response but with a significant OCP drift.²⁶ Besides drift, another

drawback of these probes comes from the adsorption of species on the sensor surface (contaminants, ions, reaction products) that can lead to a convoluted OCP response.²⁷ These limitations can strongly influence how precisely these IrO_x pH sensors capture the local pH gradient during electrochemical reactions. In addition, oxide dissolution can compromise the use of these probes in highly acidic or alkaline media.²⁸ To overcome these limitations, polymer-based potentiometric sensors²⁹ have been proposed, such as polyaniline-coated Au electrodes³⁰, and carbon electrodes modified with poly(1-naphthylamine)³¹ or poly-dopamine.³² However, many of these polymer films strongly interact with alkali metal cations which may lead to a shift in the OCP.³³ In addition, the time response is reported to strongly depend on the quality of the electropolymerization and film thickness.

Other techniques have also been used to probe the pH near the surface. Ryu et al. used the pH sensitive reaction of H₂ with cis-2-butene-1,4-diol to probe the interfacial pH during concurrent hydrogen oxidation.³⁴ Even though significant effects were observed as a function of buffer capacity and current density, the impact of the addition of cis-2-butene-1,4-diol to the electrolyte on the electrocatalysis cannot be determined and might limit the use of this technique to probe other reactions. Measurements of local pH have also been performed using a Rotating Ring-Disc Electrode (RRDE).^{35,36} However, this method is limited in terms of the electrode materials, reactions to be analyzed and lack spatial resolution. Voltammetric pH sensors have also been proposed and are interesting due to their fast response and operation in large pH ranges.^{37–40} Boltz and co-workers for instance, used the voltammetry of platinum nanoelectrodes to monitor the pH above a gas diffusion electrode during oxygen reduction.⁴¹ However, platinum can only be used to probe reactions that do not generate species that strongly interact with the surface, affecting the voltammetry. Michalak et al. developed nano pH sensors based on the cyclic voltammetry of syringaldazine polymer films attached to carbon substrates.⁴² Even though the sensor works in a large pH range, the stability of polymer films, in general, is still concerning as film detachment can hinder the pH response.

In this Chapter, we present a pH sensor based on the irreversible self-assembly of 4-nitrothiophenol on a gold ultramicroelectrode (Au-UME). After conversion, the hydroxylaminothiophenol/4-nitrosothiophenol redox couple is formed and its mid-peak potential shows a Nernstian shift of 57 mV/pH. Using hydrogen evolution as a model system, we perform pH measurements in the diffusion layer with high reproducibility. Because of the sensitivity of the

functionalized tip and to avoid possible side-effects from redox-active mediators, we also introduce an *ex situ* capacitive approach method to control the absolute tip-to-sample distance.⁴³ In contrast to potentiometric pH sensors, our probe provides high time resolution and stable response. In addition, the pH sensitivity is not affected by electrolyte species or reaction products, which allows for application in a wide variety of systems (electrocatalytic or not).

3.2 pH sensor synthesis

It has been previously shown how important the surface preparation and cleanliness of UMEs is for their use in electrocatalysis.⁴⁴ Au-UMEs were characterized in 0.1 M H₂SO₄ before functionalization (see Fig. A2 in Appendix A) in order to assure the glass is efficiently sealing the gold wire and that the surface is clean. Functionalization was performed by immersing the probe in a solution containing 4-nitrothiophenol (4-NTP). The molecules form a self-assembled monolayer at the gold surface, binding through the thiol anchor group. The free nitro group is then partially reduced electrochemically into a hydroxyl amino group by cycling the tip from 0.1 to -0.25 V vs. Ag/AgCl in 0.1 M H₂SO₄. The cyclic voltammogram (CV) of the conversion and a schematic representation of the species formed are shown in Fig. 3.1a and Fig. 3.1b, respectively. Hydroxylaminothiophenol (4-HATP) is formed through the transfer of four protons and four electrons and at positive potentials 4-HATP is reversibly oxidized to 4-nitrosothiophenol (4-NSTP) through the transfer of two protons and two electrons (see Fig. 3.1c). Thus, the mid-peak potential of the 4-HATP/4-NSTP redox couple is expected to show a Nernstian shift with pH.⁴⁵

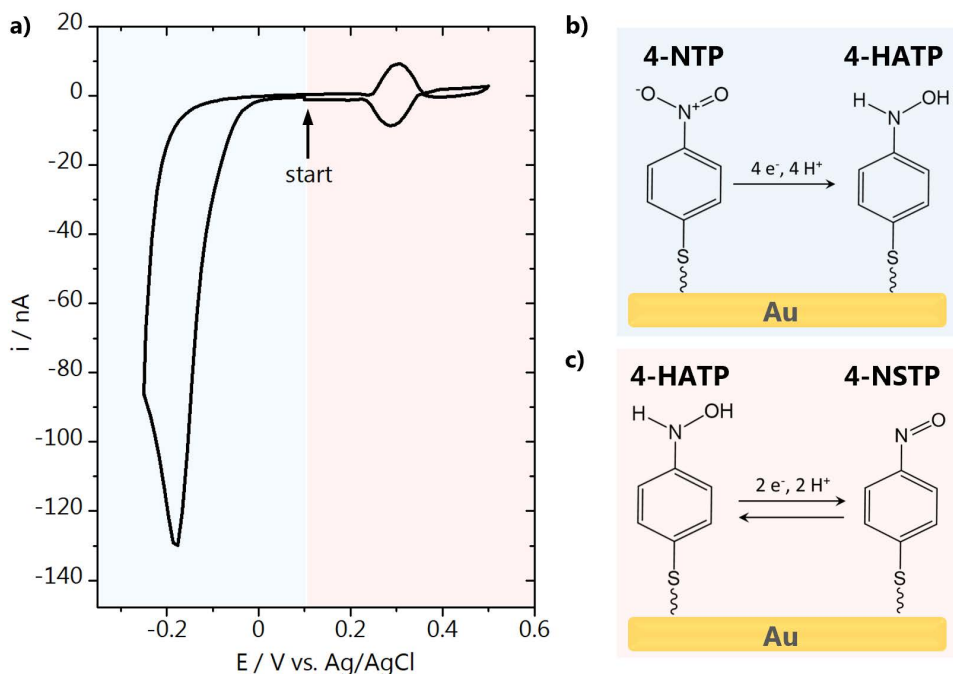


Fig. 3.1. **a)** Voltammetry (0.1 M H_2SO_4 , 100 mV s^{-1}) and schematic representation of the conversion of **b)** 4-nitrothiophenol (4-NTP) to 4-hydroxiaminothiophenol (4-HATP), and **c)** the two proton-two electron transfer reaction of the redox couple 4-HATP/4-NSTP.

The electrochemical characterization of the reversible redox couple 4-HATP/4-NSTP in Fig. 3.2a shows that the tip voltammetry is very stable over the 30 cycles performed. It is important to point out that for successful functionalization of the Au-UME the potential of the tip must be carefully controlled. It has been previously shown by Touzalin et al.⁴⁶ that at potentials lower than $-0.25 \text{ V vs. Ag/AgCl}$ (pH = 1) 4-NTP and 4-HATP are fully irreversibly reduced to 4-aminothiophenol (4-ATP). At potentials higher than $0.6 \text{ V vs. Ag/AgCl}$ the monolayer is destabilized, likely due to polymerization, leading to a decrease in the 4-HATP/4-NSTP signal intensity (although the exact mechanism is not yet clear).

To calibrate the pH sensor, the tip voltammetry was recorded in argon saturated solutions of various pH (see Fig. A.3a in Appendix A). The potential of the anodic peak as a function of pH was used to construct the calibration curves depicted in Fig. 3.2b. A linear fit of the data provides the following relationship: $\text{pH} = (0.341 - E_{\text{peak}})/0.057$ with an R^2 value of 0.99. The mid-peak potential shows a Nernstian behavior with a shift of 57 mV per pH unit. As the tip will be used to

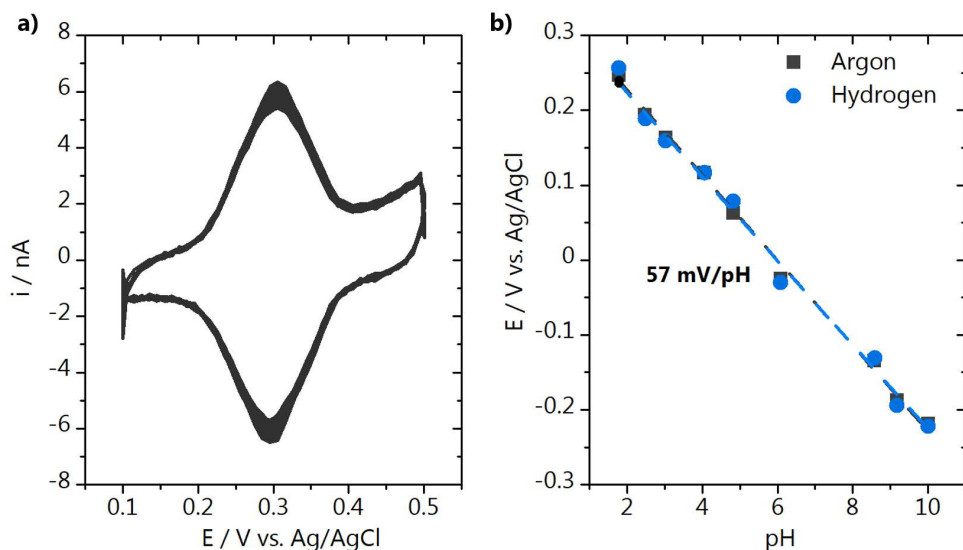


Fig. 3.2. **a)** Characterization of the electroactive redox couple 4-HATP/4-NATP in 0.1 M H_2SO_4 at 200 mVs^{-1} and **b)** calibration of the functionalized Au-UME in 0.1 M Li_2SO_4 solutions adjusted to different pH and saturated with argon or hydrogen.

probe pH changes during hydrogen evolution, it was also calibrated in hydrogen atmosphere. As can be seen in Fig. 3.2b, the presence of hydrogen does not affect the pH response. Even though the calibration curve shown in Fig. 3.2b does not include pH 7, other calibration curves were made where pH 7 was included and different from the work of Cobb et al.⁴⁷ on quinone-based pH electrodes, no significant deviation of the Nernstian response was found. The latter is probably related to the different interaction the quinone has with the substrate in comparison to the 4-nitrothiophenol self-assembled monolayer. In addition, 4-nitrothiophenol is only partially converted to 4-hydroxiaminothiophenol, and according to Cobb's work the lower the coverage of the surface, the lower the deviations.

3.3 Capacitive approach

Commonly used SECM approach techniques need a mediator or a diffusion limited reaction taking place at the tip in order to determine the tip-to-sample distance.⁴⁸ However, these methods are not ideal for our experiment, because they can contaminate the electrocatalytic system and/or destabilize the self-assembled monolayer. Furthermore, it has been shown that commonly made assumptions about the exact tip geometry lead to significant errors in the calculated tip-to-sample distance.⁴⁹ In principle, the AC-SECM^{50,51} approach could be employed,

although it is not known how stable the self-assembled monolayer is at high frequencies. Therefore, we have applied an electrolyte-free approach method that allows determining the absolute tip-to-surface distance without destabilizing the 4-NTP/4-HATP/4-NSTP monolayer. This *ex situ* method employs the capacitance between tip and sample and was recently introduced by De Voogd et al. as a pre-approach for Scanning Tunnelling Microscopy (STM) setups.⁴³

To enable the determination of the tip-sample capacitance in air, an AC potential (10 kHz, 1.41 V_{RMS}) is applied to the sample and the resulting tip current is followed with a preamplifier. The out-of-phase (Y) component of the tip current is determined using a lock-in amplifier. Fig. 3.3a shows a schematic representation of the approach configuration. The capacitance can be calculated *via*:

$$C_{tot} = \frac{Y}{2\pi fGV} \quad \text{Eq. 3.1}$$

where G is the preamplifier gain and f and V are the frequency and amplitude of the reference (sample) signal, respectively. At small tip-to-surface distances (smaller than ~10% of the tip radius), the tip and sample can be described as a parallel plate capacitor, of which the capacitance is:

$$C_{par} = \frac{\epsilon_0 A}{d} \quad \text{Eq. 3.2}$$

where ϵ_0 is the permittivity of air, A the area (of the tip), and d the tip-to-sample distance. In practice $d = d_0 - Z$, in which Z is the position of the stepper motor varied during the approach, and d_0 is the absolute surface position. At large tip-to-surface distances, which is the case during the approach, we find that the system is better described as a point charge in front of a plate, instead of a pure parallel plate capacitor. The capacitance is then given by Eq. 3.3, derived from Eq. 3 from Ref. 43. Here, the very end of the tip is described as a half sphere with radius R_{eff} and the term B accounts for the magnitude of the capacitance in the case where R_{eff} is assumed to remain constant as a function of d .

$$C_{point} = -2\pi R_{eff} \epsilon_0 * \ln(d_0 - Z) + B \quad \text{Eq. 3.3}$$

Finally, the measured capacitance as a function of the position of the stepper motor $C_{tot}(Z)$ can be fitted with Eq. 3.4. This allows to obtain the fitting parameter

d_0 which is the absolute tip-to-surface distance. The total capacitance contains also contributions that are inherent to the setup, e.g. due to the tip connection far away from the sample and the connections used.⁴³ These contributions are accounted for in the terms A_2 and L_{par}

$$C_{tot}(Z) = -A_1 * \ln(d_0 - Z) + B + \left(\frac{A_2}{L_{par} + d_0 - Z} \right) \quad \text{Eq. 3.4}$$

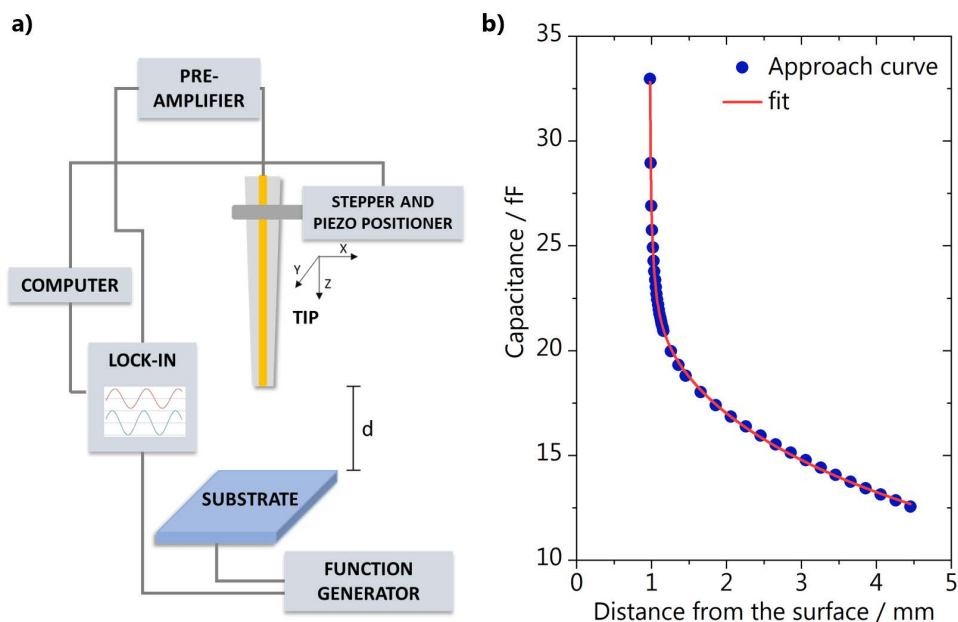


Fig. 3.3. a) Capacitive approach configuration and **b)** approach curve obtained (blue circles) with its fit using Eq. 3.4 (red line).

Fig. 3.3b shows a measured approach curve together with its fit. This enables us to approach the surface to a distance well below the tip diameter (here 10–30 μm with a 50 μm diameter tip) in a safe and reproducible way. It is important to point out that the shape of the approach curve is not affected by the probe RG (radius of the insulating layer divided by the radius of the active layer) which means that it can be employed in any SECM setup. It should be noted that, due to humidity, the measured permittivity (ϵ) differs from the permittivity of dry air (ϵ_0). In a Kelvin probe approach, this is known to significantly change the approach curve.⁵² However, as seen from Eq. 3.4 it is clear that for the capacitive approach only the

absolute capacitance changes as a function of ϵ , while the shape of the approach curve remains the same. Finally, we have successfully tested this approach technique with electrodes of different geometries and dimensions. With the appropriate electronics, the capacitive approach can also be used for significantly smaller tips than presented here. However, one should realize that, as the shape of the approach curve does not depend on the tip diameter, without detailed tip characterization the accuracy of this method is in the range of 1-3 μm .

3.4 Local pH measurements

The functionalized gold pH sensor was used to study hydrogen evolution (HER) on gold (0.1 M Li_2SO_4 , pH = 3.2) as a model system. Before the pH measurements were performed, the CV of HER was recorded at the gold substrate, which is shown in Fig. 3.4. The cathodic current observed is due to the reduction of protons ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). The reaction rate is initially governed by kinetics and below -0.8 V vs. Ag/AgCl, the reaction becomes diffusion limited. As protons are consumed at the interface and the diffusion layer thickness increases, a pH gradient is built up. This can be observed in the CV by the decrease of the cathodic current from the first to the subsequent cycles due to proton depletion. However, quantification of the local pH is not possible based on the CV alone. At potentials more negative than -1.2 V vs. Ag/AgCl and bulk pH, mainly the reduction of water would take place ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$). The SECM pH measurements were performed in the potential range highlighted in the CV, in which in principle mostly proton reduction is taking place.

SECM pH measurements were carried out with the functionalized Au-UME placed at fixed distance, 75 ± 1 μm from the surface. Hydrogen evolution was turned “on” and “off” at the gold sample while the tip voltammetry was recorded at a scan rate of 200 mV s^{-1} . An example of the shift observed in the tip voltammetry can be found in Fig. A.6 in Appendix A. The tip CVs were fitted, and the potential of the anodic peak determined as a function of time (see Fig. A.7 in Appendix A). The calibration curve shown in Fig. 3.2b was used to convert the tip peak potentials to pH. Details on the data fitting can be found in Appendix A. Results depicted in Fig. 3.5a show the pH changes taking place when HER is turned “on” and “off” at the sample at -0.75 V vs. Ag/AgCl. Each data point corresponds to the mid-peak potential extracted from each Au-UME CV. At -0.75 V vs. Ag/AgCl, protons are being consumed at the gold working electrode and the pH has an initial fast

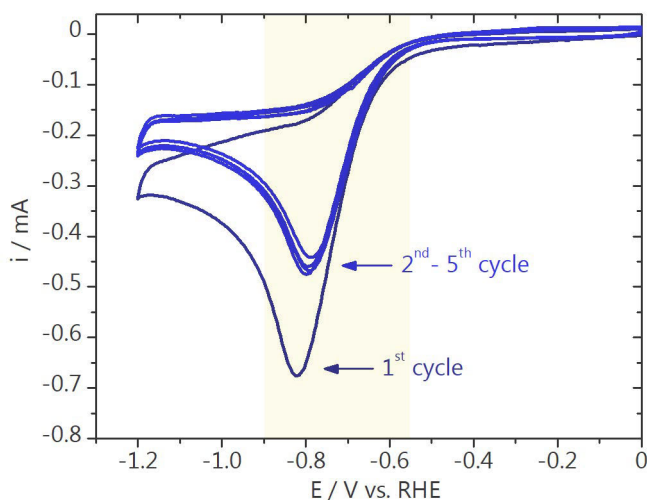


Fig. 3.4. Cyclic voltammogram of hydrogen evolution taking place at the gold sample in 0.1 M Li_2SO_4 (pH = 3.2) recorded at 100 mV s^{-1} .

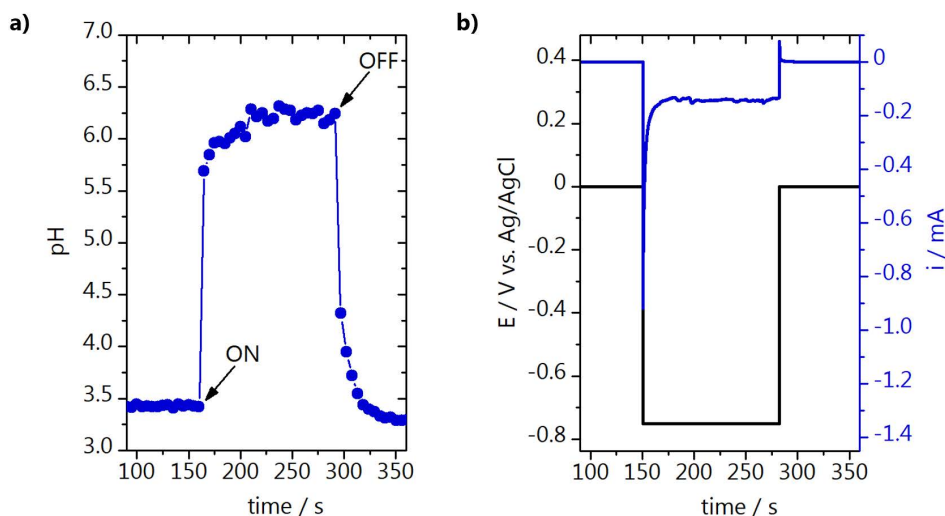


Fig. 3.5. **a)** pH measurement during hydrogen evolution in 0.1 M Li_2SO_4 (pH = 3.2) with the sample at $-0.75 \text{ V vs. Ag/AgCl}$; **b)** chronoamperometry recorded at the sample.

increase of more than two units and takes 50 seconds to reach a stable value. By observing the sample chronoamperometry curve (Fig. 3.5b), this is also the time needed for the current to reach diffusion limitation due to an initially fast increase in local pH and diffusion layer thickness. At -0.75 V the maximum pH value of 6.3 was reached. This strong pH increase can be explained by the fact that the electrolyte is not buffered. After 150 seconds, HER is turned "off" and the near-surface pH returns to the bulk pH value. Similar measurements were previously performed with an IrO_x sensor.⁵³ Comparing our results with the data presented in Figure 8 of Ref. 54, it can be seen that our probe captures the time scale of the pH changes during HER more precisely, allowing for a larger number of data points to be obtained in time, only dependent on the scan rate at which the tip voltammetry is recorded. In addition, our pH sensor is more stable, and the response does not drift in time, which is a common drawback of potentiometric sensors such as IrO_x .

Measurements were also performed at less negative sample potentials, which due to the slower consumption of protons, should lead to lower pH values than obtained at -0.75 V vs. Ag/AgCl. As depicted in Fig. 3.6 when -0.65 V vs. Ag/AgCl is applied to the sample, the pH reaches 4.75 and when HER is carried out at -0.55 V vs. Ag/AgCl only a small increase of less than one pH unit is observed. The corresponding sample chronoamperometry can be seen in Fig. A.4 in Appendix A. To assure reproducibility of the pH response, a second measurement was performed applying the same negative potentials (black curve in Fig. 3.6). The same pH values were reached for the same potentials, which also shows how thermal drift does not compromise the measurements.

Another set of HER experiments was performed where the sample potential was changed in smaller steps, to demonstrate the sensitivity of the pH probe. The results can be seen in Fig. 3.7, where the sample potential was varied from -0.6 to -0.9 V vs. Ag/AgCl in steps of 50 mV. The electrolyte bulk pH was 3 and a gradual increase in pH can be observed as a function of sample potential, irrespective of the fact that the potentials are applied in a random order. The sample chronoamperometry recorded during the experiment can be found in Fig. A.5 in Appendix A. The inset in Fig. 3.7 shows the remarkable sensitivity of our pH probe, as differences of 0.1 and 0.35 pH unit were recorded when the sample potential was -0.6 and -0.65 V vs. Ag/AgCl, respectively. In addition, measurements at more negative sample potentials show the large pH range at which the probe can be employed. Note that the absolute pH values cannot directly be compared between this measurement and the one shown in Fig. 3.6 as different spots of the

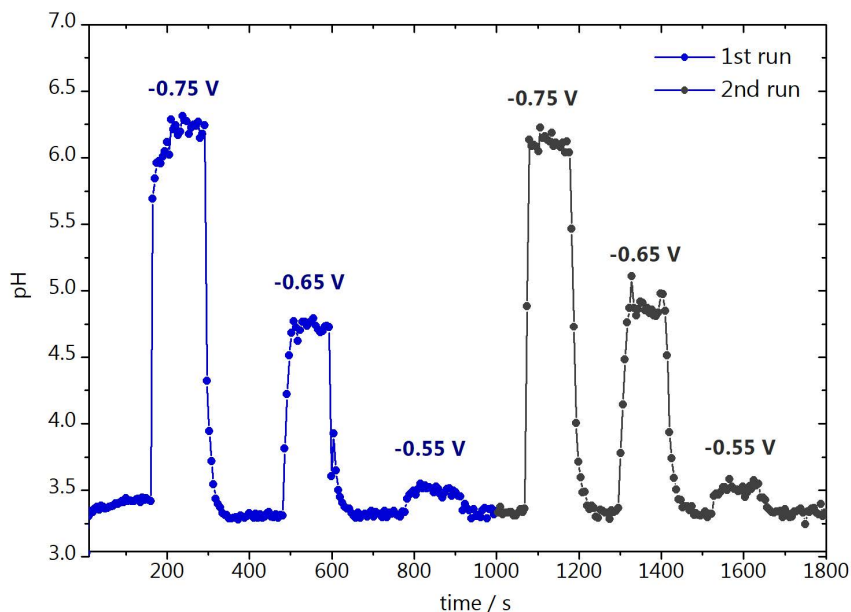


Fig. 3.6. pH measurements in the diffusion layer during hydrogen evolution in 0.1 M Li_2SO_4 (pH = 3.2) at different sample potentials. The measurement was performed in duplicate.

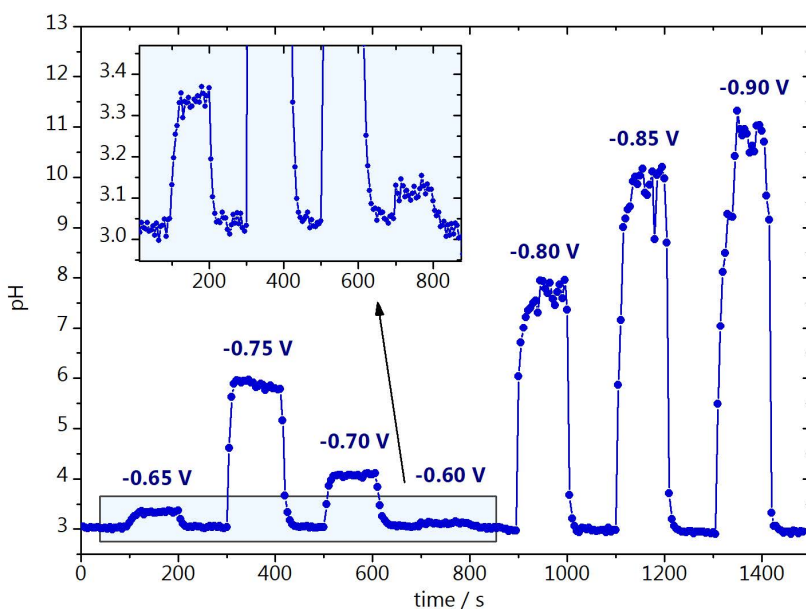


Fig. 3.7. pH measurements in the diffusion layer during hydrogen evolution in 0.1 M Li_2SO_4 (pH = 3) performed in a wider potential range. The inset shows the small pH differences recorded when the sample potential was -0.65 and -0.60 V vs. Ag/AgCl .

polycrystalline gold sample have distinct reactivities towards HER and the starting bulk pH is not the same.

It is important to point out that during the measurements, the potential window of the tip voltammetry must be adjusted due to the pH changes happening locally. Not only the 4-HATP/4-NSTP mid-peak potential shifts with pH but also the potential at which the unwanted tip reactions take place, i.e. 4-ATP formation and destabilization of the self-assembled monolayer. Therefore, the 4-HATP/4-NSTP peak intensity would decrease drastically if the potential limits were not adjusted accordingly. In addition, the time resolution of the measurement can be adjusted according to the time scale of the reaction being studied. Test CVs were recorded until up to 600 mV s⁻¹ and the tip voltammetry was still stable.

3.5 Conclusions

In this work, we have successfully developed a pH sensor based on the self-assembly of 4-nitrothiophenol on gold ultramicroelectrodes. The probe voltammetry shows a Nernstian behavior with 57 mV/pH shift, which is not affected by the electrolyte composition. To assure cleanliness and avoid destabilization of the probe, we employ a mediator- and electrolyte-free capacitive approach to determine the absolute tip-to-sample distance. We have measured the pH during hydrogen evolution with the tip placed at a constant distance, 75 μm from the surface. Results show that our pH probe provides superior time resolution compared to previously reported potentiometric IrO_x pH sensors, allowing to capture the dynamics of proton diffusion during hydrogen evolution. A gold UME of 50 μm diameter was used in this work, but the functionalization with 4-NTP can also be carried out using smaller gold UMEs for further spatially resolved measurements. This would also allow for measurements with the probe positioned closer to the surface. Summarizing, we presented a highly sensitive and selective miniature pH probe that can be applied to a wide variety of systems, changing for example the gas atmosphere, electrolyte composition, and substrate. This work provides the means for more precise determination of the spatially resolved diffusion layer pH under different reactions. Consequently, it will help better understanding and modelling electrocatalytic reactions.

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