Electrochemically induced pH change: time resolved confocal fluorescence microscopic measurements and comparison with numerical model

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Abstract

The measurement of pH near electrodes is relevant to all electrochemical reactions in aqueous solutions. In this context, confocal fluorescence microscopy is a proven technique, that can image near-electrode pH changes; however time resolved measurements, critical for a complete understanding of electrode processes, are required. In this work, for the first time we measure time resolved pH profiles formed near electrodes with confocal fluorescence microscopy. Specific factors affecting the pH measurement such as attenuation of light and the role of dye migration are discussed in detail. Using the pH-sensitive dye fluorescein, we measure the proton depletion zone formed due to oxygen reduction on a platinum electrode. Experimental results compare favorably with a one-dimensional reaction-diffusion model. This holds up to the point where the measurements reveal 3-dimensionality in the pH distribution. The method is further applied to analyse the bubble effects observed in sulphate-containing electrolytes. The work presented here is paving the way towards the use of confocal fluorescence microscopy in the measurement of 3D time resolved pH changes in numerous electrochemical settings, e.g. in the vicinity of bubbles.

Introduction

Electrochemical reactions in aqueous solutions are strongly affected by the pH near the electrode. In corrosion science, potential-pH phase diagrams (Pourbaix diagrams) best summarize this relationship. Moreover, in applications of energy storage and material conversion (e.g. CO_2 and N_2 reduction to useful products), where protons in solution are consumed, there is a direct link between the pH and the efficiency of the electrochemical cell. Measuring and understanding pH profiles near electrodes is therefore essential and can provide insight into the local surface chemistry and help design efficient electrochemical systems. This is particularly relevant in the reduction of CO_2, where sensitivity to the near electrode pH may limit the desired product formation.²⁻⁴

An effective technique to detect pH changes is the use of indicator molecules, such as fluorescein, whose fluorescence changes with pH. Unlike point measurements, e.g. via scanning electrochemical microscopy,⁵ imaging fluorescence fields allows for spatially resolved pH measurement. When coupled with confocal microscopy, this approach offers an even higher spatial resolution, and has already demonstrated its potential in electrochemical applica-
tions. For example, Unwin et al. measured three dimensional steady-state pH profiles on micro-electrodes. Cannan et al. determined the pH change accompanied by the reduction of Benzoquinone to hydroquinone. Similarly, Rudd et al. measured the pH profiles induced by the reduction of water and oxygen on gold electrodes. They considered different electrode shapes and compared their results with a steady state reaction-diffusion model. Leenheer and Atwater applied the fluorescence method in a flow cell to compare the steady state pH profiles formed (for hydrogen evolution) on patterned Au electrode surfaces. Furthermore, they measured pH profiles on various electrode materials, thereby suggesting this technique as a screening tool for identifying electrocatalysts. Similar to Rudd et al., they compared their measurements with a steady state model, one including laminar flow.

Although fluorescent measurements of spatio-temporal pH profiles near ion-selective membranes have been recently undertaken, with related electrokinetic modelling by Andersen et al., such measurements are lacking for electrolytic systems and near the electrodes. Here, besides electric field effects, large gradients in pH are created due to chemical reactions at the electrode surface. Time resolution is then essential to capture the dynamics at the electrode-electrolyte interface. One such application would be the measurement of pH profiles around growing Hydrogen bubbles in solution, which may reveal transient reaction hot-spots. Similarly, other situations involving phase change, simultaneous electrode reactions, or bulk buffer reactions during electrolysis require time resolved measurements for their accurate characterization. Certainly, a further development of time resolved measurements techniques is urgently needed to understand dynamic processes occurring at electrode/electrolyte interfaces in electrochemical processes. In spite of the need, to the best of our knowledge, a quantitative comparison of time-resolved pH measurements and modelling using fluorescent dyes is not yet available in the literature.

In this contribution we demonstrate the feasibility of using fluorescent dyes to measure spatio-temporally varying pH profiles in solution during electrochemical oxygen reduction. The experimental analysis is supplemented by the results of a time dependent reaction-diffusion model. In addition to the development of the experimental technique, our findings highlight the importance of buffer effects and supporting electrolyte concentration. It is expected that this technique will help to better tackle and understand problems such as water electrolysis and electrochemical CO$_2$ reduction among others.

**Experimental Details**

A schematic of the setup used in the experiments with the relevant dimensions is shown in Figure 1a. The electrochemical housing was made of teflon and the cell assembly was mounted on top of an inverted confocal microscope. In all measurements, a platinized titanium mesh was rolled up and placed as a ring at about 4 cm from the working electrode. This assembly successfully prevented any interference of the counter electrode reaction with the pH measurement. A 10 nm thick Platinum film evaporated on a 170 µm glass slide was used as a working electrode. A 3 nm Chromium (under) layer was used for better adhesion of the Pt film to the glass.

The sheet resistance of the resulting thin film electrode was about 69 Ω. The electrical connection to the working electrode was made with a platinized titanium point contact. A BASi® Ag/AgCl (in 3M NaCl) was used as a reference electrode. Unless otherwise stated, 0.5M NaClO$_4$ was used as electrolyte. Prior to the measurement, the pH of the solution was adjusted to a pH value of 5 by addition of appropriate amounts of 0.1M HClO$_4$. For experiments with sulphate electrolyte, Na$_2$SO$_4$ solutions were adjusted to the desired pH using 0.5M H$_2$SO$_4$. Sodium fluorescein (C$_{20}$H$_{10}$Na$_2$O$_5$, Molecular Weight: 376.27 g/mol) was used as the pH tracer. A concentration of 8 µM was used to avoid self-quenching of its fluorescence signal. The pH of the solution before the start of each experiment (as
Figure 1: (a) Schematic of the experimental setup. The electrochemical cell was placed on the inverted confocal laser scanning microscope. The transparent working electrode allowed for depth-wise ($z$) measurement of fluorescent intensity. (b) Calibration results for the pH dependence of fluorescein. The experimental data (filled circles) shown here is the mean of three measurements of intensity measurements at each pH (error bars are smaller than the marker size). A sigmoidal function (black line; see supporting information for details of fit) is fitted to all three measurements at each pH. The measurements were performed in 1 mM Na$_2$SO$_4$ containing 8µM fluorescein. pH was adjusted to the required value by addition of H$_2$SO$_4$. (c) Migration effect for different supporting electrolyte concentrations. The emission intensity ($I$) is normalized with the intensity profile before applying the current ($I_0$). The measurement of fluorescence intensity is restricted to $z > 0.1$mm due to limitations of the optical setup (see supporting information for details). The measurements were performed with a solution containing 8µM SrB. pH was adjusted to pH 5 by addition of H$_2$SO$_4$. The colour code reflects the time at which the concentrations were measured. $|i| = 5.59 \mu A/cm^2$

well as the calibration solutions shown in Figure 1b) was measured using the Hannah® Instruments Edge-pH meter that has an of ± 0.02 pH units. All chemicals were purchased from Sigma Aldrich. The experiments were carried out at constant applied currents.

Confocal microscope

An inverted laser scanning confocal fluorescent microscope (Nikon confocal microscope A1 system, Nikon Corporation, Tokyo, Japan) with a 10x dry objective (CFI Plan Fluor 10x/0.3, numerical aperture = 0.3, working distance = 16 mm) was used to measure a 1.28 mm x 1.28 mm region (512 x 512 pixel$^2$) chosen close to the center of the electrode. A 488 nm excitation laser was chosen to excite Fl, while the emission was collected in a 515-550 nm wavelength window. The pinhole (29.4 µm) cuts off any out of focus light allowing to image thin volume sections. Close to 70 measurement cross sections with 20 µm distance from each other were scanned repeatedly (in a serial fashion as shown in Figure 1a), resulting in a total measured depth of 1.4 mm. We denote the coordinate in the scanned direction as $z$. The position of the electrode surface ($z = 0$) was determined from the maxima of the laser reflections and it was found that the fluorescence signal max-
imum was located at \( z \approx 100 \, \mu\text{m} \) above the surface (see supporting information for details). Therefore, pH information was only obtained above this threshold. The scanning along \( z \) proceeded from below the electrode surface into the solution and was repeated at a typical rate of 0.5 Hz. Each fluorescein image was fitted with a Gaussian distribution, the mean of which was then taken as the measured intensity at the corresponding \( z \)-position. We find that with our parameters we operated beyond the optically thin limit, where the attenuation of the exciting laser light (along with fluorescent emission) becomes pH-dependent \(^{15} \) and cannot be neglected. Therefore an attenuation correction was implemented. Details on this as well as on intensity as well as on a depth correction to account for the multimedia geometry are provided in the supporting information.

**Fluroescein: a pH sensitive dye**

Fluorescein (Fl) is a popular choice to probe pH changes in electrochemical cells.\(^7\)\(^-\)\(^9\),\(^{16} \) The pH sensitivity of Fl arises from the existence of different protonated forms of the molecule in solution. Diehl and Markuwicz\(^{17} \) found that the presence (or absence) of the doubly charged anion corresponds to high (low) fluorescent emission. The equilibrium dissociation constants\(^{17,18} \) for the neutral (H\(_2\)Fl) and singly charged Fl anion (HFl\(^-\)) were found to be \( pK_{eq1} = 4.24 \) and \( pK_{eq2} = 6.36 \), respectively. Higher pH values therefore correspond to an increased Fl\(^2-\) concentration and in turn a higher fluorescence intensity. The relationship is highly nonlinear, however, as our calibration results in Figure 1b show. The dye is particularly pH-sensitive in the range \( 5 \lesssim pH \lesssim 10 \) (indicated by the shading in Figure 1b), as evidenced by the pronounced increase of fluorescence emission intensity measured with increasing pH within this interval. The pH dependent fluorescence emission was fitted with an analytical function to allow for a conversion from Fl intensities obtained in the experiments to pH. The laser and confocal settings were kept constant throughout the study such that the curve in Figure 1b applies to all experiments. Details on the fit and the repeatability are provided in the supporting information. Since the intensity-pH curve flattens out significantly beyond \( pH \gtrsim 8.5 \), measurement results beyond that value should be taken with caution. Lastly, since Fl is charged in solution, an electric field induced inhomogeneity in the dye distribution will make it difficult to decouple intensity changes due to migration from a pH change. An anionic\(^{19} \) pH insensitive dye, namely Sulforhodamine B (Sigma Aldrich, Molecular weight: 580.65 g/mol, 8\( \mu \)M, henceforth SRb) was therefore used to indicate the presence of dye migration. Although unlike Fl, SRb has a single negative charge in solution, due to their similar molecular weight it still serves as a good qualitative indicator of dye migration. SRb is also mildly temperature sensitive (intensity decrease \( \approx 1.2\% \) per K\(^{20} \)), but for the current densities considered in this work the temperature change is estimated (even when using resistivity of pure water) to be negligible. The measured fluorescent intensity for the highest current density (5.59 \( \mu A/cm^2 \)) in this work is presented in Figure 1c. For low supporting electrolyte concentration, i.e. \( = 10 \, \mu\text{M} \), the fluorescence intensity of the dye near the electrode surface and up to a distance of \( \approx 0.75 \) mm above the electrode decreased by up to 30\%. However, this migration effect reduces significantly for increased concentration of the supporting electrolyte, and is almost negligible for Na\(_2\)SO\(_4\) concentrations \( \geq 1\text{mM} \). A concentration of the supporting electrolyte much greater than this is therefore used in the experiments performed in this study.

**Model details**

In order to provide a reference, we also simulated the pH profiles during reaction. In the most general case, this requires the integration of the Poisson-Nernst-Planck (PNP) equations. If the concentration of the supporting electrolyte is large (compared to other ions in solution), then the whole potential drop occurs at the electrode, and ion transport can be approximated by a diffusion model.\(^{21,22} \) We there-
fore adopted a reaction-diffusion model for the simulations.

Reaction-Diffusion system
The general form of the reaction-diffusion equation is
$$\frac{\partial c_k}{\partial t} = D_k \frac{\partial^2 c_k}{\partial z^2} + f(c), \quad (1)$$
where $c_k(z,t)$ is the concentration of species $k$ and $D_k$ the diffusion constants. $f(c)$ is a non-linear function representing reaction terms, and for a chemical reaction
$$P + Q \xrightarrow[k_{\text{rev}}]{k_{\text{fwd}}} R, \quad (2)$$
is of the following form (for species $P$):
$$f(c) = -(k_{\text{fwd}}c_P c_Q - k_{\text{rev}} c_R), \quad (3)$$
where the equilibrium constant is given by $K_{\text{reaction}} = \frac{k_{\text{fwd}}}{k_{\text{rev}}} = k_{\text{fwd}}$.

Using the initial concentration $c_k(z,0) = c_k^0$, a length $L$ of the domain and a reference diffusion timescale (based on $D$, the largest of the diffusivities $D_k$), equation (1) can be made dimensionless. We then obtain:
$$\frac{\partial c_k^*}{\partial t^*} = D_{r,k} \frac{\partial^2 c_k^*}{\partial z^2} + Da \times f(c^*), \quad (4)$$
such that the non-dimensional parameters are given by a set of diffusivity ratios $D_{r,k}$ and Damkohler numbers $Da$ (e.g. for species $P$ in equation (2), $Da = \frac{k_{\text{fwd}} c_P^0 L^2}{D}$).

Here the chemical reactions considered are
$$\text{H}^+ + \text{OH}^- \xrightarrow[k_f]{k_b} \text{H}_2\text{O} \quad (5)$$
$$\text{H}^+ + \text{Fl}^2- \xrightarrow[k_{\text{fwd}}]{k_{\text{rev}}} \text{HFl}^- \quad (6)$$
where the equilibrium constants are $\frac{k_b}{k_f} = K_W$ and $\frac{k_{\text{rev}}}{k_{\text{fwd}}} = K_{\text{f,eq}}$. The $pK_a$ of H$_2$Fl is lower than the pH considered here and therefore can be ignored. Finally, the concentration of water is large and therefore essentially constant during the experiment such that the difference equations simplify to:
$$\begin{align*}
\frac{\partial c_{H^+}^*}{\partial t^*} &= \frac{\partial^2 c_{H^+}^*}{\partial z^2} - Da_1(c_{H^+}^* c_{OH^-}^* - 1) \\
&\quad - Da_2 \left( c_{H^+}^* c_{Fl2^-}^* - \frac{K_{f,eq}}{c_{H^+}^*} (1 - c_{Fl2^-}^*) \right) \quad (7a)
\end{align*}$$
$$\begin{align*}
\frac{\partial c_{OH^-}^*}{\partial t^*} &= \frac{\partial^2 c_{OH^-}^*}{\partial z^2} \\
&\quad - \frac{Da_1 c_{H^+}^* c_{OH^-}^*}{c_{H^+}^*} (1 - c_{Fl2^-}^*) \quad (7b)
\end{align*}$$
$$\begin{align*}
\frac{\partial c_{Fl2^-}^*}{\partial t^*} &= \frac{\partial^2 c_{Fl2^-}^*}{\partial z^2} \\
&\quad - \frac{Da_2 c_{H^+}^*}{c_{H^+}^*} \left( c_{H^+}^* c_{Fl2^-}^* - \frac{K_{f,eq}}{c_{H^+}^*} (1 - c_{Fl2^-}^*) \right) \quad (7c)
\end{align*}$$
where,
$$Da_1 = \frac{k_{f} c_{H}^0 L^2}{D_{H^+}}, \quad Da_2 = \frac{k_{f,Fl} TL^2}{D_{H^+}}.$$ 
$$D_{r,1} = \frac{c_{OH}^0}{D_{H^+}}, \quad D_{r,2} = \frac{c_{Fl}^0}{D_{H^+}}.$$ 

Further $T$ is the total initial concentration of fluorescein ($c_{Fl2^-} + c_{Fl2^-}$) which is used to non-dimensionalize the diffusion equation for $c_{Fl2^-}$.

All concentrations are kept constant far from the electrode ($z = L$) at their respective initial values, while flux boundary conditions are employed at the electrode surface. In particular, the consumption flux of $H^+$ is set by the Faradaic current density $i_f$ as $\frac{\partial c_{H^+}^*}{\partial z} = -\frac{|i_f| L}{FD_{H^+} c_{H^+}^*}$, with $F$ denoting the Faraday constant, while all other fluxes are zero at $z = 0$. It is important to note that $i_f$ is not the applied current density $i$, but has been modified to take the contribution of a capacitive current into account. This is achieved by using a constant capacitance similarly as done by Bonnefont et al. Assumption a Stern layer thickness $\lambda_S = 1$nm, a permittivity 10 times the vacuum permittivity $\epsilon_0$, and that the whole potential drop occurs within the Stern layer, the capacitance $C$ is estimated to be about $C \approx 88 \mu F/cm^2$. The double layer capacitance of platinum (measured in 0.1 M KClO$_4$) was found to be in a similar range (20 - 120 $\mu F/cm^2$). $i_f$ is then related to the measured time-dependent potential ($\phi$)
change by \( i_f = i - C \frac{d\phi}{dt} \). Since the exact value of C in our measurements is not known, results for \( 0 \leq C \leq 120 \) \( \mu \text{F/cm}^2 \) have also been presented in Figure 3c.

Table 1: Parameters and associated used in the model

| Parameter   | Value (units) | Parameter   | Value (units) |
|-------------|---------------|-------------|---------------|
| \( D_{\text{H}_2} \) | \( 9.3 \times 10^{-3} \) (m\(^2\)/s)\(^8\) | \( f \) | \( 8 \times 10^{-6} \) (M) |
| \( D_{\text{OH}} \) | \( 4.2 \times 10^{-9} \) (m\(^2\)/s)\(^8\) | \( k_f \) | \( k_i \) |
| \( D_{\text{OH}} \) | \( 0.42 \times 10^{-9} \) (m\(^2\)/s)\(^8\) | \( K_{\text{eq}} \) | \( 4.36 \times 10^{-7} \) (M\(^{-1}\))\(^{17}\) |
| \( k_i \) | \( 1.4 \times 10^{11} \) (M\(^{-1}\)s\(^{-1}\))\(^{27}\) | Area | \( 4 \times 10^{-5} \) (m\(^2\)) |
| \( k_b \) | \( 2.6 \times 10^{-5} \) (s\(^{-1}\))\(^{27}\) | \( C_F = 10l_{\text{ag}}/\lambda_z \) | 88 (\( \mu \text{F/cm}^2\))\(^{22}\) |

The large reaction rate constants and the associated large Damkhler numbers (\( Da \gtrsim 10^6 \)) render the system of equations very stiff. To nonetheless numerically handle them efficiently, an implicit integrating factor formulation was adopted.\(^{28,29}\) Details of this method, adaptations to our problem and its validation are presented in the supporting information.

Figure 2: Left: First cycle of the cyclic voltamogram (CV) measured at 10 mV/s for the O\(_2\) saturated and N\(_2\) bubbled solution in our setup. The shaded region shows the potential range measured in chronopotentiometric (CP) experiments. Right: The CP curves obtained for the O\(_2\) saturated case. The shaded region indicates the time over which the constant current is applied. The corresponding current density for each curve is mentioned as well.

Results and Discussion

Time resolved pH measurements

A cyclic voltamgram (CV) of an O\(_2\) saturated solution, along with the measured electrode potential for some of the constant current experiments is shown in Figure 2. For reference, an additional CV is included for the same configuration but with a solution bubbled with N\(_2\). The potential window of operation in our constant current experiments is between 0.1V and 0.5V vs Ag/AgCl (at a starting pH of 5), which translates to 0.6V - 1.1V vs RHE, and is consistent with the potential window of oxygen reduction reaction.\(^{30}\) Oxygen reduction is known to follow different reaction pathways depending on the solution pH,\(^{30,31}\) which renders the proper flux boundary conditions for OH\(^{-}\) and H\(^{+}\) complicated. However, the calculated pH profiles were found to be independent of the ion inducing the pH change. For the current densities and run-times considered here, it can be calculated that (using an initial concentration corresponding to 1 atm O\(_2\) pressure) the oxygen at the electrode surface is not completely depleted. Hence it can be concluded that oxygen reduction (and not water or proton reduction) is the primary reaction occurring at the electrode. Finally, it is important to mention that fluorescein is stable under the conditions applied.\(^{32–35}\)

The obtained emission intensity profiles and the resulting pH distributions at high supporting electrolyte concentration are summarized in Figure 3a for various current densities. In all cases considered here, \( i \) is limited to values traditionally considered minute for electrochemistry. Despite such low current densities, the pH change and the corresponding thickness of the depletion layer are significant. Figure 3a shows the attenuation corrected mean intensity of fluorescein emission as a function of distance \( z \) from the electrode surface. Independent of the applied current density, a steep front is seen to propagate into the solution already at early times, \( t < 300 \) s. This feature also translates to the corresponding pH-profiles. It should be noted, however, that intensity levels within the resulting ‘shoulder’ close to the electrode reach the saturation limit and due to the uncertainties described above, pH-results are greyed out in these instances. Nevertheless, the experimental results are in good agreement with the simulated pH profiles shown in Figure 3b (see solid lines). Interestingly, also in the simulations the pH is near constant close to the electrode.
for $|i| \geq 1.59 \mu A/cm^2$, yet with $pH = 9 - 10$ the values are slightly outside the experimental sensitivity range. Even at current densities of $\sim 1 \mu A/cm^2$, the depletion layer or the penetration depth of the pH profile reaches $\sim 1 \text{ mm}$ into the electrolyte. At higher current densities, this depletion length grows faster and extends further into the bulk of the solution.

It can be seen, however, that for the two highest current densities considered here, the intensity as well as the pH profiles recede at later times (corresponding to darker shadings of the markers), whereas the model predicts a monotonic outward propagation of the front. To enable a quantitative comparison, we track the position $z_{pH=7}$ at which the pH = 7 is encountered as a proxy for the front location. As Figure 3c shows, the pH front propagation in the experiments is well captured by the model for the two lower current density cases presented here. At higher current densities and at late times, though, the pH front in experiments either recedes or saturates. This is also true for repeat measurements made (see supporting information). However, this effect appears to be an artifact of the way the mean fluorescein intensities are calculated. Consistent with the 1D assumption, only a measure of the mean across the entire image (i.e. a plane parallel to the electrode) is considered. For example, at $t_1$ (for $|i| = 5.59 \mu A/cm^2$, see Figure 3a), this is appropriate as highlighted in Figure 4a. At $t_2$
though, the intensity distribution displayed in Figure 4a becomes distinctly inhomogeneous as seen in Figure 4b. This implies that 2D or 3D effects become relevant, which are not captured in the one-dimensional model.

To determine the location and time at which 3D effects become relevant, we consider the standard deviation ($\sigma$) normalized with the mean intensity ($\mu$) of the image as shown in Figure 4c. To minimize the effect of high frequency spatial noise, the image was box-filtered with a filter size of 50 pixels before calculating $\sigma$. Figure 4c captures the uniform image intensity for $|i| = 0.8 \, \mu A/cm^2$ as a near constant $\sigma/\mu$. In contrast, a visible peak in $\sigma/\mu$ at the depletion front $z = z_{pH=7}$ is observed for all other cases. At the two highest current densities considered, the unsteadiness in fluorescein intensity develops over time as well. The onset time ($t_{ons}$ defined as $\sigma/\mu > 0.1$) of this instability thus calculated is, in Figure 4d, found to sharply reduce with increasing current densities which is well approximated by an inverse proportionality. It is conceivable then that this instability occurs only after a certain threshold number of $H^+$ ions have been depleted from solution. The distance $\delta$ at which this non-uniformity is first measured, shows no clear trend: the non-uniformity first increases until $|i| = 3.18 \, \mu A/cm^2$ and then decreases again slightly later. Since we only look at a small portion of the electrode though, deviations from a 1-D profile can occur much earlier, at a different $\delta$. It is unlikely that the reaction at the counter electrode plays any role in the appearance of instability as it is sufficiently far away compared to the measured depletion lengths of $\sim 2$mm. Possible reasons could then be the presence of electric field effects or induced fluid flow in the system, which have not been modelled. However, despite the early appearance of inhomogeneity, the pH profiles in experiments are similar to the model results up to distances and times that are much larger (see Figure 3c: filled and open symbols, and blue/black lines in 3b). It may be possible then that the departure of pH profiles in experiments, from a 1D diffusion approximation, occurs only after a certain minimum $\sigma/\mu$ (and corresponding inhomogeneity) is reached.
Figure 5: Comparison of pH profiles for (a) perchlorate (NaClO$_4$/HClO$_4$) and (b) sulphate (Na$_2$SO$_4$/H$_2$SO$_4$) electrolytes. All measurements were performed in 0.5M supporting salt concentration containing 8µM Fl. pH was adjusted to pH 5 by addition of respective acid. pH > 8.5 has been greyed out due to the uncertainty in the measurements described in the experimental section.

**Sulphate buffer effect**

In addition to the above measurements, we proceed to evaluate the developing pH profiles in sulphate containing electrolytes, e.g. in the Na$_2$SO$_4$/H$_2$SO$_4$ system. This system is frequently used (for example sulfuric acid is commonly used to study O$_2$ reduction) but, in contrast to perchlorate electrolytes, may induce additional buffer capacity, thus changing the pH profiles. In fact, H$_2$SO$_4$ has two dissociation constants, the second corresponds to the dissociation of HSO$_4^-$ with a pKa of around 2.37–39. Figure 5 compares the pH profiles measured for the sulphate case to those obtained with perchlorate electrolyte, for the two lowest current densities. It is evident that the pH profiles develop significantly slower in sulphate-containing electrolytes. For example, for $|i| = 1.59 \, \mu A/cm^2$, the pH profiles in the Na$_2$SO$_4$/H$_2$SO$_4$ system have no clear front propagating in the solution; the profiles rather become increasingly steep close to the electrode surface with time, while for the perchlorate solution depletion lengths $z_{pH=7} \approx 1.5 \, mm$ are achieved.

To try to further explain the experimental results, we consider the $pK_a$ of HSO$_4^-$, which, although is well below our starting pH (pH = 5), due to the presence of the large concentration of SO$_4^{2-}$ in solution, creates a reservoir of HSO$_4^-$ ions which act as a source of protons in solution and stabilizes the solution against pH changes. We attempt to capture this effect in the 1D model as our results in the supplementary show. This buffer effect is most likely present in experimental measurements in literature with sulphate electrolytes. For example, Leenheer and Atwater measured the pH on patterned gold electrodes in Na$_2$SO$_4$ solutions, with different pattern shapes and area. However, their steady state simulations predicted a depletion zone much larger than experiments. Similarly, the buffering effect of Li$_2$SO$_4$ solutions may also be present in the recent measurements by Monteiro et al.

**Conclusion**

We have successfully demonstrated the use of fluorescein to measure time-resolved pH profiles in solution. The results of a time-dependent reaction-diffusion model compare reasonably well with the experimental data. However, the inhomogeneity of pH in a plane that develops at ‘high currents’ clearly shows the need for time-varying local pH measurements. The crucial aspects to consider when using fluorescence microscopy for pH measurement, like optical distortions and signal attenuation, have been carefully examined. Furthermore, the concentration of the supporting electrolyte is shown to influence migration of fluorescent dyes and should be considered to avoid pitfalls in pH measurement in electrochemical systems. For sulphate containing electrolytes, our analysis reveals buffering effects, which likely explain the difference between the measured diffusion profiles and those observed in experiments in the past.
Fluorescence microscopy offers time-resolved and relatively non-intrusive measurement of pH instantly over a large area. Since the principle of measurement presented here is applicable to other fluorescent dyes with a different pH detection range, this technique can be used for a wide range of electrochemical systems to elucidate electrode dynamics. This holds in particular for CO\textsubscript{2} reduction on gas diffusion electrodes, since the second pKa of carbonic acid lies in the fluorescein detection region. Our developed method can be directly implemented to quantify mass transport, the role of bicarbonate concentrations etc. in the electrolyte. More generally, the measurement technique presented here offers insight into the dynamics of ions in solution, important to many electrochemical systems, none more so than in electrochemical cells to unravel the role of start-stop transients. Detailed information of the pH distribution will provide a better understanding of electrode processes and aid in the overall design of electrochemical systems for eventual use in large scale electrolysis.

**Supporting Information Available**

The following files are available free of charge.

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Supporting information for:
Electrochemically induced pH change: time resolved confocal fluorescence microscopic measurements and comparison with numerical model

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Experimental Method

To determine the location of the electrode surface we measure the light reflection S1 from the working (glass slide) electrode. Figure S1 shows the mean reflection and fluorescein intensity signals measured simultaneously, starting from below the glass slide. The fluorescein signal does not provide clear information on the (electrode) surface location, hence the reflection signal is used. The presence of the glass slide causes two reflection maxima 115 µm apart, which can be used to establish the surface positions. Therefore, before starting each experiment, the reflection signal is measured (by scanning optical sections 5 µm apart) to determine where the surface of the electrode is located.

In the experiments, sections in the scanned direction are taken by the programmed movement of the optical stage (20 µm apart in the experiments in the main text). The distances measured (z_m) in this way (from the electrode surface), however, do not take into account distortion in the light path due to variations in the refractive index (air vs. aqueous electrolyte). Visser and Oud give the relationship between the actual focal distance (Δz) to stage movement (Δz_m) as Δz = Δz_mn, where n is the refractive index of the medium. To verify the appropriateness of this correction in our case, we consider the measured glass slide thickness of 115 μm (Δz_m). Using n_{glass} = 1.5, the corrected glass slide thickness then is Δz = 115 μm × n_{glass} = 172.5 μm, very close to the actual value of 170 μm. We carry out a similar correction for the refractive index of the electrolyte solution (using n_{sol} = 1.33) such that z = n_{sol}z_m. So while the total measured depth is z_{max} ≈ 1.4 mm, the corrected depth is z_{max} ≈ 1.9 mm.

Any measurement of fluorescence requires considering the path dependent attenuation of the excitation as well as the emitted fluorescent light. Since the numerical aperture of the objective used in our experiments is small, following Ohser et al., the dependence of the emitted fluorescent light (I_{em}(z)) on the excitation intensity (I_{ex}(z)) and the concentration of fluorophore (c(z)) at a point z in the solution, along with the fluorescence efficiency (α_1, pH dependent in the case of Fluorescein) can be written as:

\[ I_{em}(z) = I_{ex}(z)α_1c(z) \]
Figure S1: Surface reflection and fluorescein intensity. Maxima in the surface reflection correspond to the electrode surfaces.

Since in our case, the absorbance of the fluorophore is pH dependent, and the pH itself is pH dependent, the path dependent attenuation of the excitation intensity can be written as:

\[ I_{\text{ex}}(z) = I_{\text{ex}0} \left( e^{-\int_{z_0}^{z} \epsilon_1(pH(\tau))c(\tau)d\tau} \right) \quad (s.2) \]

where \( \epsilon_1 \) is the pH dependent attenuation coefficient of the excitation light and \( I_{\text{ex}0} \) is the excitation intensity at \( z = 0 \). Similarly if there is an attenuation \( (\epsilon_2) \) of the emitted light \( I_{\text{em}}(z) \), the measured fluorescence intensity \( I_f(z) \) goes as:

\[ I_f(z) = I_{\text{em}}(z) \left( e^{-\int_{z}^{z_0} \epsilon_2(pH(\tau))c(\tau)(-d\tau)} \right) \quad (s.3) \]

Since we use a constant concentration of fluorophore and laser settings in all our experiments, combining equations (s.1), (s.2) and (s.3):

\[ I_f(z) = I_{f0} \left( e^{-\int_{z_0}^{z} k(pH(\tau))d\tau} \right) \quad (s.4) \]

where \( I_{f0} = \alpha_1 I_{\text{ex}0}c \) is the unattenuated fluorescence intensity, and \( k = (\epsilon_1 + \epsilon_2)c \) is the overall attenuation factor. Hence a optical path history dependent correction factor of \( e^{\int_{z_0}^{z} k(pH(\tau))d\tau} \) must be multiplied with the fluorescence intensity, \( I_f(z) \), measured at a point to get the corresponding corrected value \( I_{f0} \). It should be noted that for higher numerical aperture objectives, an attenuation correction such as shown in Visser and Oud must be used.

To determine \( k \), we measured the fluorescence intensity as a function of \( z \) for different constant pH solutions \( (k \) is constant for a constant \( pH) \) similar to that shown in Figure S2a. We expect the fluorescence intensity at a particular pH to be exponentially decaying step function \( (I_{f0}(z) \) given by equation (s.4) with \( k = \text{const} \) and its maximum at the electrode surface, \( z = 0 \). The actual profiles, however, are smooth close to the electrode surface, most likely due to the point spread function (psf in the \( z \) direction) of the optical system. Taking the simplest assumption of a gaussian psf i.e. \( G(z) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{z^2}{2\sigma^2}} \) (with the standard deviation \( \sigma \)), the resulting profiles must then be a convolution of \( I_{f0}(z) \) with \( G(z) \), and should have the analytical form:

\[ I_{f0}(z) * G(z) = I_{f0} e^{-kz} e^{-\frac{z^2}{2\sigma^2}} \]

\[ \left( 1 - \frac{1}{2} \text{erfc} \left( \frac{z}{\sigma \sqrt{2}} - \frac{k\sigma}{\sqrt{2}} \right) \right) \quad (s.5) \]

where, \( \text{erfc} \) is the complementary error function. Consequently, we fit a function of the form \( I_{f0}(z) * G(z) + C \), with four fitting parameters \( I_{f0}, k, \sigma \) and \( C \) (where \( C \) is a parameter related to small constant unknown effects). The resulting fit is overlaid on the original data of constant pH solutions (average of 3 measurements) in figure S2a. The fit is reasonable, however differences in the location of their maximum indicates that the psf is likely more complicated than a gaussian function. Based on the \( I_{f0} \) and \( k \) and \( C \) obtained, we further plot \( I_{f0}(z) + C \) which shows that the psf smoothing is important only at the electrode surface. In our measurements, we therefore correct only for this attenuation and not the psf smoothing. The measurement is compromised below the location of the intensity maximum \( (I_{f,max} \text{ in Figure S2a}) \) of the profiles \((\approx 100 \mu m)\) and has not been shown in the main text. The attenuation correction factor \( k \) as a function of pH is plotted in the inset of figure, and has been fitted with a line. At the \( n \)-th stack from the electrode surface (with a distance \( \Delta z = 20 \times 1.33 \mu m \)), the measured fluorescein intensity then must be of
The general trend matches in all cases, however, there is significant spread especially at the upper limit of the pH-sensitive region. The different ionic strengths of the calibration solution could be a possible reason for these differences.\textsuperscript{S7} However, this effect is small as the red dotted line, which represents our calibration curve corrected to an ionic concentration of a 0.5M monovalent salt (using the equation in Sjöback et al.;\textsuperscript{S7} assuming that the parameter $\gamma$ in our fit behaves like an effective pKa), in Figure S2c shows. Moreover, since the fluorescence intensity at a point in the sample is related to the the local concentration of the fluorophore, the laser excitation intensity, the optical path history of the light, the voltage of the photo-multiplier tube etc., the differences could be due to a number of reasons and it is not straightforward to compare the values of fluorescence intensity, for different pH, across optical setups. Rather, laser and camera settings must remain constant between calibration and experiment for a faithful conversion of intensity values to pH. Even then, there are small differences between the repeats of our calibration measurements (new pH solutions and different electrode) in Figure S2a and these could
be traced to presence of small contaminants on the electrode surface. The inset of Figure S2a shows an example of a fluorescein intensity image (at pH = 10) obtained for each of the two calibration trials done. The difference between the repeats provides a sense of the calibration error as similar (and to varying degrees) contamination could be present in the experiments. However, since the calibration curve is similar in the lower limit of the pH-sensitive region, the effect on the location of the pH shoulder is minimal. Still, trial 2 (having the cleaner electrode) is used in our measurements and is shown Figure 1b in the main text. Lastly, the intensity dependence on pH (in Figure 1b in the main text) is fit with a function of the form

$$\ln(I_{f,max}) = \alpha + \frac{\beta}{1 + e^{-(pH-\gamma)}} \quad (s.8)$$

with fit parameters $\alpha$ (4.991±0.034), $\beta$ (2.946±0.039) and $\gamma$ (5.857 ± 0.060). A robust least-squares regression with a logistic function weight (implemented as 'nlinfit' in MATLAB) is used for fitting the data. The residuals of the regression appeared to be normally distributed (at all points except the two measurement triplicates between pH 6 and 8 that are not on the line in Figure 1b). The inverse function is therefore:

$$pH_{inv} = -\ln\left(\frac{\beta}{\ln(I_{f,max}) - \alpha} - 1\right) + \gamma. \quad (s.9)$$

The prediction interval for the non-linear fit (based on the measured calibration data) presented in Figure S3 is calculated based on Guthrie et al. and shows that at the higher ends of our pH-sensitive range, the error in measurement can be close to ±1 pH unit.

All remaining fits presented here use the 'fit' function in Matlab (R2019b).

**Details of the numerical model**

For each ion species $k$, we have a related non-dimensionalized concentration diffusion equation of the type shown in equation (4) in the main text. A second order central difference scheme is used to discretize spatial gradients.

Figure S3: The inverse function based on calibration measurements presented in the main text. At a given pH, the mean of three separate intensity measurements is shown here, since the error bars are small.

Figure S4: Comparison of results using BTCS and IIF numerical schemes. Note: only the H$^+$ and OH$^-$ ions were considered for this comparison. The relatively small effect of HFl$^-$ on the pH profiles is consequently also absent.
The numerical domain of length $L$ is divided into $N + 1$ grid points such that $\Delta z = \frac{L}{N}$. We then obtain a set of equations of the form:

$$
\frac{\partial c_k^*}{\partial t^*} = \frac{D_{r,k}}{\Delta z^2} \begin{bmatrix}
-2 & 2 & 0 & \cdots \\
1 & -2 & 1 & \cdots \\
\vdots & \vdots & \ddots & \vdots \\
0 & \cdots & 1 & -2
\end{bmatrix} \begin{bmatrix}
c_k^*(1) \\
\vdots \\
c_k^*(N)
\end{bmatrix} + \begin{bmatrix}
\pm J_k \Delta z \\
0 \\
\vdots \\
\pm J_k \Delta z
\end{bmatrix} \pm Da \times f(c^*)
$$

(s.10)

Here $c_k^* = c_k(m)$ is the (non-dimensional) spatially discretized concentration ($1 \leq m \leq N+1$, but continuous in time) of ions and $J_k$ is the constant flux of the ions at the electrode surface. In our simulations:

$$
c_{H^+}^*(N + 1) = 1 \quad \text{(s.11a)}
$$

$$
c_{OH^-}^*(N + 1) = 1 \quad \text{(s.11b)}
$$

$$
c_{F2^-}^*(N + 1) = \frac{c_{F2^-}}{T} \quad \text{(s.11c)}
$$

and,

$$
J_{H^+} = \begin{cases}
0, & \text{if } |i_{Cap}| > |i| \\
\frac{(-|i|+|i_{Cap}|)L}{FD_{H^+} + (i_{Cap})}, & \text{otherwise}
\end{cases} \quad \text{(s.12a)}
$$

$$
J_{OH^-} = 0 \quad \text{(s.12b)}
$$

$$
J_{F2^-} = 0 \quad \text{(s.12c)}
$$

where $i_{Cap}$ is the time dependent capacitive current density as described in the main text.

The above set of equations are stiff due to large reaction rate constants (and related $Da$) for the non-linear reaction terms $f(c)$. Using an implicit scheme such as Backward-Time-Central-Space (BTCS), would therefore require very small time steps and consequently a large run-time. We instead integrate in time according to the implicit integrating factor (IIF) scheme presented in Nie et al.\textsuperscript{11} A second order approximation of the $f(c)$-term is used, while employing the trapezoid rule to approximate the integration of the time dependent $i_{Cap}$.

The set of non-linear equations are then solved at each time step using the $fsolve$ function in Matlab (R2019b). The numerical scheme was validated, first with the analytical solution of the linear reaction-diffusion equation used in Nie et al.\textsuperscript{11} We further compared the results of the IIF with the BTCS scheme (for our system) for the highest current density used in this work ($|i| = 5.59 \mu A/cm^2$). The results compare well as shown in Figure S4, confirming the proper implementation of the numerical scheme.

**Repeat experiments**

Figure shows the measured pH profiles in a repeated experiment has been provided to highlight the reliability of the measurement method. A comparison of the pH front with the model results is also shown. Similar to the results presented in the main text, the experimental profiles are in good agreement at the two lower current densities and deviate from the 1D diffusion model at the two highest current densities.

**Sulphates comparison**

To account for the buffering capacity of sulphates ($\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$) we adjusted the model to include the following reaction couples:

$$
\text{H}^+ + \text{SO}_4^{2-} \xrightleftharpoons[k_f, S]{k_b, S} \text{HSO}_4^- \quad \text{(s.13)}
$$

$$
\text{Na}^+ + \text{SO}_4^{2-} \xrightleftharpoons[k_f, \text{Na}]{k_b, \text{Na}} \text{NaSO}_4^- \quad \text{(s.14)}
$$

There is an extra bulk reaction term due to $\text{HSO}_4^-$ ionization in the $\text{H}^+$ equation. Furthermore, additional reaction diffusion equations ($\text{SO}_4^{2-}$ and $\text{NaSO}_4^-$ here) and have to be taken into account. The initial concentrations of the ions are estimated based on the total dissolved $\text{Na}_2\text{SO}_4$ and pH of the solution. The dissociation constants of $\text{HSO}_4^-$\textsuperscript{S12–S14} and $\text{NaSO}_4^-$\textsuperscript{S15,S16} are taken from the literature ($K_{\text{H}SO_4} = 0.0103$ and $K_{\text{NaSO}_4} = 0.5$). Also for the forward rate constants $k_{f, \text{Na}} = k_f \times 0.1$ and $k_{f, S}\textsuperscript{S17} = k_f \times 5$ are taken.
Figure S5: Experimental repeats for all $|i|$ presented in the main text. Left: pH profile measured. pH > 8.5 has been greyed out due to the uncertainty in measurement described in the experimental section. Right: Comparison of depletion length, $z_{pH=7}$, of experiment vs model. The shaded region indicates the model results over a range of capacitance $0 \leq C \leq 120 \mu F/cm^2$ (solid line with $C = 88 \mu F/cm^2$). Open squares show pH front after the first appearance of inhomogeneity described in the main text.

Figure S6 shows a comparison of the full pH profiles for the 4 different current densities considered. The buffer effect at the two lower current densities is captured well by the model, although the profiles do not match exactly at all times. Finally, the two highest current densities have been presented here only for the sake of completeness, as (discussed in the main text) experiments at these values of $|i|$ are marked by the appearance of inhomogeneous fluorescein intensity in a plane and therefore do not follow a 1D diffusion approximation.

Figure S6: pH vs Depth for the case with sulphates: Experiments vs Simulations. (a) The experimental profiles for all $|i|$ values. (b) Numerical pH profiles based on values discussed in the text.

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